Development and Critical Evaluation of Group Contribution Methods for the Estimation of Critical Properties, Liquid Vapour Pressure and Liquid Viscosity of Organic Compounds

By

Yash Nannoolal

[B.Sc. (Eng.), M.Sc. (Eng.)]

University of Kwazulu-Natal, Durban Campus

For the degree Doctor of Philosophy (Chemical Engineering)

December 2006

The financial assistance of the National Research Foundation (NRF) towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at, are those of the author and are not necessarily to be attributed to the NRF.

Abstract

Critical properties, liquid vapour pressures and liquid viscosities are important thermophysical properties required for the design, simulation and optimisation of chemical plants. Unfortunately, experimental data for these properties are in most cases not available. Synthesis of sufficiently pure material and measurements of these data are expensive and time consuming. In many cases, the chemicals degrade or are hazardous to handle which makes experimental measurements difficult or impossible. Consequently, estimation methods are of great value to engineers.

In this work, new group contribution methods have been developed for the estimation of critical properties, liquid vapour pressures and liquid viscosities of non-electrolyte organic compounds. The methods are based on the previous work of Nannoolal (2004) & Nannoolal *et al.* (2004) with minor modifications of structural group definitions.

Critical properties, viz. critical temperature, critical pressure and critical volume, are of great practical importance as they must be known in order to use correlations based on the law of corresponding states. However, there is a lack of critical property data in literature as these data are difficult or in many cases impossible to measure. Critical property data are usually only available for smaller molecules of sufficient thermal stability.

The proposed group contribution method for the estimation of critical properties reported an average absolute deviation of 4.3 K (0.74%), 100 kPa (2.96%) and 6.4 $cm^3.mol^{-1}$ (1.79%) for a set of 588 critical temperatures, 486 critical pressures and 348 critical volumes stored in the Dortmund Data Bank (DDB (2006)), respectively. These results were the lowest deviations obtained when compared to ten well known estimation methods from literature. In addition, the method showed a wider range of applicability and the lowest probability of prediction failure and leads to physically realistic extrapolation when applied to a test set of components not included in the training set.

For the estimation of the critical temperature using the new method, knowledge about the normal boiling point is required. If there is no information on the latter property, then the previous group contribution estimation method can be employed for estimation.

Because of their great importance in chemical engineering, liquid vapour pressures have received much attention in literature. There is currently an abundance of experimental data for vapour pressures, especially for smaller molecules, but data are scarce or of low quality for larger and more complex molecules of low volatility. The estimation of liquid vapour pressures from molecular structure has met with very limited success. This is partly due to the high quality predictions required for vapour pressures for use in the design of for example distillation columns.

This work presents a new technique for the estimation of liquid vapour pressures by developing a two-parameter equation where separate parameters model the absolute value and slope while at the same time the equation is able to approximate the non-linearity of the curve. The fixed point or absolute value chosen was the normal boiling point for which a large amount of experimental data is available. A group contribution estimation of the slope was then developed which showed nearly no probability of prediction failure (high deviation). Employing experimental normal boiling points in the method, an absolute relative deviation of 6.2% in pressure for 1663 components or 68835 (68670 from DDB and 165 from Beilstein) data points was obtained. This result is in comparable accuracy or slightly higher in deviation than correlative models such as the Antoine and DIPPR equations (direct correlations). A test of the predictive capability by employing data that were not used in the training set also showed similar results. Estimations are possible up to the inflection point or a reduced normal boiling temperature of ±1.2.

If there is no information about the experimental normal boiling point, two options are recommended to obtain this value. The first and more reliable is back-calculation using the known boiling point at other pressures and the estimated slope of the vapour pressure equation. Results in this case are similar to cases where experimental normal boiling points were used. The second possibility is to estimate the normal boiling point using the method developed previously. In this case, an absolute relative deviation of 27.0% in pressure is obtained.

The saturated liquid viscosity is an important transport property that is required for many engineering applications. For this property, experimental data are limited to mostly simple and more common components and, even for these components the data often cover only a small temperature range. There have been many different approaches to estimate liquid viscosities of organic compounds. However, correlative and empirical methods are often the only or preferred means to obtain liquid viscosities.

The technique used for the estimation of the liquid viscosity is similar to that in case of liquid vapour pressures, i.e. a two-parameter equation models the absolute value, slope and the non-linearity of the curve. As there was no convenient reference point at a standard viscosity available to model the absolute value (viscosity reference temperature), an algorithm was developed to calculate this temperature which was chosen at a viscosity of 1.3 cP. This work then presents a group contribution estimation of the slope and using calculated or adjusted reference temperatures, an absolute relative deviation of 3.4% in viscosity for 829 components or 12861 data points stored in the DDB was obtained. This result is in comparable accuracy or slightly higher in deviation than correlative models such as the Andrade and Vogel equations (direct correlations). The estimation method has an upper temperature limit which is similar to the limit in case of liquid vapour pressures.

If no data are available for a viscosity close to 1.3 cP then, as in case of the vapour pressure estimation method, the temperature can be back calculated from data at other viscosity values. Alternately, the viscosity reference temperature can be estimated by a group contribution method developed in this work. This method reported an average absolute deviation of 7.1 K (2.5%) for 813 components. In case both the slope and absolute value were estimated for the liquid viscosity curve, an average absolute deviation of 15.3 % in viscosity for 813 components or 12139 data points stored in the DDB was obtained. The new method was shown to be far more accurate than other group contribution methods and at the same time has a wider range of applicability and lower probability of prediction failure.

For the group contribution predictions, only the molecular structure of the compound is used. Structural groups were defined in a standardized form and fragmentation of the molecular structures was performed by an automatic procedure to eliminate any arbitrary assumptions. To enable comparison, chemical family definitions have been developed that allow one to automatically classify new components and thus inform the user about the expected reliability of the different methods for a component of interest. Chemical family definitions are based on the kind and frequency of the different structural groups in the molecule.

Preface

The work presented in this thesis was performed at the University of Kwazulu-Natal, Durban from January 2004 to December 2006. The work was supervised by Prof. D. Ramjugernath and Prof. Dr. J. Rarey.

This thesis is presented as the full requirement for the degree of PhD in Chemical Engineering. All the work presented in this thesis is original unless otherwise stated and has not (in whole or part) been submitted previously to any tertiary institute as part of a degree.

Y. Nannoolal (983186114)

Acknowledgements

I would like to acknowledge the following people for their contribution to this work:

- Firstly, my supervisors, Prof. D. Ramjugernath and Prof. Dr. J. Rarey, for their support, ideas, wisdom and motivation during this work. Working with them has been a great learning experience in many fields.
- NRF International Science Liason, NRF-Thuthuka Programme, THRIP, University of Kwazulu-Natal Research Fund and Forschungszentrum Jülich (Germany) for financial support.
- Prof. Dr. J. Gmehling from the University of Oldenburg for his support and resourceful help.
- Mr. W. Cordes from DDBST GmBH for his support throughout the development of this work.
- On a personal note my parents, Suresh and Lalitha, my grandmother and late grandfather, my brother Dion and sister Anushka for years of support, guidance and motivation.
- My colleagues from the University of Kwazulu-Natal and University of Oldenburg for their friendship, advice and support.

Table of Contents

Abstract .... *i*
Preface .... *v*
Acknowledgements .... *vii*
Table of Contents .... *ix*
List of Figures .... *xiii*
List of Tables .... *xxi*
Nomenclature .... *xxxi*
Chapter One 1
Introduction 1
Chapter Two 7
Critical Properties 7
2.1 Introduction 7
2.2 Brief History 8
2.3 Critical Properties Literature Review 9
2.3.1 Overview of Available Critical Property Estimation Methods 9
2.3.2 Lydersen (1955) & Riedel (1949) 12
2.3.3 Ambrose (1978a), (1979) 13
2.3.4 Daubert (1980) 16
2.3.5 Klincewicz & Reid (1984) 16
2.3.6 Joback & Reid (1987) 17
2.3.7 Somayajulu (1989) 19
2.3.8 Constantinou & Gani (1994) 21
2.3.9 Tu (1995) 24
2.3.10 Marrero-Morejon & Pardillo-Fontdevilla (1999) 25
2.3.11 Marrero-Morejon & Gani (2001) 27
2.3.12 Wen & Quiang (2001) 28
2.3.13 Overall Discussion 29
Chapter Three 33
Liquid Vapour Pressure 33
3.1 Introduction 33
3.2 The Clausius-Clapeyron Equation 35
3.3 Correlative Techniques 37
3.3.1 Brief history 38
3.3.2 Theory 38
3.3.3 Correlations Based on the Clausius-Clapeyron Equation 40
3.3.4 Empirical Correlations 45
3.3.5 Discussion of Correlative Techniques 47
3.4 Estimation Methods Based on Molecular Structure 48
Chapter Four 53
Liquid Viscosity 53

4.1 Introduction 53
4.2 The Temperature Dependence of Liquid Viscosity 56
4.3 Empirical Estimation and Correlative Techniques 57
4.3.1 Correlative techniques 60
4.3.2 Discussion of Correlative techniques. 62
4.4 Group Contribution Methods 69
4.4.1 Orrick & Erbar (1974) 70
4.4.2 Van Velzen et al. (1972) 70
4.4.3 Skubla (1985) 72
4.4.4 Joback & Reid (1987) 73
4.4.5 Sastri & Rao (1992) 73
4.4.6 Discussion of Structural Techniques 74
Chapter Five 85

Liquid Theory and the Group Contribution Concept 85
5.1 Introduction 85
5.2 Liquid Theory Considerations 85
5.2.1 Enthalpy and Entropy of Phase Change 86
5.2.2 Intermolecular Forces 89
5.2.2.1 Induced Dipole - Induced Dipole Forces (Dispersive Forces, London Forces, Van der Waals Forces) 89
5.2.2.2 Dipole - Dipole (Keesom) Forces and Dipole - Induced Dipole (Debye, Induction) Forces 91
5.2.2.3 Hydrogen bonding 92
5.2.2.4 Summation of Intermolecular Forces 93
5.2.3 Influence of Molecular Structure on Intermolecular Forces 96
5.3 Group Contribution Method 97
5.3.1 First-Order Groups 97
5.3.2 Corrections 98
5.3.3 Group Interactions 100
Chapter Six 103

Computational Tools 103
6.1 Introduction 103
6.2 Software Utilities and Terminology 105
6.2.1 Development Platform and the Database 105
6.2.2 Object-Oriented Programming 106
6.2.3 Structure Query Language (SQL) 107
6.2.4 Data Access Objects (DAO) 107
6.2.5 Metalanguage 108
6.2.6 Object Linking and Embedding (OLE) 109
6.2.7 Dynamic Library Link (DLL) 109
6.3 Pure Component Property Database 110
6.4 Automatic Fragmentation 112
6.4.1 Ink-file 112
6.5 Regression 116
6.6 Filter Language 121
6.7 Property Analysis 123
Chapter Seven 129

Estimation of Critical Properties: 129
Development, Results and Discussion 129

7.1 Introduction 129
7.2 Data Verification 130
7.3 Hydrocarbon Compounds 132
7.4 Mono-functional Compounds 139
  7.4.1 Oxygen Compounds 139
  7.4.2 Nitrogen Compounds 144
  7.4.3 Sulphur Compounds 147
  7.4.4 Halogen Compounds 148
  7.4.5 Various Other Compounds 151
7.5 Multifunctional Compounds 153
7.6 Model Development 159
7.7 Discussion 161
  7.7.1 Overall Results 161
  7.7.2 Probability of Prediction Failure 162
  7.7.3 Test of the Predictive Capability 164
  7.7.4 Overall Discussion 168
Chapter Eight 173
Estimation of the Liquid Vapour Pressure Curve: Development, Results and Discussion 173
8.1 Introduction 173
8.2 Vapour Pressure Model 175
8.3 Software Platform for the Development of the Vapour Pressure Estimation Method 177
8.4 Data Verification 180
8.5 Results and Discussion 181
  8.5.1 Hydrocarbon Compounds 181
  8.5.2 Mono-functional Compounds 192
    8.5.2.1 Oxygen Compounds 192
    8.5.2.2 Nitrogen Compounds 205
    8.5.2.3 Sulphur Compounds 211
    8.5.2.4 Halogen Compounds 217
    8.5.2.5 Various Other Compounds 223
  8.5.3 Multi-functional compounds 224
  8.5.4 Model Development 237
8.6 Overall Discussion 237
  8.6.1 Overall Results 237
  8.6.2 Test of the Predictive Capability 238
  8.6.3 Normal Boiling Point Omission 239
  8.6.4 Enthalpy of Vaporisation 241
  8.6.5 Final Discussion 242
Chapter Nine 245
Estimation of the Saturated Liquid Viscosity Curve: 245
Development, Results and Discussion 245
9.1 Introduction 245
9.2 Data Verification 247
9.3 Development of a Group Contribution Method for Estimating the Viscosity of Saturated Liquids 249
  9.3.1 First Approach: Group Contribution Regression of Andrade Parameters 249
  9.3.2 Evaluation of Alternatives 250

9.3.3 Model Development 251
9.4 Results and Discussion 256
9.4.1 Hydrocarbon Compounds 256
9.4.2 Mono-functional Compounds 266
9.4.2.1 Oxygen Compounds 266
9.4.2.2 Nitrogen Compounds 279
9.4.2.3 Sulphur Compounds 286
9.4.2.4 Halogen Compounds 291
9.4.2.5 Various Other Compounds 297
9.4.3 Multi-functional Compounds 303
9.5 Overall Discussion 311
9.5.1 Overall Results 311
9.5.2 Test of the Predictive Capability 311
9.5.3 Reference Temperature Omission 315
9.5.4 Probability of Prediction Failure 317
9.5.5 Final Discussion 318
Chapter Ten 319

Conclusions 319
Chapter Eleven 323

Recommendations 323
11.1 Estimation of the Melting Point 324
11.1.1 Model Development 325
11.1.2 Melting Point Recommendations 326
11.2 QSPR – Estimation of the Normal Boiling Point Using Group Contribution and the Dipole Moment 329
11.2.1 Introduction to Computational Chemistry 331
11.2.2 GC-QSPR - Preliminary Assessment 334
11.2.3 QSPR - Conclusive Assessment 337
11.3 Additional Recommendations 339
References 343

Appendix A 367

Literature Group Contribution Tables 367
Appendix B 417

Structural Group and Correction Definitions 417
Appendix C 429

Group Contributions for the Proposed Methods 429
Appendix D 459

Property Calculation Examples 459

List of Figures

Figure 2-1: Estimated critical temperature of n-alkanes as a function of number of carbon atoms for the different models (AB and SJ overlap). 15

Figure 2-2: Dominant, recessive conjugates and conjugation operator 23

Figure 3-1: Schematic vapour pressure plot. 39

Figure 3-2: Vapour pressure plot of benzene with the Antoine equation. 42

Figure 3-3: Plot of calculated and experimental β values for ethylbenzene. 45

Figure 3-4: Molecular structure of 1,2-diisopropyl benzene. 50

Figure 4-1: Velocity gradient for a Newtonian fluid (Massey (1983)). 54

Figure 4-2: Velocity gradient for a non-Newtonian fluid 54

Figure 4-3: Volume (Gmehling (2006)) and viscosity (Onken *et al.* (1998)) plots as a function of temperature and pressure 58

Figure 4-4: Thermal conductivity as a function of density and temperature (Onken *et al.* (1998)) 59

Figure 4-5: Liquid viscosity and vapour pressure of ethanol 60

Figure 4-6: Plot of *A* and *B* parameters for n-alkanes (Andrade Equation) 64

Figure 4-7: Plot of *A* and *B* parameters for n-alkanes (Antoine Equation). 65

Figure 4-8: Plot of *A* and *B* parameters for 1-alcohols (Andrade Equation). 66

Figure 4-9: Plot of *A* and *B* parameters for n-alkanes (Vogel Equation). 66

Figure 4-10: Plot of the *C* parameter for n-alkanes. 67

Figure 4-11: Plot of 1-alcohol *A* and *B* parameters from the Vogel Equation. 68

Figure 4-12: Plot of *A* and *B* parameters for n-alkanes (Drucker Equation). 69

Figure 4-13: Plot of *A* and *B* parameters for 1-alcohols (Drucker Equation). 69

Figure 4-14: Series plot of experimental and estimated liquid viscosities for n-alkanes (Sastri and Rao method). 78

Figure 4-15: Series plot of experimental and estimated liquid viscosities for 1-alcohols (Sastri and Rao method). 79

Figure 4-16: Plot of T_0 and *B* parameters for n-alkanes (Equation 4-12). 80

Figure 4-17: Plot of T_0 and *B* parameters for 1-alcohols (Equation 4-12). 80

Figure 4-18: Series plot of experimental and estimated liquid viscosities for n-alkanes (Van Velzen method). 81

Figure 4-19: Series plot of experimental and estimated liquid viscosities for 1-alcohols (Van Velzen method)........ 82
Figure 4-20: Multiple plots (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for multi-functional alcohols........ 83
Figure 4-21: Multiple plots (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for primary amines........ 84
Figure 5-1: Illustration of dipole-dipole interactions between polar molecules (A-attraction, R - repulsion)........ 91
Figure 5-2: Hydrogen bonding (indicated by dotted line) in water........ 92
Figure 5-3: Steric contribution of the number of carbon atoms around a C-C bond........ 100
Figure 5-4: Group interactions for an alkane-diol and -triol........ 101
Figure 6-1: Flow diagram of a single property development routine........ 105
Figure 6-2: Example of a structural group definition in an ink-file........ 113
Figure 6-3: Molecular structure of a carboxylic acid group........ 113
Figure 6-4: Screen shot of building a regression case........ 118
Figure 6-5: Screen shot of regression case information........ 120
Figure 6-6: Screen shot of starting the regression........ 121
Figure 6-7: Screen shot of the generation of a filter language text file........ 122
Figure 6-8: Screen shot of the generation of estimation results........ 124
Figure 6-9: Screen shot of the generation of a filter language text file........ 125
Figure 6-10: Screen shot of deviation table in MS-Excel worksheet (not actual size)........ 126
Figure 6-11: Screen shot of the generation of a property statistical analysis........ 127
Figure 6-12: Screen shot of the multiple plot program (not actual size)........ 127
Figure 7-1: Data verification evaluation program available in DDBSP to evaluate the critical temperature and pressure........ 131
Figure 7-2: Molecular structure of two different fused aromatic compounds........ 134
Figure 7-3: Intramolecular hydrogen bond fin case of β -keto esters (A) and 1,3-dicarbonyl (B) compounds........ 157
Figure 7-4: Keto-enol tautomerism........ 157
Figure 7-5: Estimated critical temperature for n-alkanes as a function of the number of carbon atoms from different group contribution methods (AB and SJ overlap)........ 160

Figure 7-6: Fraction of the data with deviations for critical temperature larger than a given temperature. 163
Figure 7-7: Fraction of the data with deviations for critical pressure larger than a given pressure. 164
Figure 7-8: Fraction of the data with deviations for critical volume larger than a given volume. 165
Figure 7-9: Histogram of the experimental (calculated via T_c, P_c and V_c) and estimated Z_c. 171
Figure 8-1: Screen shot of the MS-Excel worksheet employed for data verification. 181
Figure 8-2: Series plot experimental and estimated liquid vapour pressures for n-alkanes. 185
Figure 8-3: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for cyclic alkanes. 186
Figure 8-4: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for alkenes. 187
Figure 8-5: Series plot of experimental and estimated liquid vapour pressures for alkynes. 188
Figure 8-6: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for aromatic compounds. 189
Figure 8-7: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for aromatic compounds. 190
Figure 8-8: Pressure deviation for mono-functional alcohols. 193
Figure 8-9: Multiple plot (Ln(P) vs. 1/T K^{-1}) of experimental and estimated liquid vapour pressures for 1-alcohols. 195
Figure 8-10: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for secondary alcohols. 196
Figure 8-11: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for tertiary alcohols. 197
Figure 8-12: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for aromatic alcohols. 198
Figure 8-13: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for alkane diols and triols. 199

Figure 8-14: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for ethers. 202
Figure 8-15: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for esters. 203
Figure 8-16: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for carboxylic acids. 204
Figure 8-17: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for primary amines. 207
Figure 8-18: Series plot of experimental and estimated liquid vapour pressures for tertiary amines from this work. 208
Figure 8-19: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for nitrous and nitrite compounds. 209
Figure 8-20: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for cyanide compounds. 210
Figure 8-21: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for sulphur compounds. 214
Figure 8-22: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for sulphur compounds. 215
Figure 8-23: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for sulphur compounds. 216
Figure 8-24: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for fluorine compounds. 219
Figure 8-25: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for chlorine compounds. 220
Figure 8-26: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for bromine compounds. 221
Figure 8-27: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for iodine compounds. 222
Figure 8-28: Series plot of experimental and estimated liquid vapour pressures for phosphate compounds from this work. 226
Figure 8-29: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for arsine compounds. 227
Figure 8-30: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for boron compounds. 228

Figure 8-31: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for silicon compounds. 229

Figure 8-32: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for multi-functional compounds. 232

Figure 8-33: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for multi-functional compounds. 233

Figure 8-34: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for multi-functional compounds. 234

Figure 8-35: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for multi-functional compounds. 235

Figure 8-36: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for multi-functional compounds. 236

Figure 8-37: Plot of experimental and estimated ΔH^v for acetone 242

Figure 9-1: Screen shot of the form employed to manage data verification. 248

Figure 9-2: Flow diagram of the procedure employed to manage data verification.... 253

Figure 9-3: Series plot of experimental and estimated liquid viscosities for n-alkanes using adjusted reference temperatures. 259

Figure 9-4: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for cyclic alkanes. 260

Figure 9-5: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for alkenes 261

Figure 9-6: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for aromatic compounds 262

Figure 9-7: Plot of adjusted and estimated viscosity reference temperatures for n-alkanes. 265

Figure 9-8: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for 1-alcohols. 269

Figure 9-9: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for secondary alcohols. 270

Figure 9-10: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for tertiary alcohols. 271

Figure 9-11: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for aromatic alcohols. 272

Figure 9-12: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for alkane diols. 273

Figure 9-13: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for ethers. 276

Figure 9-14: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for esters 277

Figure 9-15: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for carboxylic acids 278

Figure 9-16: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for primary amines 282

Figure 9-17: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for cyanides 283

Figure 9-18: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for nitrous or nitrate compounds 284

Figure 9-19: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for primary amines 285

Figure 9-20: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for sulphur compounds 288

Figure 9-21: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for sulphur compounds 289

Figure 9-22: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for sulphur compounds 290

Figure 9-23: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for fluorines. 293

Figure 9-24: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for chlorines. 294

Figure 9-25: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for bromines. 295

Figure 9-26: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for iodines. 296

Figure 9-27: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for phosphates 299

Figure 9-28: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for boron compounds. 300

Figure 9-29: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for silicon compounds. 301

Figure 9-30: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for acid chlorides. 302

Figure 9-31: Plot of adjusted ('experimental') and estimated viscosity reference emperatures for silicon compounds connected to electronegative atoms. 303

Figure 9-32: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for multi-functional compounds. 307

Figure 9-33: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for multi-functional compounds. 308

Figure 9-34: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for multi-functional compounds. 309

Figure 9-35: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for multi-functional compounds. 310

Figure 9-36: Series plot of experimental and estimated liquid viscosities for 1-alcohols from this work. 313

Figure 9-37: Series plot of experimental and estimated liquid viscosities for mono-functional carboxylic acids from this work. 314

Figure 9-38: Plot of adjusted ('experimental') and estimated viscosity reference temperatures for n-alkanes. 315

Figure 9-39: Fraction of the data with deviations for viscosity reference temperature larger than a given temperature. 317

Figure 11-1: Plot of estimated T_m, experimental T_m and T_b as a function of molecular weight for n-alkanes. 326

Figure 11-2: Plot of estimated T_m, experimental T_m and T_b as a function of molecular weight for 1-alcohols. 327

Figure 11-3: Plot of dipole moments for n-alkanes and 1-alcohols as a function of molecular weight. 336

Figure 11-4: Plot of normal boiling temperature for n-alkanes and 1-alcohols as a function of molecular weight. 336

Figure 11-5: Plot of solid and liquid vapour pressures for benzene. 340

List of Tables

Table 2-1: Overview of Group Contribution Methods for Critical Properties............ 10
Table 2-2: Critical property deviations for all methods. 30
Table 5-1: Comparison of boiling points of alkanes, ethers, alcohols and amines Atkins (1994) 93
Table 5-2: Typical potential energies of charges and dipoles Atkins (1994) 95
Table 6-1: Summary of DDB pure component property data bank (2006)................. 111
Table 7-1: Critical temperature average absolute deviations (K) of the models for the different types of hydrocarbons.. 134
Table 7-2: Critical pressure average absolute deviations (kPa) of the models for different types of hydrocarbon compounds... 135
Table 7-3: Critical volume average absolute deviations (%) of the models for different types of hydrocarbon compounds. 136
Table 7-4: Critical temperature average absolute deviations (K) for branched hydrocarbons 137
Table 7-5: Critical pressure average absolute deviations (kPa) for branched hydrocarbons 137
Table 7-6: Critical volume average absolute deviations (%) for branched hydrocarbons 137
Table 7-7: Critical temperature average absolute deviations (K) for isomeric alkanes 138
Table 7-8: Critical pressure average absolute deviations (kPa) for isomeric alkanes138
Table 7-9: Critical volume average absolute deviations (%) for isomeric alkanes 138
Table 7-10: Critical temperature average absolute deviations (K) of the models for different types of alcohol compounds.. 140
Table 7-11: Critical pressure average absolute deviations (kPa) of the models for different types of alcohol compounds.. 141
Table 7-12: Critical volume average absolute deviations (%) of the models for different types of alcohol compounds.. 141
Table 7-13: Critical temperature average absolute deviations (K) of the models for different types of oxygen (except alcohol) compounds........................... 142

Table 7-14: Critical pressure average absolute deviations (kPa) of the models for different types of oxygen (except alcohol) compounds. 143

Table 7-15: Critical volume average absolute deviations (%) of the models for different types of oxygen (except alcohol) compounds. 144

Table 7-16: Critical temperature average absolute deviations (K) of the models for different types of nitrogen compounds. 145

Table 7-17: Critical pressure average absolute deviations (kPa) of the models for different types of nitrogen compounds. 146

Table 7-18: Critical volume average absolute deviations (%) of the models for different types of nitrogen compounds. 146

Table 7-19: Critical temperature average absolute deviations (K) of the models for different types of sulphur compounds. 147

Table 7-20: Critical pressure average absolute deviations (kPa) of the models for different types of sulphur compounds. 148

Table 7-21: Critical volume average absolute deviations (%) of the models for different types of sulphur compounds. 148

Table 7-22: Critical temperature average absolute deviations (K) of the models for different types of halogen compounds. 149

Table 7-23: Critical pressure average absolute deviations (kPa) of the models for different types of halogen compounds. 150

Table 7-24: Critical volume average absolute deviations (%) of the models for different types of halogen compounds. 150

Table 7-25: Critical temperature average absolute deviations (K) of the models for various other types of compounds. 152

Table 7-26: Critical pressure average absolute deviations (kPa) of the models for various other types of compounds. 152

Table 7-27: Critical volume average absolute deviations (%) of the models for various other types of compounds. 152

Table 7-28: Groups considered to be non-additive (group & ID(s) given in brackets) 153

Table 7-29: Critical temperature average absolute deviations (K) of the models for multi-functional compounds. 155

Table 7-30: Critical pressure average absolute deviations (kPa) of the models for multi-functional compounds. 155

Table 7-31: Critical volume average absolute deviations (%) of the models for multi-functional compounds. 156
Table 7-32: Model parameters for Equations 7-2 to 7-4. 161
Table 7-33: Critical property average absolute deviations for all models. 162
Table 7-34: Test set of experimental and estimated critical temperature [K] and pressure [kPa] for 28 compounds. 167
Table 7-35: Questionable group contribution values. 169
Table 7-36: Critical property deviations for all models for the different types of intermolecular forces. 170
Table 8-1: Vapour Pressure average absolute deviations of this work for the different types of hydrocarbons (number of data points as superscript). 184
Table 8-2: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for the different types of hydrocarbons (number of data points as superscript). 191
Table 8-3: Vapour Pressure average absolute deviations of this work for branched hydrocarbons (number of data points as superscript). 192
Table 8-4: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for branched hydrocarbons (number of data points as superscript). 192
Table 8-5: Vapour Pressure average absolute deviations of this work for the different types of alcohol compounds (number of data points as superscript). 200
Table 8-6: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for the different types of alcohol compounds (number of data points as superscript). 200
Table 8-7: Vapour Pressure average absolute deviations of this work for the different types of oxygen (except alcohol) compounds (number of data points as superscript). 205
Table 8-8: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for the different types of oxygen (except alcohol) compounds (number of data points as superscript). 206

Table 8-9: Vapour Pressure average absolute deviations of this work for the different types of nitrogen compounds (number of data points as superscript) 211
Table 8-10: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for the different types of nitrogen compounds (number of data points as superscript) 212
Table 8-11: Vapour Pressure average absolute deviations of this work for the different types of sulphur compounds (number of data points as superscript) 213
Table 8-12: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for the different types of sulphur compounds (number of data points as superscript). 213
Table 8-13: Vapour Pressure average absolute deviations of this work for the different types of halogen compounds (number of data points as superscript) 218
Table 8-14: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for the different types of halogen compounds (number of data points as superscript). 223
Table 8-15: Vapour Pressure average absolute deviations of this work for various other types of compounds (number of data points as superscript). 224
Table 8-16: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for various other types of compounds (number of data points as superscript). 225
Table 8-17: Vapour Pressure average absolute deviations of this work for multi-functional compounds (number of data points as superscript) 230
Table 8-18: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for multi-functional compounds (number of data points as superscript). 231
Table 8-19: Vapour pressure average absolute deviations of this work and correlative models for all compounds. 238
Table 9-1: Viscosity average absolute deviations of this work for the different types of hydrocarbons (number of data points as superscript). 263

Table 9-2: Viscosity average absolute deviations (%) of the Andrade and Vogel models for the different types of hydrocarbons (number of data points as superscript) ... 264

Table 9-3: Viscosity absolute average deviations of this work for the branched hydrocarbons (number of data points as superscript) ... 266

Table 9-4: Viscosity absolute average deviations (%) of the Andrade and Vogel models for branched hydrocarbons (number of data points as superscript). ... 266

Table 9-5: Viscosity average absolute deviations of this work for the different types of oxygen compounds (number of data points as superscript). ... 267

Table 9-6: Viscosity average absolute deviations (%) of the Andrade and Vogel models for the different types of oxygen compounds (number of data points as superscript) ... 268

Table 9-7: Viscosity average absolute deviations of this work for the different types of oxygen (except alcohol) compounds (number of data points as superscript). ... 274

Table 9-8: Viscosity average absolute deviations (%) of the Andrade and Vogel models for the different types of oxygen (except alcohol) compounds (number of data points as superscript). ... 275

Table 9-9: Viscosity average absolute deviations of this work for the different types of nitrogen compounds (number of date points as superscript). ... 280

Table 9-10: Viscosity average absolute deviations (%) of the Andrade and Vogel models for the different types of nitrogen compounds (number of date points as superscript) ... 281

Table 9-11: Viscosity average absolute deviations of this work for the different types of sulphur compounds (number of data points as superscript). ... 286

Table 9-12: Viscosity average absolute deviations of the Andrade and Vogel models for the different types of sulphur compounds (number of data points as superscript). ... 287

Table 9-13: Viscosity average absolute deviations of this work for the different types of halogen compounds (number of data points as superscript) ... 291

Table 9-14: Viscosity average absolute deviations of the Andrade and Vogel models for the different types of halogen compounds (number of data points as superscript). ... 292

Table 9-15: Viscosity average absolute deviations of this work for the various other types of compounds (number of data points as superscript). 297

Table 9-16: Viscosity average absolute deviations (%) of the Andrade and Vogel models for various other types of compounds (number of data points as superscript)........ 298

Table 9-17: Viscosity average absolute deviations of this work for multi-functional compounds (number of data points as superscript). 305

Table 9-18: Viscosity average absolute deviations (%) of the Andrade and Vogel models for multi-functional compounds (number of data points as superscript)........ 305

Table 9-19: Liquid viscosity average absolute deviations of this work and correlative models for all compounds........ 311

Table 11-1: Normal boiling temperature average absolute deviations (K) for the different approaches in modelling the dipole moment. 338

Table A-1: Group Contributions for Lydersen (1955) & Riedel (1949) 367

Table A-2: Group Contributions for Ambrose (1978a), (1979). 368

Table A-3: Group Contributions for Daubert (1980) 370

Table A-4: Group Contributions for Klincewicz & Reid (1984) 374

Table A-5: Group Contributions for Joback & Reid (1987)........ 375

Table A-6: Group Contributions for Somayajulu (1989)........ 377

Table A-7: First order Group Contributions for Constantinou & Gani (1994)........ 383

Table A-8: Second order Group Contributions for Constantinou & Gani (1994)... 386

Table A-9: Group Contributions for Tu (1995)........ 387

Table A-10: Group (Bond) Contributions for Marrero-Morejon & Pardillo-Fontdevilla (1999). 388

Table A-11: Group-Adjacent Atom Pair Contributions for Wen & Quiang (2001).. 394

Table A-12: Group Contributions for Wen & Quiang (2001) 399

Table A-13: Group Contributions for Tu (1994) 400

Table A-14: Structural correction constants (ξ_1) for Tu (1994)........ 403

Table A-15: Structural correction values for nonring q_1 for Tu (1994) 403

Table A-16: Structural correction values for ring q_1 for Tu (1994) 403

Table A-17: Correction values for ξ_2 and q_2 for Tu (1994) 404

Table A-18: Group contributions for Orrick & Erbar (1974)........ 404

Table A-19: Group contributions for Van Velzen *et al.* (1972)........ 405

Table A-20: Configurational factors for Van Velzen *et al.* (1972) ... 406
Table A-21: Group contributions and functions for Skubla (1985) ... 407
Table A-22: Contribution of hydrocarbon groups for Sastri & Rao (1992) ... 410
Table A-23: Contribution of hydrocarbon ring structures (chain length) for Sastri & Rao (1992) ... 411
Table A-24: Contribution of halogen groups for Sastri & Rao (1992) ... 412
Table A-25: Contribution of oxygen groups Sastri & Rao (1992) ... 413
Table A-26: Contribution of hydroxyl groups for Sastri & Rao (1992) ... 414
Table A-27: Contribution of nitrogen groups for Sastri & Rao (1992) ... 415
Table A-28: Contribution of sulphur groups for Sastri & Rao (1992) ... 416
Table B-1: Group definitions (ID- identification number, PR - priority) ... 417
Table B-2: Second order groups and corrections ... 427
Table C-1: Critical temperature group contributions, number of components used for regressing these values and deviations for these components ... 429
Table C-2: Critical temperature second-order contributions, number of components used for regressing these values and deviations for these components. ... 432
Table C-3: Critical temperature group interaction contributions, interacting groups, number of components used for regressing these values and deviations for these components ... 432
Table C-4: Critical pressure group contributions, number of components used for regressing these values and deviations for these components ... 433
Table C-5: Critical pressure second-order contributions, number of components used for regressing these values and deviations for these components. ... 436
Table C-6: Critical pressure group interaction contributions, interacting groups, number of components used for regressing these values and deviations for these components ... 437
Table C-7: Critical volume group contributions, number of components used for regressing these values and deviations for these components ... 438
Table C-8: Critical volume second-order contributions, number of components used for regressing these values and deviations for these components. ... 440

Table C-9: Critical volume group interaction contributions, interacting groups, number of components used for regressing these values and deviations for these components. 441

Table C-10: Vapour-liquid equilibrium curve slope (*dB*) group contributions, number of components used for regressing these values and deviations for these components. 441

Table C-11: Vapour-liquid equilibrium curve slope (*dB*) second-order contributions, number of components used for regressing these values and deviations for these components. 445

Table C-12: Vapour-liquid equilibrium curve slope (*dB*) group interaction contributions, interacting groups, number of components used for regressing these values and deviations for these components. 446

Table C-13: Saturated liquid viscosity curve slope (*dBv*) group contributions, number of components used for regressing these values and deviations for these components. 447

Table C-14: Saturated liquid viscosity curve slope (*dBv*) second-order contributions, number of components used for regressing these values and deviations for these components. 450

Table C-15: Saturated liquid viscosity curve slope (*dBv*) group interaction contributions, interacting groups, number of components used for regressing these values and deviations for these components. 451

Table C-16: Saturated liquid viscosity reference temperature (T_v) group contributions, number of components used for regressing these values and deviations for these components. 452

Table C-17: Saturated liquid viscosity reference temperature (T_v) second-order contributions, number of components used for regressing these values and deviations for these components. 455

Table C-18: Saturated liquid viscosity reference temperature (T_v) group interaction contributions, interacting groups, number of components used for regressing these values and deviations for these components. 456

Table D-1: Estimation of the critical temperature (T_c) of 2,2,3,3-tetramethylbutane ... 459

Table D-2: Estimation of the critical pressure (P_c) of diethylene glycol monomethyl ether 460

Table D-3: Estimation of the critical volume (V_c) of trichloro silane........................ 461

Table D-4: Estimation of vapour-liquid equilibrium curve slope (*dB*) of perfluoro-2-propanone and liquid vapour pressure at 210.16K................................ 462

Table D-5: Estimation of saturated liquid viscosity curve slope (*dBv*) and reference temperature (T_v) of N,N-Diethylamine and liquid viscosity at 308.15K 463

Nomenclature[*]

a, b, c, d, e, f - adjustable parameters

C - first-order group contribution

dB - saturated liquid vapour pressure curve slope

dBv - saturated liquid viscosity curve slope

D - second-order group contribution

E - activation energy

G - gibbs energy

H - enthalpy

L - frequency of second-order group

M - molecular weight

n - number of atoms

N - frequency of first-order group

P - pressure

q - heat

r - distance from centre of molecule

R - universal gas constant

S - entropy

T - absolute temperature

U - internal energy

V - volume

W - work

Z - compressibility

Greek letters

ρ - density

μ - viscosity

μ' - dipole moment

μ'' - chemical potential

---

[*] All equations and variables are in SI units unless otherwise stated. Other symbols used are explained in the context of this work.

ω - acentric factor

Subscripts

b - boiling point
c - critical point
calc - calculated
est - estimated
l - liquid
m - melting
trans - translation
v - vapour

Superscripts

m - fusion
r - reference value
s - saturated
V - vaporization

Chapter One

Introduction

An airplane cannot lift-off without knowing the weather conditions. A lawyer cannot defend a client without knowing the crime committed. A civil engineer cannot build a tunnel without knowledge of the materials. In the same way, a chemical engineer cannot design a chemical plant without knowledge of the properties of the raw materials, products and expected by-products. The basis for any design and simulation of chemical, biochemical and environmental systems is a set of physical-chemical pure component and mixture properties.

Some engineers may perceive that properties are readily available or easily obtainable for most pure components. This is far from the truth since only a minuscule portion of chemicals have a full complement of pure component property data. Even though a large amount of data have been tabulated and correlated over the years, the rate of discovery of newer chemicals from advancement of new technology into many different and new systems is always higher than the rate at which they are measured. There is also the rapid growth in the field of combinatorial chemistry where literally millions of new compounds are synthesized and tested. Knowledge of the properties of these compounds is required to handle or separate them. Thus there are a vast number of components and experimental property data are available for relatively few.

Current physical property databases typically hold experimental data for several thousand substances. The Dortmund Data Bank (DDB (2006)), which is the primary basis of this work, contains experimental data, molecular structures and auxiliary parameters for more than 20,000 chemicals of industrial interest. The experimental data collection alone contains more than 2.5 million data tuples (data points, table lines). Pure component data alone cover more than 1 million data points.

The problem associated with obtaining experimental data for components is not always that these data cannot be measured, but mostly that it is difficult or time-consuming to synthesize the required amounts of sufficiently pure material for the experiment. In fact, measurement of these properties is in many cases cheaper than the effort to obtain even a small quantity of the pure chemical. There have been many novel apparatuses developed in recent years that can measure properties using only small samples of a pure component. The problem is that the synthesis of the chemical is time-consuming and can range from a time period of weeks to months. Many chemicals are also hazardous to handle or of limited thermal stability which makes experimental measurements difficult or even impossible.

There will always be a significant gap between demand and availability of data. For this reason, estimation methods are of great value to an engineer and knowledge about and experience with the various methods is of great importance.

There are currently many estimation methods available for a wide variety of properties. A great part of these methods is based on the group contribution concept. In many cases the group parameters were derived from the data of a relatively small number of components. Some of these methods employ purely correlative approaches without a careful analysis of the physically meaningful boundary conditions which subsequently leads to unrealistic results when the method is applied to data outside the training set (regression set).

Modern process simulation software employs various data correlations for the estimation of physical properties. However, a proper understanding of the thermodynamic assumptions underlying these correlations is needed to ensure proper application. This is also discussed by Chen *et al.* (2004) who examined the unmet needs of clients using the popular Aspen-Plus process simulator. They welcome estimation methods that employ datasets consisting of larger and more complex compounds. They also suggest that chemists and engineers have a professional scepticism about estimations methods, particularly concerning methods derived from molecular modelling and quantum mechanics. The use of experimental data not only improves the prediction but also raises the confidence level of the user.

Recently, Nannoolal (2004) & Nannoolal *et al.* (2004) proposed an estimation method for the normal boiling point that was shown to be the most accurate and has a wide range of applicability. This method is based on the group contribution approach. In addition, it is the only method that can estimate the normal boiling point of multi-functional compounds with a fair degree of accuracy by means of a group interaction approach. Following this method, it is the aim of this work to develop further estimation methods for vapour-liquid critical properties, saturated liquid vapour pressures and saturated liquid viscosities.

The first objective of this work is to develop a new estimation method for the critical temperature, pressure and volume of organic compounds with a wide range of applicability and to give a detailed analysis of its performance compared to previously published methods. Without further specification, "critical" in this work denotes the vapour-liquid critical point.

Critical properties, viz. critical temperature, critical pressure and critical volume, are of great practical importance as they are the basis for the estimation of a large variety of thermodynamic, volumetric and transport properties using the corresponding states principle. In addition, critical temperature and pressure data provide valuable information for the regression and prediction of vapour pressures at high temperature and are required by equations of state for the description of pure component and mixture behaviour.

Experimental determination of critical property data is difficult and in many cases impossible, since especially the larger and strongly associating components decompose (chemically degrade) before the critical point is reached. This means that experimental data are usually only available for smaller molecules. It is therefore vital that prediction methods be developed which are capable of not only reasonably accurate predictions, but which are also reliable with a low probability of failure when applied to extrapolation.

The second objective of this work is to develop a new estimation method for the saturated liquid vapour pressure curve of organic compounds with an accuracy that is comparable to correlative models.

The vapour pressure of a pure component is an important thermodynamic property and of fundamental interest in process design, simulation and optimisation. Recently, awareness has also been raised of the impact of pollutants on the environment where knowledge about the vapour pressure is required for the calculation of the liquid-air distribution coefficient. There is currently an abundance of experimental data for vapour pressures of smaller molecules but data is scarce or of low quality for larger and more complex molecules of low volatility. Thus predictive methods are often required to solve problems of practical importance.

Attempts to estimate liquid vapour pressures from molecular structure have met with limited success. The reason is that high quality predictions are needed for vapour pressures since it is one of the key properties for the design of, for example, distillation columns. Thus correlative techniques that require experimental data to obtain model parameters are usually the preferred means for vapour pressure calculations. Main disadvantages of these models are that they depend on the availability and experimental validity of the data and can only be used to extrapolate over limited temperature intervals.

The final objective of this work is to develop a new estimation method for the saturated liquid viscosity of organic compounds as a function of temperature with an accuracy comparable to that of correlative models. In addition, the method should be more accurate than currently used group contribution estimation methods and must be able to extrapolate with respect to temperature and chemical constitution.

The saturated liquid viscosity is an important transport property that has many engineering applications such as the design of pumps, pipelines, etc. Unfortunately, experimental data are limited to mostly simple and more common components and, even for these components the data cover only a small temperature range.

There have been many different approaches to estimate liquid viscosities of organic compounds from molecular structure. So far, fundamental theoretical methods have met with little success and no theory is available to calculate liquid viscosity from molecular properties. Thus, correlative and empirical relations are often the only means to obtain liquid viscosities. Correlative techniques, as in case of liquid vapour pressure, require experimental data to regress model parameters and cannot extrapolate over large temperature ranges. Empirical methods that use knowledge of only the molecular structure are usually only applicable to a few homologous series and report high uncertainty when applied to different types of components. Unfortunately, in some cases, these methods present the only possibility to estimate the liquid viscosity and are therefore quite commonly used.

No aspect of this work would have been possible without the availability of a large amount of experimental data, molecular structures of components involved, algorithms for the analysis and fragmentation of molecular structures using group definitions and software for data retrieval and correlation. All these were available through the DDB and the integrated software system (DDBSP).

Data were continuously entered into the DDB after work on the data bank started in 1973. The pure component property database was built up between 1991 and 1996 at the University of Oldenburg in Germany in co-operation with groups in Prague, Tallinn, Minsk, Berlin and Graz and has been further extended by DDBST GmbH since then.

For the development of the methods and tools described in this work, full access to the DDB and DDBSP was granted by DDB Software and Technology (DDBST GmbH) in Oldenburg. Whenever required, programmers at DDBST GmbH assisted in various ways. The methods developed in this work are all available within DDBSP and are used by many engineers worldwide.

During the development of the different estimation methods within this work, a large number of property estimations were performed for the new and available literature methods and compared to the experimental results stored in the DDB. Based on these results a quality assessment system was developed in order to assist the engineer in selecting the most suitable method. At the same time, this software presents information about the mean expected error in the estimated property for the respective component class. The procedure is based on a set of filter definitions that allow one to deduce the chemical "families" a component belongs to from the molecular structure.

The following chapters will give an introduction to the individual properties covered in this work and describe available estimation methods from literature and the development of the new methods. The results of the new methods will be analysed and compared to several previous methods.

The final chapter contains recommendations for further developments based on the experiences from this work.

Chapter Two

Critical Properties

2.1 Introduction

It may seem, in the ever-broadening field of chemistry and chemical engineering, that important data such as vapour pressures, heats of vaporisation, densities, heat capacities, etc, as well as other data required for the design of unit operations are readily available. However, when the literature is consulted, often very little or no data can be found. It therefore becomes the job of the engineer to estimate these types of data to the best of his knowledge. As a result, many useful and relatively accurate correlations have been developed to predict the above mentioned properties. The problem is that most of these correlations (in particular, correlations based on corresponding states principles) require knowledge of the critical point of the compound, even though properties near the critical point are mostly not needed for practical application. All components exhibit the same striking anomalies like infinite heat capacity and compressibility at the critical point. The critical point serves as the most commonly used reference point in corresponding states methods and a vast number of estimations methods based on the molecular structure of a compound are available.

This chapter will firstly present a brief review covering the phenomena of a substance at its critical point. The next part of the chapter will provide a detailed literature review on estimation methods for critical properties.

2.2 Brief History

The phenomenon of the critical point was discovered in 1822 by Tour De La (1822), (1823), who rolled a ball within a heated closed cannon barrel and noted the difference in the sound when the substance was a liquid and when it was a gas. Schmidt (1823) then predicted the critical point on the basis that there would be no latent heat of vaporisation. Skipping forward to more then a century later, Andrews (1869) discovered the essential conditions for the liquefaction of gases. Prior to this time, many investigators had tried unsuccessfully, to liquefy gases by the application of pressure and had come to the erroneous conclusion that there existed certain "permanent" gases which could not be liquefied. Andrews found that carbon dioxide could not be liquefied above 31.1 °C, even though a pressure of 300-400 atm was applied.

Further investigations led to the concept that each gas has a temperature, above which the gas cannot be liquefied regardless of the applied pressure. This led to the discovery of the critical point whereby the critical temperature (T_c) is defined as the minimum temperature of a gas at which it cannot be liquefied no matter how high the pressure. The critical pressure (P_c) (vapour pressure) is the lowest pressure which will liquefy the gas at its critical temperature. The critical molar volume (V_c) is the volume of 1 mol of the substance at the critical temperature and pressure. The critical pressure, critical volume, and critical temperature are the values of the pressure, molar volume, and thermodynamic temperature at which the densities of the coexisting liquid and gaseous phases become identical. The critical compressibility factor (Z_c) can be calculated from Equation 2-1. Other definitions also include the critical density (ρ_c), which is directly computed from the critical volume (Equation 2-2).

$$Z_c = \frac{P_c V_c}{R T_c} \tag{2-1}$$

$$\rho_c = \frac{M}{V_c} \tag{2-2}$$

The kinetic theory of gases considers two forces which act on the molecules of a gas, viz. the potential force of attraction and the kinetic force of translation. The potential force is a force which tends to cause the molecules to coalesce and form a liquid, whereas the kinetic force tends to separate the molecules into the random distribution associated with the gaseous state of matter. Since only the latter is a strong function of temperature, there is a temperature at which the kinetic energy of translation is equal to the maximum potential energy of attraction. At any temperature greater than that, only the gaseous phase can exist. An excellent analysis of the critical point, experimental apparatuses and correlations is provided by Kobe & Lynn (1953).

The difficulty with obtaining critical properties is that most components are not sufficiently stable at or near the critical temperature, and as a result experimental measurements of their critical properties are extremely difficult, if not impossible. It is therefore vital that prediction methods be developed which are capable of not only reasonably accurate predictions, but which are also reliable with a low probability of failure when extrapolating. The critical point is also difficult to capture by molecular simulation due to the very large autocorrelation length at or near this state.

2.3 Critical Properties Literature Review

2.3.1 Overview of Available Critical Property Estimation Methods

Since the first developments of group contribution methods by Riedel (1949) and Lydersen (1955), a large number of methods have been developed for the estimation of critical property data. While also various different approaches can be found in literature, the use of group contribution still seems to provide the most reliable and simple approach with which to obtain reliable results. There is a variety of estimation methods for critical property data available in the open literature. A broad overview of these methods together with a detailed discussion of their reliability was given by Poling *et al.* (2000) and earlier versions, Reid *et al.* (1987) and Reid & Sherwood (1958). In addition, several authors have evaluated the performance of models utilizing a large common set of experimental data (Yan *et al.* (2003)).

In this work, the comparison to other generally applicable methods is restricted to those which are based on the group contribution concept and are applicable over a wide range of components. Table 2-1 gives an overview on the timeline of previous major developments in group contribution methods for critical properties. Due to their practical and theoretical importance, estimation of critical properties has attracted much interest of researchers from all over the world. Critical property estimation methods restricted to individual classes of components (such as n-alkanes) were excluded from Table 2-1.

Table 2-1: Overview of Group Contribution Methods for Critical Properties

Year	Reference	Additional Information	Abbr.
1949	Riedel (1949)	-	RI
1955	Lydersen (1955)	T_b	LD
1978	Ambrose (1978a)	T_b	-
1979	Ambrose (1979)	T_b	AB
1980	Daubert (1980)	T_b	DB
1982	Fedors (1982)	-	-
1984	Joback (1984)	T_b	-
1984	Klincewicz & Reid (1984)	T_b	KR
1986	Somayajulu (1989)	T_b	SJ
1987	Joback & Reid (1987)	T_b	JR
1994	Constantinou & Gani (1994)	-	CG
1995	Tu (1995)	-	CT
1996	Wilson & Jasperson (1996)	T_b	WJ
1999	Marrero-Morejon & Pardillo-Fontdevilla (1999)	T_b	MP
2001	Marrero-Morejon & Gani (2001)	T_b	-
2001	Wen & Quiang (2001)	T_b	WQ

In addition to the methods given in Table 2-1, numerous publications cover the use of QSPR (Quantitative Structure Property Relation) correlations and popular mathematical methods like neural networks for critical property estimation. While the correlative power of these approaches has been demonstrated in many cases, the extrapolative ability of these methods is not convincing, especially to conditions well outside the training set.

Classical estimation techniques can be divided into those which require only the molecular structure and others which require further relevant properties. For typical organic compounds of interest, the ratio of T_c/T_b is often within the range of 1.4 ± 0.3. Thus knowledge of the normal boiling temperature greatly simplifies critical temperature estimation. If experimental normal boiling point or vapour pressure information is not available, group contribution estimation for this auxiliary property can be employed. These estimations are usually of better quality and have a greater range of applicability due to the much larger set of experimental data available for these properties, for example, reliable critical temperatures can be found for approximately 600 components, whilst experimental normal boiling point data in the open literature cover more than 18000 substances.

Besides the simple group additivity schemes, a number of more complex estimation routes using topological indices, Ambrose (1978a), (1979) or bond interactions, Marrero-Morejon & Pardillo-Fontdevilla (1999) will also be presented in this review.

The comparative study proposed in this work will follow similar studies undertaken by a collaboration of many researchers, Ambrose & Young (1995), Tsonopoulos & Ambrose (1995), Ambrose & Tsonopoulos (1995), Gude & Teja (1995), Daubert (1996), Tsonopoulos & Ambrose (1996), Tsonopoulos & Ambrose (2001) and Kudchadker *et al.* (2001) as well as a separate study by Yan *et al.* (2003). The difference is that, firstly, a greater number of methods will be included in this comparative study. Most of the available methods have already been implemented in the software package Artist, Cordes *et al.* (1993), which is part of the DDBSP. Estimation results were compared with a critically evaluated database in order to develop an expert system for the selection of the best model for a specific type of component. Model implementations were carefully verified, partly in cooperation with the authors.

Secondly, a re-engineered quality analysis, which was developed previously in Nannoolal (2004) & Nannoolal *et al.* (2004), will provide a more detailed and in-depth classification of organic compounds than the previous comparatives studies. These extensive comparative results should be of great value for users who rely on critical property estimation for process simulation, risk assessment or environmental models.

This chapter will briefly introduce the available methods used in this study, while a continuation of the comparative study will be undertaken in Chapter 7. The Wilson and Jasperson method will not be included as part of this study as it requires additional information apart from structure and boiling point, viz. density, and so is outside the scope of this work.

2.3.2 Lydersen (1955) & Riedel (1949)

Guldberg (1890) was the first to observe that the critical temperature can be approximated by Equation 2-3, which can also be referred to as the *Guldberg Rule*:

$$T_c = 1.5T_b \tag{2-3}$$

Riedel (1949), Vowles (1951) and Lydersen (1955) had proposed modifications of the Guldberg rule, as in the form of Equation 2-4.

$$T_c = \frac{T_b}{\theta} \tag{2-4}$$

The value of θ is generally different for each compound and can be calculated by summing up structural contributions. Vowles (1951) proposed that θ can be calculated by summing atomic contributions (also known as the zero-order or elemental contributions). This form of structural contributions is of poor accuracy and will not be considered further in this work.

Prior to Vowles, Riedel (1949) proposed 22 simple first-order groups, presented in Table A-1. Equation 2-5 was then used to calculate θ for the estimation of the critical temperature. For the critical pressure, Riedel used a combination of atomic and group contributions together with Equation 2-6. These contributions will not be presented here.

$$\theta = 0.574 + \sum_i N_i C_i \tag{2-5}$$

$$P_c = \frac{M}{(0.33 - \sum_i N_i C_i)^2} \tag{2-6}$$

Lydersen (1955) extended Riedel's method by incorporating a larger set of groups and experimental data. These groups can be found in Table A-1 in Appendix A. Lydersen also proposed a quadratic equation to estimate θ. This is presented in Equation 2-7 for the estimation of critical temperature. Equations 2-6 (with 0.34 instead of 0.33) and 2-8 are used for the estimation of critical pressure and volume, respectively. The latter two equations have become a standard, employed by many other researchers.

$$\theta = 0.567 + \sum_i N_i C_i - \left(\sum_i N_i C_i \right)^2 \tag{2-7}$$

$$V_c = 40 + \sum_i N_i C_i \tag{2-8}.$$

For the Lydersen method, an average absolute error of 10.7 K (1.71%) in critical temperature for a set of 557 components, 228 kPa (7.07%) in critical pressure for 474 components and 30.7 $cm^3.mol^{-1}$ (5.27%) in critical volume for 327 components was reported. The Riedel and Lydersen methods are among the oldest group contribution methods. The former method will not be used in the comparative study in this work since interest in this method is only for historical reasons. An extension based on a larger set of data was prepared by Joback & Reid (1987), and consequently a detailed discussion will be presented with the Joback and Reid method later on.

2.3.3 Ambrose (1978a), (1979)

In this method, the critical temperature, critical pressure and critical volume are estimated by Equations 2-9, 2-10 and 2-11, respectively. For perfluorinated compounds or compounds that contain halogens, the constant 1.242 is replaced by 1.570 in Equation 2-9, and the constant 0.339 is replaced by 1 in Equation 2-10.

$$T_c = T_b\left(1+\frac{1}{1.242+\sum_i N_iC_i}\right) \tag{2-9}$$

$$P_c = \frac{M}{(0.339+\sum_i N_iC_i)^2} \tag{2-10}$$

$$V_c = 40+\sum_i N_iC_i \tag{2-11}$$

The critical temperature model employed by Ambrose assumes that with increasing molecular weight, the critical temperature approaches the normal boiling point. The critical temperature has no relation to and is not governed by the normal boiling point and it should be considered possible for the critical temperature to be lower than the normal boiling point. However, this hypothesis cannot be proven since molecules that would exhibit this behaviour are long chain components (for example, polymers) that would readily decompose before either temperature is reached. It would therefore be an interesting alternative to regress for the constant, instead of assuming a value of 1.

Figure 2-1 shows estimated n-alkane critical temperatures for the Ambrose and various other methods (acronyms for all methods are given in Table 2-1) as a function of the number of carbon atoms. In this plot, the largest n-alkane that has an experimental critical temperature has less than 30 carbon atoms and all estimations are presented in the plot. For larger compounds, estimations were based on compounds with 30, 40, 50, 75, 100 and 150 carbon atoms and a smooth line was employed to draw the curve. Thus, the estimations between the intervals may not be correct, but these values are not required as the aim of the plot is just to demonstrate the extrapolative capabilities of the models used. For compounds with no experimental normal boiling points, values were estimated from Nannoolal (2004) & Nannoolal *et al.* (2004).

The plot provides insight into the extrapolation behaviour of the models for the case of n-alkanes. As the plot is derived from the functional form of the model equations, similar trends can be expected for other types of molecules. In the case of the Ambrose method, the extrapolation shows no physically unrealistic estimations.

The group contributions employed by Ambrose are presented in Table A-2. Within this table is a topological index, called the delta Platt number. This index is defined as the Platt number of the isomer minus the Platt number of the corresponding alkane, where the Platt number is the total number of carbon atoms three bonds apart, Platt (1947), (1952). For example, the Platt number of n-alkanes is the number of carbon atoms minus one. The use of this index is to distinguish between isomers and sterically hindered molecules. Similar parameters were developed by Nannoolal (2004). These parameters, referred to as the steric parameters, will be presented later on.

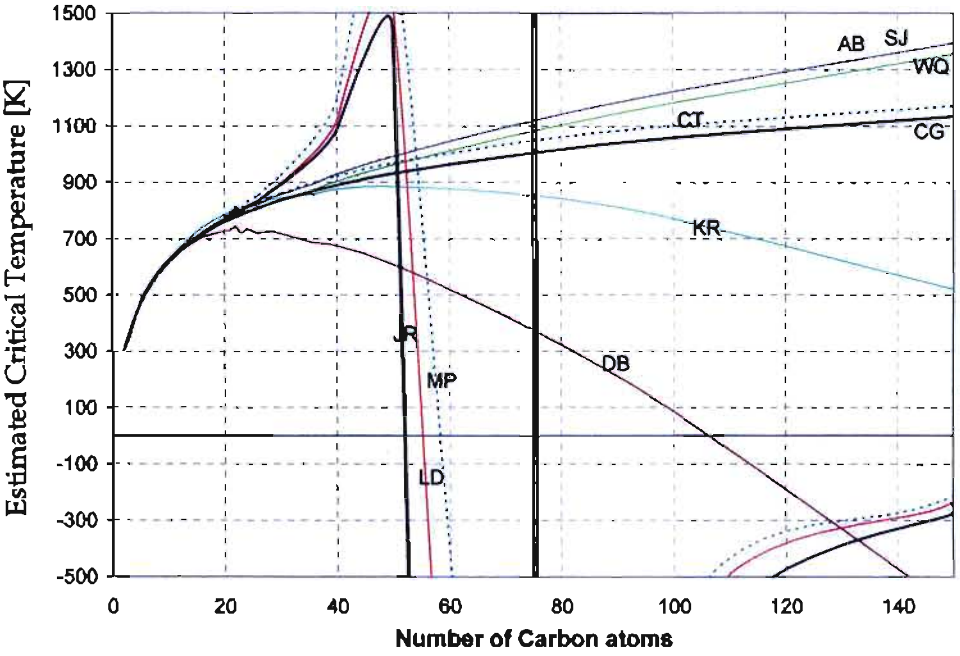


Figure 2-1: Estimated critical temperature of n-alkanes as a function of number of carbon atoms for the different models (AB and SJ overlap).

For the Ambrose method, an average absolute error of 6.0 K (1.07%) in critical temperature for a set of 528 components, 253 kPa (7.03%) in critical pressure for 412 components and 19.4 $cm^3.mol^{-1}$ (4%) in critical volume for 327 components was found.

2.3.4 Daubert (1980)

In this method, only the critical temperature and critical pressure are estimated and are given by Equations 2-12 and 2-13, respectively. For the critical temperature, an unrealistic linear relationship with the normal boiling point is assumed. In addition, the model has two competitive (intercorrelating) terms and extrapolation can be negatively affected by incorrect weighting of these terms. This is shown graphically in Figure 2-1, where the extrapolation shows unrealistic values. For the critical pressure model, both the critical temperature and normal boiling point are required.

$$T_c = 1.806T_b - \sum_i N_i C_i \tag{2-12}$$

$$P_c = \frac{1000T_c^3}{T_b^2(43.387 + \sum_i N_i C_i)} \tag{2-13}$$

Daubert classified structural groups by predefining the bonded neighbours of each group. This classification severely limits the range of applicability of the method and questions the extrapolation as many groups are redundant. Overall, 106 groups were used in the method and are presented in Table A-3. This type of technique is also used in further methods which will be presented and discussed later on in this chapter.

For this method, an average absolute error of 23.9 K (3.87%) in critical temperature for a set of 475 components and 253 kPa (7%) in critical pressure for 352 components was found. The high error reported for the critical temperature estimation is mainly a result of the incorrect assumption of a linear relationship with the normal boiling point.

2.3.5 Klincewicz & Reid (1984)

In this method, the critical temperature, critical pressure and critical volume are estimated by Equations 2-14, 2-15 and 2-16, respectively. The critical pressure and critical volume models are the standard models. For critical temperature, Klincewicz and Reid employed three competitive terms (molecular weight, normal boiling point and sum of contributions in this case) and the extrapolation is incorrect (Figure 2-1).

$$T_c = 45.40 - 0.77M + 1.55T_b + \sum_i N_i C_i \tag{2-14}$$

$$P_c = \frac{M}{(0.335 + 0.010M + \sum_i N_i C_i)^2} \tag{2-15}$$

$$V_c = 25.2 + 2.80M + \sum_i N_i C_i \tag{2-16}$$

Klincewicz and Reid employed 35 groups (Table A-4) based on a set of 398, 290 and 207 components for critical temperature, critical pressure and critical volume, respectively. The table also contains one halogen correction which is based on the work of Cramer (1980). The correction accounts for exotic instances when there are many halogens on a single carbon. Nannoolal (2004) also introduced a similar correction, which will be presented later.

The introduction of the halogen correction for the Klincewicz and Reid method resulted in a more accurate prediction of halogen compounds when compared to all methods discussed in this chapter. For the Klincewicz and Reid method, an average absolute error of 7.8 K (1.27%) in critical temperature for a set of 547 components, 246 kPa (7.57%) in critical pressure for 452 components and 17.9 $cm^3.mol^{-1}$ (4%) in critical volume for 319 components was found.

2.3.6 Joback & Reid (1987)

Joback and Reid examined many different types of estimation equations requiring group-contributions and selected Equation 2-17, 2-18 and 2-19 for the prediction of the critical temperature, pressure and volume, respectively. They assumed no interaction between groups, and structurally-dependant parameters are thereby determined by summing the number frequency of each group multiplied by its contribution.

$$T_c = \frac{T_b}{0.584 + 0.965\sum_i N_i C_i - (\sum_i N_i C_i)^2} \quad (2\text{-}17)$$

$$P_c = \frac{1}{(0.113 + 0.0032n - \sum_i N_i C_i)^2} \quad (2\text{-}18)$$

$$V_c = 17.5 + \sum_i N_i C_i \quad (2\text{-}19)$$

They employed only 41 molecular groups, which oversimplifies the molecular structure thus making several types of isomers indistinguishable. Overall this is insufficient to capture the structural effects of organic molecules and is the main reason for the poor accuracy of the method. Table A-5 presents the 41 structural groups and their respective contributions for each property. These groups are similar to Lydersen (1955) with the omission of >Si< and >B-, but with the inclusion of =N-(ring).

The multiple linear regression technique carried out, employed 409, 392 and 310 components for critical temperature, critical pressure and critical volume, respectively. In the regression procedure, optimum values are generally obtained by minimizing the sum of squares of the absolute errors determined by the difference between the estimated and experimental property values. However, Joback and Reid suggested that minimizing the sum-of-squares of the errors weighted outliers too heavily, thus the sum of absolute errors was chosen. This led to slightly higher errors for such outliers but provides an improved estimation procedure for the majority of compounds. This is not particularly useful in property estimations (especially in the case of critical properties where the data sets are relatively small) as data for the smaller compounds or compounds which are the first in their homologous series are usually easily available. Estimations are usually carried out for larger, complex or multi-functional compounds.

From the three models employed by Joback and Reid, the critical temperature model is the weakest. It should be a norm that a binomial equation (or higher order polynomials) in group contribution estimations should only be used when it can be proven where the maximum or minimum appear. For critical temperatures, no maximum or minimum are observed as a function of molecular weight and the form of the model therefore shows an incorrect extrapolation (Figure 2-1).

The only advantage of the method is that it is the simplest to use; however, the relatively small range of compounds, poor predictions and unrealistic extrapolation of the method leads to its downfall. For this method, an average absolute error of 8.8 K (1.41%) in critical temperature for a set of 543 components, 238 kPa (7.11%) in critical pressure for 452 components and 16.5 cm^3.mol^{-1} (3.73%) in critical volume for 314 components was found. Many authors have, however, followed up the work of Joback and Reid making use of the groups as a starting point.

2.3.7 Somayajulu (1989)

Somayajulu re-examined the procedures of Riedel, Lydersen and Ambrose for the group contribution calculation of critical constants and proposed new procedures in terms of group indices. These procedures were also combined with those developed by Kreglewski (1961) and Kreglewski & Zwollinski (1961), (1966).

Kreglewski proposed the use of the number of carbon atoms of a compound instead of group contributions in the estimation of critical constants. This method is restricted to homologous series and will not be discussed here. Somayajulu employed this procedure but introduced the group index (n_i - where i denotes temperature (t), pressure (p) and volume (v)), Equation 2-20.

$$n_i = \frac{C_i}{C_i(CH_3)} \qquad (2\text{-}20)$$

The molecular index (N_i) is obtained by summing the individual group indices ($\sum n_i$). With this index, the critical temperature, critical pressure and critical volume are estimated by Equations 2-21, 2-22 and 2-23, respectively. These are the same models employed by Ambrose with similar constants as well.

$$T_c = T_b\left(1 + \frac{1}{1.242 + b_t N_t}\right) \qquad (2\text{-}21)$$
$$b_t = 0.138$$

$$P_c = \frac{M}{(0.339 + b_p N_p)^2} \qquad (2\text{-}22)$$
$$b_p = 0.226$$

$$V_c = 40 + b_v N_v \qquad (2\text{-}23)$$
$$b_v = 55$$

The method incorporates a massive 179 groups for a set of 600 compounds that include inorganic groups and compounds. Table A-6 presents the structural groups and their respective contributions for each property. From the table, the contribution of the CH_3 and CH_2 groups for all properties is 1. However, the b_i parameters in Equations 2-21 to 2-23 represent the contribution of both alkyl groups, which is the same as in the case of the Ambrose method. Consequently, for n-alkanes, both methods for estimating the critical temperature overlap.

This method is a purely correlative approach. Regression results were improved by the introduction of a large number of structural groups. The method also employs a large number of second-order corrections for branched hydrocarbons and halogens (not presented here). This "overfitting" may lead to large errors for components not in the training set. For this method, an average absolute error of 8.39 K (1.44%) in critical temperature for a set of 517 components, 295 kPa (9.51%) in critical pressure for 438 components and 20.1 $cm^3.mol^{-1}$ (4.14%) in critical volume for 307 components was found. The average error for the critical pressure and volume is the highest of all methods that have or will be presented in this chapter, while the critical temperature deviation is among the highest (See Table 2-2 in Section 2.3.13).

2.3.8 Constantinou & Gani (1994)

Second-order or second level approximations are a way to provide further information about the molecular structure of the compound, such that a significantly improved prediction of properties can be made. At the same time, if these contributions are not available, a less precise estimation is still possible using only the first-order groups.

Constantinou *et al.* (1993), (1994) and Constantinou (1993) provided an additive property estimation method, which is based on conjugate operators and applicable to organic compounds. However, the generation of conjugate forms is a non-trivial issue and requires a symbolic computing environment.

Constantinou & Gani (1994) applied the method of Constantinou *et al.* (1993), (1994) based on second order conjugate forms to the group contribution concept. The method proposed a property estimation, which is performed at two levels. The basic level has contributions from first-order functional groups and the next level has second-order groups, which have the first-order groups as building blocks. Thus, their method allows for both a first-order approximation (using first-order groups) and a more accurate second-order approximation (using both first- and second-order groups).

They had considered group contribution-based computational tools, which need to accommodate two separate first-order molecular-structure descriptions, one for the prediction of pure component properties (Reid *et al.* (1987) and Lyman *et al.* (1990)) and another for mixture property estimations (Derr & Deal (1969) and Fredenslund *et al.* (1977)). To circumvent this drawback, they proposed to use as first-order groups, Table A-7, the set of groups commonly used for the estimation of mixture properties (or UNIFAC groups). A disadvantage of this selection is that a group appearing in an aliphatic ring is considered equivalent to its identical non-ring one. These groups cannot distinguish between special configurations such as multiple groups located close to each other, resonance structures, etc. For each group definition, there also does not seem to be any theoretical basis. Therefore each group has a single contribution independent of the type of compound involved. In total, there were 78 first order groups, quite similar to those used by Joback and Reid; most of the new groups being sub-divisions and quite a few of them being redundant as well.

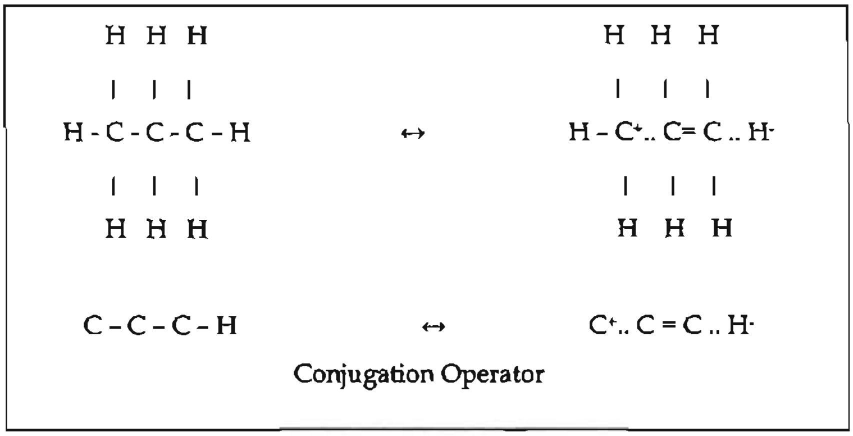
Since their estimation was primarily based upon information about the molecular structure only, the idea was to include a different level of approximation. Thus Constantinou and Gani introduced second-order groups to provide additional structural information about the compound. Their ultimate goal was to enhance the accuracy, reliability and the range of applicability of the property estimation, and reliability predict proximity effects and isomer differences. Contrary to first-order groups, there can be molecular structures which do not need any second-order groups or can be partially fragmented. The definition and identification of second-order groups, however, must have a theoretical basis. Thus, they proposed the principle of conjugation.

The theoretical background to conjugation is that compounds are represented as hybrids of many conjugates. Each conjugate form is an idealized structure with integer-order-localized bonds and integer charges on atoms. The purely covalent conjugate form is the dominant conjugate and the ionic forms are the recessive conjugates, which can be obtained from the dominant form by re-arrangement of electron pairs. A conjugation operator defines a particular pattern of electron arrangement. When applied to the dominant conjugate, an operator yields an entire class of recessive conjugates. Conjugation operators are represented by a distinct sub-chain with two or three bonds, such as C-C-C-H and O=C-C. Figure 2-2 presents a dominant conjugate, a generated recessive conjugate and the corresponding conjugation operator.

In this framework, the properties of a component are estimated by determining and combining properties from its conjugate forms. Properties of conjugate forms are estimated through conjugation operators. In the method, they used the following criteria for the identification of second-order groups:

- The structure of a second-order group should incorporate the distinct sub-chain of at least one important conjugation operator.
- The structure of a functional second-order group should have adjacent first-order groups as building blocks and it should be as small as possible.
- Second-order groups based on common operators(s) should be equally treated in the method.

- The performance of second-order groups is independent of the molecule in which the group occurs, satisfying the fundamental group contribution assumption.



$$\mathrm{H-C-C-C-H} \leftrightarrow \mathrm{H-C^{+}..C{=}C..H^{-}}$$

$$\mathrm{C-C-C-H} \leftrightarrow \mathrm{C^{+}..C=C..H^{-}}$$

Figure 2-2: Dominant, recessive conjugates and conjugation operator

Table A-8 lists second-order groups that have been defined for the method and their contributions. The idea of conjugation is primarily based on the recessive conjugate proposing another form of the molecule. Thus in the property estimation, the molecule is now a mixture of dominant and recessive conjugates. The second-order groups account for the alternate forms, or recessive conjugates. However, in many cases the possibility of a recessive conjugate form existing at atmospheric conditions is almost zero. For example, in Figure 2-2, the molecular structure of propane is presented. Propane is a non-polar covalent hydrocarbon with sp^3 carbon atoms, and the possibility of a recessive conjugate existing at atmospheric conditions is essentially zero. This would mean that a second-order group for propane is not required.

Abildskov (1994) made a limited study of this method for about 100 compounds and found that including the second order approximations improved the estimation results as often as it degrades them. With the exception of ring compounds, the improvement was rarely more than 1 to 2%. Thus the use of the second order contributions may not be worthwhile as there is no means to know when to use them.

The method employs a logarithmic model equation for the critical temperature estimation (Equation 2-24). The model can be assumed to extrapolate correctly, as seen in Figure 2-1, but higher deviations will be found since knowledge of the normal boiling point is omitted. Even with the latter drawback, Figure 2-1 shows a trend for the model which is distinctly below that of Ambrose. The critical pressure and critical volume models are presented in Equations 2-25 and 2-26, respectively.

$$T_c = 181.128 \ln\left[\sum_i N_i C_i + W\left(\sum_i L_i D_i\right)\right] \tag{2-24}$$

$$P_c = \frac{1}{(0.10022 + \sum_i N_i C_i + W(\sum_i L_i D_i))^2} + 1.3705 \tag{2-25}$$

$$V_c = -0.00435 + \sum_i N_i C_i + W\left(\sum_i L_i D_i\right) \tag{2-26}$$

The constant W is assigned a value of zero for a first-order approximation and unity in the second-order approximation, where both first and second-order group contributions are involved. 285, 269 and 251 experimental data points were used in the regression for critical temperature, critical pressure and critical volume, respectively. After the selection of data, a least squares analysis had been carried out to determine the contributions of first- and second-order groups (adjustable parameters). For this method, this work reports an average absolute error of 17.2 K (4.07%) in critical temperature for 559 components, 248 kPa (7.12%) in critical pressure for 410 components and 22.9 $\text{cm}^3.\text{mol}^{-1}$ (4.81%) in critical volume for 277 components.

2.3.9 Tu (1995)

Kurata & Isida (1955) exploited a lattice model for rod-like molecules and developed a hole theory for n-paraffin liquids. From this theory, they developed an expression for the critical temperature, Equation 2-27.

$$\frac{1}{T_c} = A + B\left(\frac{1}{2x} + \frac{1}{x^{1/2}}\right) \qquad (2\text{-}27)$$
$$x = n_c$$

Here n_c is the number of carbon atoms in the molecule. Teja *et al.* (1990) then employed this model to correlate the critical temperatures of n-alkanes. Based on their findings they proposed Equation 2-28 instead.

$$x = a + bn_c \qquad (2\text{-}28)$$

Tu (1995) employed the same relationship as Teja, but replaced n_c by the sum of group contributions, Equation 2-29. The trend in the extrapolation of the model for large molecules is similar to that of Constantinou and Gani.

$$T_c = \frac{1}{6.26897\times10^{-4} + 2{,}56086\times10^{-3}\left(\frac{1}{2x} + \frac{1}{x^{1/2}}\right)} \qquad (2\text{-}29)$$
$$x = -0.160864 + \sum_i N_i C_i$$

Tu proposed a set of 40 simple groups identical to those of the previous method, presented in Table A-9. For this method, this work reports an average absolute error of 23.3 K (4.26%) in critical temperature for a set of 572 components, which is the highest deviation of all methods presented thus far and so it will not be discussed further.

2.3.10 Marrero-Morejon & Pardillo-Fontdevilla (1999)

Pardillo & Gonzalez-Rubio (1997) had first proposed a new structural approach called Group Interaction Contribution (GIC), which considers the contribution of interactions between bonding groups instead of the contribution of simple groups. Based on the above approach (GIC), Marrero and Pardillo (1999) proposed a new method to estimate the boiling points and critical constants of pure organic compounds.

Marrero and Pardillo selected 39 simple groups, which can also be referred to as first-order groups, to generate a consistent set of group-interactions that allows one to treat a wide variety of organic compounds. These groups are similar to the method of Joback and Reid, presented earlier, with the omission of =NH and =N-(non-ring). The model equations are also similar to the models employed by Joback and Reid, Equation 2-30 to 2-32. This duplication of the models also brings the same drawbacks, i.e. the use of the binomial term in the critical temperature model results in unrealistic extrapolation as observed in Figure 2-1.

$$T_c = \frac{T_b}{0.5851 - 0.9286\sum_i N_i C_i - (\sum_i N_i C_i)^2} \tag{2-30}$$

$$P_c = \frac{1}{(0.1285 - 0.0059n - \sum_i N_i C_i)^2} \tag{2-31}$$

$$V_c = 25.1 + \sum_i N_i C_i \tag{2-32}$$

The contributions of the group-interactions are presented in Table A-10. The group-interaction structural definition proposed here should actually be known as, and from now on referred to as, a bond contribution definition because there is no physical interaction between groups but rather it's just the bonding between two defined groups. They did not calculate some bond-contributions because of the lack of property values for the compounds involved. Also, groups that were used to derive the bond contributions were from the Joback and Reid method, where the range of applicability is small and groups were poorly defined.

Due to the bond contribution approach, the range of applicability of the method is severely restricted. For example, on a data set of about 2800 components from the DDB containing boiling point information, only 1665 components were fragmented for the above-mentioned method. In addition, since the method only considers the bonded interaction between neighbouring bonds, their predictive capability usually breaks down when dealing with large, polycyclic or multi-functional compounds where the intermolecular potential between molecules (and not bonds) is relevant. The bond contributions do, however, provide a significant improved estimation in case of isomers as compared to the Joback and Reid method.

For this method, this work reports an average absolute error of 7.8 K (1.21%) in critical temperature for 458 components, 209 kPa (6.04%) in critical pressure for 381 components and 16.1 $cm^3.mol^{-1}$ (3.36%) in critical volume for 248 components.

2.3.11 Marrero-Morejon & Gani (2001)

Marrero-Morejon & Gani (2001) proposed a new group-contribution method based on three levels of approximation. The first level has a large set of simple groups that is able to partially capture proximity effects, but is unable to distinguish between isomers. For this reason, the first level of estimation is intended to deal with simple and mono-functional compounds. The second level permits a better description of poly-functional compounds and differentiation amongst isomers. Second-order groups are, however, unable to provide a good representation of compounds containing more than one ring as well as, in some cases, open-chain poly-functional compounds with more than four carbon atoms in the main chain. Thus, a further level is required to provide a better description for these types of compounds. This is accomplished by the introduction of third-order groups, which intend to represent the molecule at the third level of approximation. The third level allows estimation of complex heterocyclic and large (C = 7 to 60) poly-functional acyclic compounds. The criteria used for the identification of third-order groups are analogous to those used for second-order groups.

Overall, the method is highly complex, incorporating an extremely large number of groups (182 first-order groups (124 for T_c), 122 second-order groups (78 for T_c) and 66 third-order groups (31 for T_c)). Considering that only 587 data points were used in the regression of critical temperatures, this presents an average of less than three points per group. The definition of groups should also have a theoretical basis. It seems that a new level had been defined for cases where the previous level of approximation had failed. As with some of the methods, such as that of Somayajulu, this approach can lead to huge errors when applied outside the training set.

The complexity and correlative nature of the method has prevented and discouraged any implementation into DDBSP (DDB (2006)). However, the method has been discussed in Nannoolal (2004) with an example for the estimation of n-alkane normal boiling points. In this case, the method performed poorly. This method will not be discussed further in this work.

2.3.12 Wen & Quiang (2001)

In this method, the critical temperature is estimated by one of two different models (Equations 2-33 and 2-34). The criterion for the selection of the appropriate model is the availability of the normal boiling point. The critical pressure and critical volume are estimated by Equation 2-35 and 2-36, respectively.

$$T_c = T_b\left[1 + \left(127.754 + \sum_i N_i C_i^{'} + \sum_i L_i D_i^{'}\right) * 10^{-2}\right] \tag{2-33}$$

$$T_c = \Bigg(\Bigg(\Bigg(4.72 + \sum_i N_i C_i + \sum_i L_i D_i\Bigg) * 10^6\Bigg)^{1/2.747} \tag{2-34}$$

$$P_c = \frac{100}{(37.293 + \sum_i N_i C_i + \sum_i L_i D_i)^2} \tag{2-35}$$

$$V_c = -27.04 + \sum_i N_i C_i + \sum_i L_i D_i \tag{2-36}$$

Wen and Qiang proposed two sets of groups in their estimation of critical properties. The first is a new classification method of structural groups termed group-adjacent atom pairs which are presented in Table A-11. This classification is similar to the method of Marrero-Morejon & Pardillo-Fontdevilla (1999), except they used adjacent atoms instead of bonds. The second classification employs 13 simple groups consisting of the elements O, N and S as corrections to group-adjacent atom pairs, presented in Table A-12.

The use of group-adjacent atom pairs would possibly have an advantage over bond contributions as it results in a larger range of applicability with fewer parameters. But discussed in Nannoolal (2004) with an example for the estimation of n-alkane normal boiling points. In this case, the method performed poorly. This method will not be discussed further in this work.

2.3.12 Wen & Quiang (2001)

In this method, the critical temperature is estimated by one of two different models (Equations 2-33 and 2-34). The criterion for the selection of the appropriate model is the availability of the normal boiling point. The critical pressure and critical volume are estimated by Equation 2-35 and 2-36, respectively.

$$T_c = T_b\left[1+\left(127.754+\sum_i N_i C_i' + \sum_i L_i D_i'\right) * 10^{-2}\right] \tag{2-33}$$

$$T_c = \left(\left(4.72+\sum_i N_i C_i + \sum_i L_i D_i\right) * 10^{6}\right)^{1/2{,}747} \tag{2-34}$$

$$P_c = \frac{100}{(37.293+\sum_i N_i C_i + \sum_i L_i D_i)^2} \tag{2-35}$$

$$V_c = -27.04 + \sum_i N_i C_i + \sum_i L_i D_i \tag{2-36}$$

Wen and Qiang proposed two sets of groups in their estimation of critical properties. The first is a new classification method of structural groups termed group-adjacent atom pairs which are presented in Table A-11. This classification is similar to the method of Marrero-Morejon & Pardillo-Fontdevilla (1999), except they used adjacent atoms instead of bonds. The second classification employs 13 simple groups consisting of the elements O, N and S as corrections to group-adjacent atom pairs, presented in Table A-12.

The use of group-adjacent atom pairs would possibly have an advantage over bond contributions as it results in a larger range of applicability with fewer parameters. But

Table 2-2: Critical property deviations for all methods.

Methods	T_c			P_c			V_c		
	NC[*]	MAPE[†]	AAD[‡] (K)	NC	MAPE	AAD (kPa)	NC	MAPE	AAD ($cm^3.mol^{-1}$)
AB[§]	528	1.07	6.0	412	7.03	253	242	3.99	19.4
MP	458	1.21	7.8	381	6.04	209	248	3.36	16.1
KR	547	1.27	7.8	452	7.57	246	319	3.96	17.9
WQ	506	1.26	7.8	-	-	-	-	-	-
JR	543	1.41	8.8	452	7.11	238	314	3.73	16.5
SJ	517	1.44	8.4	438	9.51	295	307	4.14	20.1
LD	557	1.71	10.7	474	7.07	228	327	5.37	30.7
DB	475	3.87	23.9	352	7.00	253	-	-	-
Methods not requiring T_b:									
WQ	506	2.97	16.7	421	5.67	197	294	4.99	22.1
CG	559	4.07	17.2	410	7.12	248	277	4.81	22.9
CT	572	4.26	23.3	-	-	-	-	-	-

As was discussed before, critical properties for higher molecular weight compounds are almost impossible to measure. Thus, a very important criterion of a new model for critical properties has to be its extrapolative capability. A means to test this capability is to estimate properties for compounds far outside the range of the data used in the regression. This was shown in Figure 2-1.

It was discussed earlier on that quadratic equations should not be employed in group contribution estimations; this was illustrated in Figure 2-1. At the same time, terms that are in competition with each other (as in case of the Klincewicz and Reid model) should not be regressed simultaneously. Overall, in Figure 2-1, five of the ten models shown presented unrealistic extrapolations. This work will concentrate in equal

---

[*] Denotes number of components
[†] Denotes mean absolute percentage error
[‡] Denotes average absolute deviation
[§] Abbreviations defined in Table 2-1

amounts on the extrapolative capabilities and the probability of prediction failure of the models developed.

Chapter Three

Liquid Vapour Pressure

3.1 Introduction

It is a well-known fact that when increasing the temperature, phase changes of a substance occur in the following direction (a solid can also directly turn into gas):

Solid → Liquid → Gas

Each of these changes requires an input of heat to the system at constant temperature and pressure. The amount of heat is equal to the sum of the change in internal energy and work (Equation 3-1).

$$q = \Delta U + W \tag{3-1}$$

For the case of reversible processes, this is equivalent to Equation 3-2.

$$\Delta H = \Delta U + \Delta(PV) \tag{3-2}$$

The phase changes in the directions considered involve disorientation and in most cases a spacial separation of the molecules in the phase (in the case of water the mean distance between molecules is smaller in the liquid than in the solid phase resulting in a lower density of the coexisting solid). In most cases, only a small portion of the phase change enthalpy is required for the volume change. The major part is needed for the required increase in internal energy. This increase in internal energy consists of a relatively small change in translational, rotational and vibrational energy[*] and to the largest part an increase in potential energy.

---

[*] All these are forms of kinetic (thermal) energy at the molecular level.

On the other hand, these phase changes can also be characterized by an increase in the 'randomness' of the system or the degree of spread of their quantum states. At any particular temperature and pressure, the stable phase is that which has the smallest values of its chemical potential (μ'') or Gibbs free energy per mol. Thus, considering the liquid and vapour phases, if the relation in Equation (3-3) is observed, then the liquid is the more stable of the two. Conversely, if the relation is switched around, then the vapour phase is more stable. Chemical equilibrium is observed between these two phases when the chemical potentials of all components are equal in both phases. Chemical equilibrium can also be characterized by the compromise between energy and entropy, or in molecular terms, between energetically favoured order and energetically disfavoured disorder.

$$\mu_l'' < \mu_v'' \tag{3-3}$$

Consequently, at any given temperature and for any pure substance, if the vapour phase is in thermodynamic equilibrium with a liquid (or solid) phase, then the vapour pressure is identical to the system pressure. This vapour pressure is also often denoted as the saturated vapour pressure.

There have been many different representations of the vapour pressure-temperature relationship for pure liquids. This is due not only to the importance of the physical property itself, but also its relation to other properties, such as the latent heat of vaporization. For practical calculations, a convenient interpolation formula is required, since the experimental data are usually fragmented and located at inconvenient temperature and pressure intervals. Parameters of such a vapour pressure model are either obtained by regression of experimental data (correlative technique) or estimation techniques, for example from molecular structure.

One important data point on the vapour pressure curve is the normal boiling temperature, where the vapour pressure is equal to 1 atm. Many structure estimation techniques for the normal boiling temperature have been developed in the past, the most reliable being the one developed in the previous work, Nannoolal (2004) & Nannoolal *et al.* (2004). The added complexity when going from the fixed point (normal boiling point) to the vapour pressure as a function of temperature is that this is now a temperature dependant property. In addition, vapour pressure data are needed within high precision for important processes such as distillation. Therefore, correlative techniques based on reliable experimental data are almost always preferred to structure estimation techniques.

Possibly because of the above reasoning, there is a lack of structure estimation methods for the vapour pressure presented in literature, whereas there is an abundance of literature on correlative techniques. The typical procedure consists of estimating the normal boiling temperature and the vapour-liquid critical point and connecting these by a reliable correlation equation.

The purpose of this work is to develop a method for the prediction of vapour pressures that does not require knowledge of the critical point. This chapter will thus focus rather on correlative techniques with very little emphasis to structure estimations methods (as compared to Chapter 2) in order to find a suitable equation for this purpose.

3.2 The Clausius-Clapeyron Equation

In the case of a single component system with two phases α and β in equilibrium, the chemical potentials of the component in both phases are functions of temperature and pressure only.

The line of intersection of the two chemical potential surfaces corresponds to the phase equilibrium curve. Along this line, the relationship described in Equation 3-4 must be satisfied:

$$\mu_{\alpha}^{''} = \mu_{\beta}^{''} \tag{3-4}$$

Then at a neighbouring point, Equation 3-5 applies, which means that any incremental change in the chemical potential is equal (Equation 3-6).

$$\mu_{\alpha}^{''} + d\mu_{\alpha}^{''} = \mu_{\beta}^{''} + d\mu_{\beta}^{''} \tag{3-5}$$

$$d\mu_{\alpha}^{''} = d\mu_{\beta}^{''} \tag{3-6}$$

At equilibrium, temperature and pressure are constant. The chemical potential is dependant on temperature and pressure, a change in temperature results in a simultaneous change in pressure if equilibrium is to be maintained. Consequently, Equation 3-6 can be expressed in the following way for a pure component system:

$$\left(\frac{\partial \mu_{\alpha}^{''}}{\partial T}\right)_{P} dT + \left(\frac{\partial \mu_{\alpha}^{''}}{\partial P}\right)_{T} dP = \left(\frac{\partial \mu_{\beta}^{''}}{\partial T}\right)_{P} dT + \left(\frac{\partial \mu_{\beta}^{''}}{\partial P}\right)_{T} dP \tag{3-7}$$

An alternate form of the elemental property equation of the Gibbs function can be written as follows:

$$d(nG) = -(nS)\,dT + (nV)\,dP + \sum \mu_{i}^{''}\,dn_{i} \tag{3-8}$$

At equilibrium, $d(nG) = dn_i = 0$. It therefore holds that

$$\left(\frac{\partial \mu_{i}^{''}}{\partial P}\right)_{T} = V \tag{3-9}$$

$$\left(\frac{\partial \mu_{i}^{''}}{\partial T}\right)_{P} = -S \tag{3-10}$$

Substituting Equations 3-9 and 3-10 into Equation 3-7 yields:

$$-S_{\alpha}dT + V_{\alpha}dP = -S_{\beta}dT + V_{\beta}dP \tag{3-11}$$

Here S represents the molar entropy and V the corresponding molar volume of the substance in the two phases α and β. At equilibrium, where the chemical potentials of both phases are equal, transition between the two phases is reversible and the change in molar entropy can be rewritten with respect to molar enthalpy (H) and temperature (Equation 3-12).

$$S_\alpha - S_\beta = \frac{H_\alpha - H_\beta}{T} \tag{3-12}$$

Re-arranging Equation 3-11 to match the left hand side of Equation 3-12 and substituting into the latter equation, the well-known Clausius-Clapeyron equation is obtained.

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \tag{3-13}$$

The Clausius-Clapeyron equation allows one to calculate the pressure change dP which is necessary in order to maintain phase equilibrium when there is a temperature change dT.

Equation 3-13 only holds for single component systems since the chemical potentials in both phases were assumed to be functions of temperature and pressure only. It may be noted that the equation still applies for substances that contain several chemical species (for example, H_2O, OH^-, H_3O^+, $(H_2O)_2$) where reaction equilibrium is observed. If the total number of chemical species is X, then between them there are $X - 1$ chemical reaction and stoichiometric restrictions. There is thus only one independent component and one independent chemical potential. In connection with the phase rule, such a system has one degree of freedom when there are two phases present. Thus an arbitrarily chosen temperature change will give rise to a definite pressure change, as given by the integral of Equation 3-13. For the same reason the left-hand side of this equation is complete and not merely a partial differential.

3.3 Correlative Techniques

There are a number of compilations of vapour pressure correlations presented in the open literature. Poling *et al.* (2000) and the previous editions of this book, Reid *et al.* (1987) and Reid & Sherwood (1958) present methods to estimate and correlate the vapour pressure that appear to be the most accurate and common. There are also a number of more detailed reviews, for example by Majer *et al.* (1989), Thompson (1946), Vetere (1988) and many reviews published by Ambrose (1972), (1977), (1978b), (1980), (1986) and Ambrose *et al.* (1978).

3.3.1 Brief history

The very earliest vapour pressure equation was given by Dalton (1801), who suggested that the pressure increased in geometric progression and temperatures in arithmetic progression (Equation 3-14).

$$\log P = A + BT \tag{3-14}$$

This relation was quickly disproved when accurate measurements were made available. However, the gentle curvature of the vapour pressure data suggested the approximate validity of the rule.

3.3.2 Theory

The Clausius-Clapeyron equation (Equation 3-13) can be rearranged into the following form:

$$\frac{d \ln P^{S}}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H}{R \Delta Z} \tag{3-15}$$

The advantage is that in this form, both sides of the equation vary only slightly with temperature. Most vapour pressure estimations and correlations were derived from Equation 3-15 via integration. For integration, an assumption must be made regarding the dependence of $\Delta H^V/\Delta Z^V$ on temperature. Also a constant of integration is obtained which must be evaluated from a single vapour pressure point. The simplest approach is to assume that, with $B = \Delta H^V/R\Delta Z^V$,

- The volume of the liquid (V_l) is negligible as compared to the volume of the gas (V_v) ($Z_l=0$) and the vapour is an ideal gas ($Z_v=1$).
- The heat of vaporization is constant over the temperature range involved.

Based on these assumptions, integration of Equation 3-15 leads to Equation 3-16, with the constant of integration denoted as A and P^o a standard pressure (e.g. 1 atm).

$$\ln\frac{P^S}{P^o}=A-\frac{\Delta H^V}{RT}=A-\frac{B}{T} \tag{3-16}$$

The assumptions listed above are only valid over a limited temperature range and far away from the critical point. However, because both ΔH^V and ΔZ^V depend on temperature in a similar form and both become zero at the critical point, Equation 3-16 is approximately valid up to this point (Figure 3-1). At lower temperatures, ΔZ^V is very close to one and constant while ΔH^V increases slightly with decreasing temperature. Thus, $\Delta H^V/\Delta Z^V$ does not vary much with temperature.

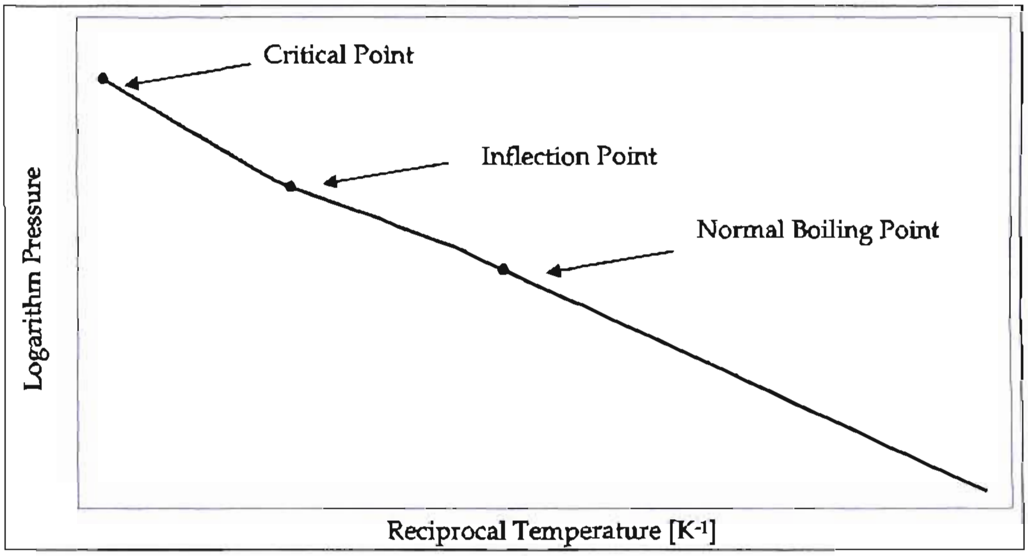


Figure 3-1: Schematic vapour pressure plot.

3.3.3 Correlations Based on the Clausius-Clapeyron Equation

The application of Equation 3-16 to more accurate data reveals that *1/T* does not give a true picture of the vapour pressure relationship. There are deviations that exceed reasonable experimental error and extrapolation is unwise even over short temperature ranges.

Antoine (1888b) modified Equation 3-16 by simply substituting *(T + C)* for *T* in the correlation of water vapour pressures. In a later publication, Antoine (1888a) applied the modification to over 20 compounds and mixtures. This equation, Equation 3-17, is now the well-known Antoine equation.

$$\ln P^S = A - \frac{B}{T+C} \tag{3-17}$$

An extensive study of the Antoine equation was carried out by Schmidt (1917) for 114 liquids and 24 solids, and nearly straight lines were obtained when plotting the *ln (P)* vs. *1/(C+T)*. Cox (1923) proposed a graphical correlation in which the ordinate, represented by P, is on a log scale, and a straight line with a positive slope is drawn. The line is taken to represent the vapour pressure of a reference compound (generally water). If the vapour pressure of the reference compound is accurately known as a function of temperature, the abscissa scale can be marked in temperature units. When the vapour pressure and temperatures scales are prepared in this way, vapour pressure for other compounds are generally found to be straight lines, especially for homologous series. For these types of series, a useful phenomenon is noted on Cox charts. The straight line for each member of a homologous series converges to a fixed point when extrapolated. This is known as the infinite point and is useful for providing a single value of the vapour pressure for a new member of the series. Calingeart & Davis (1925) showed that the temperature scale on the Cox chart is nearly equivalent to the function *1/(T+C)* of the Antoine equation, when applied to several classes of compounds using a value of *C=-43 K (or C = 230 K - 273 K)*. Thus the Cox chart resembles a plot of the Antoine equation.

The C parameter in the Antoine equation is generally referred to as a temperature or graphically a slope correction. Both characterizations are equally applicable. As a slope correction, the use of the constant C reduces systematic deviations which cause bowing of the straight line when the logarithm pressure is plotted against *(1/T)*. In the earliest developments, it was found that C lies between -50 and -30, but with more extensive data available, this was quickly disproved. A correlation was proposed by Thompson (1959) relating C to the normal boiling point (Equation 3-18).

$$C = 18 - 0.19T_b \tag{3-18}$$

The Antoine equation is arguably the most popularly used vapour pressure correlation as there are a large number of tabulated values for the parameters, *A*, *B* and *C* (Dykyj *et al.* (1999), (2000), (2001)). At the same time, the parameters are not difficult to regress when experimental data are available. Determination of Antoine constants is often performed using multi-linear regression of the equation:

$$T\ln\left(\frac{P}{P^0}\right) = (AC - B) + (AT) + C\left[-\ln\left(\frac{P}{P^0}\right)\right] \tag{3-19}$$

where P^0 is the reference pressure (usually 1 atm)

This regression avoids using a slow non-linear algorithm and the requirement for initial values of the parameters.

The Antoine equation provides a good representation of the vapour pressure-temperature relationship over a limited temperature range and extrapolation over very small temperature ranges generally yields reasonable results.

The parameter C should not be freely regressed to data in a limited temperature range and should always be in a physically meaningful range. Figure 3-2 shows a plot of logarithmic vapour pressure against reciprocal temperature for benzene with two lines (*X* and *Y*) for different temperature ranges, and consequently, two different sets of the parameters *A*, *B* and *C*. Line X is based on the entire temperature range and can be considered to be very accurate (line X overlaps with experimental data). However, line

Y is based on a smaller temperature range (350 - 370 K) and it can be plainly seen that the extrapolation will yield erroneous results (the parameter *C* for line *Y* is physically improbable). Secondly, the equation should not be applied to temperatures at or above the inflection point (Figure 3-1), usually around a reduced temperature of 0.75 - 0.8.

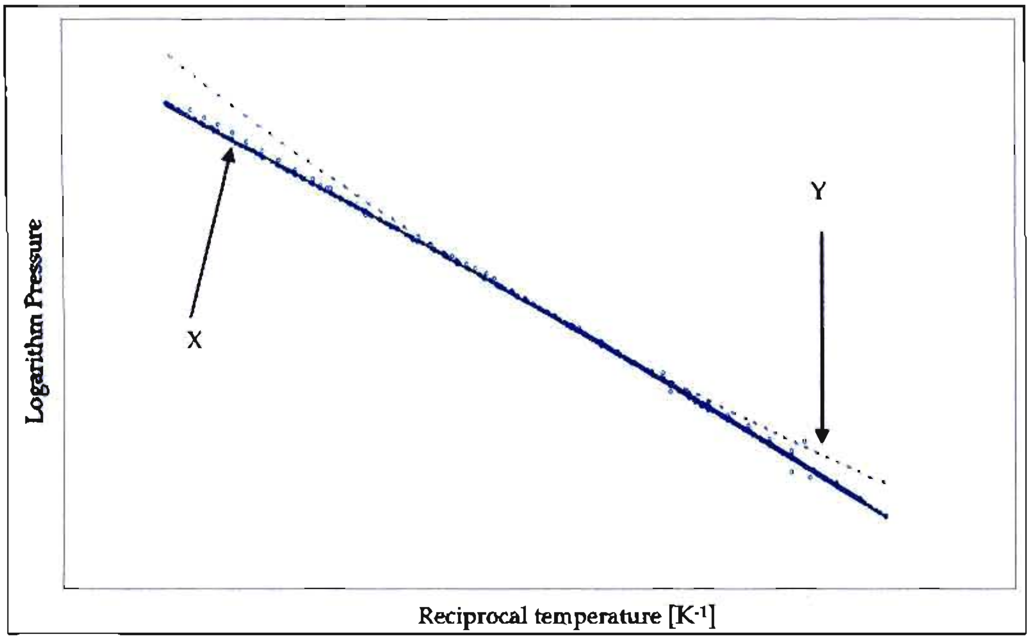


Figure 3-2: Vapour pressure plot of benzene with the Antoine equation.

Another approach from Equation 3-15 is to represent *B* by a polynomial equation (Equation 3-19).

$$B = B_0 + B_1 T + B_2 T^2 + B_3 T^3 + \ldots \qquad (3\text{-}19)$$

Substitution followed by integration leads to Equation 3-20.

$$\ln P^S = A + \frac{B_o}{T} + B_1 \ln T + B_2 T + \frac{B_3}{2} T^2 + \ldots \qquad (3\text{-}20)$$

With a sufficient number of coefficients, this equation is valid over the entire temperature range up to the critical point.

From Equation 3-20, many researchers have derived similar forms to correlate the vapour pressures. One of the simpler forms of Equation 3-20 is to assume that B_2, B_3 ... = 0. This is known as the Kirchhoff equation (Kirchhoff (1858)) despite Rankine (1849) having used it earlier (Equation 3-21). It is usually written in the form:

$$\ln P^S = A - \frac{B}{T} + C\ln\left(\frac{1}{T}\right) \tag{3-21}$$

Another popular form is the DIPPR 101 equation (DIPPR (1992)), which uses the temperature raised to the power of a constant (E) as an additional term, Equation 3-22, to account for the higher order terms.

$$\ln P^S = A - \frac{B}{T} + C\ln\left(\frac{1}{T}\right) + DT^E \tag{3-22}$$

Riedel (1954) proposed a vapour pressure equation of the form:

$$\ln P^S = A - \frac{B}{T} + C\ln\left(\frac{1}{T}\right) + DT^6 \tag{3-23}$$

The term T^6 permits a depiction of the inflection point at high temperatures. To determine the constant in Equation 3-23, Riedel defined the parameter α (Equation 3-24); here P_r^s is the reduced vapour pressure.

$$\alpha \equiv \frac{d\ln P_r^s}{d\ln T_r} \tag{3-24}$$

From a study of experimental data, Plank & Riedel (1948) found a constraint which is presented in Equation 3-25.

$$\frac{d\alpha}{dT_r} = 0 \rightarrow T_r = 1 \tag{3-25}$$

Using this constraint, Riedel showed that:

$$\ln P_r^S = A' - \frac{B'}{T_r} + C'\ln\left(\frac{1}{T_r}\right) + D'T_r^6 \tag{3-26}$$

Where

$$\begin{aligned} &A' = -35Q, B' = -36Q, C' = 42Q + \alpha_c, \\ &D' = -Q, Q = K(3.758 - \alpha_c) \end{aligned} \tag{3-27}$$

In Equation 3-27, α_c is α at the critical point. Riedel chose the value of K to be 0.0838. However, Vetere (1991) found improved prediction results for alcohols and acids by using different expressions for K (not discussed here).

As it is not desirable to determine α_c from Equation 3-24, an alternate solution is to use Equation 3-28 and 3-29, by means of the knowledge of the normal boiling point.

$$\alpha_c = \frac{3.758K\Psi_b + \ln\left(\frac{P_c}{1.10325}\right)}{K\Psi_b - \ln T_{br}} \tag{3-28}$$

$$\psi_b = -35 + \frac{36}{T_{br}} + 42\ln T_{br} - T_{br}^6 \tag{3-29}$$

The obvious advantage of the Riedel method is that it requires only knowledge of the normal boiling point, critical temperature and critical pressure. Figure 3-3 shows a plot of experimental and calculated β (defined in Equation 3-30) values for the Antoine and Riedel method. The term β provides a means of assessing the temperature dependence of the ratio of the heat of vaporization and the compressibility factor. Thus, as discussed before, it can be considered to have a compensatory effect over the entire region below the inflection point. The use of the higher order term in the Riedel method allowed the description of the inflection point, Figure 3-3, however the curve diverges at lower pressures. The Antoine equation is able to capture the lower vapour pressures but leads to problems when approaching the inflection point.

$$\beta = \frac{d\ln P^S}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H}{R\Delta Z} \tag{3-30}$$

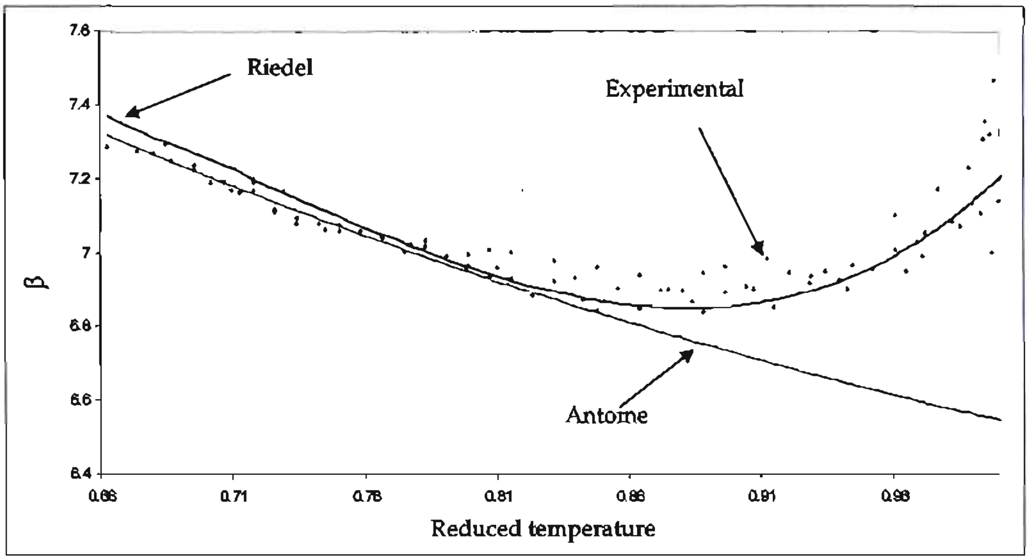


Figure 3-3: Plot of calculated and experimental β values for ethylbenzene.

An interesting approach by Abrams *et al.* (1974) links the parameters in Equation 3-20 ($B_4, B_5 \ldots = 0$) to molecular properties via the kinetic theory of vapour pressure but this will not be discussed in this work.

3.3.4 Empirical Correlations

The application of the correlation equations described above does not allow fitting of experimental data from the triple point to the critical point within reasonable accuracy and a reasonable number of parameters. Most of these correlations are only applicable to certain regions on the vapour pressure curve. Consequently, more empirical techniques have been employed.

An excellent review of many empirical correlations of the vapour pressure prior to 1910 is presented in Chwolson (1910). Following this, there were a number of useful correlations developed that can be found in some of the references mentioned earlier. However, the development of these correlations will not present an added advantage in the proposed work. Consequently, this work will only look at the popular Wagner correlation equation.

Wagner (1973), (1977) employed an intricate statistical technique to develop a vapour pressure equation for argon, nitrogen and water, applicable to the entire liquid region for which experimental information is available. In this method, the terms and coefficients were chosen according to strict statistical criteria. The resulting model is presented in Equation 3-31.

$$\ln P_r^s = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{T_r} \qquad \tau = 1 - T_r \tag{3-31}$$

A further improved form of Wagner equation was developed by Ambrose (1986) and Ambrose & Ghiassee (1987), Equation 3-32. Both forms are able to adequately describe the vapour pressure as a function of temperature over the entire liquid region.

$$\ln P_r^s = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^5}{T_r} \tag{3-32}$$

There have also been a number of forms of the Wagner equations including a fifth term. However, Ambrose (1986) recommended that, except for special cases, the use of the fifth term cannot be justified and is not necessary.

Mcgarry (1983) published values of constants for Equation 3-31 for 250 liquids. For Equation 3-32, Poling *et al.* (2000) published values of constants for 92 liquids.

It was shown earlier that extrapolation of the Antoine equation is not reliable. The same may be true for the above two models. However, one procedure that has been recommended, (Ambrose *et al.* (1978), Ambrose (1980), Mcgarry (1983) and Ambrose & Ghiassee (1987)) is to use both equations above, and determine the constants by a constrained fit to the data. For this type of fit, there are three constraints that are normally used to reproduce vapour pressure behaviour for all substances, viz.:

1. A minimum in the $\Delta H^V/\Delta Z^V$ vs. T_r at some reduced temperature, typically between 0.8 and 1, must be observed. Ambrose & Ghiassee (1987) pointed out

that this constraint should cause both parameters, *B* and *C*, in Equations 3-31 and 3-32 to have different signs.

2. The second constraint was identified by Thodos (1950), which requires that there be an inflection point in the lnP^s vs. $1/T$ plot.
3. The third constraint employs the Watson equation (Thek & Stiel (1966)), Equation 3-33, to insure that the low temperature behaviour of the vapour pressure equations leads to the temperature dependence of the enthalpy of vaporization predicted by Equation 3-33. Alternatively, the low temperature behaviour can also be established by combining vapour pressure information with thermal data.

$$\Delta H^{V2} = \Delta H^{V1}\left(\frac{1-T_{r2}}{1-T_{r1}}\right)^{n} \qquad (3\text{-}33)$$

3.3.5 Discussion of Correlative Techniques

Only a few of the many vapour pressure correlations published in literature have been discussed here. The models presented appear to be among the most accurate and widely used in estimating vapour pressure data.

The Antoine equation presents a reliable and simple means of estimating and correlating vapour pressure data below the inflection point, as long as estimation is based on interpolation or extrapolation over a small temperature range. At very low temperatures, *T* approaches the value of -*C* and the Antoine equation diverges and becomes unrealistic. From the inflection point to the critical point, the Riedel model is adequate with only the normal boiling point and critical properties required and no information between these points needed. For a more complicated approach, and where extrapolation and high accuracy is needed, the Wagner equation (Equation 3-31 and 3-32) is recommended. Poling *et al.* (2000) published estimation results for the above three correlations for acetone, 1-octanol and tetradecane where the temperature range covers the melting point or triple point to the critical point. In all cases the Wagner equation was the most accurate, with the Antoine equation being more accurate than the Riedel below the inflection point (and Riedel more accurate above the inflection), as expected. However, the disadvantage of the Wagner equation over the Antoine equation is that it requires knowledge of the critical point. This severely limits the range of applicability of the method.

As suggested earlier, the proposed group contribution vapour pressure estimation method will only be applicable to temperatures below the inflection point. For this reason, the objective will be to develop this method within the accuracy of the Antoine and DIPPR 101 equations. The Riedel and Wagner equations were presented here as a means to correlate data from the inflection point to the critical point (this will not be investigated in this work). Thus, the combination of the latter two methods and the proposed method would be useful in describing vapour pressure behaviour over the entire liquid region, and in cases where there is no critical point information, this can be estimated with the method that will be presented in this work.

3.4 Estimation Methods Based on Molecular Structure

There are very few methods for vapour pressure estimation based on molecular structure present in literature. Most methods employ a group contribution approach in estimating the parameters (*A*, *B*, *C* ...) of some of the models presented in this chapter. These methods generally develop correlations only for certain homologous series. One of these methods was based on the UNIFAC approach, Fredenslund *et al.* (1977). This was first presented by Jensen *et al.* (1981) and extended by Yair & Fredenslund (1983). However, the method requires complicated calculations and input of other physical properties such as the second viral coefficient. The method is also only applicable to a pressure range from 1 kPa to 300 kPa with some success in estimating the vapour pressures.

Tu (1994) proposed a vapour pressure estimation method with a simpler calculation and applicable to a broader pressure range. Tu assumed a quadratic temperature dependence of $\Delta H^V/\Delta Z^V$, and derived Equation 3-34 for the estimation of the vapour pressure.

$$\ln P^S M = \left[\sum_i N_i \left(A_i + \frac{B_i}{T'} - C_i \ln T' - D_i T' \right) \right] + Q \qquad (3\text{-}34)$$
$$T' = \frac{T}{100}$$

Q is defined as a component specific correction and can be calculated from Equations 3-35 to 3-39.

$$Q = \sum_{i=1}^{2} \xi_i q_i \qquad (3\text{-}35)$$

There are two types of specific compound corrections proposed by Tu. The first (i = 1) is a structure correction.

$$\xi_1 = s_0 + s_1 N_{as} + s_2 N_{bs} + s_3 N_{es} \qquad (3\text{-}36)$$

Equation 3-36 only applies to alkylbenzenes, for other compounds ξ_1 = 1. For non-ring and ring compounds, Equations 3-37 and 3-38 are employed, respectively.

$$q_1 = \alpha_{1n} + \frac{\beta_{1n}}{T} - \gamma_{1n} \ln T - \delta_{1n} T \qquad (3\text{-}37)$$

$$q_1 = \alpha_{1r} + \frac{\beta_{1r}}{T} - \gamma_{1r} \ln T - \delta_{1r} T \qquad (3\text{-}38)$$

The second term in the sum (Equation 3-35) (i = 2) is a functional group correction.

$$\xi_2 = f_0 + f_1 N_{cm} + f_2 N_{cm}^2 + f_3 N_{cm}^3 + f_4 N_{cm}^4 \qquad (3\text{-}39)$$
$$q_2 = \alpha_2 + \frac{\beta_2}{T} - \gamma_2 \ln T - \delta_2 T$$

In Equations 3-36 to 3-39, ξ_1 and ξ_2 are structural and functional group correction factors, and q_1 and q_2 are structural and functional group corrections, respectively; α_i, β_i, γ_i and δ_i are correction constants for correction type i, and subscripts n and r denote non-ring and ring compounds, respectively. Equation 3-36 is employed to describe the effect of alkyl substituents on the vapour pressure of substituted benzenes. N_{as} is the number of carbon atoms on the alkyl substituent, N_{bs} is the number of branched alkyl substituents, N_{es} is the number of neighbouring alkyl substituents and s_0, s_1, s_2 and s_3 are constants. For example, the N_{cs}, N_{bs} and N_{es} of 1,2-diisopropyl benzene (Figure 3-4) is 6, 2 and 1, respectively. The effect of the functional groups on the vapour pressure is corrected according to N_{cm}, the number of carbon atoms on the molecule, and the constants of the functional group correction factor, f_0, f_1, f_2 and f_3. The predicted constants, A_i, B_i, C_i and D_i in Equation 3-34 are given in Table A-13. For Equations 3-36 to 3-39, the tabulated values of the corrections and constants are presented in Tables A-14 to A-17.

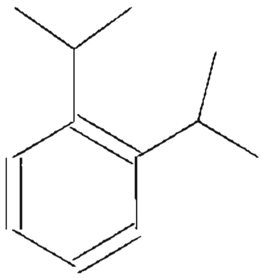


Figure 3-4: Molecular structure of 1,2-diisopropyl benzene.

In total, Tu employed 216 group values and 135 correction values for a set of only 336 components (5287 data points). From the sets of groups and corrections defined in Tu's work, it can be assumed that this method can only be applied to certain homologous series, or components within the data set. At the same time the regression of the constants, A_i, B_i, C_i and D_i, is difficult as the parameters intercorrelate and thus, an error within one influences other values.

Tu reported an average absolute percentage error of 5% for the above data set, within a temperature range of 90-643K or pressure range of 0.01-8103 kPa. Estimation of multi-functional compounds would produce high errors as additional functional corrections would have to be defined. Also, components that do not belong to a particular homologous series, for example highly branched alkanes or fused aromatics, are questionable in their estimation. Thus, the proposed work by Tu has a limited range of applicability. At the same time, Tu did not use a test set of components that were not used in the regression, to test the predictive capabilities of the method.

Voutsas *et al.* (2002) developed a simple method for the prediction of vapour pressures from information about the normal boiling point only. As compared to the method of Tu, Voutsas did not use functional groups and corrections but instead, defined certain values for different homologous series. This method also has a more theoretical and meaningful derivation than the method of Tu, but carries the same limitations. There are also a few other group contribution methods, which are similar to the approach employed by Tu, but restricted to individual classes of components.

Another approach to estimate fluid properties is the 'two reference fluids' estimation method first proposed by Lee & Kesler (1975). In the Lee-Kesler method, a fluid's properties are obtained by interpolation between the properties of a simple fluid ($\omega = 0$) and a reference fluid ($\omega \neq 0$). Ambrose & Patel (1984) used either propane and octane or benzene and pentafluorotoluene as the reference fluids. From an example calculation of vapour pressures of acetone, using propane and octane as the reference fluids, Reid *et al.* (1987) reported average absolute percentage errors as much as five times greater than the Antoine equation. Ambrose and Patel also suggested that an interpolation in the acentric factor, Equation 3-40, would produce more reliable estimates. However, the disadvantage of the method is that knowledge of critical properties is required which severely reduces the range of applicability of the method.

$$\omega^{reference1} < \omega < \omega^{reference2} \tag{3-40}$$

There are also a number of more complex estimation techniques employing QSPR correlations or molecular properties from molecular mechanics. Using only the molecular structure, there is a predictive approach using a COSMO solvation model (Klamt (1995) and Klamt *et al.* (1998)). Sandler *et al.* (2004) developed a general predictive method based on the calculation of the solvation free energy that consists of three parts; the electrostatic, dispersion and cavity formation contributions. The electrostatic contribution is determined by a quantum mechanical COSMO solvation model. For the cavity term, a thermodynamic perturbation theory for hard sphere molecules is employed, and the dispersion term is modelled using a mean field proportional to the density and molecular surface area. The method also includes a number of parameters to account for variations in molecular structure, functional groups and size of the molecule. This approach, which requires a fair amount of computational expertise, is derived from the chemical potential of pure substances and reports extraordinarily high errors of 76% for a set of only 317 compounds.

Thus currently, there is no estimation method that is able to accurately predict the vapour pressure of a large variety of organic compounds from the molecular structure. As presented in this work, most are only applicable to certain homologous series or have the limitation of requiring knowledge of critical properties. Thus the purpose of this work is to develop a group contribution method to estimate the vapour pressures of a wide variety of organic compounds. The Antoine and DIPPR equations with tabulated or newly regressed parameters will be used for comparison.

Chapter Four

Liquid Viscosity

4.1 Introduction

If a shearing stress is applied to any segment of a confined fluid, the fluid will move with a velocity gradient such that its maximum velocity is at the point where the stress is applied. Now if the local shear stress per unit area at any point is divided by the velocity gradient, the ratio obtained is defined as the viscosity of the fluid. Thus, viscosity is the measure of the resistance of a fluid to deformation under shear stress. More commonly, it can be perceived as "thickness", or resistance to flow. Viscosity can also be thought of as a measure of fluid friction. Thus, water is "thin" and has a low viscosity, whereas vegetable oil is "thick" and has a high viscosity.

In general, in any flow, layers move at different velocities and the fluids "thickness" arises from the shear stress between the layers that ultimately oppose any applied force. Isaac Newton postulated that for straight, parallel and uniform flow, the shear stress, τ, between layers is proportional to the velocity gradient in the direction perpendicular to the layers (Equation 4-1).

$$\tau = -\mu \frac{\partial u}{\partial y} \tag{4-1}$$

Here, the constant μ denotes the coefficient of viscosity, viscosity or dynamic viscosity. Many fluids satisfy Newton's criterion and are known as Newtonian fluids (Figure 4-1). Non-Newtonian fluids exhibit a more complicated behaviour between shear stress and the velocity gradient than simple linearity (Figure 4-2).

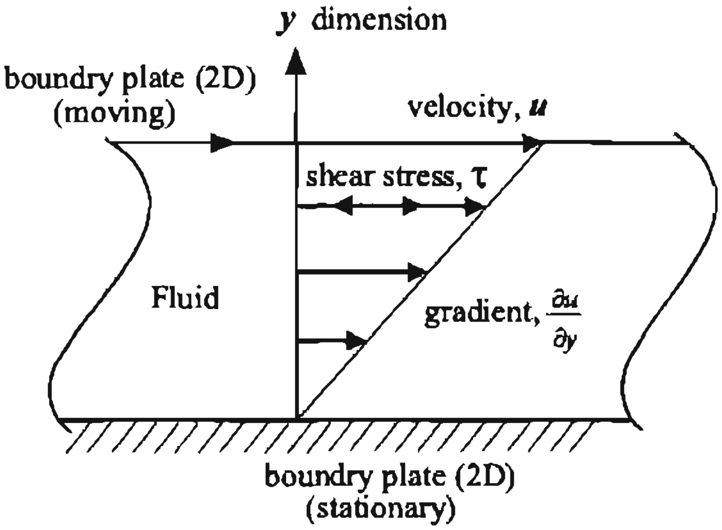


Figure 4-1: Velocity gradient for a Newtonian fluid (Massey (1983)).

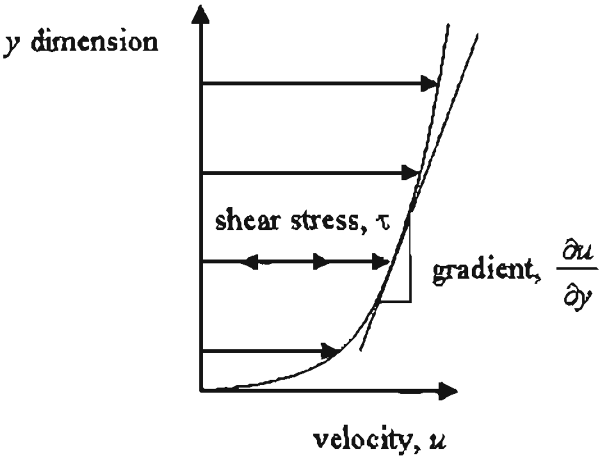


Figure 4-2: Velocity gradient for a non-Newtonian fluid (Massey (1983)).

Since viscosity is defined as the ratio of shearing stress per unit area and a velocity gradient, it has the dimensions (force)*(time)/(length)^2. In scientific terms, it can also be expressed as poises (p), where 1 poise denotes a viscosity of 0.1 N.s.m^{-2}.

The viscosity of gases at low densities and sufficiently high temperatures (perfect gas) can be described by a simple equation taking into account the mean free path and transported momentum difference. On the basis of molecular considerations, the dilute gas region may be best defined by the Boltzmann equation for monatomic gases. A vast amount of literature exists for the dilute gas region, of which a comprehensive review is provided by Touloukian *et al.* (1975).

The liquid viscosity on the other hand is governed by higher order collisions, and thus, is out of the scope of the Boltzmann equation. Besides being significantly larger, liquid viscosity shows temperature dependence opposite to that of gases. In addition, it shows significant density dependence which is not present in gases. Both these facts suggest that the mechanisms governing liquid viscosity are totally different from those leading to gas viscosities. Application of gas models to liquids can therefore not be successful. Thus, no complete and rigorous theory has yet been developed for the dense region.

Models for the interpretation of liquid viscosity range from simplified models such as Eyring's activated state theory and its successive modifications to approaches like Enskog's hard sphere theory, and finally include rigorous mechanical approaches in the form of the distribution function or time-correlation functions methods. All of the above approaches have failed to correctly predict the experimental findings from molecular properties. With respect to statistical mechanics, a good detailed review is provided by Stephan & Lucas (1969), who also cited further reviews by Gubbins (1973), Steele (1969), Rice & Gray (1965), Mazo (1967), Rice *et al.* (1968) and Brush (1961). These types of methods will not be discussed in this work.

The problem of viscosity thus provides a typical example for the fact, that, even when building a theory for a single property or a set of physical properties on an understanding of its microscopic behaviour, no suitable predictive model may be obtained.

Andrade (1934a) suggested that in building a theory of liquid viscosity for practical application, it should be at least partly or even half of an empirical nature. This would allow the description of any irregularities in the experimental data by an empirical approach while retaining a physically meaningful description of the overall trend. This suggestion is the strategy that is used in this work with application to all properties.

A large variety of rigorous statistical mechanical theories, empirical and correlative techniques have been mentioned thus far. In this work, only empirical and correlative techniques will be discussed.

4.2 The Temperature Dependence of Liquid Viscosity

As argued above, liquid and gas viscosity are governed by different mechanisms. This can be deduced from the fact that the viscosity of liquids decreases with rising temperature, whereas the viscosity of gases increases. In a gas, a tangential force is produced between two parallel layers by the transport of individual molecules from one layer to another that results in a transfer of momentum. The molecules collide with one another and move freely over a certain distance. The same theory does not hold for a liquid where the molecules mostly reside in longer-living structures and only perform short lasting "jumps" to other positions (the motions of the molecules are always in a field of intermolecular forces).

A number of previous researchers have recognized that friction by transport, which occurs in the gaseous mechanism, is inadequate to explain liquid viscosity. There are various possible mechanisms of which the forces of collision seem to be the only proven factor. A communication of momentum from layer to layer takes place at the extreme liberation of molecules oscillating about an equilibrium position. This means that the liquid viscosity decreases with temperature because the temperature agitation interferes with the interchange of momentum at the extreme liberations. Thus, to account for the temperature variation, there must be a mutual potential energy of the molecules which is necessary if transfer of momentum is to take place. This energy is negative, since the molecules approach one another under conditions where the forces of attraction are large. Then, in accordance with the Boltzmann exponential distribution law, the number of cases favourable for transfer will decrease as the temperature rises and this rate of decrease is governed by the magnitude of the potential energy involved.

There have been many attempts to apply the kinetic theory of gases to liquids. However, the assumption of the attractive forces in gases being negligible makes it rather evident that this theory cannot be applied to liquids. In the ordinary sense, a liquid is governed by intermolecular forces, and in some aspects more closely resembles a solid than a gas.

4.3 Empirical Estimation and Correlative Techniques

The first advancement to these types of techniques was the representation of viscosity over a wide region of states in terms of temperature and density. It is especially useful to plot the residual viscosity (viscosity at a specified temperature and density minus its value at the same temperature and zero density) as a function of density (Equation 4-2).

$$\mu(T,\rho)-\mu_0(T) = f(\rho) \tag{4-2}$$

This concept was originally developed for another transport phenomenon (thermal conductivity (Abas-zade (1952)) and has been extensively discussed for interpolation and extrapolation purposes by Brebach & Thodos (1958), Shimotake & Thodos (1958), Groenier & Thodos (1961), Eakin & Ellington (1965), Dillier *et al.* (1970) and Lucas & Stephan (1973). From Equation 4-2, one isotherm in the dense fluid region is sufficient, together with the dilute gas viscosities as a function of temperature, to obtain data for all fluid states for which PVT data are available. Given also that PVT-data are more readily available than the dense fluid viscosity data; this concept is valuable for obtaining approximated viscosity values. However, Roger & Brickwedde (1965) and Kestin & Wang (1968) suggested that this concept is barely valid at high and low densities where the temperature dependence of viscosity becomes significant. In view of these factors, a more accurate representation should be obtained for the temperature dependence of viscosity in the different states.

In this work, the separate correlation of viscosity in terms of temperature and density is not considered. In addition to the fact, that a suitable equation of state is required, density data along the vapour-liquid equilibrium curve would have to be iteratively calculated from given temperature values. It is more convenient to represent saturated liquid viscosity data as an explicit function of temperature. An explicit equation for viscosity for the entire regime of states, as a function of temperature and pressure, is not possible because of the infinite gradients at the critical point. This led to the subdivision of the total fluid region into various sub regions such as the dilute gas, dense gas, and two liquid regions, one close to the critical point and one at lower temperatures.

Figure 4-3 shows that the general form of the viscosity behaviour is not very different from the PVT-behaviour of a fluid and thus an equation, for example Van der Waals, may possibly be able to reproduce this behaviour over the whole range for many components with the critical point as the reference point. In case of transport properties, the property diverges when approaching the critical point (Figure 4-4), so that an equation of state would not be valid within this region and a fictious critical viscosity, thermal conductivity, etc. would be required. In addition, a Van der Waals type equation would falsely predict a decrease of gas viscosity with temperature.

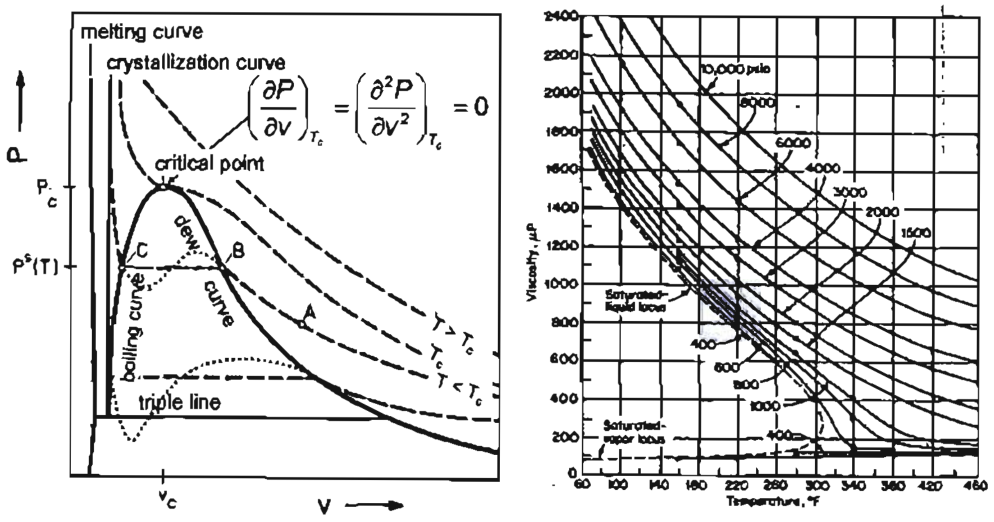


Figure 4-3: Volume (Gmehling (2006)) and viscosity (Onken *et al.* (1998)) plots as a function of temperature and pressure.

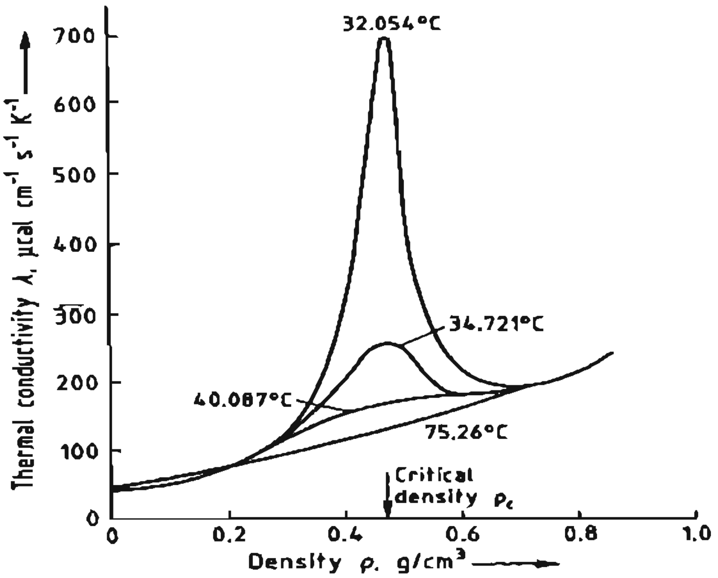


Figure 4-4: Thermal conductivity as a function of density and temperature (Onken *et al.* (1998)).

Correlations are also not readily available at or near the critical point and since the viscosity usually becomes low near this state, there is some degree of technical interest, for example in case of supercritical extraction, etc. However, this work will only consider the liquid region below the critical point with special attention to low temperatures.

There are also numerous correlations for viscosity which employ the interrelationships between viscosity and various other thermodynamic and transport properties. Among these relationships is the example of linking the viscous energy in Eyring's reaction rate expression to the internal energy of vaporization. This can also be extended to including specific volume and molar entropy of vaporization. There are also other correlations related to using the sonic velocity and, at high pressure, the compressibility factor.

Relations between viscosity and other transport properties may also be rigorously found from kinetic theory. There are relations between viscosity and thermal conductivity and diffusion coefficients. The quality of such relations between the various transport properties is subject to restrictions of irreversible thermodynamics, where mathematical transformations of transport properties exhibit different type of fluxes and generally don't interrelate. For these reasons, these types of methods will not be discussed in this work.

4.3.1 Correlative techniques.

The effect of temperature on liquid viscosity is analogous to that in case of liquid vapour pressure. However, the viscosity of liquids decreases with increasing temperature either under isobaric or saturated liquid conditions. This behaviour can be seen in Figure 4-5, where the liquid viscosity and vapour pressure of ethanol is plotted as a function of temperature.

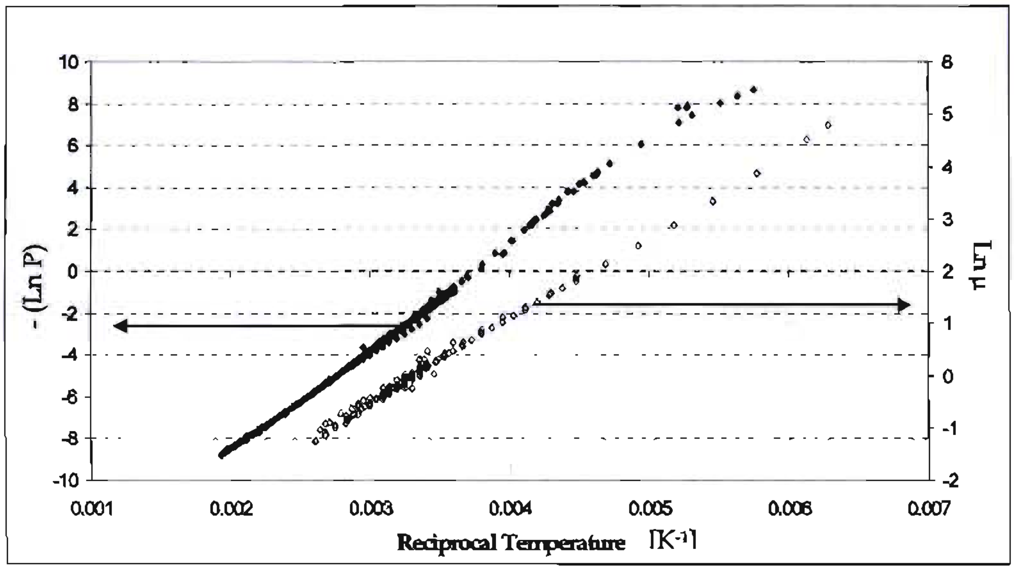


Figure 4-5: Liquid viscosity and vapour pressure of ethanol.

In accordance with the proposed theory, for the transfer of momentum to take place, the molecules must possess a mutual potential energy (*E*). If the frequency of vibration (*v*) is assumed to be constant, the variation of viscosity with temperature will be governed by the fraction of molecules attaining this energy at extreme liberation. From the Boltzmann distribution formula, Andrade (1934b) proposed that for the ratio of the number of molecules possessing energy (*E*) at temperature *T* to the number possessing the same energy at temperature T' is:

$$\frac{\mu_T}{\mu_{T^*}} = e^{\frac{E}{k}\left(\frac{1}{T}-\frac{1}{T^*}\right)} \tag{4-3}$$

An approximate formula for temperature variation of viscosity can thus be described by Equation 4-4.

$$\frac{\mu_T}{\mu_{T^*}} = e^{\frac{E}{kT}} . e^{-\frac{E}{kT^*}} \tag{4-4}$$

For a temperature range from the melting point to a temperature slightly above the normal boiling point (generally in the region of 0.8 of the reduced temperature), Equation 4-4 can be expressed in a more general form (Equation 4-5).

$$\ln \mu = A + \frac{B}{T} \tag{4-5}$$

This form was first proposed by de Guzman (1913), but is more commonly know as the Andrade equation. There have been many variations proposed to improve its correlative accuracy; many include a function of the molar volume in the *A* or *B* parameter (Bingham & Stookey (1939), Cornelissen & Waterman (1955), Eversteijn *et al.* (1960), Girifalco (1955), Gutmann & Simmons (1952), Innes (1956), Marschalko & Barna (1957), Medani & Hasan (1977), Miller (1963a), (1963b), Telang (1945) and Van Wyk *et al.* (1940)). Vogel (1921) proposed another variation by the introduction of a third constant (Equation 4-6), quite similar to the Antoine equation for vapour pressures. For this form of the equation, there are a number of reported values for the parameters *A*, *B* and *C* in literature.

$$\ln \mu = A + \frac{B}{T+C} \tag{4-6}$$

Equation 4-5 requires at least two data points to determine the two constants. Lewis & Squires (1934) proposed from empirical facts that the sensitivity of viscosity to temperature variations appears to depend only on the value of the viscosity. This is also known as the Lewis-Squires chart, which can be expressed in the form an equation (Equation 4-7).

$$\mu^{-0.2661} = \mu_k^{0.2661} + \frac{T - T_k}{233} \tag{4-7}$$

Here μ is the liquid viscosity at temperature T, and μ_k is the known liquid viscosity at T_k. This equation is only approximate and has errors reported by Poling *et al.* (2000) from 5 to 15% (or greater).

Porter (1912) was the first to draw attention to the relationship between liquid viscosities and vapour pressures, when he showed that the logarithm of viscosity for mercury and water depends linearly on the logarithm of vapour pressure. Drucker (1918) proposed an analytic formulation of this relation, Equation 4-8.

$$\ln \mu = A + B \ln P \tag{4-8}$$

However, Drucker reported that large deviations from Equation 4-8 were observed for strongly associating liquids. Mitra & Chakravarty (1954) showed that for strongly associating liquids, the parameter B is a function of temperature, and recommended to employ Equation 4-9 (where C is a component-specific parameter).

$$\ln \mu = A + B \ln P - C(\ln \mu)^2 \tag{4-9}$$

There are numerous other viscosity-correlating methods that have been proposed. A number of these are summarized and reviewed by Stephan & Lucas (1969), Poling *et al.* (2000), Reid *et al.* (1987), Reid & Sherwood (1958), Viswanath & Natarajan (1989), Mehrotra (1991), Mehrotra *et al.* (1996) and Monnery *et al.* (1995).

4.3.2 Discussion of Correlative techniques.

In order to develop a group contribution method for a temperature dependant property, the data for each component are often first correlated using a simple equation. It is imperative in the correlation that the parameters have minimal interrelation. In addition, the correlative parameters employed should have physical significance and relate to the chemical constitution of the respective compound. In this work, the different correlative methods are not evaluated based on their accuracy to reproduce experimental data, but with respect to their ability to yield reproducible parameters that have a minimum dependence on experimental data irregularities.

All reviews cited earlier, assess correlative models based on their interpolative and extrapolative capabilities when applied to random compounds. Another means to assess their correlative power and to test whether the models have a semi-theoretical background is to examine their correlation with chemical constitution.

Batschinski (1913) was the first to find a relationship between liquid viscosity and molar volume. This was later modified by Lucas & Lucas (1986), who derived Equation 4-10 (where V_{ref} is the volume of the liquid at which $\mu = 1cp$). Lucas and Lucas consequently found that by plotting V_{ref} and V_o for n-alkanes, the relationship to chemical constitution was linear. Thus, the new relationship is effective in producing sensible parameters which are now dimensional physical quantities. This relationship proves that the viscosity increases linearly with increasing molar volume.

$$\mu = \frac{V_{ref} - V_o}{V - V_o} \qquad (4\text{-}10)$$

In order to examine the semi-theoretical background of the correlative models, it is important to understand the parameters associated with these models. Consider the Andrade equation which was derived from the simple activation energy type expression (Equation 4-5), where the *A* parameter relates to the molar volume of the liquid (fixed point). The *B* parameter correlates with the potential energy (slope) and should solely depend on the type of molecule (as with the *A* and *B* parameters in the Clausius-Clapeyron equation in Section 3.3.2). Figure 4-6 plots the n-alkane *A* and *B* parameters as a function of molecular weight from the Andrade Equation.

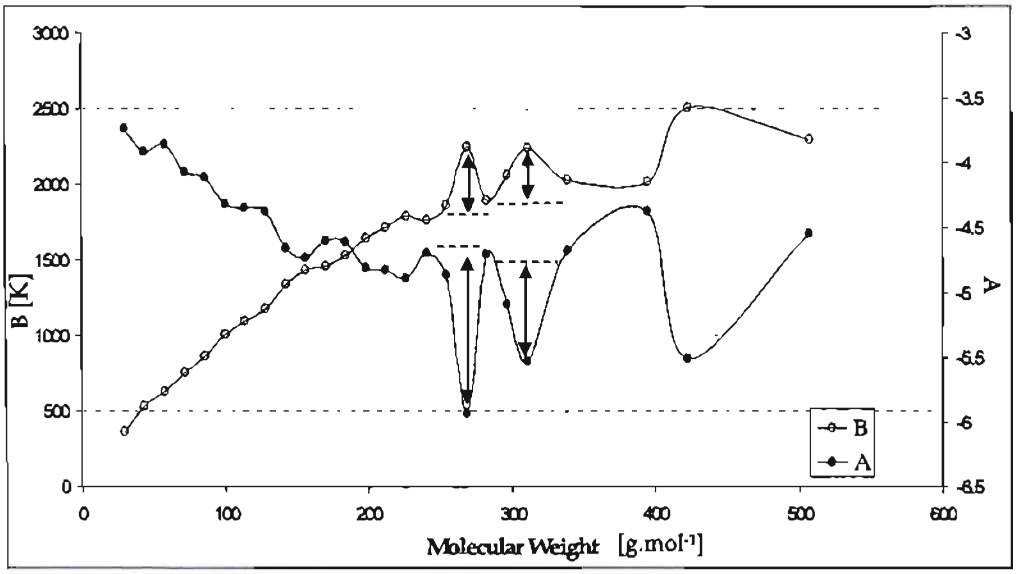


Figure 4-6: Plot of *A* and *B* parameters for n-alkanes (Andrade Equation).

Both trends in Figure 4-6 depict meaningful results. Some scatter is observed but this is the result of the insufficient quality of experimental data for higher alkanes. This is the general problem with viscosity data since they usually cover a certain range of temperatures. Very little data over the same temperature range are available for a set of components in a homologous series. The data are also confined to small temperature ranges which limit a meaningful analysis of the parameters. In the case of vapour pressure data, experiments usually cover a wider temperature range and are generally less influenced by the pressure range. Thus, the parameters, for example, of the Antoine equation (*A* and *B*) are relatively smooth (Figure 4-7) within a homologous series.

It also should be noted that the intercorrelation of parameters is dependant on the temperature range (as discussed in Section 3.3.3). For example, it can be seen in Figure 4-6 that for several components where one parameter deviates from the general trend, the other parameter deviates in the opposite direction proportionately (consider the length of the both parameters deviation for one component, where the ratio is similar to another component). Thus, the deviations for the two parameters from the general trend are strongly intercorrelated. Another reason for the observed deviation can lie in the poor quality of data. But in general, the plots provide a means of assessing the quality of the parameters, and in essence, their interpolative and extrapolative capabilities (parameters for components that deviate from the general trend would be deemed questionable).

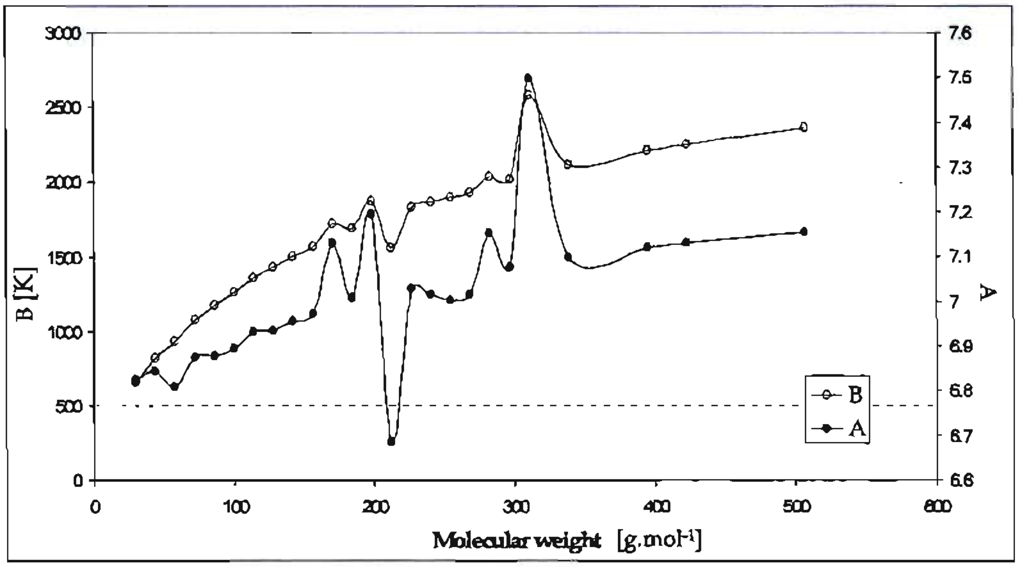


Figure 4-7: Plot of *A* and *B* parameters for n-alkanes (Antoine Equation).

The deviation of the *B* parameters from the general trend in Figure 4-6 also may imply that the parameters are temperature dependent. Thus, it has to be tested beforehand whether the correlative equation is able to cover a large viscosity-temperature range. If this is not the case then a correlative equation will yield different parameters for different viscosity ranges. The general trends from Figure 4-6 can also be seen for 1-alcohols (Figure 4-8), a homologous series that exhibits hydrogen bonding.

For the Vogel equation, a plot of the *A* and *B* parameters is presented in Figure 4-9 for n-alkanes. When compared to the Andrade plot, there is a significantly larger scatter and no evident trend.

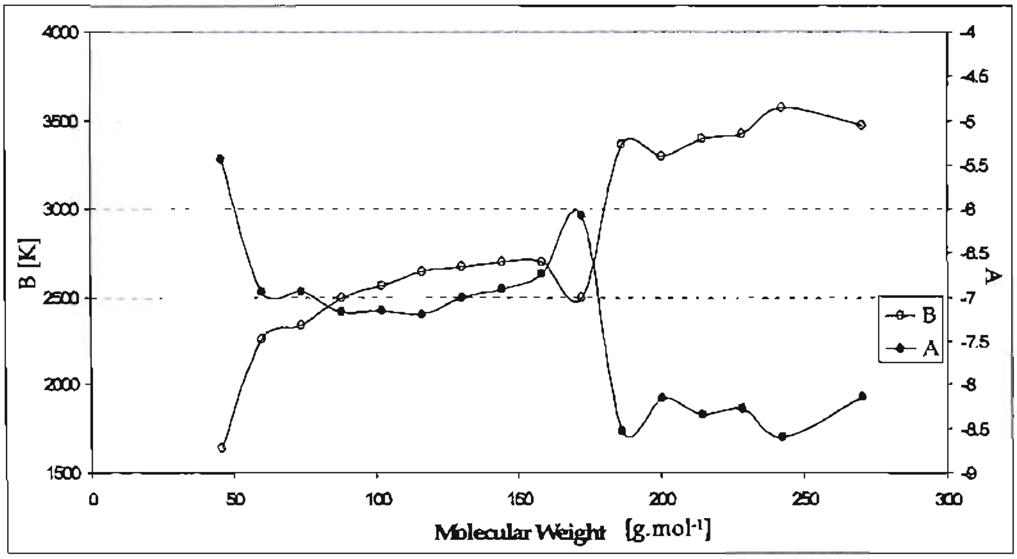


Figure 4-8: Plot of *A* and *B* parameters for 1-alcohols (Andrade Equation).

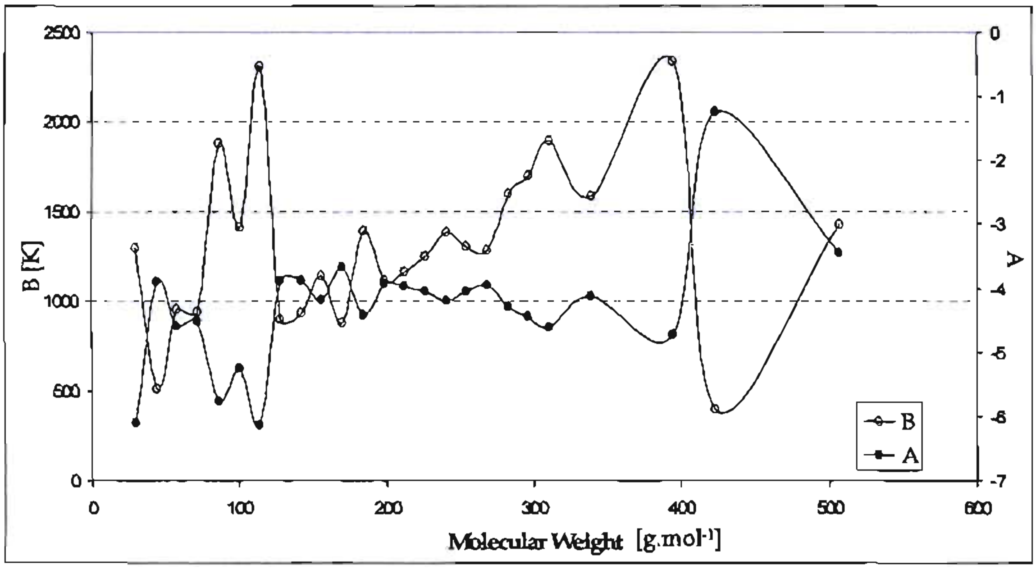


Figure 4-9: Plot of *A* and *B* parameters for n-alkanes (Vogel Equation).

The C parameter of the Vogel and Antoine equation is also plotted for n-alkanes in Figure 4-10. For the Antoine equation, an obvious trend is evident with almost no scatter. However, for the Vogel equation, although the trend depicted by the C parameter bares some resemblance to the Antoine C parameter, a large scatter is observed.

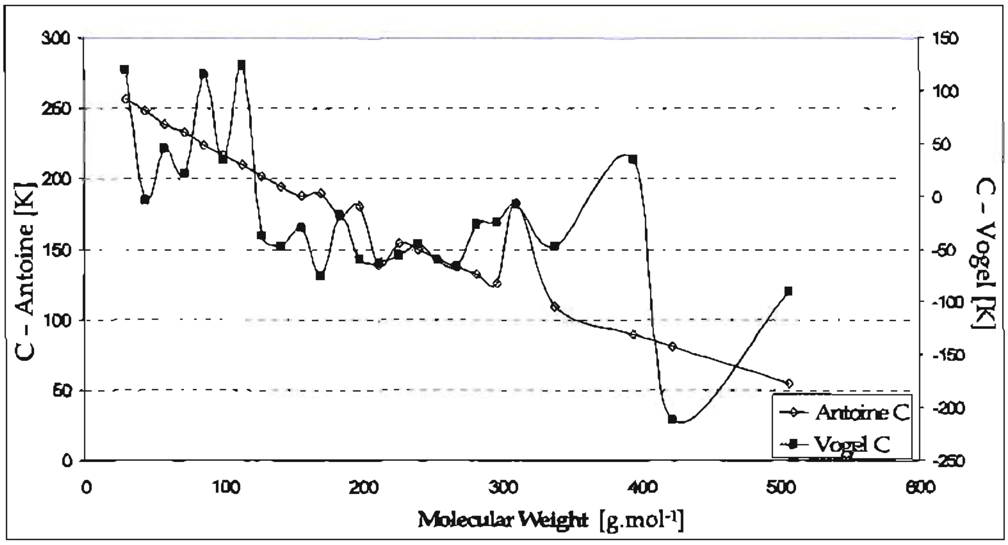


Figure 4-10: Plot of the C parameter for n-alkanes.

From the presentation of both plots for the Vogel parameters, even for the simple n-alkanes series exhibiting weak London forces, no observable trend is evident. The introduction of the C parameter was on the basis of removing the temperature dependence of the *B* parameter, but the trend depicted by the latter does not substantiate this theory. Even considering the fragmentation of data, the trends depicted by the Andrade equation should show some resemblance to the scatter of the Vogel equation. To substantiate the Vogel plots, a plot of the *A* and *B* parameters for 1-alcohols is presented in Figure 4-11. Similar results are observed as in the case of the previous two plots.

The introduction of the *C* parameter in the Vogel equation leads to a strong intercorrelation of the *A* and *B* parameters. This implies that the extrapolative capabilities of the Vogel equation are questionable and the equation should not be used outside the temperature range of the data.

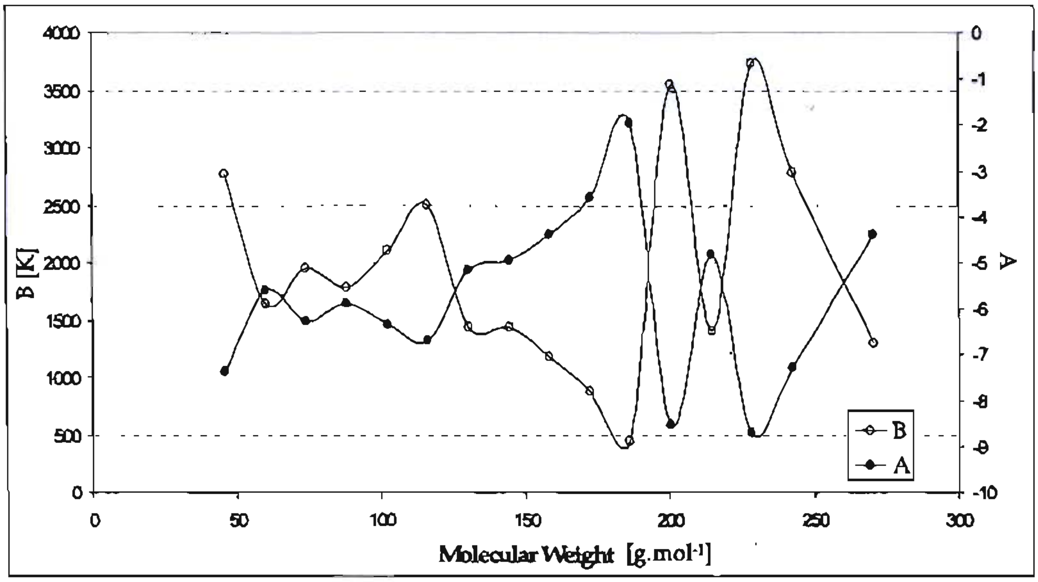


Figure 4-11: Plot of 1-alcohol *A* and *B* parameters from the Vogel Equation.

The Andrade and Vogel models are arguably the most popular and commonly employed correlations for liquid viscosity. A third correlation will also be discussed which is most commonly employed in the group contribution estimation of liquid viscosity. This is the viscosity-pressure relationship, first suggested by Drucker, Equation 4-8. A plot of the *A* and *B* parameters for n-alkanes is presented in Figure 4-12. The *A* parameter is not influenced by the size of the molecule. More interestingly, the *B* parameter seems to have a minimum which is extremely difficult to correlate with respect to chemical constitution.

As a further example, a plot of the *A* and *B* parameters for 1-alcohols is presented in Figure 4-13. Both parameter trends exhibit either a minimum or maximum. Thus, it can be concluded that the parameter trends obtained for the Drucker equation are not suitable for group contribution method development. Different series yielding different trends makes a group contribution estimation of these parameters almost impossible.

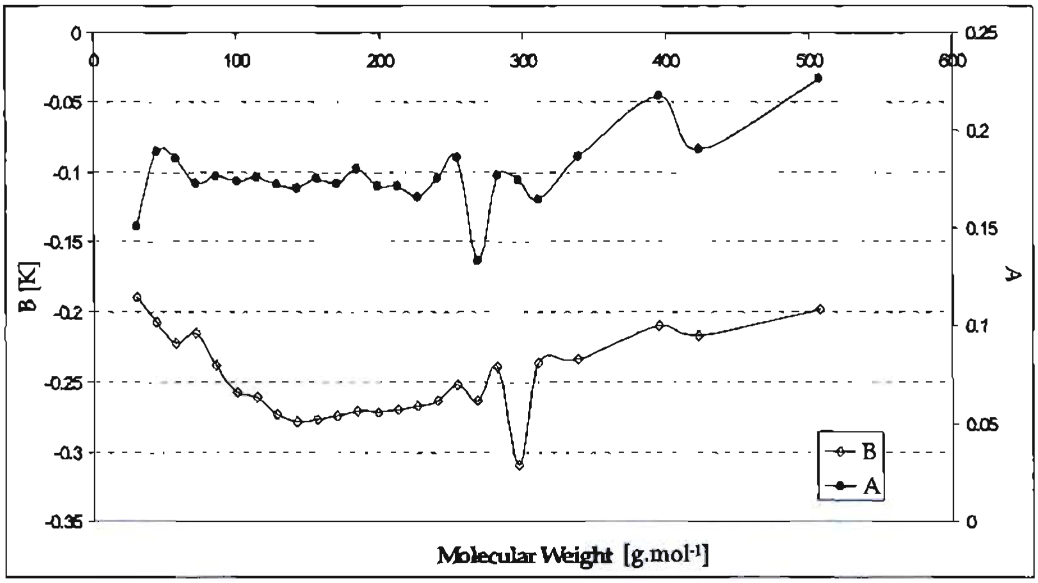


Figure 4-12: Plot of *A* and *B* parameters for n-alkanes (Drucker Equation).

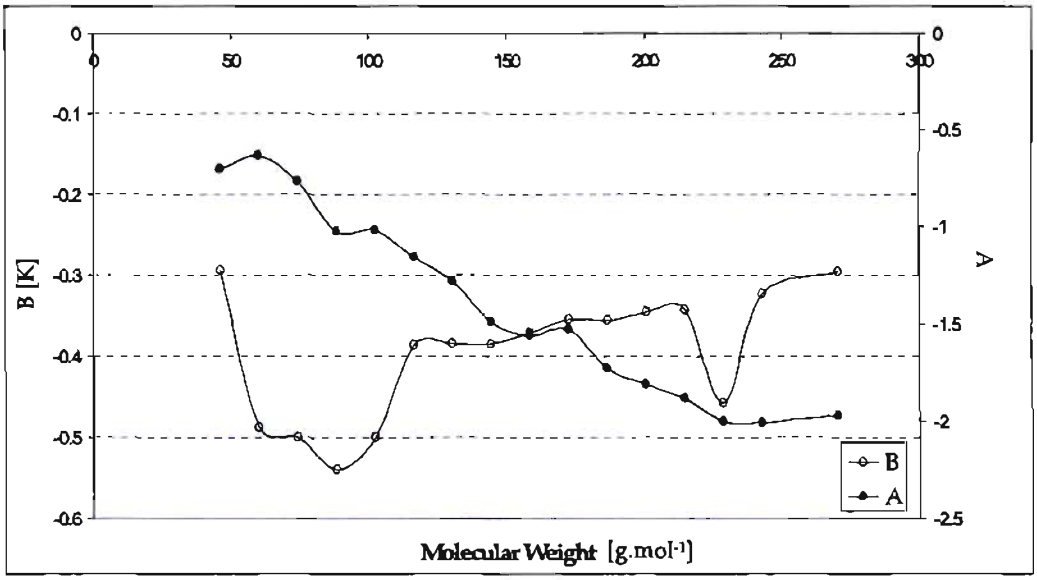


Figure 4-13: Plot of *A* and *B* parameters for 1-alcohols (Drucker Equation).

4.4 Group Contribution Methods

These types of methods employ group or structural parameters that are generally available for certain homologous series, or a list of different structural groups. Most methods use some variation of Equation 4-5 and are applicable up to a reduced temperature of 0.7-0.8. As the proposed method will be based on the same approach, a thorough description and discussion of several methods of this type will be presented here.

4.4.1 Orrick & Erbar (1974)

This method employs a very simple group contribution approach to estimate the values of A and B for Equation 4-5.

$$\ln\frac{\mu_L}{\rho_L M} = A + \frac{B}{T} \tag{4-11}$$

The equation requires a liquid density value at 20 °C or at the melting point (whichever is higher). The method incorporates 28 simple structural groups for both parameters and is only applicable to hydrocarbons as well as halogenated (except fluorinated) and oxygenated compounds. Structural groups are given in Table A-18. The authors report mean absolute percentage error of approximately 15% for 188 organic liquids. This method requires knowledge of liquid density and will therefore not be discussed any further.

4.4.2 Van Velzen et al. (1972)

Van Velzen and co-workers proposed an estimation method in which viscosity depends solely on temperature and chemical constitution. The basis of this method is the Andrade equation (Equation 4-5). By choosing a reference point of μ = $1cP$, it follows that $T_0 = -B/A$. With a slight modification of the original equation, the following equation was proposed:

$$\ln\mu = B\left[\frac{1}{T} - \frac{1}{T_0}\right] \tag{4-12}$$

This equation contains two parameters; T_0 which is the intercept of the log viscosity-temperature line with the abscissa, and B which is the slope of the line. Van Velzen observed that both parameters are functions of n_c, the number of carbon atoms. For the homologous series of n-alkanes and by a regression analysis, he found that for $n_c \leq 20$:

$$T_o = 28.86 + 37.439n_c - 1.3547n_c^2 + 0.02076n_c^3 \tag{4-13}$$

$$B = 24.79 + 66.885n_c - 1.3173n_c^2 + 0.00377n_c^3 \tag{4-14}$$

And for $n_c > 20$:

$$T_o = 238.59 + 8.164n_c \tag{4-15}$$

$$B = 530.59 + 13.740n_c \tag{4-16}$$

In order to be applicable to isomeric alkanes, the principle of the effective carbon number (*ne*) was introduced. The effective carbon number (also referred to as the equivalent chain length) is the chain length of a hypothetical n-alkane with viscosity equal to 1cP at the temperature where the viscosity of the compound in question is also 1cP. *ne* can be calculated from the total number of carbon atoms in the molecule and one or more structural and/or configuration factors (Δn) (Equation 4-17).

$$ne = n_c + \Delta n_c \tag{4-17}$$

In the same way, B is calculated as the sum of B_a, which is the value of B for the hypothetical alkane with the equivalent chain length *ne*, and ΔB, which is the correction factor depending on the chemical constitution of the compound (Equation 4-18). Generally, Δn_c is not a constant, but a function of n_c, whereas in most cases ΔB is a function of *ne*.

$$B = B_a + \Delta B \tag{4-18}$$

For compounds with more than one functional group both Δn and ΔB are cumulative. Thus, the equivalent chain length can be found from Equation (4-19)

$$ne = n_c + \Delta n_{c1} + \Delta n_{c2} \ldots \tag{4-19}$$

Once ne is known, T_0 can be calculated from Equation 4-13 or 4-15, inserting ne for n_c. B_a is found from Equation 4-14 or 4-16, inserting B_a and ne for B and n_c. Subsequently the required viscosity can be calculated from Equation 4-12, as both B and T_0 are now available. There exists one important difference between the calculation of ne and B. In case of two or more identical functional groups, the corrections Δn_c can be applied additively. On the contrary, for the calculation of B, the functional correction ΔB has to be applied only once.

Table A-19 and A-20 provides the various functions for Δn_c and ΔB for a number of functional groups and structural configurations, respectively. These values were obtained by a careful statistical evaluation employing 314 compounds and close to 4500 data points. The authors reported average deviations of 10 to 15% for this data set.

4.4.3 Skubla (1985)

Skubla (1985) employed Equation 4-8 and, by the least squares method, calculated values for parameters A and B for 199 compounds, or 4144 data points. The vapour pressure was calculated from the Antoine equation, however for 1-olefins, some n-alkyl-cyclohexanes and n-alkylbenzenes, it was calculated front the Frost—Kalkwarf equation.

The parameters A and B were divided into structural contributions Δa and Δb and were expressed in the given homological series as a function of the number of carbon atoms. Values of the structural contributions Δa and Δb are given in Table A-21. Parameters A and B can then be easily calculated for any compound by adding the corresponding contributions Δa and Δb. This method is only applicable to certain homologous series and restricted to the range of carbon atoms defined for the functional groups.

4.4.4 Joback & Reid (1987)

Joback and Reid proposed a model (Equation 4-20) that is similar to the Andrade equation (Equation 4-5). In this case, the slope and intercept are functions of simple functional groups (Table A-5), which are also used in their estimation of normal boiling points and critical properties (described in Section 2.3.7 of this work and in Nannoolal (2004)).

$$\ln \mu = \ln M + \frac{\sum N_i C_{bi} - 597.82}{T} + \sum N_i C_{ai} - 11.202 \tag{4-20}$$

This method has a very limited range with only half of the groups employed for the estimation of critical properties having contributions to estimate the liquid viscosity. For this reason, this method will not be discussed further.

4.4.5 Sastri & Rao (1992)

Sastri & Ramana Rao (1970) proposed an alternate form of the Andrade equation by choosing to equate the reciprocal temperature to the logarithm of the vapour pressure (Equation 4-21). This relation is the same as was first proposed by Porter (1912).

$$\ln \mu = A - N \ln P \tag{4-21}$$

Sastri & Rao (1992) then applied Equation 4-21 at the normal boiling point, Equation 4-22, and by simple substitution, Equation 4-23 was derived.

$$\mu_b = A \tag{4-22}$$

$$\ln \mu = \mu_b - N \ln P \tag{4-23}$$

Here μ_b is the viscosity at the normal boiling point (T_b) and P the vapour pressure. Below the normal boiling point, for the vapour pressure calculation, Sastri and Rao employed Equation 4-24.

$$\ln P = (4.5398 + 1.0309 \ln T_b)\left(1 - \frac{\left(3 - \frac{2T}{T_b}\right)^{0.19}}{\frac{T}{T_b}} - 0.38\left(3 - \frac{2T}{T_b}\right)^{0.19} \ln\left(\frac{T}{T_b}\right)\right) \qquad (4\text{-}24)$$

This vapour pressure equation is not necessarily the most accurate equation for vapour pressure predictions but must be used with Equation 4-21. This is because the group contributions used to estimate μ_b and N have been determined when P was calculated with Equation 4-21. μ_b and N are determined by Equations 4-25 and 4-26, respectively. The values μ_b and N were regressed for 314 compounds, or 4500 data points. The functional groups employed for the parameters in Equations 4-25 and 4-26, are presented in Tables A-22 to A-28.

$$\mu_b = \sum \Delta\mu_b + \sum \Delta\mu_{bcor} \qquad (4\text{-}25)$$

$$N = 0.2 + \sum \Delta N + \sum \Delta N_{cor} \qquad (4\text{-}26)$$

Above the normal boiling point, the authors propose an alternate equation based on the Andrade equation. This relationship requires knowledge of critical properties and is out of the scope of the proposed work.

4.4.6 Discussion of Structural Techniques

A recent method presented by Hsu *et al.* (2002) reported an average absolute percentage deviation of 4.14% for 482 organic liquids or 4627 data points. The property prediction model employs 91 funtional groups in a four-parameter equation (Equation 4-27). Unfortunately, the method is not available via the DDBSP and a comparison to the proposed method cannot be undertaken. However, the method requires a critical point which, would not only improve the accuracy of the method, but conversely, severely limit the range of applicability. In addition, the four-constant equation is bound to have interrelation of the parameters which will question the extrapolative capabilities of the method. At this point though, this discussion is just speculation, but the method will not be discussed further.

$$\ln \mu = \sum_i N_i \left[a_i + b_i T + \frac{c_i}{T^2} + d_i \ln P_c \right] \tag{4-21}$$

Of the five group contribution methods for the estimation of liquid viscosity presented in this chapter, the methods of Orrick & Erbar (1974) and Joback & Reid (1987) have the smallest range of applicability and will not be discussed further.

The method of Skubla employed group contributions to estimate the *A* and *B* parameters of the Drucker (Equation 4-8) relationship. However, as discussed in Section 4.3.2, the trends depicted for these parameters for different homologous series not only yielded inconsistent results, but also deviated within the members of each homologous series. In other words, different homologous series yield different trends and no function is able to correlate the trend within the homologous series itself. For this reason, Skubla employed different functions for different series as well as for different members of the series. This not only questions the extrapolative capabilities of the method, but questions the assumption of group contribution methods, which entails that individual groups are additive. Thus, the Skubla method is mainly applicable to components involved within its development, and for this reason, will not be discussed further.

Sastri and Rao also employed the viscosity-pressure relationship, but derived a new equation by fixing one parameter to the viscosity at the normal boiling temperature. However, this modification has no specific advantage as the equation is identical to the former equation. Accordingly, the same discussion as with the Skubla method applies here as well. For illustration purposes though, some results will be presented for this method in this chapter.

The estimation of the liquid viscosity of n-alkanes from the Sastri and Rao method is presented in Figure 4-14. For the fixed point, μ_b was assumed to be constant for compounds with less than eight carbon atoms, which from Figure 4-12 is actually correct. However, with increasing molecular weight the viscosity curve deviates further away from the experimental data. It can be assumed that the error in the estimation of the slope is caused by the fact that data for higher molecular weight compounds were not included in the training set.

The estimation of the liquid viscosity of 1-alcohols from the Sastri and Rao method is presented in Figure 4-15. Contrary to the estimation of n-alkane viscosities, errors lie in the estimation of both the fixed point and slope. This is evident in cases where it can be seen that the slope deviates from the trend of experimental data or the calculated curve is parallel to the data. This is a perfect example of intercorrelation from the simultaneous regression of both parameters. Also, it is evident that the viscosity-pressure relationship does not obey the group contribution assumption, and in both methods that employ this model, a large number of corrections were added to overcome this limitation.

Van Velzen modified the Andrade equation to include a component-specific reference temperature where the viscosity is 1 poise. The introduction of a reference temperature, rather than a reference viscosity, has a theoretical advantage (discussed in Chapter 9). In case of vapour pressure, a fixed pressure of one atmosphere leads to a reference temperature (the normal boiling point).

Figures 4-16 and 4-17 show plots of T_0 and B for n-alkanes and 1-alcohols, respectively. The trends within each homologous series are smoother than those shown earlier and at the same time, both series exhibit similar trends. Thus, the new model developed by Van Velzen has a clear advantage over the models presented earlier.

The estimation of the liquid viscosity of n-alkanes from the Van Velzen method is presented in Figure 4-18. The method is able to accurately estimate the viscosity of these components, except in case of the smaller compounds. However, it is also noticeable that for the highest molecular weight compounds the slope starts to deviate. In essence, the Van Velzen method overestimates the slope of the smaller compounds and with increasing molecular weight, starts to underestimate it. A reason might be that data for the larger compounds were not in the training set of the method.

Van Velzen only employed six compounds in the regression of primary alcohols (not necessarily 1-alcohols), which can be assumed to be low molecular weight compounds. From the multiple plots of 1-alcohols in Figure 4-19, it is clearly evident that the method fails with increasing molecular weight. Thus it can be assumed that the higher molecular weight compounds were not in the training set. Another instance of the poor performance outside the regression set is seen in the multiple plot for diols in Figure 4-20. Van Velzen employed only two compounds in the regression set, which were probably 1,4-butanediol and 1,5-pentanediol and the estimation of the other diols not in the regression is poor with errors in the slope and fixed point. For primary amines (six compounds employed in regression set), the multiple plot presented in Figure 4-21 yields further poor results. The poor results for components outside the training set of the Van Velzen method could be due to the polynomial terms used to estimate the individual parameters (use of polynomial terms were discussed in Chapter 2). From all the methods presented in this work, the Van Velzen method is the most accurate. At the same time, the method is only applicable to a few members of some homologous series.

From the discussion of estimation methods for temperature dependent properties presented in this and the preceding chapter, it becomes obvious that nearly all of the methods are only applicable to certain homologous series and perform nowhere near the accuracy of correlative methods. One re-occurring observation is that the intercorrelation of parameters from a simultaneous regression of all compounds makes it difficult, or nearly impossible, to develop this type of method for applicability to a wide range of organic compounds. The assumption of linearity within a homologous series for each parameter is also mostly not valid. It is the aim of this work, with respect to liquid vapour pressure and viscosities, to develop methods that are applicable to a wide range of compounds and in comparable accuracy to correlative models.

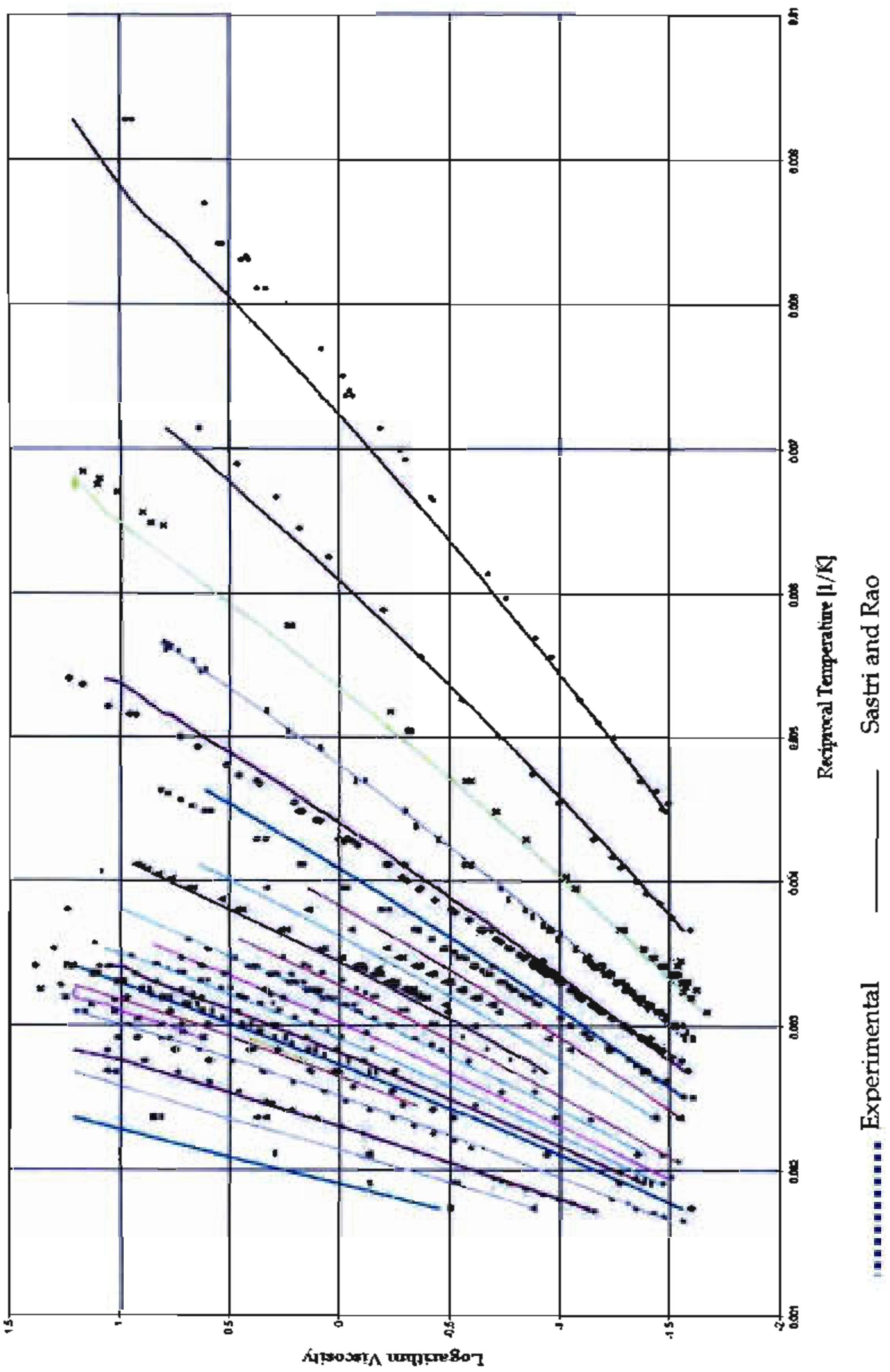


Figure 4-14: Series plot of experimental and estimated liquid viscosities for n-alkanes (Sastri and Rao method).

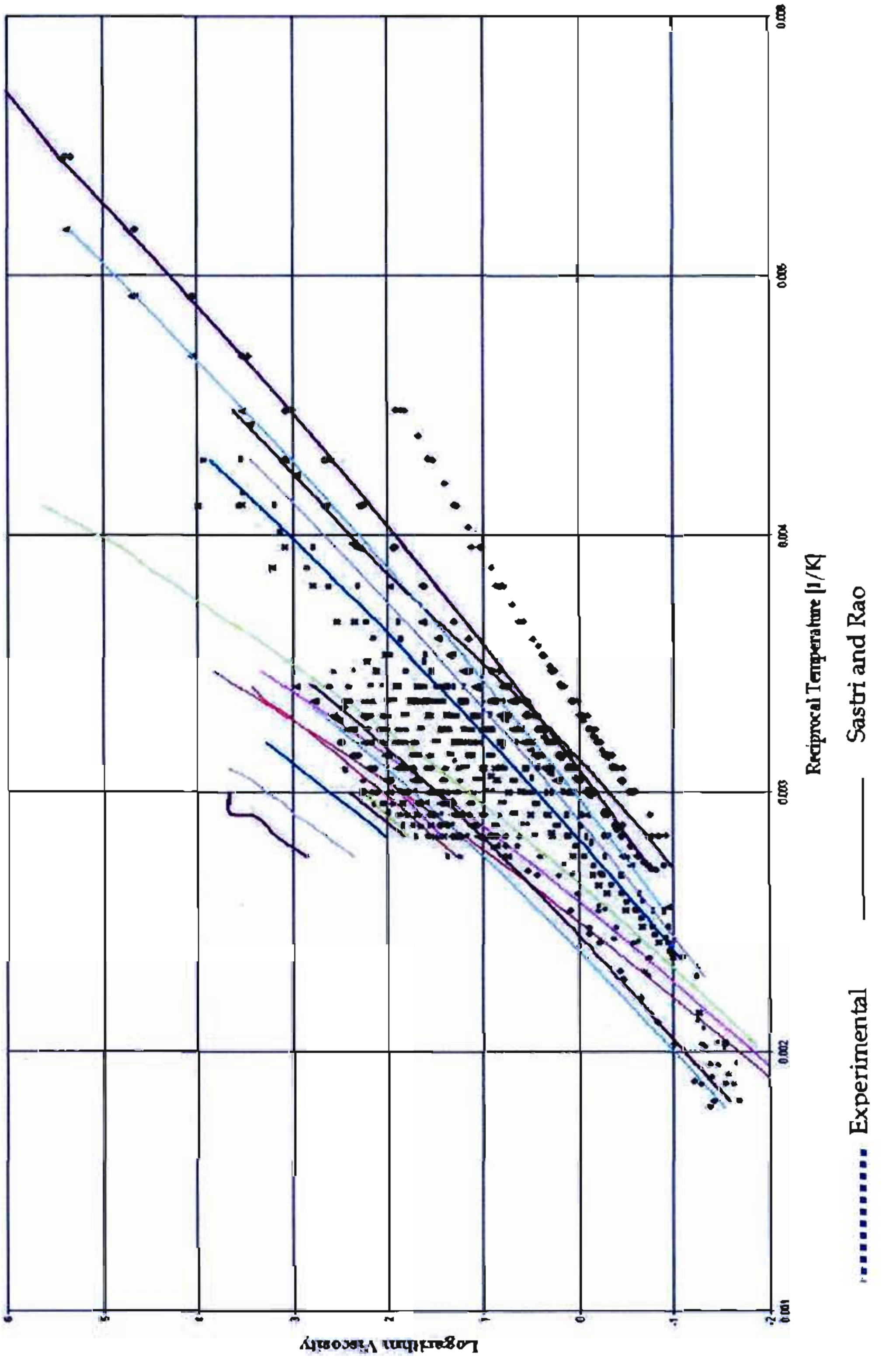


Figure 4-15: Series plot of experimental and estimated liquid viscosities for 1-alcohols (Sastri and Rao method).

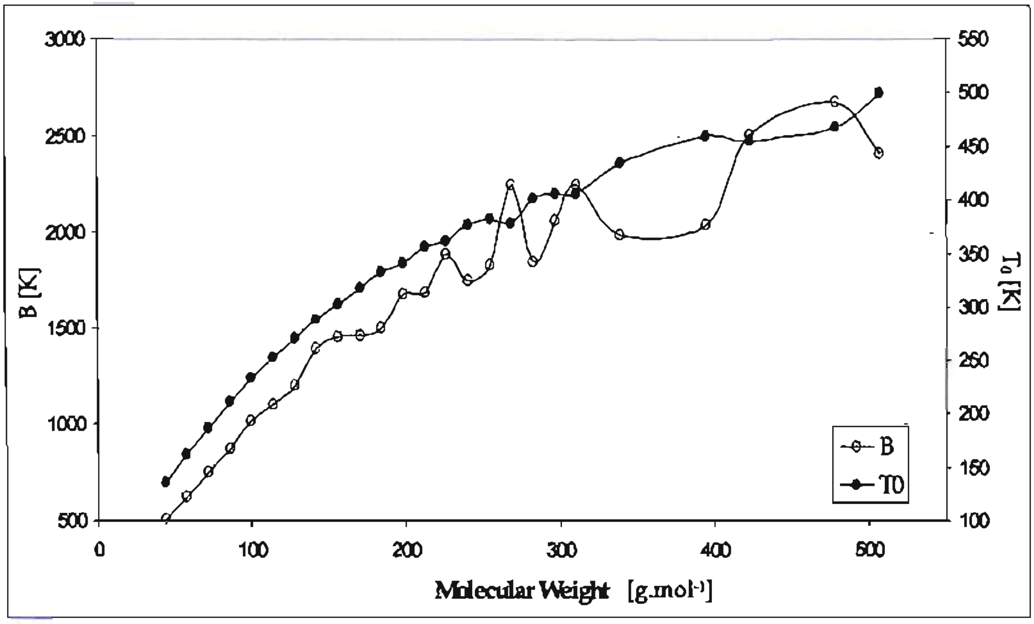


Figure 4-16: Plot of T_0 and B parameters for n-alkanes (Equation 4-12).

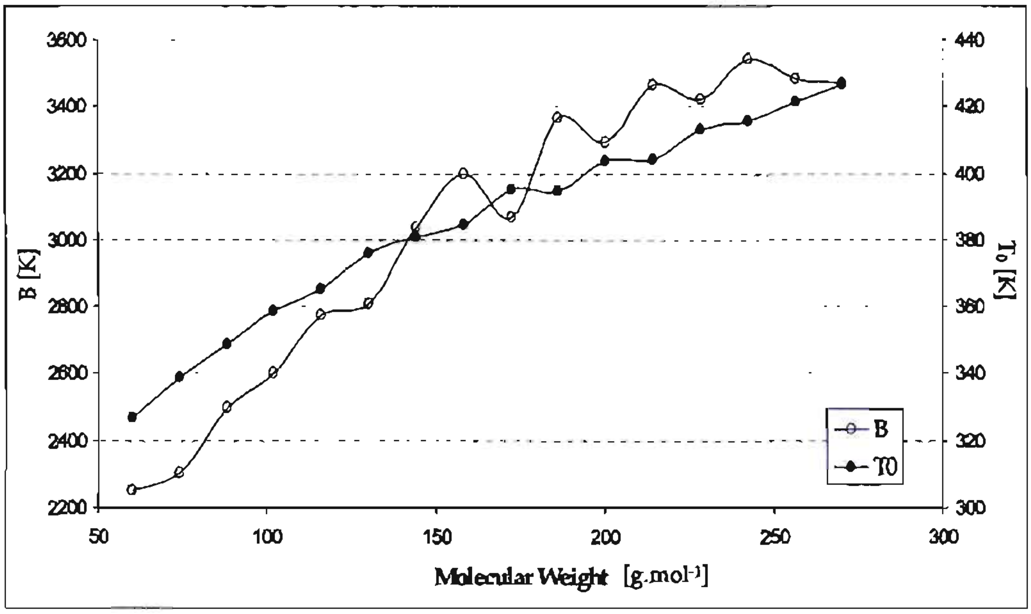


Figure 4-17: Plot of T_0 and B parameters for 1-alcohols (Equation 4-12).

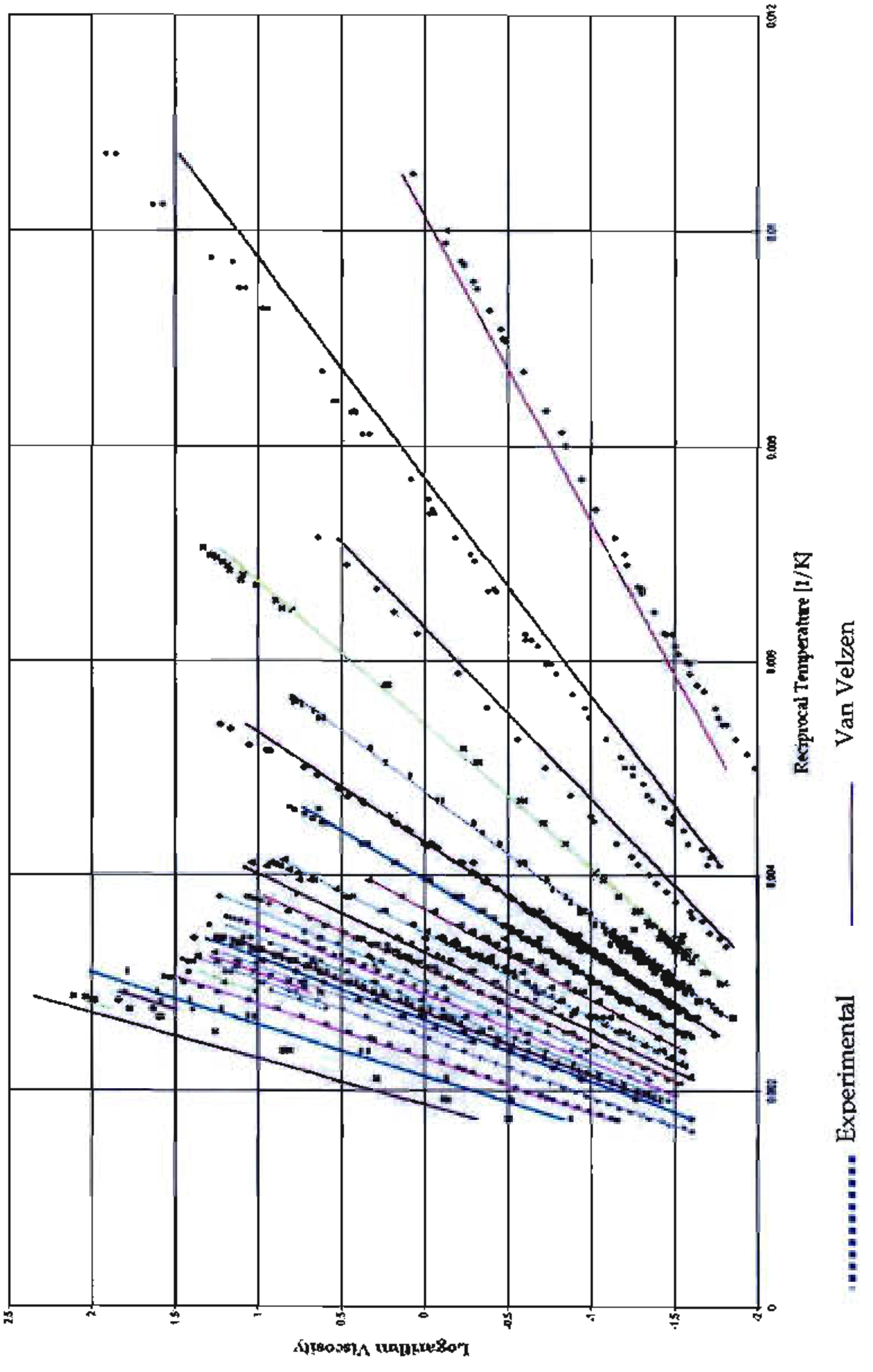


Figure 4-18: Series plot of experimental and estimated liquid viscosities for n-alkanes (Van Velzen method).

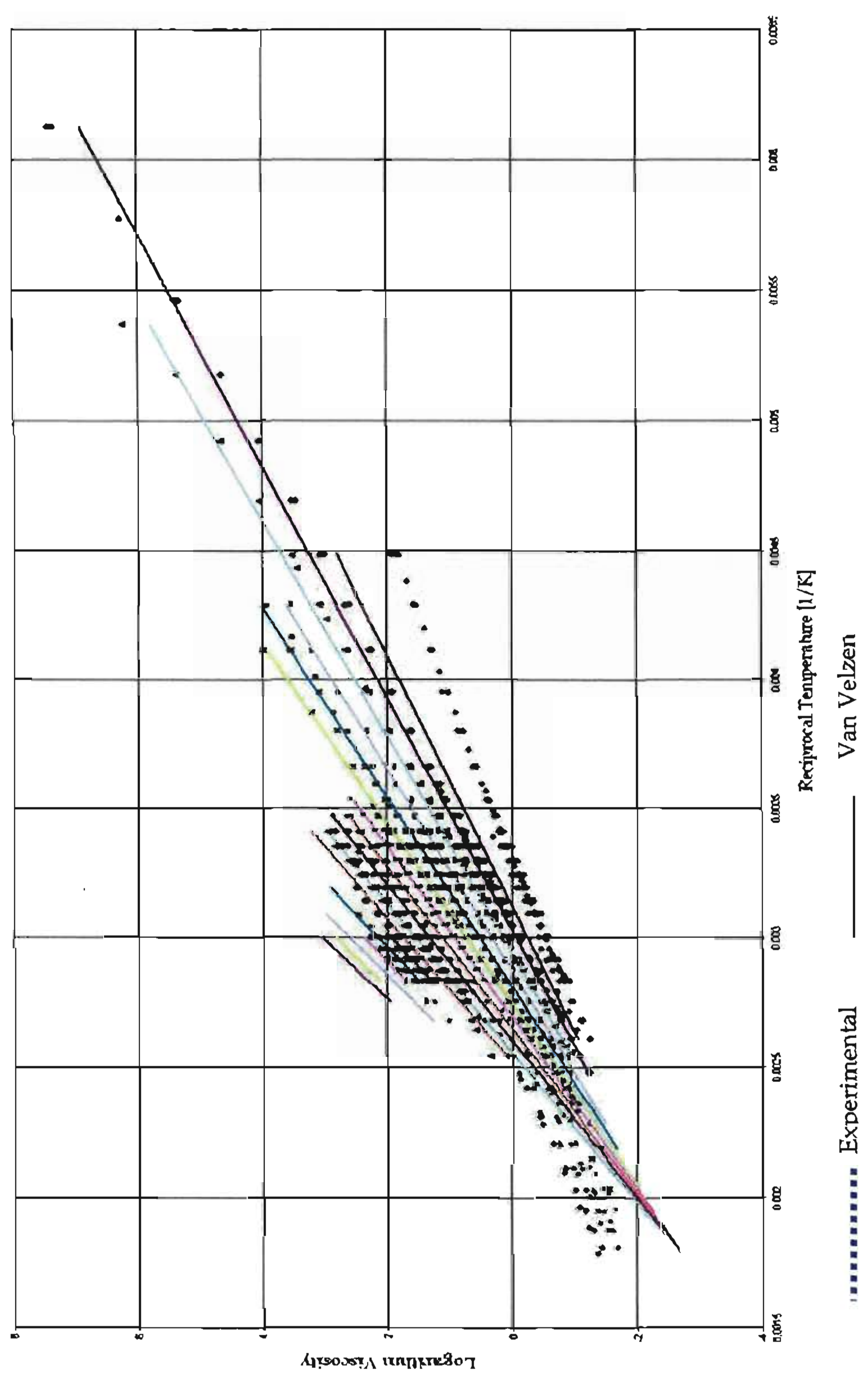


Figure 4-19: Series plot of experimental and estimated liquid viscosities for 1-alcohols (Van Velzen method).

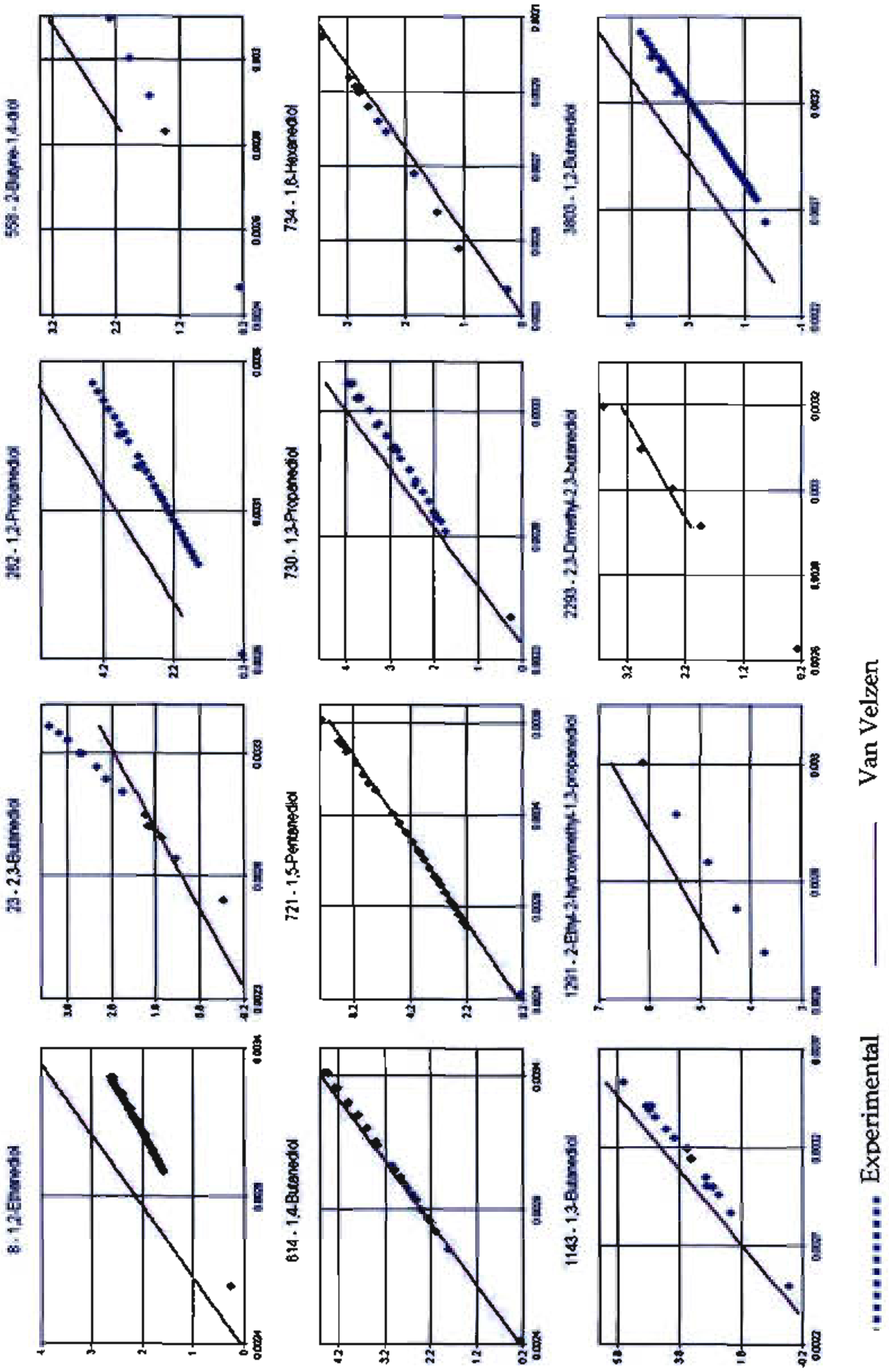


Figure 4-20: Multiple plots (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for multi-functional alcohols.

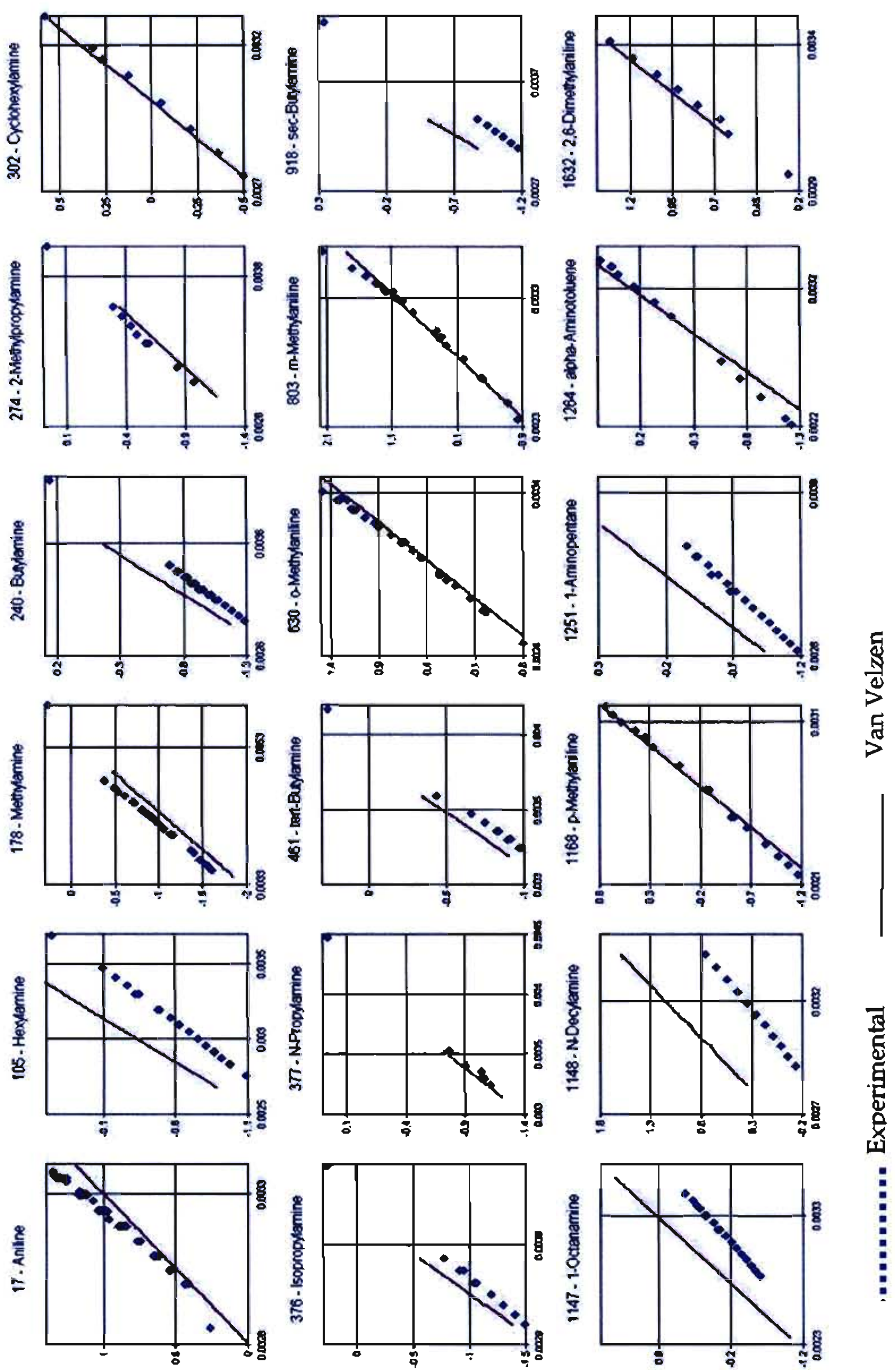


Figure 4-21: Multiple plots (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for primary amines.

Chapter Five

Liquid Theory and the Group Contribution Concept

5.1 Introduction

In this work, estimation methods for various pure component properties like liquid vapour pressure, normal boiling point, critical properties and liquid viscosity have been developed. At the beginning of the development though, it was important to carefully examine the dependencies of these properties on other thermodynamic variables and to gain an understanding of molecular and electronic structures, types of inter- and intramolecular interactions, etc, which determine the value of interest. In addition, awareness should be raised of the physically realistic range, the functional dependence of these values on other variables like temperature and pressure, the physically meaningful boundary conditions and expected behaviour in case of extrapolation outside the range of the proposed method. Therefore, the first part of this chapter will describe important aspects of the behaviour of organic compounds and their physical properties.

The proposed work is an extension of Nannoolal (2004), where the estimation of normal boiling points of organic compounds by a group contribution method was presented. The same approach will be employed in this work in a further elaborated and slightly modified form. For this reason, the second part of this chapter will describe the previously published method as this is required to follow the arguments presented in this work.

5.2 Liquid Theory Considerations

Different theories, many of them of extraordinarily complexity, are available to describe the structure and dynamics of the liquid state. Despite intensive research, none of these theories have led to sufficiently reliable results when applied to property estimation of realistic fluids. For this reason, empirical and semi-empirical methods are usually employed.

It can be argued that empirical methods based on for example the group contribution concept present a mere curve fitting exercise without any theoretical background. This type of argument can stem from, for example, the experiences with the extrapolative capabilities of group contribution estimation methods for critical properties (Figure 2-1 in Section 2.3.3). As discussed, half of these methods led to incorrect extrapolations for high molecular weight compounds. At the same time, the other half of these methods gave meaningful extrapolations. Thus different users employing different methods will have different impressions about group contribution techniques. This is one of the reasons where the above mentioned argument arises.

It is generally accepted, that group contribution methods should not be purely correlative, but should utilize any available knowledge about the functional dependence on other available properties and observe any known boundary conditions. This was discussed in the previous chapter in Section 4.1.

The aim of this section is to summarize some of the theoretical aspects required for the development of the new group contribution methods. Nannoolal (2004) contains a similar discourse that will be partly repeated here but with further elaboration and revision. The reason for this is to provide a solid background before attempting to present the model development and results.

5.2.1 Enthalpy and Entropy of Phase Change

For any phases α and β in equilibrium, the following relationship can be derived (see Nannoolal (2004) for derivation):

$$T = \left(\frac{\Delta H^{\alpha\beta}}{\Delta S^{\alpha\beta}}\right)_P \tag{5-1}$$

The above relationship is valid for any two phases in equilibrium and for systems with any number of components. Special cases are for example:

- solid → liquid (melting or fusion curve)
- solid → vapour (sublimation or deposition curve)
- liquid → vapour (vaporisation or condensation curve)

This work will only deal with properties along the vaporisation curve (saturated liquid vapour pressure curve, normal boiling point, critical properties and saturated liquid viscosity).

In case of pure components, the change of enthalpy between the phases is the difference between the molar enthalpy of the saturated phases at the same temperature and equilibrium pressure. To move a molecule from the liquid into the vapour phase, intermolecular attraction must be overcome. Thus, increasing attractive forces between the molecules will lead to a higher enthalpy of vaporization. At any point along the vaporisation curve and sufficiently remote from the critical point, the total interaction between the molecules in the vapour phase is small compared to the liquid phase. Consequently, the enthalpy of vaporization is related to the total intermolecular interaction in the liquid phase.

The change of enthalpy required to cross the phase boundary has a significant influence on, for example, the vapour pressure. A molecule in the liquid phase must have a kinetic energy greater than the potential energy in order to escape into the vapour phase. The portion of the molecules having a thermal energy larger than a certain value can be described using the Boltzmann expression $exp(-\Delta E/RT)$. This leads to an approximate logarithmic dependence of vapour pressure on reciprocal temperature.

Entropy corresponds to the number of possible arrangements (positions and/or energy levels) that are available to a system at any given state. The population (probability of occupation) ratio of two states of different energy can be calculated from the energy difference ΔE and the thermal energy RT. The more ways (arrangements) a particular state can be realised, the greater the likelihood (probability) that this state will occur.

(Nature spontaneously proceeds towards the states that have the highest probabilities of existing).

The following text contains a description of the molecular basis of entropy and its effect on chemical reactions or phase changes (cited by Barrow (1985)). "The equilibrium of A and B in which B has the higher entropy, for example, can be understood in terms of the fact that for some reason there are more available quantum states corresponding to B. There are therefore more ways of distributing the atoms in these states so that a molecule of type B is formed than there are ways of arranging the atoms in the quantum states so that a molecule of type A is formed. The tendency of A to change over to B, even if no energy driving force exists, is therefore understood to be due to the driving force that takes the system from a state of lower probability, i.e., of few quantum states and a few possible arrangements, to one of higher probability, i.e., one of many available quantum states and more possible arrangements. The qualitative result from this discussion is: *A substance for which the molecules have more available quantum states has the higher probability and therefore the higher entropy.*"

"The molecular explanation of the entropy change in a process is basically quite simple. In practice, of course, it is not always easy to see whether a process, or reaction, produces a system with more, or less, available quantum states or energy levels. Thus, for the liquid-to-vapour transition a large entropy change increase occurs. The difficulties encountered in a molecular understanding of the liquid state make it very difficult to evaluate this entropy increase from the molecular model."

In the case of evaporation, the change in entropy is nearly solely determined by the change of translational freedom (i.e. the gain of translational entropy when going from a confined space in the liquid to the available vapour phase volume). This is why according to Trouton's rule the entropy of vaporisation at the normal boiling temperature is approximately identical for a large number of components. Deviations in most cases result from non-ideal gas phase behaviour.

"Some gas-phase molecules, like CH_4 have for example negligible entropy due to rotation and vibration. Others like CCl_4, have a large contribution from this motion; about half the entropy of gaseous CCl_4 is due to rotational and vibrational contributions. But molecules like CH_4 and CCl_4 seem to obey Trouton's rule equally well. Thus it seems that no major changes in the rotational and vibrational entropies are occurring upon vaporisation", Barrow (1985).

5.2.2 Intermolecular Forces

One obvious argument for the existence of intermolecular forces is the existence of phases. Without these forces, the condensed phase, liquid and solid, would not exist since these are the forces that hold the molecules together. Even in a gas, the presence of strong intermolecular interactions can cause non-ideal behaviour. In liquids and solids the molecules are much closer together and are influenced significantly by intermolecular forces. Thus, this section will briefly describe the types of forces and their influence on the properties of liquids and solids. Most of the arguments will be based on the excellent description of these forces presented by Tesconi & Yalkowsky (2000).

5.2.2.1 Induced Dipole - Induced Dipole Forces (Dispersive Forces, London Forces, Van der Waals Forces)

If an induced dipole interacts with another induced dipole, the result is an induced dipole-induced dipole or dispersion (London) interaction. The magnitude of this type of interaction depends on the ionisation potential and polarizability of the molecules concerned. The ionisation potential is the energy required to remove the most loosely held electron in the molecule. It generally decreases with molecular size and degree of unsaturation, but does not vary greatly between simple and complex molecules and can be considered to be constant for many organic compounds except perfluorinated components. Polarizability is a measure of the ease with which a dipole can be induced in a molecule. It is proportional to molecular volume, which can be considered to be additive, and since ionisation potentials is roughly constant, the induced dipole-induced dipole interaction can also be assumed for most compounds to be additive.

London (dispersive) forces are weak attractive forces that are important over only extremely short distances. They exist for all types of molecules in condensed phases.

London forces are the only kind of intermolecular attractive forces present among symmetrical non-polar molecules. Without London forces, these molecules could not condense to form liquids or solidify to form solids. Although Van der Waals forces generally refer to all intermolecular attractions, the name is also used interchangeably with "London forces". As London forces diminish very quickly with growing distance, one can distinguish roughly between molecules "in contact" and "not in contact". The energy difference between these two states is the London interaction for one molecular contact. Application of the Boltzmann distribution law shows, that a significant proportion of the molecules in a liquid can be assumed to be in mutual contact. This is the reason why models based on the number of intermolecular contacts perform analogous to those which calculate the total energy by special integration of the intermolecular potential times radial distribution function.

Polarizability increases as "electron clouds" (i.e. the space in which the probability of finding the electron exceeds a certain predefined value) become larger and more diffuse with growing distance from the nucleus (towards heavier atoms) and decreases from metals towards halogens and noble gases within one period of the periodic system of elements due to the increasing charge of the nucleus (which at the same time leads to a contraction of the Van der Waals-radii). In addition, it depends on the number of polarisable electrons. Therefore, London forces are generally stronger for molecules that are larger or have more electrons. The increasing effectiveness of London forces of attractions becomes important even in the case of some polar covalent molecules. For example, it accounts for the increase in boiling point in the sequences $HCl < HBr < HI$ and $H_2S < H_2Se < H_2Te$. The difference in electronegativities decreases in these sequences, and the increasing London forces override the decreasing permanent dipole-dipole forces (discussed later). A similar effect can be seen in the trend of the boiling points of the halogens from fluorine to iodine.

While the centre of potential is usually assumed to be in the centre of the molecule, the centre of the dispersive force lies approximately in the position of the nucleus of the individual atoms. Thus, dispersive forces do not diminish with increasing size of the molecules as this does not move the centres of attraction further apart. To account for this, the simple Kihara potential contains a parameter c that places the centre of attraction at some place between the centre ($c=0$) of the molecule and the Van der

Waals radius (*c*=*1*). Modern potentials place several potential functions at different points inside the molecule to approximate a realistic anisotropic potential.

5.2.2.2 Dipole - Dipole (Keesom) Forces and Dipole - Induced Dipole (Debye, Induction) Forces

A dipole-dipole interaction between polar molecules results from the attraction or repulsion of opposite or liked charged atoms of different molecules, respectively (Figure 5-1). Dipole-dipole interactions are also known as Keesom forces. For non-hydrogen bonding molecules (see later), these interactions influence the orientation of the molecules in the liquid (or solid). They are also a function of the magnitude of the molecule's local dipole moment and the positioning of the molecule with respect to its neighbouring groups. This implies that these interactions may not always be additive. But, since the positioning of the molecules in most liquids is aligned for maximum dipolar interaction, the interactions are in most cases additive.

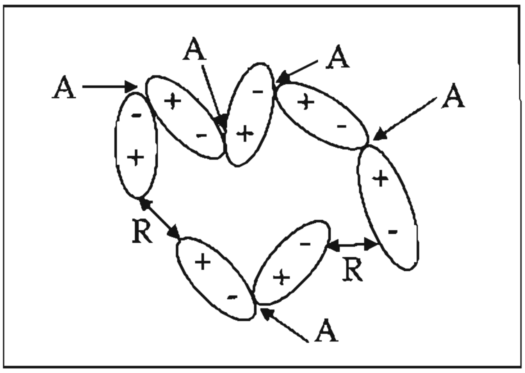


Figure 5-1: Illustration of dipole-dipole interactions between polar molecules (A-attraction, R - repulsion).

An induced dipole occurs when one molecule with a permanent dipole repels another molecule's electrons, 'inducing' a dipole moment in that molecule, in the same manner as an electric field induces a dipole in a conductor. An induced dipole interacting with a dipole creates an induced dipole-dipole or Debye interaction. The strength of these interactions depends on the polarizability and magnitude of its local dipole moments. As with dipole-dipole interactions, induced dipole-dipole interactions are in most cases additive. In addition to the dipole-dipole and dipole-induced-dipole forces, similar effects are present in case of quadrupoles and multipoles. While quadrupole effects of this kind are usually small, multipole effects are even less important.

5.2.2.3 Hydrogen bonding

Hydrogen bonded to oxygen, nitrogen or fluorine (and to a lesser extent, sulphur, chlorine and phosphorus) forms a special case of very strong interaction known as hydrogen bonding. A hydrogen bond leads to the partial sharing of a hydrogen atom by two highly electronegative atoms (Figure 5-2). In practically every case, this hydrogen is not equally shared. The atoms entering into the bond must include both an acceptor and donor. A weak hydrogen bond can also be formed between a donor atom and the electrons in a π orbital of a sp or sp^2 carbon.

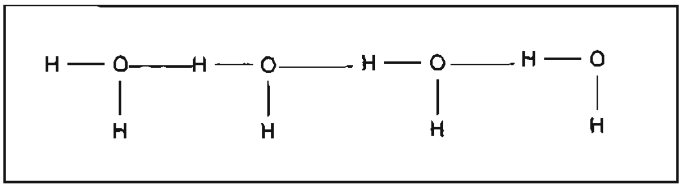


Figure 5-2: Hydrogen bonding (indicated by dotted line) in water

If a hydrogen bond is formed between two different molecules, then this is known as intermolecular hydrogen bonding. If the bond is internal, i.e. within the molecule itself, then this is known as intramolecular hydrogen bonding. Intramolecular hydrogen bonding is a special case in which steric effects support the formation of an intramolecular bond that results in a significant decrease of the enthalpy of vaporization. In many cases, this phenomenon is difficult to detect by group contribution methods (some examples are given in Nannoolal (2004)).

The increase in attractive forces in the liquid phase increases the heat of vaporization. The extra energy required to break these bonds is the main reason why molecules with hydrogen bonds have much higher boiling points. The boiling point of water illustrates this behaviour, with a boiling point of 100 °C and a molecular weight of 18 g.mol^{-1}. The closest alkane in size is methane, which has a molecular weight of 16 g.mol^{-1} and a normal boiling point of -167.7 °C. Also, alcohols and amines, molecules with hydrogen bonding, generally have higher boiling points (Table 5-1) than alkanes and ethers (the oxygen is bonded to two carbons and does not form a hydrogen bond, but induced dipole-dipole forces do exist) of comparable molecular weight.

The strongest hydrogen bonds are linear, where two electronegative atoms and the hydrogen between them lie on a straight line and for acceptor and donor atoms with a higher electronegativity or polarizability. Nitrogen is less electronegative than oxygen, which means that hydrogen bonds between amines are weaker than hydrogen bonds in alcohols. Amines, therefore, have lower boiling points than alcohols (Table 5-1) of comparable molecular weight.

Table 5-1: Comparison of boiling points of alkanes, ethers, alcohols and amines Atkins (1994)

Compound	**NBP**[*]	**Compound**	**NBP**	**Compound**	**NBP**
$CH_3CH_2CH_3$	-42.1	$CH_3CH_2CH_2CH_3$	-0.5	$CH_3\ CH_2CH_2CH_2CH_3$	36.1
CH_3OCH_3	-23.7	$CH_3OCH_2CH_3$	10.8	$CH_3CH_2OCH_2CH_3$	34.5
CH_3CH_2OH	78.0	$CH_3CH_2CH_2OH$	97.4	$CH_3CH_2CH_2CH_2OH$	117.3
$CH_3CH_2NH_2$	16.6	$CH_3CH_2CH_2NH_2$	47.8	$CH_3CH_2CH_2CH_2NH_2$	77.8

5.2.2.4 Summation of Intermolecular Forces

The properties observed for organic compounds on the macroscopic level are determined by the properties of individual molecules and the interactions between them. The polar or non-polar character of a molecule will clearly be important in determining the nature of its interactions with other molecules. These interactions can be considered the result of the effects described above. Thermodynamic properties of pure substances are to a large extent determined by these effects.

The various molecular interactions may not always be additive, as they can also be competitive. The orientation of the molecules most favourable to satisfy one type of

---

[*] Normal boiling point in °C

interaction may not be ideal for another type. Molecules tend to arrange themselves in a manner to maximize the forces of attraction by bringing sites of opposite charges together and minimizing the forces of repulsion by separating regions of like charges. The result is a compromise to achieve the lowest possible potential energy without an improbable lowering of the entropy. Consequently, since these forces may not always be additive, a group contribution method will use an average value of the effect of a fragment in several compounds.

Hydrogen bonds are especially competitive as only one bond can exist between the hydrogen and the acceptor site. This leads to the non-additivity of group contributions in the case of hydrogen-bonding groups (see below).

Molecules have kinetic energy as a result of their velocities relative to some fixed frame of reference. They also have potential energy from their positions relative to one another. Molecules in the condensed phase are in a region of highly negative potential energy due to the attractive forces exerted by the neighbouring molecules. By supplying energy in the form of heat, molecules in the liquid phase can acquire sufficient kinetic energy to overcome the potential energy of attraction and escape into the vapour phase. The vapour pressure (or vapour phase fugacity, chemical potential) will thus provide a means to measure the tendency of a molecule in a condensed phase to escape into the vapour phase. The larger the vapour pressure, the greater the escaping tendency (fugacity). Thus, observation of a large vapour pressure at a low temperature implies that relatively little kinetic energy is required to overcome the potential interactions between the molecules in the condensed phase.

Table 5-2 presents typical potential energies for the different types of interactions.

Table 5-2: Typical potential energies of charges and dipoles Atkins (1994)

Interaction Type	Distance Dependence	Typical Energy [kJ.mol^{-1}]	Comments
Ion-Ion	1/r	250	Only between ions
Hydrogen bond A-H...B	-	20	A,B = N, O or Fl
Ion-Dipole	1/r^2	15	
Dipole-Dipole	1/r^3	2	Between stationary polar molecules
	1/r^6	0.3	Between rotating polar molecules
London	1/r^6	2	Between all types of molecules

The ion-ion interaction has by far the highest potential energy. These types of liquid compounds are generally referred to as molten salts or in case of low melting points "ionic liquids". In most cases they have no measurable vapour pressures and will .not be considered in this work. Apart from this interaction, molecules with hydrogen bonding tend to have higher bonding energies than molecules with dipole-dipole interactions and London forces. This result's in a higher thermal energy needed to separate the molecules. While the potential energy from London forces is almost the same as the dipole-dipole interaction energy, these forces are only effective over a short distance than the latter one. Thus (similar to adhesion glue) they lead to an energy difference between molecules "in contact" and "not in contact". This leads to the formation of long-living structures and a significant difference between the size of transport properties like viscosity, thermal conductivity or thermal conductivity in sub-critical liquids (held together by intermolecular forces, internal pressure) and supercritical fluids of similar density (held together by pressure applied externally).

5.2.3 Influence of Molecular Structure on Intermolecular Forces

In many cases, molecular structure has an important influence on intermolecular forces. Several cases will be discussed here.

The dipole moment of a bond is defined as the product of the total amount of positive or negative charge and the distance between their centres. In a molecule with only one covalent bond, the dipole moment of the whole molecule is identical to the dipole moment of the bond. Molecules with dipole moments are attracted to one another because they align themselves in such a way that the positive end of one dipole is close to the negative end of another dipole. These electrostatic attractive forces are called dipole-dipole interactions (discussed earlier).

As the dipole moment of a molecule depends strongly on the relative position of the groups and a group contribution method only has knowledge about the type and frequency of the groups, this interaction is sometimes difficult to predict. Dipole moments are on the other hand available from the results of quantum-mechanical or semi-empirical calculations and can be introduced into an estimation method without the need for an experiment. This will be investigated in Chapter 11.

Steric hindrance (or steric strain) is the strain put on a molecule when atoms or groups are too close to each other. Generally, this leads to increased polarizability and has a pronounced effect on the properties of non-polar compounds. In other cases steric hindrance may for example prevent conjugation of unsaturated bonds as in the case of 2,5-dimethyl benzoic acid, where the acid anion is not stabilised by delocalisation as compared to benzoic acid. A detailed discussion of steric hindrance together with some examples is presented in Nannoolal (2004).

There are also various other factors that influence the liquid (condensed) phase, some of which were also described in Nannoolal (2004). However, the theory presented so far is adequate for an understanding of fluid behaviour within the context of this work.

5.3 Group Contribution Method

The proposed work will employ innovative techniques for the development of state of the art property prediction models for the properties mentioned earlier. Understanding and application of these models requires knowledge about the underlying group contribution concept. Thus, this section will present a summary of the group contribution model developed in Nannoolal (2004), and the theory prior to this section helps provide meaning to the scientific and mathematical basis of this model.

5.3.1 First-Order Groups

Group contribution is one of the simplest forms of estimation for any desired property since it only requires the knowledge of the molecular structure. In the development of a group contribution model, the first and most important assumption is that the influence of individual groups on an observable property is additive and very similar for this group in different molecules.

There are numerous approaches to the classification of functional groups by different authors. A number of these approaches have been discussed in Chapters 2 and 4 of this work. With respect to the normal boiling point, methods developed for their estimation have also been developed for critical properties which were presented earlier. The two exceptions were Cordes & Rarey (2001) and Stein & Brown (1994), discussed in Nannoolal (2004).

Nannoolal (2004) suggested that from the examination of the various group contribution approaches, the method of Cordes & Rarey (2001) was the most successful. As a result, the group contribution model presented here is based on the idea that the specification of the chemical neighbourhood of a structural group plays a significant role in property predictions. Thus, it became evident for the definition of first-order functional groups, that:

- there is no need to distinguish between carbon or silicon as a neighbour atom;

- very electronegative (N, O, F and Cl) or aromatic neighbours often significantly influence the contribution of a structural group;
- it is usually of great importance whether a group is part of a chain, ring or aromatic system;
- the effect of conjugated unsaturated bonds on each other must be taken into account. Therefore in all groups containing the C=O double bond, a correction had to be introduced in case of conjugation (for example, C=C-C=O);
- Steric hindrance results in a slight delocalization (increased "softness") of electrons that leads to stronger dispersive interactions.

The definition of the first-order groups for the estimation of the normal boiling is presented in Nannoolal (2004) & Nannoolal *et al.* (2004). These definitions will not be repeated here, however, the modified version for the estimation of critical properties, vapour pressure and liquid viscosity, will be presented later together with a table of the changes made.

There are two important rules when fragmenting a molecule with the proposed group contribution method. The first is that the molecule must be entirely fragmented with the group definitions available and the second is that for cases where a fragment may belong to different groups, the groups with the lower priority number (higher priority) must be chosen. Priority numbers were assigned during method development. An important criterion for priorities is that a group that can be constructed out of other smaller groups needs to have a higher priority than all the smaller groups.

5.3.2 Corrections

The use of higher order groups or corrections by previous methods has generally been of a correlative nature and tends to seriously affect the ability to extrapolate. Therefore, these groups should be used economically and only in cases where an obvious effect on the physical property, which could not be captured by the individual group contributions, is evident.

This applies mostly to proximity effects, where two groups show a significant behaviour affecting the physical properties only if they are located in a certain position to each other. In case the relative position is of no concern, the effect can be described using group interactions (see below). Numerous examples exist for these types of effects. In most cases they can be described by the introduction of an additional (larger) group rather than by a second order group. A very pronounced example is the combination of an alcohol group (-OH) and the C-O double bond group leading to a carboxylic acid.

In case the effect is similar for several cases, a correction contribution is more efficient. For example, instead of introducing additional conjugated versions of the ketone, aldehyde, carboxylic acid and ester group, one C=C-C=O correction group has proven sufficient to describe this effect both in cases of isolated conjugated C=C-bonds and carbonyl-carbon attached to an aromatic system.

A number of corrections developed by Cordes & Rarey (2001) were also employed in the method of Nannoolal (2004) and are presented in Table B2, ID = 123 to 129.

One of the major disadvantages of the former method was its inability to differentiate amongst hydrocarbon isomers. A detailed analysis of hydrocarbon compounds revealed rather high deviations for some, but not all highly branched isomers. One way to improve the results would have been to introduce several larger groups, as done by many authors employing higher order corrections. Introducing these types of groups can greatly reduce errors for certain components in the available database but may lead to large errors when estimating properties of new components, which would require yet another large group correction. Instead, a steric correction was introduced, which counts the number of carbon atoms connected to the partners of a C-C bond (ID = 130 - 133 in Table B2), Figure 5-3. A detailed discussion of these groups is presented in Nannoolal (2004) & Nannoolal *et al.* (2004). This effectively describes the effect of steric hindrance on polarizability.

Several other corrections were discussed in detail in Nannoolal (2004) & Nannoolal *et al.* (2004) (see ID 119 - 122 and 134 in Table B2). For example, for the case of carbonyl groups with a carbon–carbon bond in conjugation with the carbonyl double bond, a correction (C=C–C=O - ID = 134) was introduced. The correction takes into account the ability of the electronegative oxygen to polarize the electrons in the conjugated system resulting in a significantly larger charge separation (higher dipole moment) than in case of the isolated carbonyl double bond.

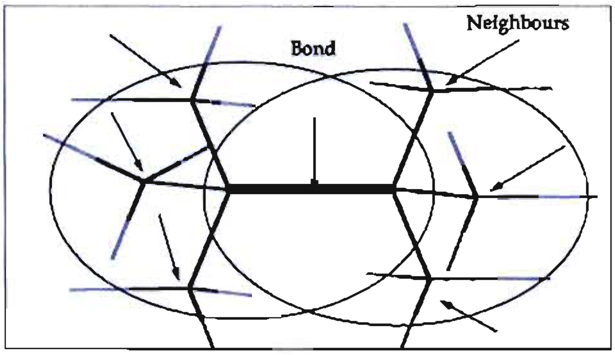


Figure 5-3: Steric contribution of the number of carbon atoms around a C-C bond.

5.3.3 Group Interactions

One of the advancements in the method of Nannoolal (2004) was the introduction of group interactions for the estimation of multi-functional compounds (Figure 5-4). Prior to this, no method could reliably estimate properties for these types of compounds within a fair degree of accuracy. Most methods showed extraordinarily large errors.

The idea behind group interactions is that, for compounds where there are two or more strongly associating groups, the assumption of simple additivity no longer holds. For example an alcohol group (-OH) in the homologous series of 1-alcohols will have a similar effect on the property of each 1-alcohol, the CH2-groups added to generate other members of the series behaves additively. Increasing the number of hydroxyl-groups will greatly overestimate association as these groups behave (to a certain extend) non-additive but competitive or exhibit chain formation that is not present in alcohols with only one OH-group. These effects are shown in Figure 5-4.

Although halogen compounds may act as hydrogen bonding acceptors, halogen groups can be considered to behave additively due to the weakness of these bonds. The same holds for other groups containing π-electrons. This omission does not lead to significantly worse results or any serious estimation failures.

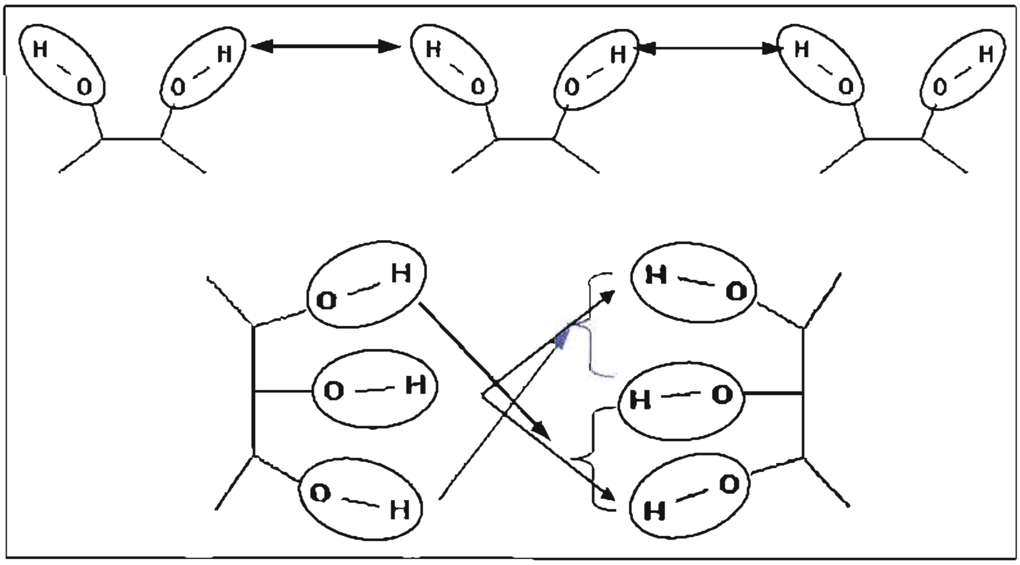


Figure 5-4: Group interactions for an alkane-diol and -triol.

As a conclusion, introduction of groups, corrections and interactions should never be based on trial and error, but must be rationalized by the molecular understanding of the effects governing the size of the physical property to be estimated. In addition, the effect must be of sufficient influence. If the expected uncertainty of estimation lies around 6 K (for a normal boiling point), there is no need to improve the result for a few components by 1 or 2 K by introducing additional groups.

Exaggerating the number of groups might lower the mean deviation in case of the training set of data but can have catastrophic consequences in extrapolation.

In other cases, data that require additional groups may not be available in the training set. The groups should be introduced anyway either with a missing or estimated group contribution value. There are for example no boiling point data for components containing both the carboxylic acid and amine group. It is common knowledge that these components form zwitterions with a negligible vapour pressure. Introducing the COOH-NH2 interaction with a very large contribution might not yield the correct value but leads to a much more reliable result than omitting the interaction.

Chapter Six

Computational Tools

6.1 Introduction

Computational tools play an important role in chemical engineering ranging from a simple calculation of vapour pressures using for example the Antoine equation to the dynamic simulation of chemical plants. However, with numerous software packages and smaller software tools being readily available, the number of engineers engaging in software development is steadily decreasing. Today, computer programming in chemical engineering is strongly marked by the use of available functionality in process simulation software, data bank programs, etc. A typical program written by an end-user is rather simple and exploits thermodynamic or unit operation models from, for example, Aspen Plus, data bank functionality from MS-Access or another SQL (discussed later) data bank product, etc. A very commonly used language is VBA (in conjunction with MS-Excel) due to the fact that most chemical engineers are well acquainted with this program.

In academic research on the other hand, new and innovative functionality is often required that cannot be found in commercial software.

In this work, standard software was used wherever possible to maximise efficiency. MS-Excel-VBA was used to link the different tools owing to its simplicity and compatibility to commercial software. In addition, most scientific and engineering software contain documentation and example files for the simple programmatic access to its functionality via VBA.

For the development of group contribution methods, the most important required tools are:

- A database containing a large amount of reliable experimental data to be used as a training and test set.
- A procedure to fragment molecules into their structural groups. Most of the older methods were developed using manual fragmentation. This is not only tedious and time consuming but also discourages modifications and investigations of alternate approaches.

Further important tools include:

- A regression routine that can safely handle a large number of parameters, both linear and non-linear. As this is not commercially available, it was developed within a previous work. To ensure maximum performance, the routine was implemented as a DLL-file in Compaq FORTRAN.
- Analysis tools (report generators) for the results from a regression or to assess the performance of literature methods in comparison to the method under development. This type of comparison (both tabular and graphical) is very specific and is an important tool in this work.
- A data bank for the storage of regression settings, experimental and regressed data, as well as model parameters. For this task, MS-Access proved to be sufficient and can be easily accessed from VBA.
- Various data verification tools. The quality and consistency of the data in the training set significantly influences the quality of the derived method. Several tools were available in the DDB Software Package (DDBSP) in addition to new tools that had to be developed within this work.

This chapter introduces the different tools in more detail. A flow diagram of the development routine for a single property is presented in Figure 6-1.

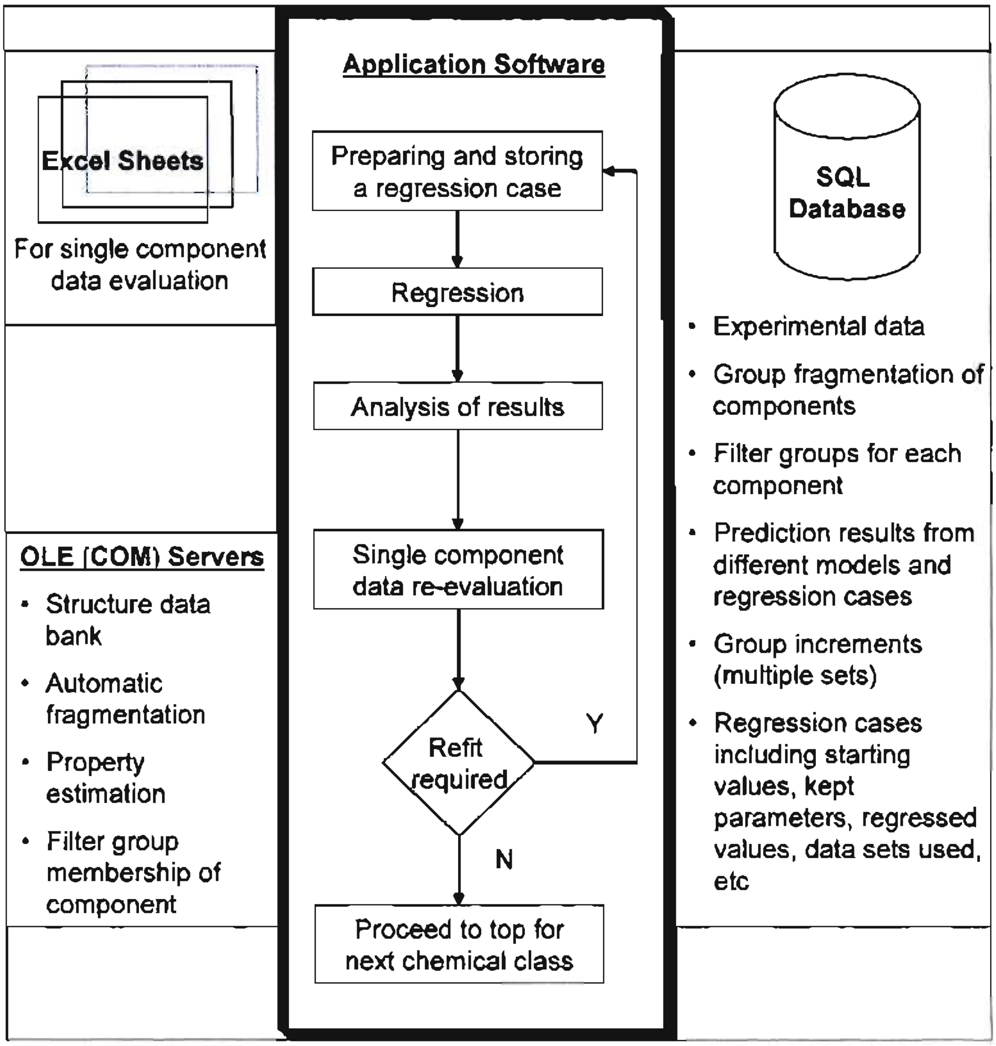


Figure 6-1: Flow diagram of a single property development routine.

6.2 Software Utilities and Terminology

6.2.1 Development Platform and the Database

The previous work, Nannoolal (2004), utilized Microsoft Excel (MS-Excel) and Visual Basic for Applications (VBA), a powerful programming language integrated into Excel, as the developmental platform. MS-Excel was employed as the user interface for storage and analyzing data, etc, and VBA as the programming language. There are many advantages and disadvantages of this platform but the main justification for a redesign of the software lies in the lessons learned in the previous approach.

Instead of storing data and regression results for different properties in several MS-Excel workbooks, a database was created in Microsoft Access (MS-Access). Use of SQL for retrieval, filtering and manipulation of data allowed more simple automation, flexibility and efficiency that required less complex programming code. MS-Excel was still employed as the software "front-end" as it allows simple presentation of the data in the form of tables and diagrams. The complete program code was written in VBA inside the front-end MS-Excel design workbook. Database features were accessed via DAO (discussed later).

There are numerous obvious advantages in using a database, instead of storing data in MS-Excel. For example, the normal boiling point of ethanol can be stored in an MS-Excel worksheet where the reference to the cell would be the row and column number. Instead, in a database, the value can be stored in a unique Table for normal boiling point data together with a field pointing to the source of the experimental value and a pointer to the component entry in a basic data table. So the database provides a fixed point of reference via indexes and links between tables whereas in MS-Excel the reference is the cell position. The program code is also interchangeable in the database with respect to the different properties by changing the names of the tables to be accessed, provided the table names contain the same basic fields. Overall, the database is much easier and simpler to use, maintain and modify than in case of storage of data in MS-Excel sheets.

6.2.2 Object-Oriented Programming

An object in computing terms is a software bundle of properties (variables), methods and events. For example, software objects are often used to model real-world objects found in everyday life. The idea behind object-oriented programming is that a computer program can be seen as a collection of individual or multiple units, or objects, which act on each other, as opposed to a traditional view in which a program may be seen as a collection of functions, or simply as a list of instructions to the computer (procedural programming). Each object is capable of receiving messages, processing data, and sending messages to other objects and can be viewed as independent, with a distinct role or responsibility.

Object-oriented programming is claimed to promote greater flexibility and maintainability in programming, and is widely popular in large-scale software engineering. Furthermore, object-oriented programming is an easier approach to learn for new computer programmers than previous approaches. It is often simpler to develop and to maintain, lending itself to more direct analysis, coding, and understanding of complex situations and procedures than other programming methods. In this work, object oriented programming was employed in various ways. Some examples are presented in the following sections.

6.2.3 Structure Query Language (SQL)

SQL is the most popular computer language used to create, retrieve, modify and manipulate data stored in database management systems. This language has evolved from its original use to include object-oriented database management systems.

SQL has a limited or specific purpose, to query data from a database. Thus, it is not a programming language such as VBA, but is a declarative language.

For example, a query using an SQL statement can be of the form "Select * from VAP where T > 500". This query selects all fields from a table named "VAP" and records where the field "T" is greater than 500 (in this case the query temporarily creates a table (dynaset) of vapour pressure data where the temperature is greater than 500 K). The use of SQL is extensive and can become extremely complicated. In early developments, it was only employed to store and retrieve data from the database. However, with growing knowledge of the language, manipulation and modification by means of built-in functions such as mathematical operators extended the use of SQL.

6.2.4 Data Access Objects (DAO)

Data Access Objects (DAO 3.6) is an object oriented interface created by Microsoft which allows Microsoft Access and Visual Basic to employ the Jet or ODBC Direct database engine. DAO enables the user to access and manipulate data in local or remote databases, and to manage the databases, their objects and structure via a programming language. DAO works by creating a "Workspace" object in which all database operations are performed. The workspace object then acts as a session object that exists within a larger database engine object. There are two types of database objects, a Jet and an ODBC Direct database engine. The latter database engine is not employed in this work.

The Jet database engine object consists of multiple objects, namely a workspace object and a series of error objects. The workspace object consists of group and user objects and a database object. The database object consists of container objects such as query definition objects (send a query to the database via SQL), Recordset objects (which are defined by a set of field objects), relation objects (which show the relationship between different fields in the database) and table definition objects (which consist of fields and indexes).

DAO is slowly becoming an outdated object (it will not feature in the new Microsoft 64-bit operating systems), but it provides all the necessary communication with the database for development in this work. Newer version objects for communicating with a database are network oriented and of no advantage to this work.

6.2.5 Metalanguage

A metalanguage is a symbolic language used to describe and act upon constructs of another programming language (base language). One could describe any computer program or user interface as a metalanguage.

A metalanguage is built upon a base language, which is usually a much more complicated language, for example VBA. The metalanguage is mostly a very simple programming language located in a user-friendly interface, for example, MS-Excel. In this work, as well as the previous work, the use of a metalanguage was to develop a filter language (discussed later on).

6.2.6 Object Linking and Embedding (OLE)

OLE or nowadays COM is primarily used to access objects from other components. These objects are typically documents or programs created by another component that supports OLE (COM) and are called OLE (COM) objects. A component that provides its documents or programs to be linked or embedded in other components is called an OLE (COM) server. A component in which documents or programs can be linked or embedded is called an OLE (COM) container. For example, a Microsoft Word document can be embedded in a Microsoft Access form and the user can then edit this document in Microsoft Word. In this case, Microsoft Word is the OLE (COM) server, and Microsoft Access is the OLE (COM) container.

An OLE (COM) server was created in the DDBSP Artist program by one of their programmers. The OLE (COM) server, "Rechenmodul", is defined as an object and is linked to all components, properties, methods such as the fragmentation of groups, filters and estimations from group contribution methods, contained in the Artist program. Thus, the OLE (COM) server serves as a link between VBA and Artist.

6.2.7 Dynamic Library Link (DLL)

A DLL is a file containing a collection of subroutines, functions or data blocks designed to perform a specific class of operations. The file format for a DDL is the same as a Windows executable (EXE) file, but with the extension dll. DLL files can contain code, data and resources in any combination. Functions within DLLs are called by applications as necessary to perform the desired operation.

In this work, a multi-linear least squares fit (discussed later) of between 500 to 50000 data points and at most 400 parameters is performed. Since VBA is not a compiling language, the regression can take an unreasonably long time to conclude, especially considering that the non-linear fit (outer loop) calls the linear fit (inner loop) for an objective function evaluation multiple times (typically between 100 and 5000 iterations). Thus, the overall performance depends mainly on the efficiency of the multi-linear regression routine. For this reason, this routine was converted to Compaq

Visual FORTRAN 6.6c (a popular programming language used mainly for mathematical applications) and compiled and linked as a DLL. This increased the overall performance by approximately two orders of magnitude.

6.3 Pure Component Property Database

The first and most obvious requirement for the development of any pure component property estimation method is the availability of a sufficiently large training set of reliable experimental data. Fortunately, the Dortmund Data Bank (DDB (2006)), the largest database for thermo-physical properties for components of technical interest, was available in this work. Data were continuously entered into the DDB after work on the data bank started in 1973 and were extensively used, for example, for the calculation of phase equilibrium data and model development. Due to its intensive use for research and application problems, this set of data may be regarded as reliable. The pure component property database was built up since 1991 at the University of Oldenburg in Germany in co-operation with groups in Prague, Tallinn, Minsk, Berlin and Graz and currently contains properties for 16 398 components from 19 962 references (1 069 318 data points). A summary of the pure component property data bank of the DDB is presented in Table 6-1.

Additional data were added to the training set from the Beilstein database (Beilstein (2002)) for specific structures of interest. In addition, from the work of Nannoolal (2004), molecular structures for approximately 16000 components were stored in the form of connection tables so that the molecules could easily be fragmented. Currently, the present database (DDB and data found in Beilstein) contains normal boiling point temperatures for almost 19000 components. However, the additional experimental data from Beilstein mostly were reported by organic chemists in articles dealing with the synthesis of new components and are often of limited reliability. The benefit of the Beilstein data however is that data can serve as a test set and in some cases can be added to the training set for structural or interaction groups for which no data are available in the DDB. In this work, only 165 vapour pressure points were added from the Beilstein database to the training set.

Table 6-1: Summary of DDB pure component property data bank (2006)

Property	Compounds	References	Sets	Points
Viscosity	2211	2424	15285	96570
Vapour Pressure	6144	6303	23354	162393
Critical Property Data	957	885	3279	3285
Triple Point	234	180	294	294
Kinematic Viscosity	611	234	1413	6379
Density	7303	5975	39407	288476
Melting Point	4832	2670	11399	12692
Molar Heat Capacity (C^P)	2386	1831	9773	172556
Virial Coefficients	260	326	828	4575
Heat of Vaporisation	2408	1042	4883	11056
Heat of Fusion	1423	837	2060	2105
Thermal Conductivity	771	909	8801	82022
Surface Tension	2054	635	4589	20220
Entropy	1460	899	2580	7975
Std. Heat of Combustion	1268	393	1471	1480
Std. Heat of Formation	2775	1191	3975	4009
Enthalpy ($H - H_0$)	273	172	461	7126
Enthalpy ($H - H_{298}$)	20	17	27	458
Gibbs Energy of Form (/T)	58	25	62	927
Gibbs Energy of Form	33	25	36	104
G-function	1208	563	1896	28327
Enthalpy ($H - H_{298}$) (/T)	3	2	3	76
Enthalpy ($H - H_0$) (/T)	96	47	113	1892
Transition Temperature	383	331	755	855
Heat of Transition	360	305	628	643
Molar Heat Capacity (C^V)	84	79	931	10382
Mass Heat Capacity (C^V)	7	4	15	474
Ideal Gas Heat Capacity	1285	708	2251	30827
Dielectric Constant	334	114	589	3252
Speed of Sound	474	274	2392	20286

Diffusion Coefficient	8	3	22	129
Flash Point	1	1	1	1
Molar Saturation Heat Capacity	30	10	66	1051
Heat of Sublimation	14	2	14	14
Enthalpy of Sublimation	69	19	116	222
Entropy of Transition	2	1	2	4
Entropy of Formation	4	2	4	4
Enthalpy	47	18	77	3776
Entropy ($S - S_0$)	2	2	2	85
Entropy ($S - S_{298}$)	1	1	1	8
Thermal Expansion Coefficient	26	3	50	334
Compressibility (isothermal)	2	1	14	154

6.4 Automatic Fragmentation

Fragmentation of molecules into defined structural groups can be a tedious and time consuming procedure. Thus, a crucial requirement for pure component property estimation development is an automatic procedure to fragment molecules into the different structural groups. As the DDB software also required the fragmentation of molecules for use in a program called Artist (which estimates pure component properties using a large number of different estimation methods), an automatic procedure was developed by Cordes *et al.* (1993) to fragment molecules into their respective groups. The same procedure was employed in Nannoolal (2004), and was also employed here. The structural definition of the groups of any method can be conveniently stored in a group definition file (ink-file).

6.4.1 Ink-file

The ink-file is a text file with the extension ink. It provides structural information (quite similar to connection tables) for the defined groups. Thus for any method, an ink-file can be developed and the automatic procedure will fragment molecules according to the group definitions in this file.

The syntax of the structural group definition in an ink-file can be best explained by using an example. Figures 6-2 and 6-3 shows the definition of a carboxylic acid group in an ink-file and the molecular structure, respectively (the numbers in brackets at the beginning of each line are used for explanation purposes only and are not part of the ink-file)

```
(1)    Carboxylic acid§COOH§
(2)     4 3 44 44
(3)    C 3 2 K 0 Yes
(4)    O 1 1 K 0 Yes
(5)    O 1 1 K 0 Yes
(6)    C 4 1 * 0 No
(7)    1 2 2 K
(8)    1 3 1 K
(9)    1 4 1 K
```

Figure 6-2: Example of a structural group definition in an ink-file

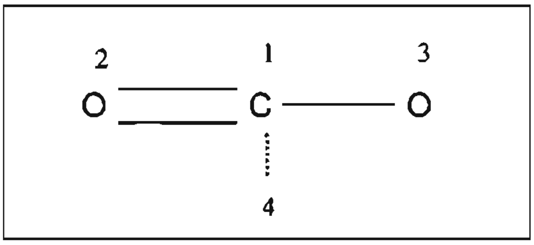


Figure 6-3: Molecular structure of a carboxylic acid group

The individual lines in the ink-file contain the following information:

Line 1:

Contains the name and a shortened name of the group between the section sign operator (§). The shortened name was employed as verification in the filter language in the previous work, but is not required anymore.

Line 2:

This line has 4 items, which must be separated by a space. The first item is the number of atoms in the group, here '4'. The second item is the number of bonds, here '3'. Third and fourth item are main group and subgroup and entirely dependant on the method, for example, 2 separate numbers are needed for the UNIFAC method. In this work, both identifiers are identical.

Lines 3-6:

These six lines provide information about the four atoms and contain 6 items each. First item is the element symbol, the second and third items are the maximum number and minimum number of neighbours, respectively. For example, in Figure 6-3, the carbon atom can only have a maximum of three neighbours because of the presence of the double bond, and a minimum of two neighbours as the two oxygen atoms ('2' and '3') are a permanent part of the group (hydrogen atoms are not counted as neighbours). The fourth item is the neighbourhood of the atom; here for example, 'K' represents chain. The fifth item is the charge, '0' for no charge, and the sixth item is whether the item should be included as part of the group. The latter item is Boolean with the term 'Yes' meaning to fragment the particular element as part of the group and 'No' to exclude it. The latter term is particularly useful to describe the neighbourhood of the group which is not part of the group. This complies with the general rule that an element can only be fragmented once. For example, if atom '4' is a -CH group, then the carboxylic acid requires this group for the fragmentation to occur, but the -CH is not fragmented as part of a carboxylic acid. Instead it will be fragmented separately.

Lines 7-9:

These three lines provide information about the three bonds and contain 4 items each. First and second items are the reference numbers of the atoms connected by the bonds, for example, '1' refers to line 3, '2' refers to line 4. The third item is the bond type, '1' - single bond, '2' - double bond, '3' - triple bond. The fourth item defines whether the bond is part of a chain (K), ring (R), aromatic system (A), non-aromatic (N) or any bond (*).

General notes:

- The number of atoms and number of bonds in line (2) must correspond to the number in the elemental and bonds description, respectively. For example, '4' atoms correspond to line 3-6, '3' bonds correspond to line 7-9.
- Hydrogen atoms do not have to be included into the group definition; they are automatically added in the procedure. For example, the oxygen, number '3' in Figure 6-3, has 1 maximum and minimum number of neighbours as defined in the ink file. However, oxygen has 2 bonds and thus the procedure will automatically assign hydrogen as the missing bond.
- * refers to all atoms, [] is used to group more than one atom, Li *et al.* (1996) is used to exclude atoms, where a combination of elements can be included that are separated by a comma.

In the previous work, a separate program was employed to fragment the molecules. The output is a comma separated variable (CSV) file that was imported into the MS-Excel file. The second order corrections presented in Chapter 5 also used a separate ink file for the fragmentation. Only the steric corrections and group interactions were generated separately by VBA code and a metalanguage program (described in Nannoolal (2004)), respectively.

In this work, as the method for the estimation of normal boiling points had been already implemented into the DDBSP Artist program, the fragmentation is easily obtained via the OLE (COM) server. In this case, there are two ink files, one for the groups and the other for corrections. The exceptions are the steric corrections, which are internally coded in the fragmentation routine, and the group interaction fragmentation which uses separate text files that are similar to the format of the metalanguage. For the latter fragmentation, there are two text files, the first describes an interaction group with the predefined group numbers (for example, a single OH interaction group will have the group number belonging to the short chained, primary, secondary and tertiary alcohol first-order groups). The second is the group interaction contribution together with its unique ID number and contribution (for example OH-NH).

The input to the OLE (COM) server is now the method and property name and an array of the unique identification numbers for each molecule (DDB numbers). The obvious advantage to employing this technique is that the fragmentation is not only faster and efficient, but also takes into account all of the above groups and corrections simultaneously, whereas, this was done separately in the previous work. As both regression and calculation routines employ the same fragmentation routine, inconsistencies are avoided. The fragmentations are then stored in the MS-Access database for further use in regression and analysis of results.

There are three further important rules concerning the fragmentation. Firstly, no atom can be assigned to more than one group, and, secondly, the entire molecule must be fragmented or the error 'group assignment failed' is returned by the OLE (COM) method. The third rule states that no larger group may consist of smaller groups that are given a higher priority in the ink-file. For example, if the OH group appears before the COOH group, part of COOH group would be assigned to the OH group and the COOH would not be found. This criterion can be verified by a special test method available in the fragmentation routine.

6.5 Regression

The regression algorithm developed in the previous work was used here without modification. It performs a simultaneous regression of model and group parameters and consists of an inner and outer regression loop. The outer loop optimizes any non-linear constants by minimizing the sum of squared errors between the calculated and experimental property values. This common objective function leads to a slightly higher mean absolute deviation as larger deviations are overweighed. The inner loop performs the multi-linear least squares fit of the linear group parameters.

The non-linear algorithm employed was the Simplex method (Nelder & Mead (1965)). This method requires only function evaluations; not derivatives with respect to the parameters. It is not very efficient in terms of the number of function evaluations that it requires and is generally slow near the optimum solution. However, considering the small number of non-linear parameters to be optimized (0 to 6), it is sufficiently fast and generally recognised as a very safe and robust algorithm.

Function minimization on a set of linear equations can be performed quickly and efficiently by employing a multi-linear least squares regression. The general form of the algorithm was modified to exclude the constant parameter a_0 in Equation 6-1.

$$y_i = a_0 + \sum_{j=1}^{M} a_j x_{ij} \tag{6-1}$$

where x_{i1}, x_{i2}, ..., x_{iM} are the variables that y_i depends on.

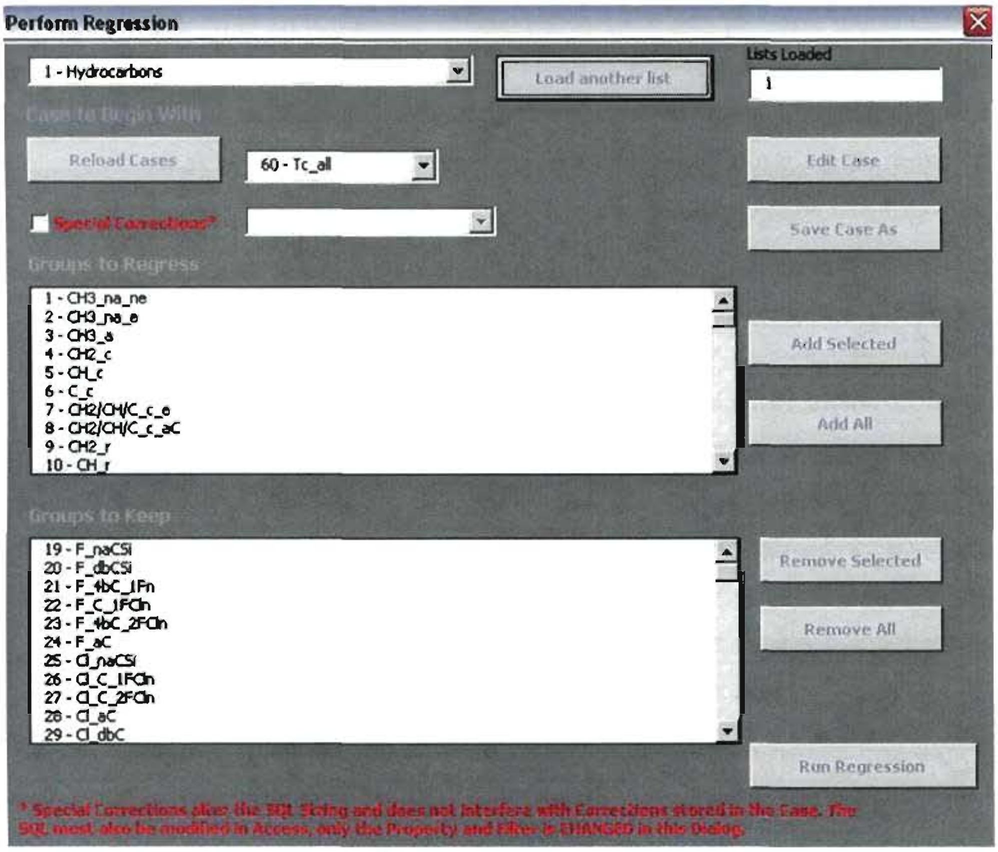
The modified form is presented in Equation 6-2, where M is the number of structural groups, including second-order corrections. The aim of this form is to provide a means by which individual groups can be regressed separately. If this was done using Equation 6-1, the regression would produce incompatible values for the constant a_0.

$$y_i = \sum_{j=1}^{M} a_j x_{ij} \tag{6-2}$$

A thorough description and derivation of the regression algorithm, including the Simplex method and multi-linear least squares fit, is presented in Nannoolal (2004). As this algorithm was successful in the previous work, it was also employed here. However, even though the routines for this algorithm remained the same, the entire software involving the regression has been redesigned for efficient regression of the different classes of compounds.

The user interface of the regression software now consists of a number of forms. Input and output of the regression procedure as well as all further specifications are stored in a regression case. In essence, the regression software can be controlled entirely by the form presented in Figure 6-4.

In order for this form to be functional, a default case is built. The reason is that the selection of groups requires a fragmentation method to be chosen first that is stored in the case. If the fragmentation method (group contribution method) is changed, the groups will need to change, so the case will need to be edited first and then reloaded.



1 - Hydrocarbons

Lists Loaded: 1

Case to Begin With: 60 - Tc_all

☐ Special Corrections*

Groups to Regress

1 - CH3_na_ne
2 - CH3_na_e
3 - CH3_a
4 - CH2_c
5 - CH_c
6 - C_c
7 - CH2/CH/C_c_e
8 - CH2/CH/C_c_aC
9 - CH2_r
10 - CH_r

Groups to Keep

19 - F_naCSi
20 - F_dbCSi
21 - F_4bC_1Fn
22 - F_C_1FCln
23 - F_4bC_2FCln
24 - F_aC
25 - Cl_naCSi
26 - Cl_C_1FCln
27 - Cl_C_2FCln
28 - Cl_aC
29 - Cl_dbC

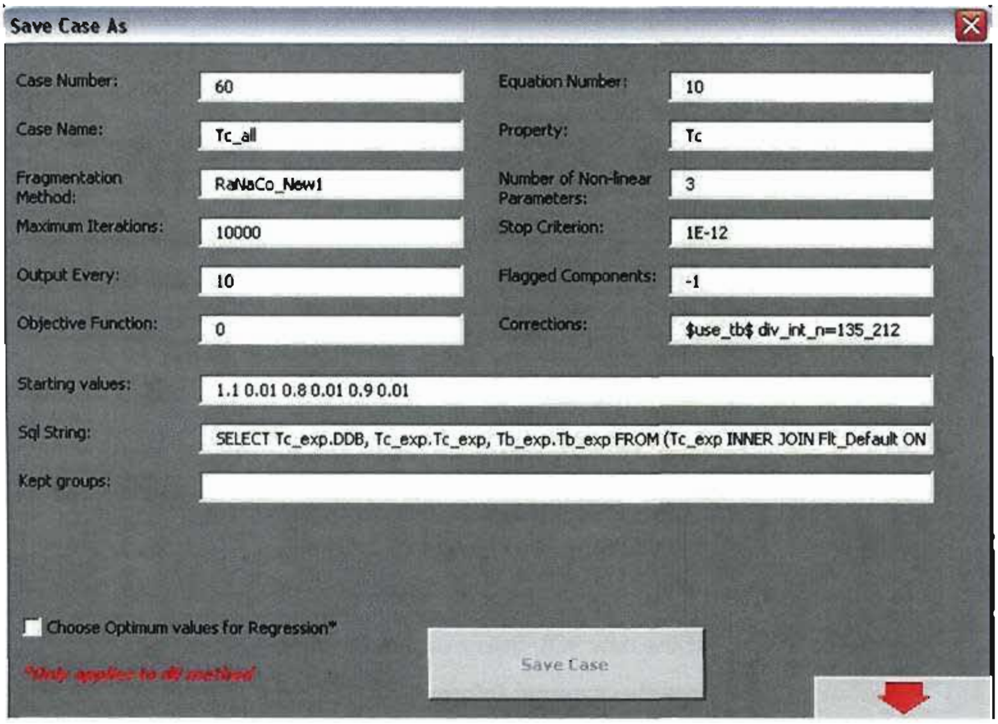
* Special Corrections alter the SQL String and does not interfere with Corrections stored in the Case. The SQL must also be modified in Access, only the Property and Filter is CHANGED in this Dialog.

Figure 6-4: Screen shot of building a regression case

Once a case is loaded (by the command button 'Load Cases', renamed to 'Reload Cases' after the combobox accompanying the command is already filled), a filter indicated by the first combobox (contains '1 - hydrocarbons') must be chosen. This filter contains information about the class of compounds and alters the data set employed in the regression by choosing only groups that belong to components in that filter. The groups belonging to the fragmentation method can then be regressed or kept and listed in the listboxes 'Groups to Regress' and 'Groups to Keep', respectively. Groups can be moved easily between these two listboxes. However, a restriction is that if groups that do not belong to the current filter are moved into the listbox containing all the groups to regress, this does not result in an addition of components to the dataset. At the same time, a routine is included within the regression that automatically removes groups for which there are no data. Thus, moving the kept groups would be redundant. Consequently, an option was developed where multiple filters can be loaded ('Load another list').

Once the parameter settings for a case are built from the form in Figure 6-4, the current case can be edited or a new case created by the same two command buttons. A new form will appear which contains all the settings for the case (Figure 6-5) of which most are self explanatory. The key settings worth mentioning are firstly, the 'Sql string'. This textbox contains the SQL query that retrieves all data required in the regression. The filter chosen from Figure 6-4 will alter this query. However, if the regression case employs molecular properties, then the option 'special corrections' in Figure 6-4 must be checked. The reason for this is that the new SQL query cannot be altered in the code. Secondly, the setting 'Corrections' provides external information that may be required in the code. Finally, the setting 'Starting Values' contains initial values listed sequentially together with the step widths required for the Simplex method.

Once all the settings for a regression case are determined, the regression can then be performed by choosing the command 'Run Regression' in Figure 6-4. A new form will appear to run the regression (Figure 6-6). There are two important settings here; the first is 'Regress with kept values'. This setting chooses a previous regression case and searches for non-zero group contributions. These groups are then moved from the right hand side of Equation 6-2 to the left. The aim of this is to regress groups that are not common to the regression cases (different filters). For example, if a regression of 1-alcohols is performed, the hydrocarbons group values should be kept. This allows the testing of the individual performance of the alcohol groups and not the alcohols and hydrocarbon groups together. The second setting is the 'Regress without non-linear values'. This setting bypasses the Simplex method and only performs the multi linear least squares fit. The aim of this setting is to not allow the non-linear values to compete with the group values when testing individual groups.

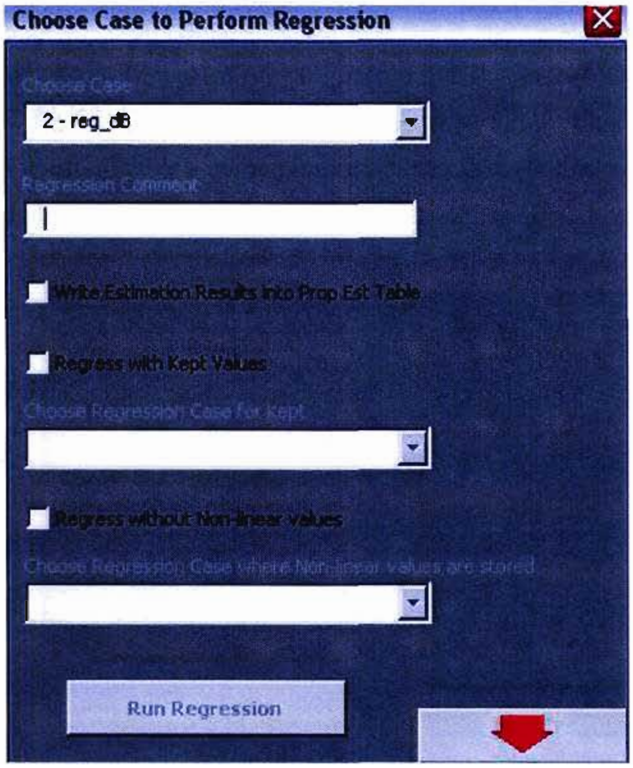


Case Number: 60
Equation Number: 10
Case Name: Tc_all
Property: Tc
Fragmentation Method: RaNaCo_New1
Number of Non-linear Parameters: 3
Maximum Iterations: 10000
Stop Criterion: 1E-12
Output Every: 10
Flagged Components: -1
Objective Function: 0
Corrections: use_tb div_int_n=135_212
Starting values: 1.1 0.01 0.8 0.01 0.9 0.01
Sql String: SELECT Tc_exp.DDB, Tc_exp.Tc_exp, Tb_exp.Tb_exp FROM (Tc_exp INNER JOIN Flt_Default ON
Kept groups:

☐ Choose Optimum values for Regression*
*Only applies to all method

Figure 6-5: Screen shot of regression case information

The regression of all components and groups is generally an error free procedure. However, regression of individual groups can pose a problem if two or more groups are collinear. Implementation of a singular value decomposition algorithm presented in Press *et al.* (1986) to decompose the collinear matrix has proven to be unsuccessful as the results were undesirable. Alternately, collinearity will only occur in the case when two or more groups in the regression have the exact same frequency for each component (the columns are collinear). For example, in the regression of 1-alcohols, an alcohol group and a CH_2 group connected to an electronegative group are collinear. An easy solution is, considering that this regression will be performed by keeping hydrocarbons group values (the CH_2 mentioned above requires an electronegative neighbour and thus will not have a value in the regression of hydrocarbon compounds), to set the group to a realistic non-zero value. The regression will now compute that since the value is non-zero, it will not be included in the regression. Although the final group values are incorrect, these values are not significant at this stage as the final results of the property prediction are still correct. For this reason, another algorithm presented in Press *et al.* (1986) to test for collinearity has been implemented in this work.



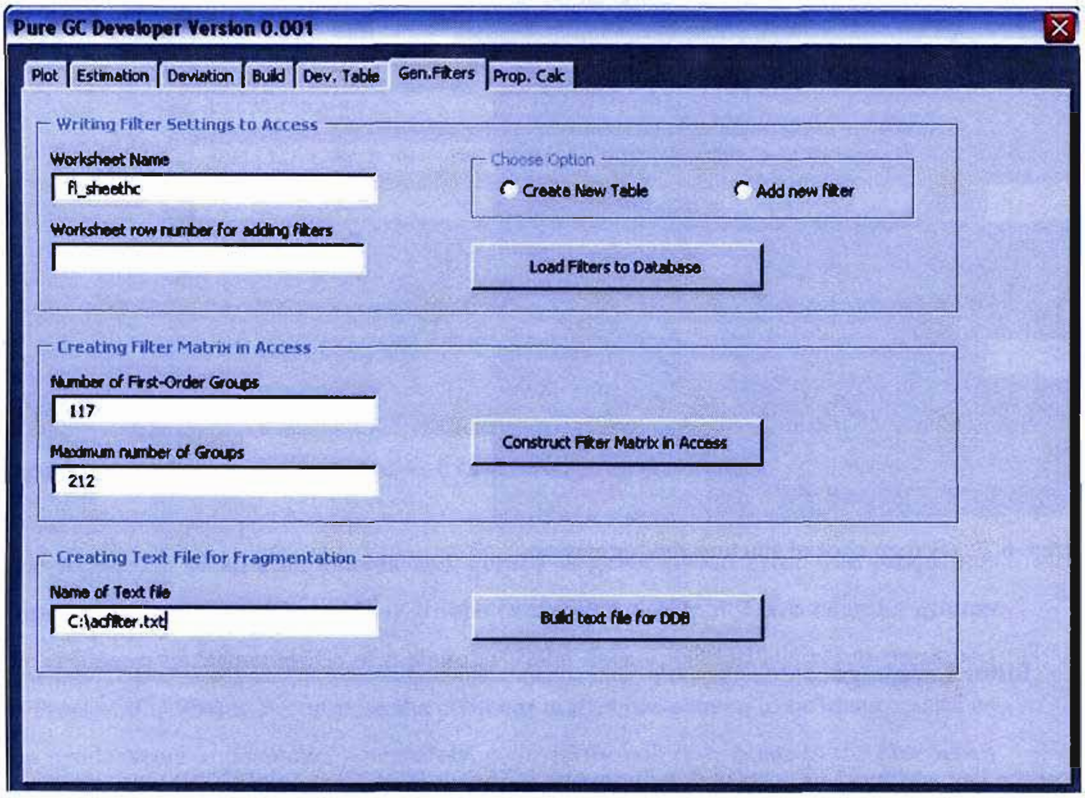
Choose Case: 2 - reg_dB

Figure 6-6: Screen shot of starting the regression

6.6 Filter Language

One of the key and most important developments in the work of Nannoolal (2004) was a filter language. This was developed using the metalanguage concept with an MS-Excel worksheet containing the metalanguage and VBA as the base code. The concept of the filter language is that it breaks organic compounds into defined specific classes and subclasses of compounds, for example, hydrocarbons and n-alkanes. Thus, a filter result (such as n-alkanes) is a collection of components derived and based on the chemical similarities of its members.

The description and definition of the metalanguage filter program including its commands and sub-commands is presented in the previous work. The concept employed previously is still used in this work. However, as the filter language has been implemented into the DDBSP Artist software to develop a quality database, the entire base code has been converted by a DDBSP programmer into C++ (programming language). The obvious advantage of the new base code is not only that it is faster, but it is also easily accessible from the OLE (COM) server. The metalanguage code is now located in a text file. This file serves as the input for the OLE (COM) server. The text file is prepared via the form presented in Figure 6-7.



Worksheet Name: fl_sheethc

Worksheet row number for adding filters:

Number of First-Order Groups: 117

Maximum number of Groups: 212

Name of Text file: C:\acfilter.txt

Figure 6-7: Screen shot of the generation of a filter language text file

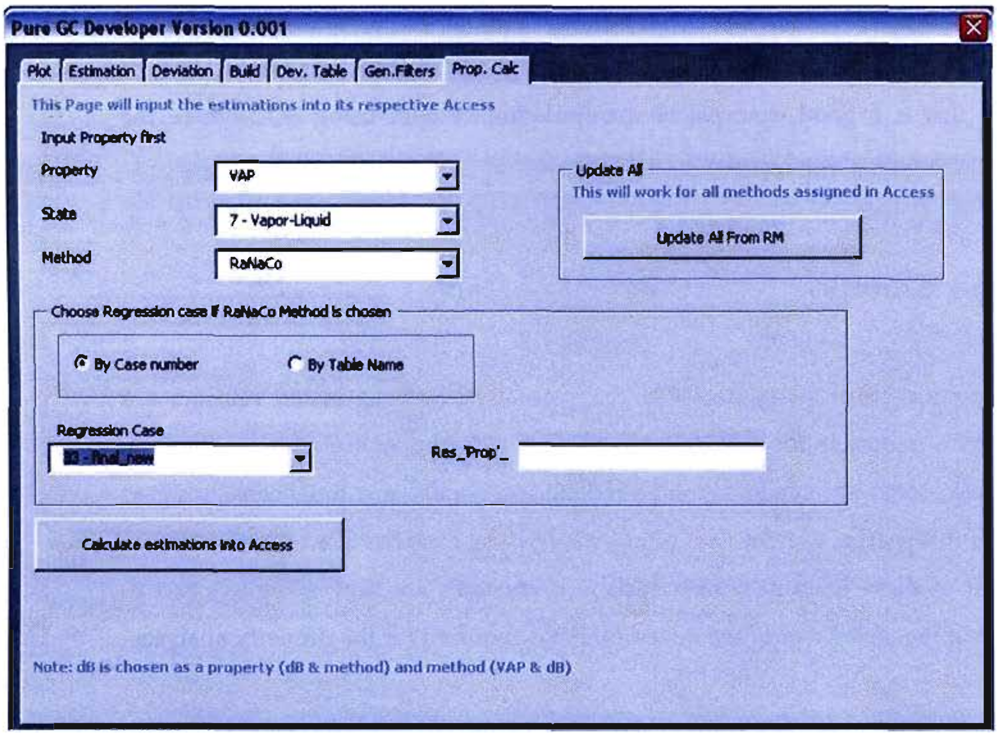
The metalanguage MS-Excel worksheet (discussed in previous work) can still be employed for implementation of new filters and modification of current filters, of which the first frame ('Writing Filter Settings to Access') imports the filters to the database. The filters are stored in a memo data field (which can store up to 65535 characters). Alternately, the filters can be modified within the memo data field in the MS-Access table. For preparation of the metalanguage text file, the filters are reconstructed into a matrix form (second frame 'Creating Filter Matrix in Access') and the text file is then easily generated (third frame 'Creating Text File for Fragmentation'). The output of the filter language from the OLE (COM) server is a set of filter groups generated for each component. The great advantage of the membership to filter groups with each component is that a set of components belonging to a particular filter or combination of filters can be easily found by running a query (using SQL). For example, in the regression program described earlier, a regression can be run for any filter or a combination of filters that are derived from the filters stored for each component (this is a good example of manipulation of data using SQL where the "InStr" function is employed to search for text in a cell).

6.7 Property Analysis

The pure component property database, fragmentation and regression routines are important tools required for the development of a group contribution estimation method. These tools are obviously required and generally are time consuming to develop. For this reason, a great deal of knowledge and time has been invested in the development of these tools presented earlier. These tools are now extremely fast to employ so that the major part of the development is required for the property analysis.

Once a regression has been performed, the results can be easily outputted. However, for a temperature dependant property where the estimation is based on another derived parameter (this will be discussed later on) that is estimated by the proposed group contribution method, the new parameter will have to recalculate property values. This is achieved by the form presented in Figure 6-8. This form also has the facility to calculate estimation results for methods presented in Chapters 2, 3 and 4, most of which are generated from the OLE (COM) server. The 'Update All' command calculates all estimation results for methods chosen from a table in the database.

The results of the estimation (also results from other methods) are outputted into a MS-Excel worksheet using the form presented in Figure 6-10. For a temperature dependant property where the estimation is based on another derived parameter, the results outputted will be the deviations of the new parameter for each component, together with average deviations of the temperature dependant property in different pressure ranges. Alternately, if the checkbox in Figure 6-9 is checked, the results for each data point are outputted. The use of this output is in principle for data verification (discussed later on).



This Page will input the estimations into its respective Access

Input Property first

Property: VAP

State: 7 - Vapor-Liquid

Method: RaNaCo

This will work for all methods assigned in Access

● By Case number ○ By Table Name

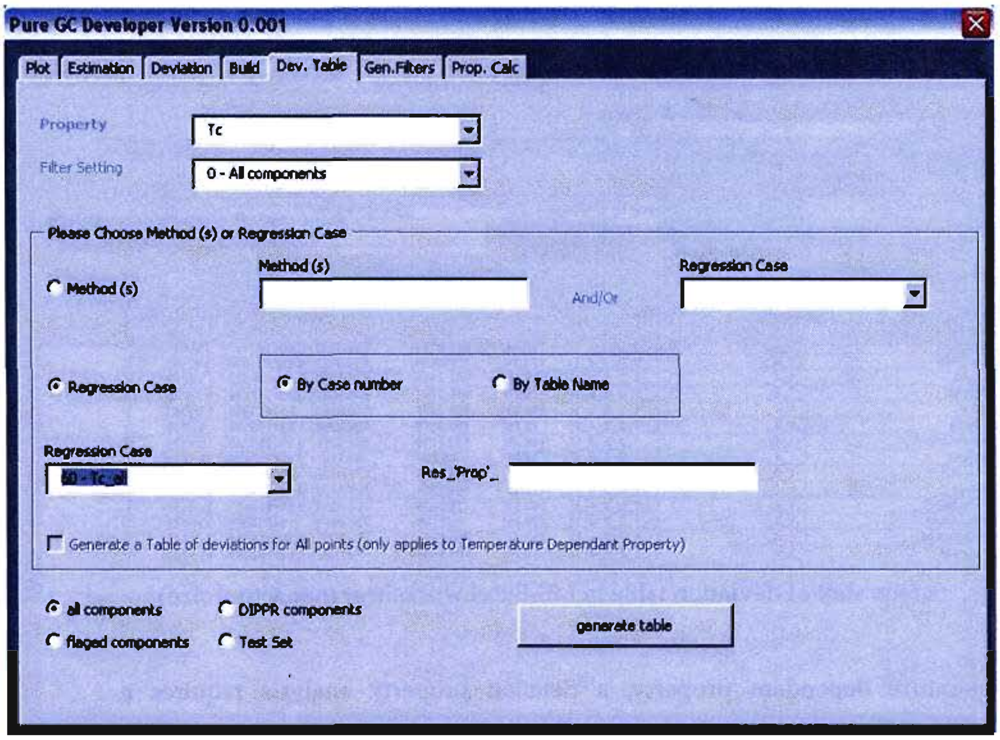
Regression Case: [illegible] - Final_new

Res_Prop'_

Note: dB is chosen as a property (dB & method) and method (VAP & dB)

Figure 6-8: Screen shot of the generation of estimation results

A screen shot of the results printout in an Excel worksheet is presented in Figure 6-10. Within this worksheet are two comboboxes that store lists for the filters and groups. By choosing any filter or group, or both, this will filter out components that belong to that filter or group. The 'Generate STL' command button generates an STL list of components highlighted in the worksheet. This file can for example be opened by the program Artist, which will then show graphical representations of the molecular structures.



Property: Tc

Filter Setting: 0 - All components

○ Method (s)

● Regression Case

● By Case number ○ By Table Name

Regression Case: 60 - Tc_all

Res_'Prop'_

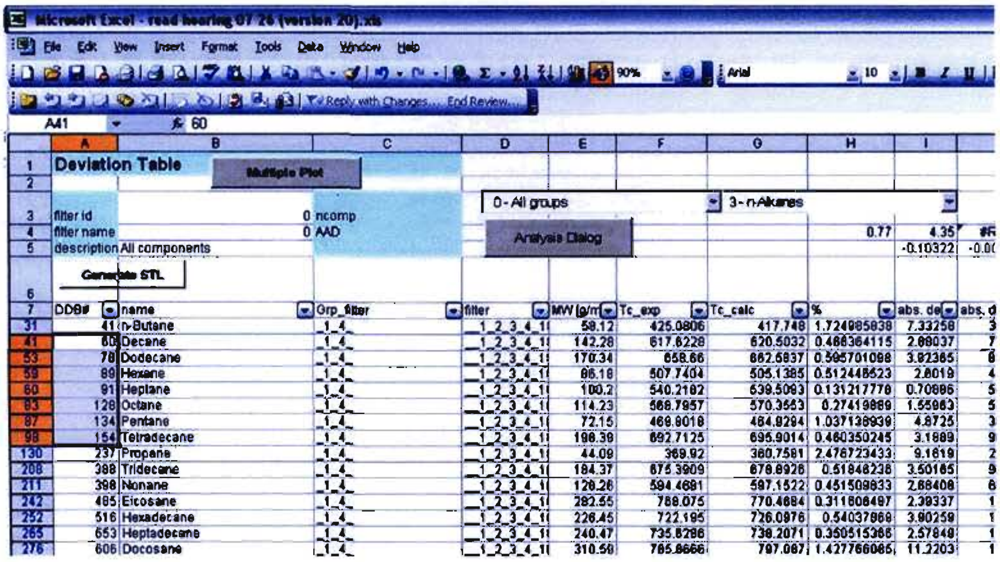
☐ Generate a Table of deviations for All points (only applies to Temperature Dependant Property)

● all components ○ DIPPR components

○ flaged components ○ Test Set

Figure 6-9: Screen shot of the generation of a filter language text file

The major purpose of the filter language in the previous work was to generate a statistical analysis of deviations for any property and for the various different estimation methods available. This software is presented in Figure 6-11. Once a property is chosen (state required for temperature dependant properties), a list of available estimation and correlative methods is generated (regression case is required for the proposed work), and the statistical analysis prints the average absolute deviations and number of components for all filters and selected methods into the chosen worksheet. In the case of temperature dependant properties, an added enhancement is the inclusion of mean deviations for the pre-defined pressure ranges chosen.



Deviation Table

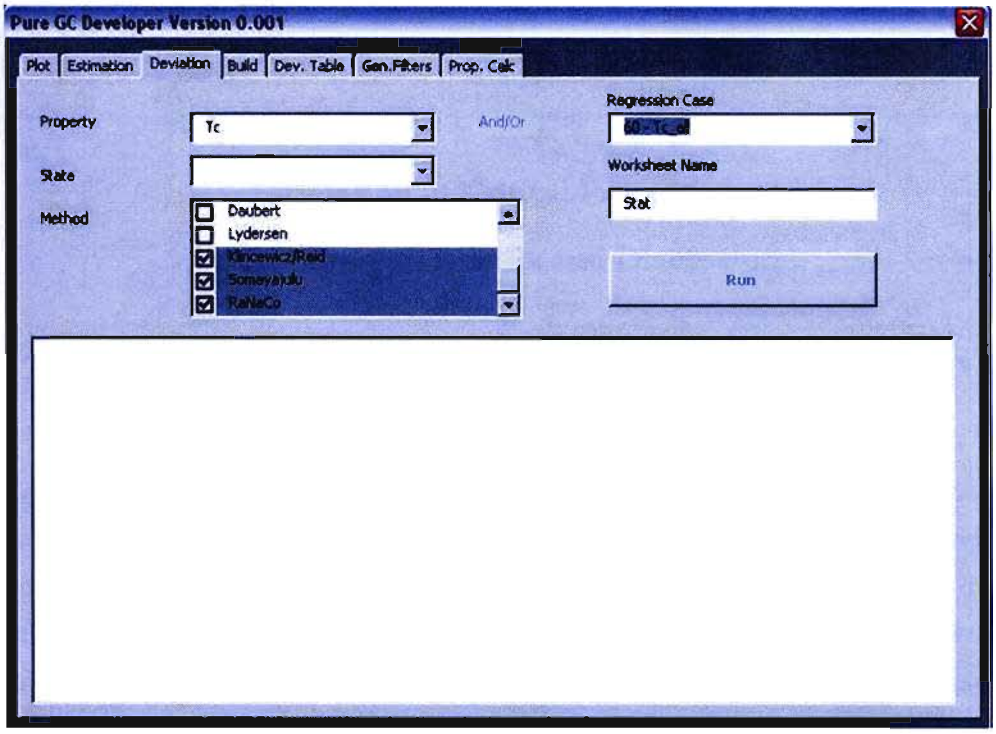
filter id 0 ncomp
filter name 0 AAD 0.77 4.35 #R
description All components -0.10322 -0.0(

DDB#	name	Grp_filter	filter	MW (g/m	Tc_exp	Tc_calc	%	abs. de	abs. d
41	n-Butane	_1_4_	_1_2_3_4_1(	58.12	425.0806	417.748	1.724985838	7.33258	3
60	Decane	_1_4_	_1_2_3_4_1(	142.28	617.6228	620.5032	0.466364115	2.88037	7
78	Dodecane	_1_4_	_1_2_3_4_1(	170.34	658.66	662.6837	0.595701098	3.92365	6
89	Hexane	_1_4_	_1_2_3_4_1(	86.18	507.7404	505.1385	0.512448523	2.6019	4
91	Heptane	_1_4_	_1_2_3_4_1(	100.2	540.2182	539.5093	0.131217770	0.70886	5
128	Octane	_1_4_	_1_2_3_4_1(	114.23	568.7957	570.3553	0.27419889	1.55963	5
134	Pentane	_1_4_	_1_2_3_4_1(	72.15	469.8018	464.9294	1.037138939	4.8725	3
154	Tetradecane	_1_4_	_1_2_3_4_1(	198.39	692.7125	695.9014	0.460350245	3.1889	9
237	Propane	_1_4_	_1_2_3_4_1(	44.09	369.82	360.7581	2.476723433	9.1619	2
388	Tridecane	_1_4_	_1_2_3_4_1(	184.37	675.3909	678.8926	0.51846236	3.50165	9
398	Nonane	_1_4_	_1_2_3_4_1(	128.26	594.4681	597.1522	0.451509833	2.68408	6
485	Eicosane	_1_4_	_1_2_3_4_1(	282.55	768.075	770.4684	0.311606497	2.39337	1
516	Hexadecane	_1_4_	_1_2_3_4_1(	226.45	722.195	726.0976	0.54037868	3.90259	1
653	Heptadecane	_1_4_	_1_2_3_4_1(	240.47	735.6286	738.2071	0.350515366	2.57849	1
606	Docosane	_1_4_	_1_2_3_4_1(	310.58	785.8666	797.087	1.427766085	11.2203	1

Figure 6-10: Screen shot of deviation table in MS-Excel worksheet (not actual size)

For a temperature dependant property, a detailed property analysis requires a graphical representation. This is achieved by a 'Multiple Plot' program, developed from an ActiveX control, presented in Figure 6-12. The program plots any number of charts for many components together with estimation results from other methods. The program can also generate a series plot on one chart, however, in this case only one method can be chosen as it becomes impossible to distinguish between methods. Examples of the output of the program are presented in Chapter 4. This program is the most important tool in the development of a temperature dependant estimation method.

The tools presented in this section are the basic requirements for a property analysis. Overall, the computational tools presented in this Chapter have been designed to provide an efficient, flexible and more detailed study of property estimation methods. The aim of these tools was to support the method development and to provide innovative tools in the property analysis.



Property: Tc

State:

Method:
- ☐ Daubert
- ☐ Lydersen
- ☑ Klincewicz/Reid
- ☑ Somayajulu
- ☑ RaNeCo

Regression Case: 60 - Tc_all

Worksheet Name: Stat

Figure 6-11: Screen shot of the generation of a property statistical analysis

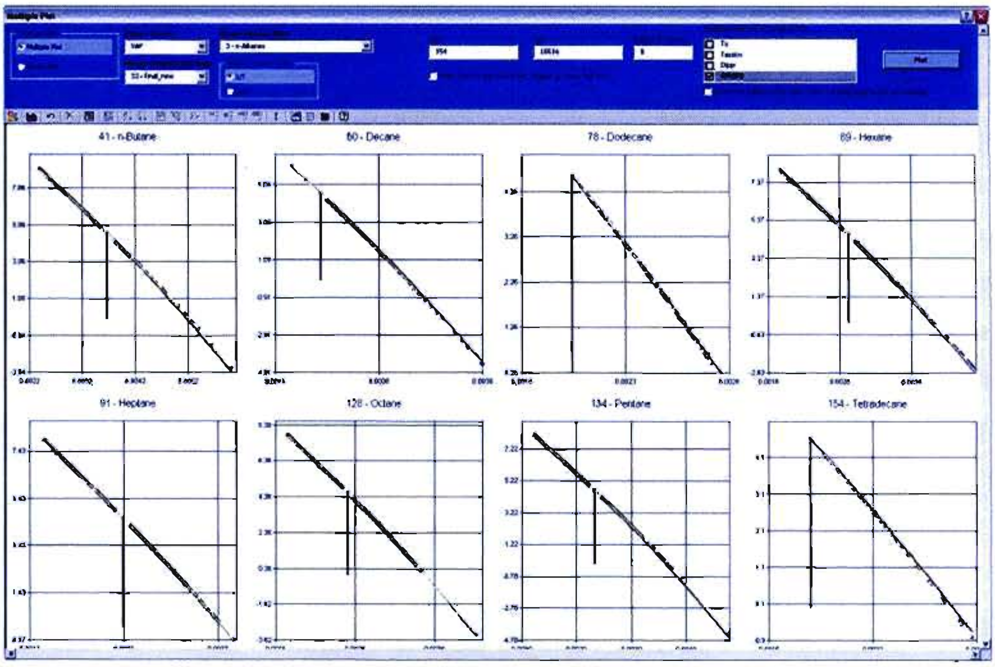


Figure 6-12: Screen shot of the multiple plot program (not actual size)

Chapter Seven

Estimation of Critical Properties:
Development, Results and Discussion

7.1 Introduction

Many authors start developing group contribution methods with methods for critical properties (T_c, P_c, V_c). This is generally not a wise decision since there is a relatively small set of data available (as compared to normal boiling point data where the amount of available data is at least five times larger). Due to the limited amount of data, a rather small set of structural groups is sufficient to model the behaviour. Many specific structural phenomena that strongly affect physical properties will need to be added later when the same model is extended to for example the normal boiling point.

Since both the critical properties and normal boiling points of organic compounds are influenced by the same set of molecular properties (energetic interaction, size and form), the same group contribution scheme (Section 5.3) as developed for the latter property, Nannoolal (2004) & Nannoolal *et al.* (2004), is employed in this work. This has the advantage that the required differentiation can be derived from and validated using a much larger set of experimental data. If this hypothesis holds, one data point of good quality is sufficient to calculate a group contribution increment. At the same time, numerous contributions cannot be determined due to the lack of data. While this limits the applicability of the method, it greatly reduces the probability of prediction failures. Even without experimental data to verify this assumption, it is highly probable that a contribution that affects the normal boiling point would also affect critical properties.

The objective of this work was to develop a new estimation method for the critical temperature, pressure and volume of organic compounds with a wide range of applicability and to give a detailed analysis of its performance compared to ten well-known previously published methods (Chapter 2). This chapter will be structured in a manner so as to introduce the development route and blend together the results and discussion.

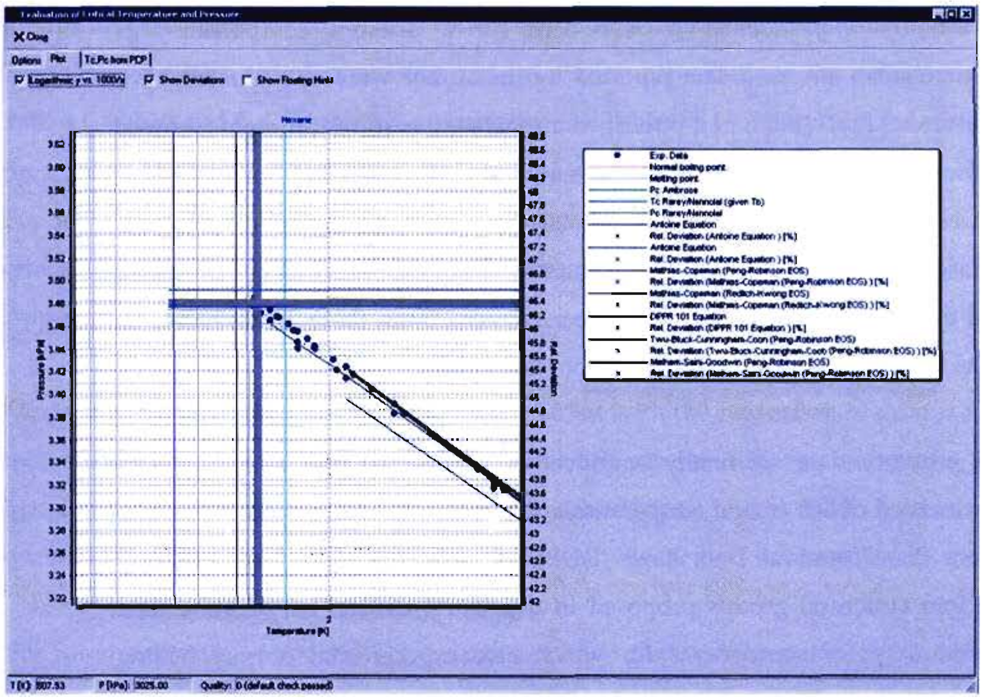
A quality or reliability analysis of such an estimation method is of significant practical importance as a tool to assess process model reliability in chemical process design and optimization. Different authors have previously reported less extensive tests of critical property estimation methods in the past based on a smaller set of data, fewer methods and less differentiation with respect to classes of chemically similar compounds. This analysis will provide a means to assess the quality of the proposed method.

7.2 Data Verification

The quality and prediction capabilities of any method strongly depend on the amount and quality of the experimental data used for its development. In the case of minimizing the RMSD, data points with large errors are strongly overweighed and therefore have a significant impact on the regression results. For example, in the case of a set of 20 components, 19 of these components show virtually no experimental error while the one component shows an error of 20 K. The sum of squared errors is 400 K^2. The same total error would result if all 20 components have a deviation of 4.47 K each. Thus, errors in a few unreliable data points are usually greatly reduced by a simultaneous regression, but this significantly increases the deviation for the reliable data. From the regression results, it is then difficult to identify unreliable data.

In the case of critical property data, there is only a small set of experimental data available. The reason for this is that higher molecular weight and strongly associating components readily decompose before the critical point is reached. This also makes experimental measurements rather difficult and experimental errors are frequent. Thus, it must be presumed that errors in experimental measurement exist.

Fortunately, in the DDB, data were carefully examined and partly revised within the development of a generally applicable volume translated group contribution equation of state (Ahlers & Gmehling (2001), (2002a), (2002b) and Wang *et al.* (2003)) and within the development of pure component data correlations for process control. During this work, available critical property data were verified using a large amount of other types of data like vapour pressure, density, heat of vaporization, heat capacity, etc. Figure 7-1 shows a screenshot of the program that can be used to verify critical property data which is available in DDBSP.



T (K): 507.53   P [kPa]: 3025.00   Quality: 0 (default check passed)

Figure 7-1: Data verification evaluation program available in DDBSP to evaluate the critical temperature and pressure.

Within this work, further verification of experimental data was also carried out. Analyzing data for each component individually can be a tedious and time consuming procedure. Thus, the detection of unreliable data generally involved considering components with high deviations, and those that can be considered to be exotic. Data verification usually consisted of verifying:

- Outdated references.
- Critical points extrapolated from lower pressure data.
- Outlying data points for components where data were also reported by other authors.

- References of the DDB data in the Beilstein database. The latter database values were not employed in this work.

For all data, copies of the original references were available at DDBST GmbH. In many cases where data were questionable, the original reference was re-evaluated. In cases where an author's experimental measurement for a selected component was considered unreliable, all other data reported by the author were re-evaluated. For example, Nesterova *et al.* (2000) had published critical temperatures for eight isomeric compounds with all having the same critical temperature but different boiling points. The improbability that these eight isomers should have identical critical temperatures leads to the assumption that the published values were not experimental but estimated by a method that could not differentiate between isomers. Thus, these values had to be considered as unreliable and were removed from the data set.

The critical property data set finally employed in this work after extensive data evaluation consisted of 588 critical temperatures, 486 critical pressures and 348 critical volumes from the Dortmund Data Bank (DDB), all of which could be completely fragmented into structural groups proposed in this work. Critical temperature data were included only for components for which also experimental normal boiling temperatures were available.

7.3 Hydrocarbon Compounds

Hydrocarbon compounds are the most simple and basic of all organic compounds. For this reason, any group contribution method must give an accurate and consistent estimation for these types of compounds. Consistent means that an estimation method must be able to estimate all classes and sub-classes of hydrocarbon compounds within a fair degree of accuracy.

Since group contribution is based on the assumption of simple additivity, hydrocarbon fragments are also found in most other components and poor predictions for any class of hydrocarbons will also lead to higher deviations for compounds involving other groups. Thus, work started by regressing group contributions for saturated, unsaturated and aromatic compounds.

For the critical properties group contribution method, the group definition, description, identification number (ID), priority (PR) and examples, for first-order groups and second-order corrections can be found in Tables B-1 and B-2 in Appendix B, respectively. The group, correction and interaction contributions are presented in Tables C-1, C-2 and C-3 for the critical temperature, Tables C-4, C-5 and C-6 for critical pressure and Tables C-7, C-8 and C-9 for critical volume, in Appendix C, respectively. For the proposed method, a detailed procedure is provided for the calculation of critical properties for three different components in Tables D-1, D-2 and D-3 in Appendix D.

Model development for group contributions started with the regression of groups for n-alkanes. Many regressions were then performed on the different subclasses of hydrocarbons as well as the full set of hydrocarbons. Within each regression, questionable data were verified and possible flaws in the method were analysed.

For fused aromatic compounds, it became apparent that a differentiation would be required between the two compounds presented in Figure 7-2. By definition, a fused aromatic atom is an aromatic atom connected to three aromatic atoms. For both compounds in Figure 7-2 the encircled carbon atoms are fused aromatic atoms. However, compound *B* has a non-aromatic bond and compound *A* an aromatic bond between the aromatic carbons. Consequently, a new group was introduced for compounds where a non-aromatic bond connects two fused aromatic carbons (Group ID = 214).

The results for the different types of hydrocarbons for the critical temperature are presented in Table 7-1. Except for fused aromatics, cyclic alkenes and alkynes, the results are comparable to the method of Ambrose (AB) while all other methods perform significantly worse in many cases. This is surprising as the Ambrose method represents one of the oldest but highly regarded work in this comparison and it should be expected that it would have served as a reference for all later developments.

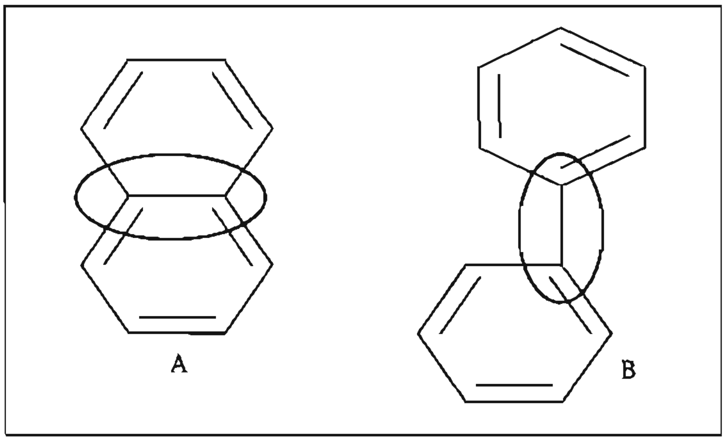


Figure 7-2: Molecular structure of two different fused aromatic compounds.

In case of fused aromatics, the Ambrose method is only applicable to 2 components and the proposed method to 5 components. In cases like this, the deviations are not comparable as they do not result from the same set of data.

Table 7-1: Critical temperature average absolute deviations (K) of the models for the different types of hydrocarbons.

	Average Absolute Deviations (K) (Number of components in Superscript)										
	PR[*]	**JR**	**CG**	**MP**	**AB**	**CT**	**WQ**	**DB**	**LD**	**SJ**	**KR**
Hydrocarbons (HC)	3.5^{141}	5.7^{141}	10.3^{142}	7.1^{123}	3.1^{134}	13.6^{143}	5.0^{124}	14.3^{140}	6.4^{141}	4.9^{141}	7.4^{141}
Saturated HC	3.1^{78}	5.3^{78}	7.6^{80}	7.8^{78}	2.5^{78}	8.5^{60}	3.6^{78}	16.7^{78}	6.3^{78}	5.5^{78}	5.8^{78}
Non-aromatic HC	3.3^{104}	5.2^{104}	7.5^{105}	7.0^{96}	2.8^{103}	8.0^{106}	3.8^{69}	14.7^{104}	6.3^{104}	4.9^{104}	5.7^{104}
Unsaturated HC	3.8^{26}	5.0^{26}	7.1^{25}	3.8^{16}	3.8^{25}	6.5^{26}	4.9^{11}	8.6^{26}	6.3^{26}	3.2^{25}	5.5^{29}
n-Alkanes	4.4^{25}	11.2^{25}	5.9^{27}	17.5^{25}	4.2^{26}	4.9^{27}	2.3^{25}	30.8^{25}	13.1^{25}	4.2^{25}	11.6^{25}
Alkanes (non-cyclic)	3.3^{65}	5.7^{65}	6.4^{67}	7.6^{65}	2.3^{65}	7.1^{67}	2.4^{65}	13.1^{65}	6.8^{65}	5.8^{66}	6.3^{65}
Alkanes (cyclic)	2.1^{13}	3.4^{13}	14.0^{13}	8.6^{13}	3.8^{13}	15.9^{13}	9.8^{13}	34.8^{13}	3.9^{13}	3.9^{13}	3.4^{13}
Aromatic HC	4.1^{37}	6.9^{37}	18.0^{37}	7.1^{27}	3.8^{31}	29.4^{37}	8.0^{36}	13.1^{36}	6.5^{37}	4.7^{37}	12.6^{36}
Fused aromatic HC	6.8^{5}	8.8^{5}	13.3^{6}		2.4^{2}	49.1^{6}	6.9^{5}	12.6^{5}	8.1^{5}	8.2^{6}	9.5^{6}
Alkenes HC	4.5^{22}	4.6^{22}	7.1^{22}	3.1^{14}	2.7^{22}	5.8^{22}	4.3^{7}	9.0^{22}	5.6^{22}	3.0^{22}	5.8^{22}
Alkenes (cyclic HC)	6.4^{4}	7.6^{4}	12.8^{4}	5.9^{2}	3.3^{4}	6.9^{4}	5.5^{3}	37.3^{4}	6.4^{4}	5.6^{4}	9.7^{4}
Alkynes HC	0.1^{3}	9.3^{3}	7.4^{3}	7.0^{3}	12.4^{3}	10.1^{3}	7.1^{3}	7.4^{3}	11.6^{3}	4.7^{3}	3.4^{3}

---

[*] Denotes Proposed Method (PR). All other abbreviations in the table are referenced to Table 2-1. These definitions will not be repeated again in this chapter.

The results for the different types of hydrocarbons for the critical pressure are presented in Table 7-2. The proposed method again performs similar to the Ambrose method while all other methods perform significantly worse.

Table 7-2: Critical pressure average absolute deviations (kPa) of the models for different types of hydrocarbon compounds.

	Average Absolute Deviations (kPa) (Number of components in Superscript)									
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**DB**	**LD**	**SJ**	**KR**
Hydrocarbons (HC)	72^{140}	104^{140}	139^{139}	213^{130}	71^{132}	106^{128}	143^{129}	124^{140}	127^{140}	188^{140}
Saturated HC	56^{80}	97^{80}	90^{80}	134^{80}	54^{78}	80^{80}	80^{77}	104^{80}	146^{80}	129^{80}
Non-aromatic HC	69^{99}	95^{99}	93^{96}	230^{96}	62^{98}	86^{89}	86^{84}	108^{99}	133^{99}	131^{99}
Unsaturated HC	75^{19}	86^{19}	108^{18}	653^{18}	97^{18}	137^{6}	113^{17}	123^{19}	77^{19}	138^{19}
n-Alkanes	43^{27}	72^{27}	63^{27}	68^{27}	65^{25}	40^{27}	69^{25}	71^{27}	71^{27}	226^{27}
Alkanes (non-cyclic)	59^{68}	100^{68}	78^{68}	72^{68}	39^{66}	70^{68}	68^{65}	99^{68}	153^{68}	137^{68}
Alkanes (cyclic)	39^{12}	80^{12}	160^{12}	486^{12}	138^{12}	134^{12}	198^{12}	136^{12}	107^{12}	86^{12}
Aromatic HC	103^{41}	128^{41}	248^{41}	164^{32}	92^{36}	152^{39}	297^{36}	164^{41}	113^{41}	326^{41}
Fused aromatic HC	60^{4}	156^{4}	382^{4}		18^{2}	245^{4}	604^{4}	318^{4}	34^{4}	108^{4}
Alkenes HC	74^{15}	80^{16}	108^{15}	804^{14}	93^{15}	125^{5}	90^{15}	67^{15}	71^{16}	134^{15}
Alkenes (cyclic HC)	33^{1}	38^{1}	432^{1}	272^{1}	434^{1}	163^{1}	370^{1}	8^{1}	12^{1}	252^{1}
Alkynes HC	105^{3}	142^{3}	104^{3}	87^{3}	115^{3}	129^{3}	285^{2}	248^{3}	97^{3}	148^{3}

In the case of Table 7-3, the proposed method outperforms all other methods including the Ambrose method. Higher deviations were found for cyclic alkenes in which case three of the four compounds were isomers. The difference between the highest and lowest critical volumes among these isomers was an astonishing 33 $cm^3.mol^{-1}$. However, as there were no other means to verify these data, except for those already mentioned, they had to be included in this work.

It should be noted that, in the above and all further tables, the measure of performance of different methods is influenced by the database used. As the training set used in this work differs from that of other authors, small differences are insignificant. In the case of the deviations for cyclic alkanes shown in Table 7-1, models with deviations in the range of 2 to 4 K all perform equally well and the differences are insignificant.

However, 5 of the 11 methods show much higher deviations and are not suitable for this type of components.

Table 7-3: Critical volume average absolute deviations (%) of the models for different types of hydrocarbon compounds.

	Average Absolute Deviations (%) (Number of components in Superscript)								
	PR	JR	CG	MP	AB	WQ	LD	SJ	KR
Hydrocarbons (HC)	1.6^{96}	2.4^{96}	4.3^{96}	2.4^{83}	2.9^{92}	3.9^{84}	2.8^{96}	3.1^{96}	3.1^{96}
Saturated HC	1.7^{57}	2.8^{57}	3.3^{57}	2.7^{57}	3.0^{57}	3.5^{57}	3.0^{57}	3.6^{57}	3.1^{57}
Non-aromatic HC	1.9^{74}	2.6^{74}	3.1^{74}	2.4^{70}	2.8^{74}	4.2^{63}	2.6^{74}	3.3^{74}	2.9^{74}
Unsaturated HC	2.5^{17}	2.0^{17}	2.5^{17}	1.2^{13}	2.3^{17}	11.0^{6}	2.3^{17}	2.6^{17}	2.4^{17}
n-Alkanes	1.0^{17}	6.0^{17}	5.3^{17}	4.7^{17}	5.8^{17}	4.7^{17}	6.8^{17}	5.8^{17}	6.1^{17}
Alkanes (non-cyclic)	1.8^{49}	3.1^{49}	3.1^{49}	2.6^{49}	3.3^{49}	2.9^{49}	3.3^{49}	3.9^{49}	3.5^{49}
Alkanes (cyclic)	0.9^{8}	1.4^{8}	5.1^{8}	3.6^{8}	1.0^{8}	7.1^{8}	0.9^{8}	1.4^{8}	0.9^{8}
Aromatic HC	0.6^{22}	1.7^{22}	8.0^{22}	2.3^{13}	3.0^{16}	2.9^{21}	2.6^{22}	2.3^{22}	3.8^{22}
Fused aromatic HC	1.2^{3}	1.5^{3}	9.2^{3}		9.0^{2}	1.4^{3}	1.5^{3}	1.6^{3}	5.6^{3}
Alkenes HC	2.9^{14}	1.8^{14}	2.6^{14}	0.9^{10}	2.3^{14}	18.4^{3}	2.1^{14}	2.7^{14}	2.3^{14}
Alkenes (cyclic HC)	4.9^{4}	3.4^{4}	5.0^{4}	1.6^{1}	4.3^{4}	19.4^{3}	3.1^{4}	4.5^{4}	3.6^{4}
Alkynes HC	0.8^{3}	2.6^{3}	2.1^{3}	2.1^{3}	2.4^{3}	2.7^{3}	3.1^{3}	2.3^{3}	2.8^{3}

Tables 7-4 to 7-6 present results for all components where steric corrections were used to account for cumulated branching and isomeric effects for critical properties. These type of components can be described equally well using the steric parameters presented in this work and the delta Platt number employed in the Ambrose method as both approaches describe the same structural effects in a similar manner. All other methods give larger errors for at least one of the component groups. Overall, the steric parameter reports a more consistent set of results as compared to the Ambrose method.

Table 7-4: Critical temperature average absolute deviations (K) for branched hydrocarbons

	Average Absolute Deviations (K) (Number of components in Superscript)										
	PR	**JR**	**CG**	**MP**	**AB**	**CT**	**WQ**	**DB**	**LD**	**SJ**	**KR**
$(C,C{=})C{-}CC_3$	0.0^{2}	6.6^{2}	40.4^{2}	14.6^{2}	3.4^{2}	28.4^{1}	20.3^{2}	33.3^{2}	27.8^{2}	3.7^{2}	19.7^{2}
$C_2C{-}CC_2$	2.9^{12}	3.4^{12}	16.9^{12}	5.0^{12}	2.6^{12}	13.9^{12}	6.4^{12}	15.9^{12}	3.8^{12}	12.1^{12}	5.0^{12}
$C_3C{-}CC_2$	2.8^{7}	4.8^{7}	13.2^{7}	2.4^{6}	1.7^{7}	8.2^{7}	3.1^{7}	13.4^{7}	4.5^{7}	12.0^{7}	6.0^{7}
$C_3C{-}CC_3$	1.4^{3}	1.5^{3}	10.4^{3}	1.1^{3}	1.7^{3}	12.6^{3}	2.6^{3}	0.9^{3}	5.2^{3}	16.6^{3}	2.8^{3}

Table 7-5: Critical pressure average absolute deviations (kPa) for branched hydrocarbons

	Average Absolute Deviations (kPa) (Number of components in Superscript)									
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**DB**	**LD**	**SJ**	**KR**
$(C,C{=})C{-}CC_3$	73^{3}	281^{3}	250^{3}	168^{3}	116^{3}	164^{3}	278^{2}	236^{3}	200^{3}	194^{3}
$C_2C{-}CC_2$	87^{11}	120^{11}	301^{11}	41^{11}	222^{10}	58^{11}	250^{10}	163^{11}	348^{11}	53^{11}
$C_3C{-}CC_2$	56^{6}	191^{5}	105^{5}	42^{5}	14^{6}	84^{5}	51^{5}	215^{5}	409^{6}	83^{5}
$C_3C{-}CC_3$	58^{3}	304^{3}	68^{3}	58^{3}	17^{3}	109^{3}	92^{3}	342^{3}	510^{3}	180^{3}

Table 7-6: Critical volume average absolute deviations (%) for branched hydrocarbons

	Average Absolute Deviations (%) (Number of components in Superscript)								
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**LD**	**SJ**	**KR**
$(C,C{=})C{-}CC_3$	0.0^{2}	6.6^{2}	8.4^{2}	-	8.9^{2}	6.2^{2}	9.2^{2}	9.6^{2}	6.4^{2}
$C_2C{-}CC_2$	2.1^{10}	3.6^{10}	1.8^{7}	3.2^{8}	1.7^{7}	8.7^{10}	3.0^{10}	5.6^{10}	3.6^{10}
$C_3C{-}CC_2$	2.6^{5}	4.0^{6}	2.3^{5}	1.6^{5}	3.3^{5}	2.8^{5}	3.7^{5}	6.5^{5}	3.6^{5}
$C_3C{-}CC_3$	0.0^{1}	0.2^{1}	8.3^{1}	1.3^{1}	3.0^{1}	0.8^{1}	1.9^{1}	3.9^{1}	0.1^{1}

The delta Platt number is a topological index that is quite complicated to calculate and which may require computational tools. The main application of the delta Platt number is to differentiate amongst isomers. Tables 7-7 to 7-9 present estimated critical properties of C_7H_{16} to $C_{10}H_{22}$ and their isomers. In this analysis, the Ambrose method is more accurate than the proposed method in most cases. Also, the Marrero and Pardillo (MP) method is fairly accurate with the use of bond contributions. However, it was shown in Nannoolal (2004), for the normal boiling point which has a much larger data set, that the Marrero and Pardillo gave higher deviations with increasing molecular weight and isomer count. Nevertheless, the proposed work is able to adequately differentiate among isomer compounds. The main reason of the lower quality in case of hydrocarbons, compared to the Ambrose method, lies in the fact that the parameters were simultaneously regressed to all critical property data. A regression to only hydrocarbons would produce similar results as found for the Ambrose method.

Table 7-7: Critical temperature average absolute deviations (K) for isomeric alkanes

		Average Absolute Deviations (K)										
Compound	**NI**[*]	**PR**	**JR**	**CG**	**MP**	**AB**	**CT**	**WQ**	**DB**	**LD**	**SJ**	**KR**
C_7H_{16}	9	2.8	1.7	4.4	1.3	0.5	5.1	6.9	2.1	2.1	1.6	4.4
C_8H_{18}	18	1.9	2.0	6.6	1.7	0.8	6.6	8.3	2.5	2.0	2.3	6.2
C_9H_{20}	6	2.0	3.5	12.1	2.0	2.3	11.8	13.7	3.2	2.1	4.4	11.4
$C_{10}H_{22}$	3	2.9	2.0	7.3	0.7	1.8	4.6	9.3	1.6	1.4	4.9	8.7

Table 7-8: Critical pressure average absolute deviations (kPa) for isomeric alkanes

		Average Absolute Deviations (kPa)									
Compound	**NI**	**PR**	**JR**	**CG**	**MP**	**AB**	**WQ**	**DB**	**LD**	**SJ**	**KR**
C_7H_{16}	9	60	69	56	67	12	63	33	81	169	62
C_8H_{18}	18	54	93	69	49	14	71	60	99	201	77
C_9H_{20}	6	36	144	82	51	20	90	77	152	264	106
$C_{10}H_{22}$	3	59	162	67	56	8	71	118	163	238	86

Table 7-9: Critical volume average absolute deviations (%) for isomeric alkanes

		Average Absolute Deviations (%)							
Compound	**NI**	**PR**	**JR**	**CG**	**MP**	**AB**	**WQ**	**LD**	**SJ**	**KR**
C_7H_{16}	9	1.4	1.6	1.6	1.2	1.5	1.3	1.7	2.5	1.7
C_8H_{18}	18	2.2	2.5	2.3	1.7	2.4	2.4	2.5	3.4	2.4

---

[*] Denotes number of isomers

For all classes of hydrocarbons and all three critical properties, the proposed method leads to reliable predictions. Large deviations were observed for small components, which are among the first in its homologous series. It is often the case that first members of their respective homologous series do not follow the trend of that series. Fortunately, experimental data are generally widely available for these simple substances and thus there is no need for group contribution estimation. For example, in case of ethane, a deviation of -9.2 K, -210 kPa and -5.2 % for critical temperature, critical pressure and critical volume, respectively, was obtained.

7.4 Mono-functional Compounds

Mono-functional compounds in this work are defined as compounds with a hydrocarbon backbone and only one strongly associating or hydrogen bonding group, for example OH, NH_2, etc. The group contribution approach is based on the additivity of group increments with respect to the estimated property. In the case of hydrogen-bonding or otherwise strongly associating groups, the assumption of simple additivity is not valid. Thus, the research approach employed throughout this work involved the scientific analysis of a functional group, a class or subclass of compounds.

7.4.1 Oxygen Compounds

The results for the different types of alcohol compounds for the critical temperature are presented in Table 7-10. For mono-functional alcohols, only the Ambrose and Somajayulu methods report a lower deviation, while the latter method has a small range of applicability (54 compounds). Large deviations were only observed for the first members in the homologous series, such as ethanol (8.4 K), 2-propanol (22.8 K) and tert-butanol (15.2 K).

Table 7-10: Critical temperature average absolute deviations (K) of the models for different types of alcohol compounds.

	Average Absolute Deviations (K) (Number of components in Superscript)										
	PR	**JR**	**CG**	**MP**	**AB**	**CT**	**WQ**	**DB**	**LD**	**SJ**	**KR**
1-Alcohols	7.1^{18}	23.0^{18}	11.4^{19}	17.8^{18}	2.4^{18}	5.5^{19}	20.5^{18}	66.1^{18}	24.9^{18}	4.9^{18}	11.1^{18}
Alcohols [*]	6.4^{68}	21.1^{68}	18.5^{64}	16.9^{68}	8.1^{68}	24.2^{79}	17.9^{67}	44.2^{67}	28.0^{66}	14.1^{54}	13.0^{68}
Primary alcohols	7.4^{26}	21.0^{26}	12.0^{27}	16.0^{26}	2.6^{26}	7.0^{27}	18.0^{25}	58.0^{25}	22.3^{26}	5.4^{25}	10.0^{26}
Secondary alcohols	6.6^{23}	18.2^{23}	8.3^{26}	13.3^{23}	4.6^{23}	18.1^{26}	11.6^{23}	14.8^{23}	19.3^{23}	-	9.5^{23}
Tertiary alcohols	8.1^{4}	11.9^{4}	12.3^{4}	10.3^{4}	7.6^{4}	38.6^{4}	8.6^{4}	13.7^{4}	13.0^{4}	-	8.4^{4}
Aromatic alcohols	4.2^{13}	4.4^{13}	8.9^{13}	3.5^{13}	4.3^{13}	-	10.2^{13}	21.1^{13}	36.0^{13}	3.8^{12}	14.5^{13}
Alkane diols, triols	13.1^{5}	72.9^{5}	116.0^{5}	62.8^{6}	45.6^{5}	109.0^{5}	55.8^{5}	84.6^{5}	73.9^{5}	60.3^{3}	44.7^{5}

For the case of alkane diols and triols, the proposed method leads to acceptable deviations while all other methods (including Ambrose) should not be used. During the development of the proposed method, slightly higher deviations for mono-functional compounds were accepted in order to improve the estimation in the case of multi-functional alcohols. The largest deviation was found in case of glycerol (30.9K), the first and only compound in its series in the training set (the only alkane triol).

The results for the critical pressure are presented in Table 7-11. For mono-functional alcohols, the proposed method reports the lowest deviation of all methods. In the case of aromatic alcohols, a large deviation was observed for phenol (375 kPa), which is the first compound in its series. The higher deviation is accepted as the extrapolation to higher molecular weight components is of greater importance. This error contributes largely to the overall average as only data for four components are present.

For alkane diols and triols, a large error was observed in the case of 1,3-propanediol (422 kPa), the largest error observed for multi-functional alcohols. However, in this case the reference, VonNiedernhausern *et al.* (2000), stated an experimental error of ±600 kPa, so even the large estimation error is still within the accuracy of the experimental value.

---

[*] Includes multi-functional compounds

Table 7-11: Critical pressure average absolute deviations (kPa) of the models for different types of alcohol compounds.

	Average Absolute Deviations (kPa) (Number of components in Superscript)									
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**DB**	**LD**	**SJ**	**KR**
1-Alcohols	48^{16}	67^{16}	159^{16}	57^{16}	133^{16}	72^{16}	128^{16}	73^{16}	89^{16}	159^{16}
Alcohols *	101^{66}	258^{66}	389^{66}	249^{66}	345^{64}	245^{66}	284^{63}	290^{66}	327^{44}	306^{65}
Primary alcohols	72^{24}	74^{24}	164	72^{24}	137^{24}	96^{24}	137^{23}	84^{24}	80^{23}	170^{24}
Secondary alcohols	63^{13}	156^{13}	171^{13}	198^{13}	157^{13}	185^{13}	128^{13}	149^{13}	-	247^{13}
Tertiary alcohols	130^{3}	266^{3}	168^{3}	102^{3}	255^{3}	236^{3}	36^{3}	274^{3}	-	293^{3}
Aromatic alcohols	230^{4}	204^{4}	247^{4}	227^{4}	160^{4}	339^{4}	280^{4}	434^{4}	156^{4}	170^{4}
Alkane diols, triols	268^{6}	865^{6}	1963^{6}	778^{6}	1534^{5}	543^{6}	935^{6}	679^{3}	1002^{3}	617^{5}

The results for the critical volume are presented in Table 7-12. For mono-functional alcohols, the proposed method outperforms all other methods, where the largest deviation was found in case of ethanol (2.7%). Unfortunately, there were no experimental data for multi-functional alcohol available.

Table 7-12: Critical volume average absolute deviations (%) of the models for different types of alcohol compounds.

	Average Absolute Deviations (%) (Number of components in Superscript)								
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**LD**	**SJ**	**KR**
1-Alcohols	1.2^{10}	2.5^{10}	2.5^{10}	2.7^{10}	2.6^{10}	2.5^{10}	2.8^{10}	2.7^{10}	2.7^{10}
Alcohols *	1.0^{40}	3.6^{40}	4.2^{40}	3.7^{37}	3.9^{38}	3.6^{40}	3.3^{40}	3.9^{18}	4.0^{40}
Primary alcohols	1.3^{11}	2.3^{11}	2.3^{11}	2.7^{11}	2.6^{11}	2.6^{11}	2.6^{11}	2.4^{11}	2.6^{11}
Secondary alcohols	1.1^{20}	2.9^{20}	3.9^{20}	2.9^{19}	3.9^{20}	3.3^{20}	3.1^{20}	-	3.3^{20}
Tertiary alcohols	0.0^{1}	2.6^{1}	3.4^{1}	0.2^{1}	5.9^{1}	0.2^{1}	3.8^{1}	-	3.0^{1}

The results for the different types of other oxygen compounds (without alcohols) for the critical temperature are presented in Table 7-13. For almost all classes of compounds, the proposed method performs significantly better than the other methods. Due to the additional conjugated bond correction for carbonyl compounds (C=C-C=O), the proposed method yields significantly better results for these

---

* Includes multi-functional compounds

components (note that this is a single correction regressed to all carbonyl compounds that have this effect and not regressed separately for each class). Large deviations were observed for the smaller compounds such as acetic acid (15.8 K) and 2-methyltetrahydrofuran (23.7 K).

Table 7-13: Critical temperature average absolute deviations (K) of the models for different types of oxygen (except alcohol) compounds.

	Average Absolute Deviations (K) (Number of components in Superscript)										
	PR	**JR**	**CG**	**MP**	**AB**	**CT**	**WQ**	**DB**	**LD**	**SJ**	**KR**
Ethers	4.6^{27}	3.7^{27}	8.8^{23}	3.4^{27}	4.0^{27}	10.8^{24}	7.5^{25}	29.3^{26}	4.5^{27}	2.6^{22}	4.6^{27}
Epoxides	2.1^{2}	2.9^{2}	114.0^{1}	3.7^{2}	7.6^{2}	-	8.7^{2}	42.0^{2}	4.5^{2}	-	1.2^{2}
Aldehydes (no =-=O)	2.3^{9}	11.0^{9}	6.2^{6}	4.4^{9}	5.5^{9}	6.8^{9}	4.0^{9}	37.7^{9}	12.7^{9}	46.6^{8}	4.5^{9}
Aldehydes (=-=O)	0.0^{1}	17.6^{1}	5.9^{1}	4.1^{1}	8.4^{1}	37.9^{1}	3.2^{1}	8.7^{1}	20.4^{1}	2.4^{1}	5.9^{1}
Ketones(no =-=O)	2.8^{21}	6.3^{21}	4.8^{30}	5.9^{21}	4.0^{19}	7.2^{20}	4.6^{21}	10.1^{21}	6.9^{21}	11.2^{21}	4.4^{19}
Ketones(=-=O)	2.9^{2}	0.2^{1}	33.1^{1}	-	2.3^{1}	51.6^{2}	4.9^{1}	49.3^{1}	1.9^{1}	28.6^{1}	4.3^{1}
Non-cyclic carbonates	0.0^{2}	79.6^{2}	12.0^{1}	51.0^{1}	10.6^{1}	-	-	-	74.5^{2}	9.1^{1}	8.3^{1}
Carboxylic acids	5.1^{12}	6.5^{12}	11.6^{12}	4.6^{12}	6.9^{12}	11.7^{12}	5.4^{12}	8.6^{12}	7.4^{12}	7.1^{12}	8.5^{12}
Esters	3.7^{37}	5.6^{37}	7.2^{37}	5.4^{36}	4.6^{37}	17.7^{37}	4.0^{36}	30.1^{37}	4.8^{37}	4.9^{37}	4.7^{37}
Formic acids esters	2.3^{6}	-	8.8^{6}	2.6^{6}	3.6^{6}	-	-	26.4^{6}	14.9^{6}	1.4^{6}	4.5^{6}
Lactones	0.0^{1}	0.1^{1}	183.0^{1}	-	-	-	-	8.4^{1}	8.6^{1}	-	-
Anhydride chains	0.0^{1}	2.5^{1}	37.1^{1}	-	1.3^{1}	-	-	7.6^{1}	0.5^{1}	39.7^{1}	6.4^{1}
Aromatic oxygen	1.8^{3}	6.5^{3}	-	2.4^{2}	10.4^{1}	55.0^{3}	2.5^{3}	-	5.4^{3}	3.0^{3}	4.1^{3}
Oxygenated (w/o alcohols) *	4.4^{184}	8.9^{180}	14.3^{171}	6.8^{164}	5.6^{159}	23.5^{180}	11^{175}	37.8^{148}	10^{176}	10.8^{169}	7^{162}

The results for the critical pressure are presented in Table 7-14. For almost all classes of compounds, the proposed method is in comparable accuracy with Ambrose's method and yields significantly better results than the other methods. As in the case of critical temperature, the largest deviations were also observed for the smaller compounds, acetic acid (782 kPa), 2-methyltetrahydrofuran (448 kPa) and methyl formate (427 kPa). The large average absolute deviation for formic acid esters (in total three components)

---

* Includes multi-functional compounds

is a result of the large deviation in case of methyl formate. It can be assumed that the extrapolation to larger compounds will perform significantly better.

Table 7-14: Critical pressure average absolute deviations (kPa) of the models for different types of oxygen (except alcohol) compounds.

	Average Absolute Deviations (kPa) (Number of components in Superscript)									
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**DB**	**LD**	**SJ**	**KR**
Ethers	157^{23}	165^{23}	126^{18}	125^{23}	118^{23}	117^{21}	184^{18}	143^{23}	108^{16}	257^{23}
Epoxides	0^{1}	228^{1}	498^{1}	888^{1}	498^{1}	780^{1}	167^{1}	233^{1}	-	714^{1}
Aldehydes (no =-=O)	90^{6}	189^{6}	229^{6}	235^{6}	208^{6}	171^{6}	-	407^{6}	4479^{6}	181^{6}
Aldehydes (=-=O)	0^{1}	115^{1}	293^{1}	106^{1}	175^{1}	73^{1}	-	418^{1}	2^{1}	610^{1}
Ketones(no =-=O)	65^{15}	67^{14}	147^{16}	147^{13}	71^{12}	73^{14}	228^{14}	171^{14}	151^{14}	94^{12}
Ketones(=-=O)	40^{2}	5^{1}	548^{2}	-	179^{1}	50^{1}	711^{1}	440^{1}	480^{1}	301^{1}
Non-cyclic carbonates	0^{2}	1656^{2}	327^{1}	748^{1}	339^{1}	-	-	1365^{2}	342^{1}	284^{1}
Carboxylic acids	146^{12}	291^{12}	463^{12}	614^{12}	153^{12}	333^{12}	310^{12}	360^{12}	134^{12}	160^{12}
Esters	89^{16}	104^{15}	126^{15}	63^{14}	72^{15}	51^{14}	189^{14}	97^{15}	59^{15}	140^{16}
Formic acids esters	236^{3}	-	238^{3}	540^{3}	186^{3}	-	92^{3}	299^{3}	166^{3}	315^{3}
Lactones	0^{1}	268^{1}	392^{1}	-	-	-	1409^{1}	429^{1}	-	-
Anhydride chains	0^{1}	250^{1}	615^{1}	-	430^{1}	-	1016^{1}	264^{1}	680^{1}	248^{1}
Aromatic oxygen	64^{1}	198^{1}	-	572^{1}	468^{1}	530^{1}	-	416^{1}	204^{1}	512^{1}
Oxygenated (w/o alcohols)[*]	103^{143}	278^{128}	242^{106}	231^{113}	165^{111}	194^{114}	295^{89}	233^{141}	483^{123}	234^{125}

The results for the critical volume are presented in Table 7-15. The proposed method yields significantly better results than all other methods. Large errors were observed again only for small molecules (first members in homologous series). It should be noted at this point that due to the limited number of critical volumes available, there are instances where group increments had to be calculated from a single point. This cannot be avoided, but as the group fragmentation scheme was developed using a greater set of data (normal boiling point data), the group definition is sufficient to describe the behaviour of the different classes of components. Different reliable data points will lead to nearly identical group increments.

---

[*] Includes multi-functional compounds

Table 7-15: Critical volume average absolute deviations (%) of the models for different types of oxygen (except alcohol) compounds.

	Average Absolute Deviations (%) (Number of components in Superscript)								
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**LD**	**SJ**	**KR**
Ethers	2.5^{15}	1.9^{15}	3.3^{11}	2.1^{14}	2.5^{15}	3.6^{14}	2.2^{15}	1.5^{10}	2.6^{15}
Epoxides	0.0^{1}	8.4^{1}	4.7^{1}	7.6^{1}	1.4^{1}	19.8^{1}	0.3^{1}	-	5.7^{1}
Aldehydes (no =-=O)	0.5^{5}	6.8^{6}	5.1^{5}	5.3^{4}	1.1^{6}	5.4^{6}	7.5^{5}	23.7^{6}	4.4^{6}
Aldehydes (=-=O)	0.0^{1}	5.7^{1}	11.7^{1}	-	0.4^{1}	7.1^{1}	4.9^{1}	0.7^{1}	7.2^{1}
Ketones(no =-=O)	0.8^{25}	4.9^{24}	6.1^{25}	4.0^{23}	5.6^{24}	4.3^{24}	5.8^{24}	5.8^{24}	5.1^{24}
Ketones(=-=O)	0.0^{2}	3.0^{1}	2.4^{2}	-	2.4^{1}	2.7^{1}	3.3^{1}	0.1^{1}	2.7^{1}
Non-cyclic carbonates	0.0^{1}	2.7^{1}	3.2^{1}	-	0.8^{1}	-	0.9^{1}	1.4^{1}	1.3^{1}
Carboxylic acids	4.0^{4}	2.9^{4}	3.5^{4}	2.8^{4}	3.8^{4}	2.8^{4}	3.7^{4}	3.2^{4}	3.2^{4}
Esters	0.7^{9}	1.2^{9}	1.3^{9}	1.5^{8}	1.6^{9}	1.6^{9}	1.4^{9}	1.4^{9}	1.9^{9}
Formic acids esters	1.0^{3}	-	1.6^{3}	2.0^{3}	0.8^{3}	-	6.7^{3}	0.5^{3}	1.7^{3}
Aromatic oxygen	3.8^{3}	4.3^{3}	-	0.2^{2}	1.3^{1}	2.0^{3}	3.9^{3}	4.5^{3}	6.3^{3}
Oxygenated (w/o alcohols)[*]	2^{95}	5.1^{83}	6.8^{71}	4.8^{77}	4.1^{73}	5.6^{60}	8.6^{93}	6.2^{86}	5.4^{86}

7.4.2 Nitrogen Compounds

The results for the different types of nitrogen compounds for the critical temperature are presented in Table 7-16. The proposed method yields significantly better results than the other available methods and has a greater range of applicability. For all mono-functional nitrogen compounds, there were no relatively large deviations. The slightly higher than average deviations were, as usual, for the smaller components such as dimethylamine (12.7 K), propionitrile (14 K) and quinoline (19.3 K).

The only available data point in the filter 'Nitrous & Nitrites' is for nitromethane. Although it has been discussed earlier that one point is sufficient group contribution increment, this group should be used with great caution as nitromethane is the first compound in its series.

---

[*] Includes multi-functional compounds

Table 7-16: Critical temperature average absolute deviations (K) of the models for different types of nitrogen compounds.

	Average Absolute Deviations (K) (Number of components in Superscript)										
	PR	**JR**	**CG**	**MP**	**AB**	**CT**	**WQ**	**DB**	**LD**	**SJ**	**KR**
Primary amines	3.8^{8}	7.1^{8}	14.7^{8}	6.7^{7}	7.3^{8}	21.9^{8}	6.8^{7}	7.6^{8}	8.6^{8}	8.0^{8}	2.8^{8}
Secondary amines	3.5^{9}	4.3^{9}	14.3^{9}	3.1^{9}	4.5^{9}	19.9^{7}	2.9^{9}	19.6^{9}	5.9^{9}	5.2^{7}	5.2^{9}
Tertiary amines	5.5^{4}	3.5^{4}	13.9^{4}	2.8^{4}	3.5^{4}	16.1^{4}	4.7^{4}	23.2^{4}	3.6^{4}	3.6^{4}	8.3^{4}
Amines[*]	3.2^{24}	9.8^{24}	19.6^{24}	7.7^{22}	9.1^{24}	28.8^{23}	18.7^{23}	17.3^{23}	11.5^{24}	11^{20}	5.4^{24}
N in 6-membered rings	5.0^{12}	8.3^{12}	38.1^{11}	1.0^{10}	3.7^{11}	26.8^{12}	5.7^{12}	6.6^{1}	-	16.1^{12}	8.9^{12}
Cyanides	5.9^{7}	7.4^{7}	6.2^{5}	10.5^{7}	8.2^{7}	58.8^{7}	9.7^{6}		8.6^{7}	10.7	7.9^{7}
Di amides	2.0^{2}	-	-	-	9.9^{1}	-	-	-	2.6^{1}	-	11.7^{1}
Nitrous & nitrites	0.0^{1}	0.3^{1}	-	0.4^{1}	0.3^{1}	-	0.5^{1}	-	0.3^{1}	0.6^{1}	0.6^{1}
Nitrogenated (w/o Amines)[*]	6.0^{33}	6.5^{22}	28.1^{16}	5.0^{16}	6.7^{19}	35.7^{22}	13.2^{21}	6.6^{1}	7.8^{8}	16.7^{26}	8.3^{23}

The results for the critical pressure are presented in Table 7-17. For primary amines, the higher average absolute deviation is as a result of large deviations for methylamine (794 kPa) and 2-methylpropylamine (601 kPa). These are the first components in their series. The average absolute deviation for the other six primary amines is 138 kPa. For all mono-functional and multi-functional nitrogen compounds (including amines), the proposed method yields a remarkable improvement when compared to all other methods.

The results for the critical volume are presented in Table 7-18. The proposed method nearly always leads to the lowest deviations and no extremely high deviations (>5 %) were found. The only exception is in case of pyridine (7 %) which is the smallest component in the 6-membered nitrogen ring series.

---

[*] Includes multi-functional compounds

Table 7-17: Critical pressure average absolute deviations (kPa) of the models for different types of nitrogen compounds.

	Average Absolute Deviations (kPa) (Number of components in Superscript)									
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**DB**	**LD**	**SJ**	**KR**
Primary amines	278^{6}	437^{6}	282^{6}	193^{7}	402^{6}	383^{7}	464^{6}	380^{6}	342^{6}	544^{6}
Secondary amines	126^{6}	338^{6}	398^{6}	281^{5}	306^{5}	315^{6}	445^{6}	356^{6}	388^{7}	267^{6}
Tertiary amines	101^{4}	111^{4}	177^{4}	62^{4}	132^{4}	198^{4}	509^{4}	118^{4}	138^{4}	185^{4}
Amines*	148^{26}	487^{25}	483^{23}	400^{21}	508^{23}	556^{22}	493^{22}	472^{25}	496^{22}	486^{25}
N in 6-membered rings	118^{3}	85^{3}	165^{2}	113^{3}	40^{3}	121^{3}	-	-	241^{3}	128^{3}
Cyanides	157^{6}	176^{6}	228^{5}	152^{6}	269^{6}	149^{5}	-	253^{6}	250^{6}	218^{6}
Di amides	0^{1}	-	-	-	-	-	-	-	-	-
Nitrous & nitrites	0^{1}	410^{1}	-	20^{1}	18^{1}	1^{1}	-	40^{1}	407^{1}	437^{1}
Nitrogenated (w/o Amines)*	100^{13}	263^{12}	208^{7}	177^{10}	192^{9}	313^{11}	-	263^{6}	255^{12}	176^{12}

Table 7-18: Critical volume average absolute deviations (%) of the models for different types of nitrogen compounds.

	Average Absolute Deviations (%) (Number of components in Superscript)								
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**LD**	**SJ**	**KR**
Primary amines	2.6^{5}	6.8^{6}	4.2^{3}	3.3^{3}	6.7^{5}	4.1^{4}	7.4^{5}	6.0^{5}	4.8^{5}
Secondary amines	0.8^{3}	5.8^{3}	4.2^{3}	3.9^{3}	9.6^{3}	4.4^{3}	5.0^{3}	7.7^{2}	7.5^{3}
Tertiary amines	1.7^{1}	1.1^{1}	1.4^{1}	1.2^{1}	1.8^{1}	1.2^{1}	4.6^{1}	2.1^{1}	2.8^{1}
Amines*	1.4^{12}	4.6^{12}	9.1^{10}	3.2^{8}	7.7^{12}	5.8^{11}	6.1^{12}	5.4^{9}	7.5^{12}
N in 6-membered rings	3.1^{4}	4.3^{4}	5.4^{3}	6.1^{3}	3.9^{4}	8.7^{4}	-	4.6^{4}	6.1^{4}
Cyanides	0.0^{1}	0.0^{1}	0.2^{1}	1.0^{1}	0.3^{1}	0.9^{1}	0.3^{1}	0.2^{1}	2.5^{1}
Di amides	0.0^{1}	-	-	-	10.2^{1}	-	1.1^{1}	-	2.7^{1}
Nitrous & nitrites	0.0^{1}	0.1^{1}	-	0.1^{1}	0.2^{1}	0.1^{1}	0.2^{1}	0.2^{1}	0.2^{1}
Nitrogenated (w/o Amines)*	2.6^{10}	3.3^{6}	4.1^{4}	5.7^{5}	4.4^{6}	10.7^{8}	0.7^{2}	6.3^{17}	5^{9}

---

* Includes multi-functional compounds

7.4.3 Sulphur Compounds

The results for the different types of sulphur compounds for the critical temperature are presented in Table 7-19. The proposed method in most cases yielded the lowest deviation. There were no large deviations (>20 K) for any of the sulphur compounds.

Table 7-19: Critical temperature average absolute deviations (K) of the models for different types of sulphur compounds.

	Average Absolute Deviations (K) (Number of components in Superscript)										
	PR	JR	CG	MP	AB	CT	WQ	DB	LD	SJ	KR
Thiols	4.2^{7}	3.0^{7}	9.5^{5}	0.7^{6}	4.4^{7}	11.8^{7}	2.8^{6}	10.7^{6}	4.7^{7}	1.4^{6}	9.0^{7}
Thioether	7.7^{7}	9.1^{7}	16.5^{7}	7.7^{7}	9.4^{7}	15.4^{6}	4.5^{6}	24.9^{7}	10.1^{7}	10.2^{6}	12.8^{7}
Aromatic thioether	1.6^{3}	8.2^{3}	-	0.5^{1}		52.5^{3}	4.9^{3}	-	8.3^{3}	3.7^{3}	2.6^{3}
Sulfolane (O=S=O)	0.0^{1}	-	-	-	-	-	30.4^{1}	-	-	-	-
Sulphur compounds *	4.1^{22}	5.9^{21}	13.0^{12}	4.2^{14}	6.8^{15}	29.4^{20}	8.1^{19}	18.4^{13}	7.2^{20}	6.1^{19}	11.0^{21}

The results for the critical pressure are presented in Table 7-20. The larger deviation in case of thiols is caused by the two components which are both the first members in their homologous series (methanethiol (472 kPa) and ethanethiol (350 kPa)). The difference in critical pressures between these two components is an astonishing 18 bar. The reference for methanethiol is rather old (Berthoud & Brum (1924)) and as there were no other data available, both components were included in the training set. In this case, group parameters should be used with caution.

The results for the critical volume are presented in Table 7-21. A moderately large error was found in case of methanethiol (9.5%). Data were reported in one reference of 1924 (see above) and a second from 1961 (Janik & Janik (1961)).

---

* Includes multi-functional compounds

Table 7-20: Critical pressure average absolute deviations (kPa) of the models for different types of sulphur compounds.

	Average Absolute Deviations (kPa) (Number of components in Superscript)									
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**DB**	**LD**	**SJ**	**KR**
Thiols	411^{2}	431^{2}	240^{1}	14^{2}	181^{2}	210^{2}	641^{2}	173^{2}	185^{2}	280^{2}
Thioether	150^{3}	218^{3}	97^{3}	177^{3}	106^{3}	178^{3}	158^{2}	101^{3}	112^{3}	113^{3}
Aromatic thioether	77^{3}	98^{3}	-	10^{1}	-	338^{3}	-	526^{3}	352^{3}	497^{3}
Sulfolane (O=S=O)	0^{1}	-	-	-	-	1963^{1}	-	-	-	-
Sulphur compounds *	125^{12}	338^{11}	132^{4}	95^{6}	136^{5}	652^{12}	399^{4}	259^{10}	237^{11}	303^{11}

Table 7-21: Critical volume average absolute deviations (%) of the models for different types of sulphur compounds.

	Average Absolute Deviations (%) (Number of components in Superscript)								
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**LD**	**SJ**	**KR**
Thiols	4.9^{3}	4.8^{3}	16.5^{1}	0.6^{2}	4.1^{3}	0.7^{2}	4.2^{3}	1.6^{2}	3.4^{3}
Thioether	1.2^{3}	3.1^{3}	2.7^{3}	2.5^{3}	2.9^{3}	2.6^{3}	2.9^{3}	2.9^{3}	2.7^{3}
Aromatic thioether	2.3^{3}	1.3^{3}	-	0.0^{1}	-	28.5^{3}	3.0^{3}	1.3^{3}	3.0^{3}
Sulfolane (O=S=O)	0.0^{1}	-	-	-	-	58.4^{1}	-	-	-
Sulphur compounds *	1.9^{13}	3.5^{12}	6.1^{4}	1.6^{6}	3.6^{6}	19.1^{12}	3.4^{11}	2.8^{11}	2.7^{12}

7.4.4 Halogen Compounds

For halogen compounds, no distinction between mono-functional compounds and multi-functional compounds is made. Although some halogen compounds may act as hydrogen bonding acceptors, the halogen groups can be considered to behave additive due to the weakness of these bonds.

The results for the different types of halogen compounds for the critical temperature are presented in Table 7-22. The filter 'halogen saturated' refers to a saturated hydrocarbon backbone with any number of halogen atoms defined to it. The proposed method yielded consistently good estimation results and no large deviations (>14 K).

---

* Includes multi-functional compounds

Table 7-22: Critical temperature average absolute deviations (K) of the models for different types of halogen compounds.

	Average Absolute Deviations (K) (Number of components in Superscript)										
	PR	**JR**	**CG**	**MP**	**AB**	**CT**	**WQ**	**DB**	**LD**	**SJ**	**KR**
Saturated Fluorine	3.1^{5}	4.0^{5}	48.1^{5}	2.2^{6}	7.6^{5}	22.6^{5}	3.6^{4}	19.9^{3}	5.4^{6}	6.3^{5}	4.6^{5}
Fluorinated	2.1^{21}	7.9^{21}	28.1^{25}	3.0^{20}	9.2^{21}	28.9^{25}	2.4^{18}	5.8^{19}	9.1^{21}	2.8^{21}	3.2^{21}
Saturated chlorine	4.5^{14}	4.7^{14}	6.5^{13}	-	4.9^{14}	12.9^{14}	4.8^{14}	7.8^{13}	4.5^{14}	5.2^{13}	6.6^{14}
Chlorinated	4.6^{17}	5.1^{17}	6.6^{16}	-	4.9^{17}	11.9^{173}	4.8^{16}	7.0^{16}	5.1^{17}	4.7^{16}	6.5^{17}
Saturated bromine	2.6^{2}	2.6^{2}	3.6^{2}	-	5.7^{2}	5.1^{2148}	7.6^{2}	16.0^{2}	10.4^{2}	8.0^{2}	1.7^{2}
Brominated	2.2^{3}	3.1^{3}	5.8^{3}	-	4.2^{3}	5.7^{3}	5.3^{3}	11.7^{3}	8.5^{3}	5.8^{3}	2.2^{3}
Iodinated	4.2^{3}	2.6^{3}	6.5^{3}	0.1^{3}	1.4^{3}	11.5	0.1^{2}	0.2^{2}	2.7^{3}	3.0^{3}	4.1^{3}
Halogenated Compounds ·	3.6^{128}	6.0^{115}	30.9^{128}	3.8^{60}	6.4^{115}	39.8	6.3^{111}	9.9^{82}	7.2^{121}	8.9^{121}	5.7^{116}

In the case of critical pressure (Table 7-23), the number of fluorine components in the training set is almost twice of that in case of the critical temperature. The reason is that for many fluorinated compounds no experimental normal boiling point was available and these compounds were excluded from the training set.

Larger deviations were observed for the smaller components such as chloroform (422 kPa), ethylbromide (251 kPa) and propylbromide (457 kPa). Chloroform can be considered to be an exotic compound with a high hydrogen bonding index. The two bromine compounds are the first members in their homologous series. For all eight bromine compounds, the average absolute deviation is 212 kPa. If the two bromine components mentioned earlier are removed, the deviation is only 124 kPa.

The results for the critical volume (Table 7-24) only contain one slightly higher deviation (1,2-Dichloroethane (8.6 % or 19 $cm^3.mol^{-1}$)) where the reference (Hojendahl (1942)) reported an experimental error of ±15 $cm^3.mol^{-1}$. Thus, the estimation error for this component is still close to the accuracy of the experimental value.

· Includes multi-functional compounds

Table 7-23: Critical pressure average absolute deviations (kPa) of the models for different types of halogen compounds.

	Average Absolute Deviations (kPa) (Number of components in Superscript)									
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**DB**	**LD**	**SJ**	**KR**
Saturated Fluorine	112^{32}	242^{32}	318^{32}	122^{32}	524^{27}	163^{31}	367^{20}	304^{32}	511^{32}	249^{32}
Fluorinated	109^{43}	244^{43}	289^{43}	107^{42}	496^{36}	136^{40}	298^{31}	320^{43}	415^{43}	211^{43}
Saturated chlorine	211^{9}	685^{9}	200^{8}	-	533^{9}	290^{9}	606^{5}	275^{9}	173^{8}	416^{9}
Chlorinated	183^{11}	593^{11}	281^{8}	-	477^{11}	324^{11}	578^{6}	279^{11}	155^{9}	483^{11}
Saturated bromine	354^{2}	238^{2}	753^{2}	-	978^{2}	172^{2}	1532^{2}	1026^{2}	263^{2}	236^{2}
Brominated	295^{3}	367^{3}	530^{3}	-	653^{3}	195^{3}	1082^{3}	882^{3}	225^{3}	392^{3}
Iodinated	125^{1}	14^{1}	130^{1}	14^{1}	48^{1}	1^{1}	7^{1}	193^{1}	235^{1}	11^{1}
Halogenated Compounds [*]	119^{122}	395^{112}	330^{91}	131^{63}	559^{91}	179^{99}	355^{60}	304^{121}	331^{116}	287^{112}

Table 7-24: Critical volume average absolute deviations (%) of the models for different types of halogen compounds.

	Average Absolute Deviations (%) (Number of components in Superscript)								
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**LD**	**SJ**	**KR**
Saturated Fluorine	1.9^{28}	4.2^{28}	6.1^{21}	3.0^{25}	19.0^{3}	5.7^{25}	4.6^{28}	3.8^{28}	4.2^{28}
Fluorinated	2.1^{38}	4.9^{38}	5.8^{31}	3.0^{34}	8.3^{5}	4.9^{33}	4.5^{38}	3.3^{38}	3.5^{38}
Saturated chlorine	3.8^{4}	4.0^{4}	2.3^{2}	-	6.5^{3}	4.4^{4}	4.1^{4}	4.8^{3}	3.6^{4}
Chlorinated	3.0^{6}	4.7^{6}	4.1^{4}	-	6.0^{4}	5.5^{6}	6.2^{5}	3.7^{4}	5.1^{6}
Saturated bromine	2.1^{1}	2.5^{1}	2.6^{1}	-	1.1^{1}	0.0^{1}	2.4^{1}	0.8^{1}	0.2^{1}
Brominated	1.1^{2}	1.6^{2}	3.4^{2}	-	1.4^{2}	0.1^{2}	2.3^{2}	0.6^{2}	3.0^{2}
Iodinated	0.0^{1}	0.2^{1}	4.7^{1}	0.1^{1}	0.3^{1}	0.0^{1}	1.5^{1}	0.0^{1}	0.2^{1}
Halogenated Compounds [*]	2.3^{94}	5.0^{80}	5.1^{81}	5.3^{45}	7.6^{18}	5.0^{74}	6.3^{87}	4.4^{89}	4.4^{60}

The filter of 'Halogenated Compounds' contains a significant number of components with combinations of different halogen groups and other strong associating or hydrogen bonding groups. Nevertheless, no especially high deviations were found for this filter.

---

[*] Includes multi-functional compounds

From all available methods, the Klincewicz & Reid (1984) method presents an accuracy closest to the proposed method and a range of applicability which is almost similar. The reason for the accuracy is the result of the inclusion of a halogen correction proposed by Cramer (1980). However, this correction only differentiates between the numbers of halogens on any atom. The proposed method employs five halogen corrections (also applicable to multi-functional compounds) which are more directly linked to the different electronic configurations. This is one of the reasons for the much improved accuracy as compared to the older method.

7.4.5 Various Other Compounds

The results for the various other compounds for the critical temperature are presented in Table 7-25. In the case of the regression of silicon compounds, the groups were entirely re-engineered regarding the number of electronegative neighbours of a silicon atom. Previously, there were three silicon groups; viz. silicon connected to an oxygen, to either fluorine or chlorine and any other atom. As the number of electronegative neighbours influences the electronic configuration of the molecule, the groups were reconstructed to account for the number of electronegative neighbours on a silicon atom. A new correction was also developed for silicon atoms to differentiate between different halogen and oxygen atoms. The modification was also applied for the estimation of the normal boiling point with similar success.

The proposed method now yields the most accurate results as well as an extended range of applicability compared to all other available methods. The only method with a similar range of applicability is that of Somayajulu (1989). Although the latter method reports a lower average absolute deviation than the proposed method, the range of compounds is smaller (17). For these 17 components, the proposed method reports a deviation of 8.0 K. From all silicon compounds, only one compound showed a large deviation, Dodecamethylpentasiloxane (32.4 K).

The results for the critical pressure and critical volume are presented in Table 7-26 and 7-27, respectively. The proposed method yields better overall results and an extended range of applicability for both properties. There were no large deviations for the critical pressure (>250 kPa) and critical volume (>5%).

Table 7-25: Critical temperature average absolute deviations (K) of the models for various other types of compounds.

	Average Absolute Deviations (K) (Number of components in Superscript)										
	PR	JR	CG	MP	AB	CT	WQ	DB	LD	SJ	KR
Tin	0.0^{1}	-	-	-	-	-	44.6^{1}	-	-	0.9^{1}	-
Boron	0.0^{1}	-	-	-	-	-	119.0^{1}	-	11.3^{1}	6.5^{1}	-
Silicon	2.6^{2}	-	-	-	-	-	-	-	10.7^{2}	8.9^{2}	-
Silicon to oxygen	9.5^{16}	-	-	-	-	-	-	-	16^{13}	9.5^{11}	-
Silicon (*en* [*])	8.4^{23}	-	-	-	-	-	-	-	12.5^{19}	8.2^{17}	-

Table 7-26: Critical pressure average absolute deviations (kPa) of the models for various other types of compounds.

	Average Absolute Deviations (kPa) (Number of components in Superscript)									
	PR	JR	CG	MP	AB	WQ	DB	LD	SJ	KR
Tin	0^{1}	-	-	-	-	-	-	-	520^{1}	-
Boron	0^{1}	-	-	-	-	2470^{1}	-	1236^{1}	703^{1}	-
Silicon	147^{2}	-	-	-	-	-	-	108^{2}	132^{2}	-
Silicon to oxygen	53^{13}	-	-	-	-	-	-	74^{13}	79^{9}	-
Silicon (*en* [*])	55^{23}	-	-	-	-	-	-	90^{22}	113^{18}	-

Table 7-27: Critical volume average absolute deviations (%) of the models for various other types of compounds.

	Average Absolute Deviations (%) (Number of components in Superscript)								
	PR	JR	CG	MP	AB	WQ	LD	SJ	KR
Silicon	0.0^{1}	-	-	-	-	-	28.0^{1}	4.0^{1}	-
Silicon to oxygen	2.0^{6}	-	-	-	-	-	41.8^{8}	4.4^{8}	-
Silicon (*en* [*])	2.2^{17}	-	-	-	-	-	33.3^{15}	3.7^{15}	-

---

[*] Denotes silicon connected to any electronegative neighbour. This filter also includes all multi-functional compounds.

7.5 Multifunctional Compounds

The second-order group interactions correct the flawed assumption of additivity in the case of strongly associating groups exhibiting a hydrogen bonding interaction (Section 5.3.3).

The list of groups considered to be non-additive is presented in Table 7-28. Minor changes were introduced compared to the list of groups published earlier (Nannoolal *et al.* (2004)). For instance, since tertiary amines are 'shielded' by three carbon atoms, the probability of a hydrogen bonding interaction is extremely small. Thus, the tertiary amine group is considered now to be additive. There has also been a modification to the 'Nitro' interaction group as compared to the previous method. The interaction group now includes the functional groups nitrate (ID - 72) and nitrous attached to a non-aromatic carbon (ID - 68). This decision is based on the numerically similar group contribution values as well as the similar chemical nature of the groups.

Table 7-28: Groups considered to be non-additive (group & ID(s) given in brackets)

Abbr.	**Group Name (Group) (ID (s))**	**Abbr.**	**Group Name (Group) (ID (s))**
OH	Alcohol (-OH) (34,35,36,37)	Ats	Aromatic Sulphur (-S(a)-) (56)
OH(a)	Phenol (-OH(a)[*]) (37)	SH	Thiol (-SH) (53)
COOH	Carboxylic Acid (-COOH) (44)	NH_2	Primary Amine (-NH_2) (40, 41)
EtherO	Ether (-O-) (38)	NH	Secondary Amine (>NH) (42,97)
Epox	Epoxide (>(OC2)<) (39)	OCN	Isocyanate (-OCN) (80)
Ester	Ester (-COOC-) (45,46,47)	CN	Cyanide (-CN) (57)
Ketone	Ketone (-CO-) (51,92)	Nitro	Nitrate (72) & Nitrous (68, 69)
Alde	Aldehyde (-CHO) (52,90)	AN5	(a) N-5-ring (=N(a)-(r5)) (66)
AO	Aromatic Oxygen (-O(a)-) (65)	AN6	(a) N-6-ring (=N(a)-(r6)) (67)
Teth	Sulfide (Thioether) (-S(na)-) (54)		

---

[*] Denotes aromatic

The group interaction contribution (*GI*) is calculated via Equation 7-1:

$$GI = \frac{1}{n}\sum_{i=1}^{m}\sum_{j=1}^{m}\frac{C_{i-j}}{m-1} \qquad \text{(Where } C_{i-j} = C_{j-i}\text{)} \qquad (7\text{-}1)$$

Here C_{i-j} is the group interaction contribution between group *i* and group *j* (where $C_{i-i} = 0$, as the interaction of a group with itself is accounted for by the first-order contribution), *n* is the number of atoms (except hydrogen) and *m* is the total number of interaction groups in the molecule. The total group interaction contribution decreases with the size of the molecule. To take this into account, the sum of group interactions is divided by the number of non-hydrogen atoms in the molecule (*n*). The group interaction contribution is added to the summation of group contribution values for first-order groups and second-order corrections.

The results for all multi-functional components with non-additive behaviour for the critical temperature, critical pressure and critical volume are presented in Tables 7-29 to 7-31. In these tables, only deviations for components including the specific interaction group together with any other interaction group are reported. For example, under "OH", deviations for components including the "OH" interaction group together with any other interaction group are reported.

In almost all cases, all other methods yield extraordinarily large deviations. This is a general problem with most group contribution methods from literature.

For the critical temperature, there were large deviations for dodecamethylpentasiloxane, glycerol and 2,2-diethoxypropane (30 K). The first two components were already discussed earlier, the latter component represents a special case as both ether groups connect to the same carbon atom which has four large neighbours (steric hindrance). Apart from these components, there were no relatively large (>25 K) deviations for the other components.

Table 7-29: Critical temperature average absolute deviations (K) of the models for multi-functional compounds.

	Average Absolute Deviations (K) (Number of components in Superscript)										
	PR	JR	CG	MP	AB	CT	WQ	DB	LD	SJ	KR
OH	5.8^{17}	42.6^{17}	50.9^{17}	37.8^{17}	21.9^{17}	61.7^{17}	36.6^{17}	95.3^{17}	44.9^{17}	39.5^{13}	23.3^{17}
OH(a)	0.0^{1}	4.7^{1}	35.8^{1}	15.4^{1}	4.6^{1}	-	28.1^{1}	40.5^{1}	53.0^{1}	2.0^{1}	14.4^{1}
NH_2	0.0^{3}	24.1^{3}	39.8^{3}	22.9^{3}	20.5^{3}	68.4^{3}	27.9^{3}	41.5^{3}	24.8^{3}	29.7^{3}	18.3^{3}
NH	0.0^{2}	14.8^{2}	27.3^{2}	15.8^{2}	7.0^{2}	53.0^{1}	6.5^{2}	35.6^{2}	21.7^{2}	25.7^{1}	4.9^{2}
COOH	12.8^{3}	-	-	-	-	-	-	-	-	0.4^{1}	-
Ether	7.4^{44}	17.3^{31}	20.6^{27}	16.8^{28}	8.8^{30}	30.7^{29}	18.8^{30}	92.4^{25}	18.3^{41}	15.6^{32}	16.1^{31}
Epoxide	0.0^{1}	31.2^{1}	46.8^{1}	17.9^{1}	28.8^{1}		29.9^{1}	24.3^{1}	28.7^{1}		49.6^{1}
Ester	1.5^{8}	3.9^{8}	8.8^{6}	3.5^{7}	3.6^{8}	13.7^{8}	7.5^{6}	87.4^{7}	4.7^{8}	3.3^{7}	14.9^{6}
Ketone	0.0^{1}	-	-	-	-	157.0^{1}	46.9^{1}	-	-	-	-
Teth, AtS, AO, AN5	6.9^{6}	5.0^{3}	-	6.4^{1}	-	17.1^{3}	41.1^{3}	-	-	22.9^{3}	6.8^{3}
All GI components	6.7^{54}	21.2^{47}	33.4^{39}	21.4^{41}	14.6^{42}	43.6^{44}	21.5^{46}	84.6^{36}	23.5^{54}	18.2^{46}	18.4^{47}

Table 7-30: Critical pressure average absolute deviations (kPa) of the models for multi-functional compounds.

	Average Absolute Deviations (kPa) (Number of components in Superscript)									
	PR	JR	CG	MP	AB	WQ	DB	LD	SJ	KR
OH	128^{17}	608^{17}	972^{17}	566^{17}	651^{17}	500^{17}	597^{17}	589^{17}	735^{13}	592^{17}
OH(a)	0^{1}	572^{1}	198^{1}	172^{1}	116^{1}	213^{1}	335^{1}	446^{1}	86^{1}	113^{1}
NH_2	0^{3}	1668^{3}	1575^{3}	1672^{3}	1930^{3}	1727^{3}	1501^{3}	1839^{3}	1788^{3}	1767^{3}
NH	0^{2}	107^{2}	481^{2}	114^{2}	348^{2}	161^{2}	295^{2}	210^{2}	25^{1}	246^{2}
Ether	73^{33}	353^{23}	328^{19}	260^{20}	228^{22}	319^{22}	318^{20}	197^{33}	258^{26}	318^{23}
Epoxide	0^{1}	737^{1}	298^{1}	126^{1}	245^{1}	139^{1}	180^{1}	351^{1}	-	920^{1}
Ester	74^{7}	150^{7}	136^{7}	204^{6}	134^{7}	188^{7}	538^{6}	135^{7}	155^{6}	155^{7}
Ketone	0^{1}	306^{1}	-	121^{1}	-	130^{1}	-	279^{1}	509^{1}	50^{1}
Teth, AtS, AO, AN5	0^{5}	600^{5}	-	514^{1}	-	1030^{6}	-	181^{2}	285^{6}	207^{5}
All GI Components	77^{50}	488^{40}	850^{31}	401^{34}	530^{34}	451^{39}	536^{31}	323^{47}	378^{40}	406^{40}

Table 7-31: Critical volume average absolute deviations (%) of the models for multi-functional compounds.

	Average Absolute Deviations (%) (Number of components in Superscript)								
	PR	**JR**	**CG**	**MP**	**AB**	**WQ**	**LD**	**SJ**	**KR**
OH	0.7^{6}	4.6^{5}	6.7^{5}	9.0^{4}	5.2^{5}	7.4^{5}	4.6^{6}	4.9^{6}	10.1^{5}
OH(a)	0.0^{1}	27.7^{1}	16.5^{1}	-	12.3^{1}	7.7^{1}	11.3^{1}	15.7^{1}	8.7^{1}
NH	0.0^{2}	0.5^{2}	13.7^{2}	2.9^{1}	10.2^{2}	6.6^{2}	1.8^{2}	1.0^{1}	14.4^{2}
OCN	3.9^{4}	-	-	-	-	-	-	6.5^{4}	-
Ether	2.6^{19}	7.4^{12}	9.6^{9}	7.7^{10}	8.4^{10}	8.8^{12}	20.3^{19}	6.3^{17}	7.8^{12}
Epoxide	0.0^{1}	31.9^{1}	38.7^{1}		35.4^{1}	16.4^{1}	34.1^{1}	-	35.9^{1}
Ester	3.1^{3}	3.9^{3}	6.5^{3}	5.0^{3}	4.3^{3}	4.4^{3}	4.4^{3}	4.6^{3}	2.6^{3}
Ketone	0.0^{1}	43.0^{1}	-	67.0^{1}	-	46.8^{1}	40.0^{1}	37.8^{1}	48.2^{1}
Teth, AtS, AO, AN5	0.0^{5}	4.4^{5}	-	9.4^{1}	-	19.6^{5}	3.7^{2}	4.0^{5}	3.3^{5}
All GI Components	2.0^{32}	8.6^{21}	11.0^{13}	10.9^{14}	8.7^{14}	12.0^{21}	18.0^{25}	6.5^{29}	9.3^{21}

For the critical pressure, there were large deviations for 1,3-propanediol and 1,2-butanediol (407 kPa). The first component has already been discussed and the latter component exhibits an additive dipole moment. Apart from these components, there were no relatively large (>300 kPa) deviations for the other components.

For critical volume, no relatively large deviations (>5 %) were observed. The only exception was 1,8-octanediisocyanate where the isocyanate group contribution value is questionable (this will be shown later).

Caution should be taken when estimating properties of multi-functional compounds as additional effects not captured by group contribution can have a strong influence. For instance, β-keto esters (A) and 1,3-dicarbonyl (B) compounds (Figure 7-3), tautomeric effects lead to the formation of an intramolecular hydrogen bond. For these components, the critical temperature is lower than estimated.

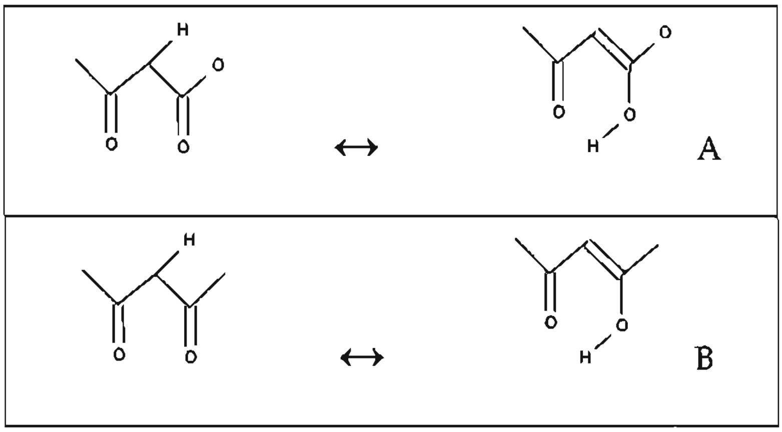


Figure 7-3: Intramolecular hydrogen bond fin case of β -keto esters (A) and 1,3-dicarbonyl (B) compounds.

Keto-enol tautomerism (Figure 7-4) is basically always present in liquid ketones but the equilibrium is usually close to 100% ketone. Different effects stabilize the enol form and in some cases can even lead to equilibrium very close to pure enol.

One such effect is the formation of an intramolecular hydrogen bond like discussed above for 1,3-diketones. In this case, the resulting enol has lower total intermolecular interactions and thus a lower boiling point and critical temperature. Another effect is the formation of a larger resonance stabilised π-electron system (aromatic or non-aromatic). Phenol for example represents an enol stabilised by aromaticity. In this case, both the boiling point and critical temperature are usually higher than estimated.

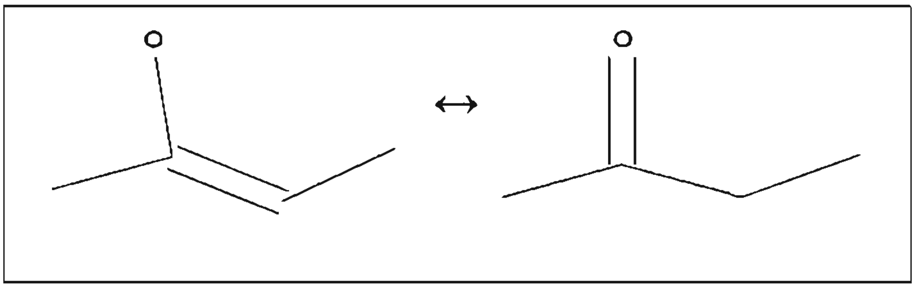


Figure 7-4: Keto-enol tautomerism.

One of the most drastic interactions is observed between a -COOH and NH_2 group. In this case, zwitterions (amino acids) are formed and group contribution estimations should never be employed for these compounds. A zwitterion (from German "Zwitter" — "hybrid," "hermaphrodite") is a compound with anionic and cationic groups in the same molecule. At neutral *pH* most zwitterions are therefore negatively charged anions and positively charged cations at the same time. Zwitterions usually have a high solubility in water due to their charged groups and a poor solubility in most organic solvents with practically no vapour pressure.

Special groups have been defined for the latter two cases, 1,3-diketones (ID- 118) and COOH-NH_2 (ID - 218). No group contribution value is given to disable property estimation for these compounds.

The only disadvantage of employing group interactions is the lack of physical property data for multi-functional compounds. A relatively large number of interaction groups are required to predict the properties of only a few components. For instance, for critical temperature, critical pressure and critical volume, there are 20, 18 and 15 interaction groups for 64, 50 and 32 components, respectively. This is only about 2.1 to 3.2 points per group. However, for the normal boiling point estimation, there were 73 groups for 398 components.

Interaction groups have a significant effect on the physical properties and therefore need to be included. If no interaction contribution is available, the estimation results will be systematically wrong. For normal boiling temperatures, it could be shown that the interaction contribution is similar for different compounds. They can therefore be derived from the data for one component but in this case will depend entirely on the quality of the data for this compound.

The limited number of experimental data points also leads to a problem that not all of the required group interaction contributions could be regressed. Discarding group interaction contributions for polyol compounds increases the average absolute deviation in critical temperature from 5.8 K to 21.6 K, which is similar to the deviations of the Ambrose (1978a) and Klincewicz & Reid (1984) methods (see Table 7-10). All other models perform significantly worse. Thus, the new model can also be recommended in cases where group interaction parameters are not available. In this case, one should expect higher uncertainty of the result.

7.6 Model Development

An important feature of a group contribution method, beside the correlation of available data, is its ability to safely interpolate and extrapolate. This is especially true for critical property data estimation as the majority of available data are for rather small molecules. Usually, group contribution methods are regularly applied to very different substances, even in some cases to polymers with molecular weights orders of magnitude larger than the components in the experimental data base.

While analyzing the results for ten different estimation methods from literature, it became apparent that five of these produce physically unrealistic extrapolations. Figure 7-5 (similar to Figure 2-2 except for the inclusion of the proposed method estimations) presents the estimated critical temperature for n-alkanes as function of the number of carbon atoms. As this erroneous behaviour is caused by the functional form of the model equation, similar unrealistic extrapolations can be expected for all types of large molecules.

The development of a property prediction model started by employing various models in the regression of the different classes and subclasses of compounds. Models that were applicable to the trends obtained from the different classes of compounds and that can safely interpolate and extrapolate were tested in the final regression of all compounds. The following models were employed due to their correlative power and safe extrapolation ability:

$$T_c = T_b \left(b + \frac{1}{a + \left(\sum_{i}^{m} N_i C(T_c)_i + GI \right)^c} \right) \tag{7-2}$$

$$\frac{P_c}{kPa}=\frac{M^b}{\left(a+\sum_i^m N_i C(P_c)_i+GI\right)^2} \tag{7-3}$$

$$\frac{V_c}{cm^3 mol^{-1}}=\frac{\sum_i^m N_i C(V_c)_i+GI}{n^a}+b \tag{7-4}$$

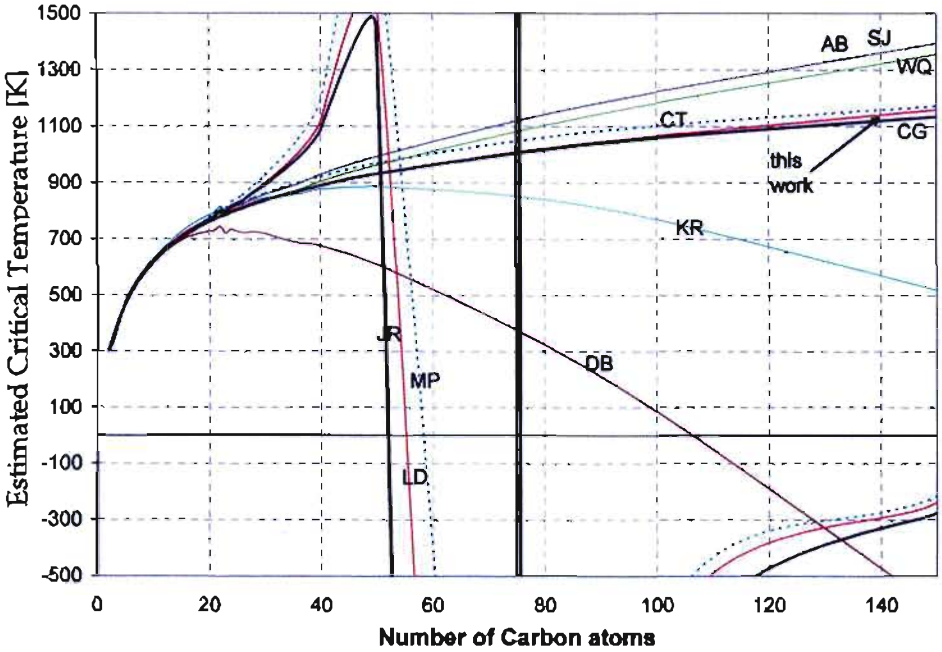


Figure 7-5: Estimated critical temperature for n-alkanes as a function of the number of carbon atoms from different group contribution methods (AB and SJ overlap).

For equations 7-2 to 7-4, the summation of group contributions includes *GI* (Equation 7-1). For these models, *m* indicates the total number of groups, N_i and C_i the frequency and group contribution value of group *i*, respectively. The model parameters for each property are presented in Table 7-32.

Table 7-32: Model parameters for Equations 7-2 to 7-4.

Property	a	b	c
T_c	0.9889	0.6990	0.8607
P_c	0.00939	-0.14041	-
V_c	-0.2266	86.1539	-

The model for T_c is similar to the model employed by Ambrose (1978a) with the exception that the parameter *b* replaces the value of 1 employed by Ambrose. It was suggested earlier on in Chapter 2 that a value of one leads to $T_c \rightarrow T_b$ with increasing number of group contribution increments. However, since it is considered possible for T_c to have values smaller than T_b for very large compounds (for example, polymers), the variable *b* was regressed to experimental data. A value of *b* lower than one was accepted. Several authors have also employed a quadratic function (see Chapter 2) in their models; this resulted in physically unrealistic local maxima or minima (see Figure 7-5, parts of some trends is intentionally omitted for illustration purposes). For the equation used to estimate P_c, a quadratic function was employed in this work but it was verified, that the location of the maximum does not lead to problems in extrapolation. For V_c, there is a relatively small dependence on the number of atoms as is reflected by the small negative value of *a*.

7.7 Discussion

7.7.1 Overall Results

The results for the estimation of all critical properties of all applicable components for the available methods are presented in Table 7-33. The average absolute percentage error of the proposed method for all properties is significantly lower than that of the other methods. The proposed method also combines the lowest deviation with the broadest range of applicability (i.e. number of components for which the property can be estimated).

Table 7-33: Critical property average absolute deviations for all models

Methods	T_c			P_c			V_c		
	NC[*]	MAPE[†]	AAD[‡] (K)	NC	MAPE	AAD (kPa)	NC	MAPE	AAD (cm^3/mol)
This work	588	0.74	4.3	486	2.96	100	348	1.78	6.4
Ambrose	528	1.07	6.0	412	7.03	253	242	3.99	19.4
Marrero Pardillo	458	1.21	7.8	381	6.04	209	248	3.36	18.1
Klincewicz/Reid	547	1.27	7.8	452	7.57	248	319	3.86	17.9
Wen/Qiang(Tb)	506	1.26	7.8	-	-	-	-	-	-
Joback	543	1.41	8.8	452	7.11	238	314	3.73	16.5
Somayajulu	517	1.44	8.4	438	9.51	285	307	4.14	20.1
Lydersen	557	1.71	10.7	474	7.07	228	327	5.37	30.7
Daubert	475	3.87	23.9	352	7.00	253	-	-	-
Methods not requiring T_b:									
Wen/Qiang	506	2.97	16.7	421	5.67	197	294	4.99	22.1
Gani, Constantinou	559	4.07	17.2	410	7.12	248	277	4.81	22.8
Chein-Hsiun Tu	572	4.26	23.3	-	-	-	-	-	-

7.7.2 Probability of Prediction Failure

The method, apart from being more accurate than previous methods, also has a significantly improved probability of predicting properties within a smaller prediction error. This is shown in Figures 7-6 to 7-8 for critical temperature, critical pressure and critical volume, respectively. These plots serve as the most important criterion for the reliability and extrapolation capability of any group contribution model. The curves in the plots were calculated using all estimations possible for each method and were not limited to a common set of data.

---

[*] Denotes number of components

[†] Denotes mean absolute percentage error

[‡] Denotes average absolute deviation

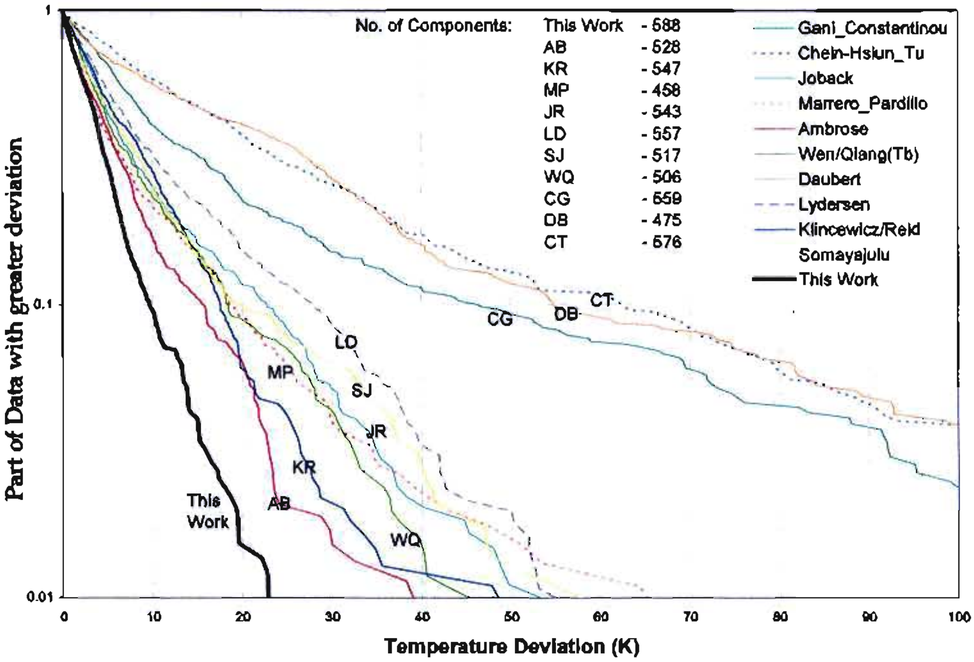


Figure 7-6: Fraction of the data with deviations for critical temperature larger than a given temperature.

From the plot of the critical temperature, for the proposed method, the curve indicates that only 10 % of the data are estimated with a deviation greater than 10 K and approximately 2.5 % with a deviation greater than 20 K. Also, besides the proposed method, the Ambrose method performed significantly better than all other methods. The large deviations observed for the Constantinou & Gani (1994) and Tu (1994) methods are partly caused by the fact that these methods estimate the critical temperature without information about the normal boiling temperature (note that the estimation from the method of Wen & Quiang (2001) that does not require knowledge of the normal boiling point is not plotted).

Besides the average deviations of the models and the information from Figures 7-6 to 7-8, one should also be aware of the problems of JR, LD, MP, DB and KR with respect to extrapolation to large molecules (Figure 7-5).

The authors can only recommend, besides the new method presented in this paper, the methods of Ambrose (AB) and to a lesser extent KR (for not too large molecules) for critical property data estimation. The other methods should be used with great caution in case of multi-functional compounds.

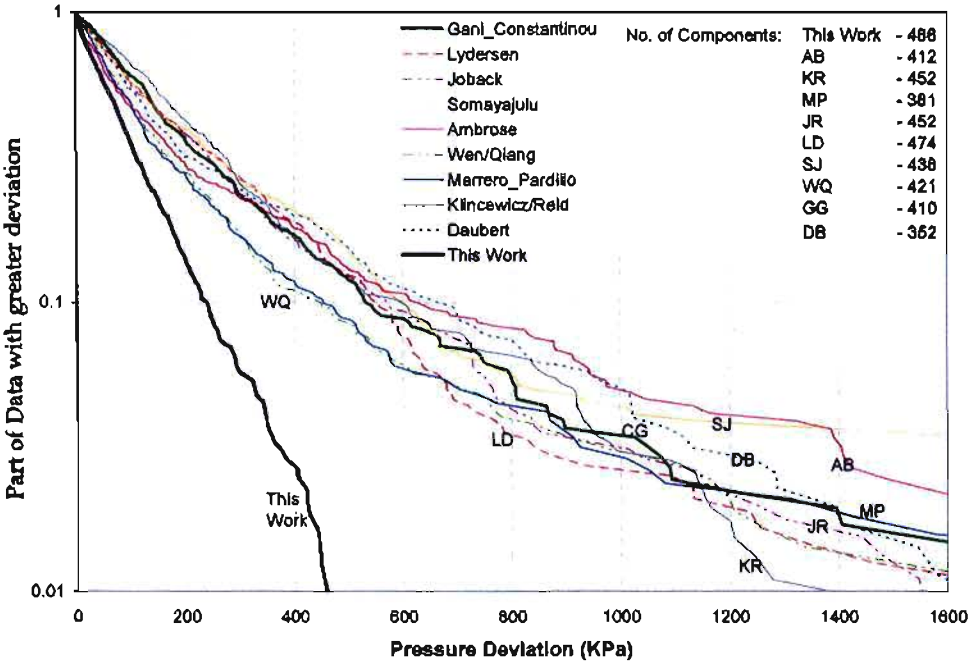


Figure 7-7: Fraction of the data with deviations for critical pressure larger than a given pressure.

7.7.3 Test of the Predictive Capability

Thus far, the proposed method has proved to be accurate, consistent and has a greater range of applicability. However, to test the predictive capability of a correlation, the estimation of a test set of data not used in the regression should be employed. This procedure provides a means to verify both the applicability of the model and the reliability of the data employed to obtain the regressed parameters. The problem with this kind of test, in the case of critical property data, is that only a small set of experimental data is available. This means that it is necessary to include all data in the regression of model parameters in the training set. However, there is one limited test of this type that can be conducted, and this was employed in this work. It should, however, be noted that the Ambrose (1978a) method did not use this form of test.

Instead, the author proceeded very carefully to ensure that the different model parameters were set to physically realistic values.

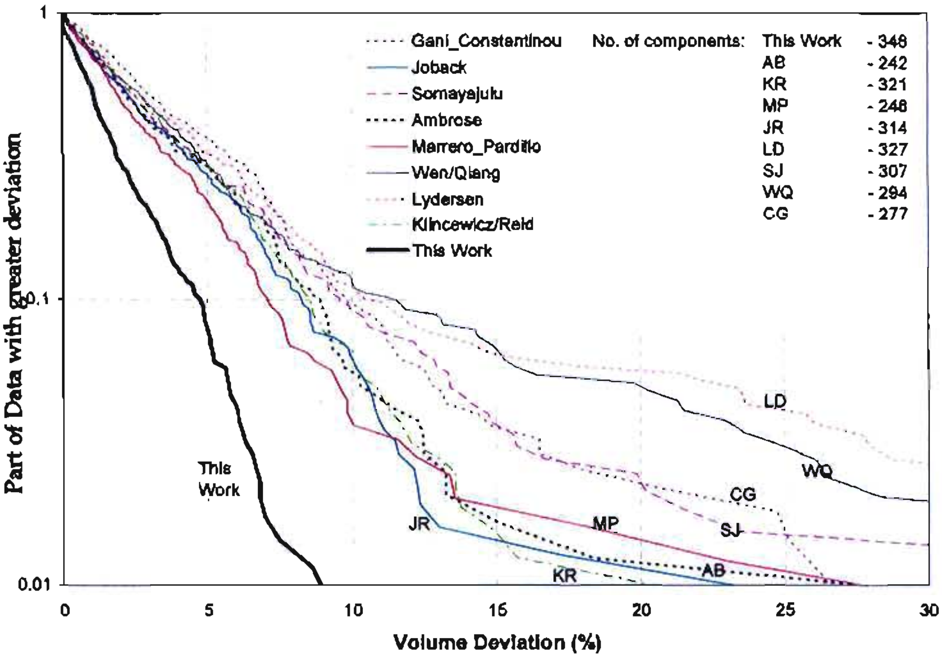


Figure 7-8: Fraction of the data with deviations for critical volume larger than a given volume.

The test conducted was for the case of critical temperatures. There were data for 67 components which were not used in the regression of model parameters due to the lack of reliable experimental information on the normal boiling point. When estimating the critical temperatures for these components using T_b values that were estimated from the method of Nannoolal (2004) & Nannoolal *et al.* (2004), an average absolute deviation of 10.87 K (1.93 %) was obtained. This compares favourably to other methods which do not require the normal boiling temperature, Constantinou & Gani (1994): 19.9 K for 56 components, Tu (1995): 39.8 K for 58 components and Wen & Quiang (2001): 14.5 K for 52 components.

For the normal boiling point estimation, the absolute average deviation of the previous method was 6.52 K for all 2812 components in the training set and 6.37 K for 199 components in the test set.

Estimating all critical temperature data in the training set using estimated instead of experimental T_b values increases the absolute average deviation by about 5 K from 4.31 K (0.74 %) to 9.21 K (1.65 %). From these results, it is deduced that the deviation in critical temperature for the test set is around 6 K while another 5 K can be attributed to the error in normal boiling point estimation. This compares well to the deviation of 4.31 K in the training set as the test set contains numerous data for exotic compounds that are also of questionable reliability.

A second test was performed on the estimation of the critical temperature and pressure from 28 compounds recently published by VonNiedernhausern *et al.* (2006a), (2006b), (2006c). This type of test is of limited applicability as the experimental data are only reported by one author. The results of the estimation are presented in Table 7-34 (some of the components presented in this test set also appear in the training set but with different property values). For the critical temperature, the proposed method yields significantly better results than the other available methods. For the critical pressure, larger deviations are seen for all methods. This author reports large experimental errors in some cases, for example ±5% for phenyl isocyanate. In addition, a previous publication in 2000 using the same experimental apparatus reported an experimental error of ±600 kPa for 1,3-propanediol (mentioned earlier in Section 7.4.1). Thus it can be assumed that the data for critical pressures are of limited reliability and the test results should not be considered representative.

				Critical Temperature Absolute Deviations (K)													Critical Pressure Absolute Deviations (kPa)									
Component name	T_b	T_c	P_c	WQ*	WQ	AB	PR*	PR	CT*	DB	LD	KR	SJ	JR	CG*	MP	WQ	AB	PR	DB	LD	KR	SJ	JR	GC	MP
2-Propenoic acid butyl ester	420.2	601.2	2840			2.3	19.8	14.9	9.3	33.4	3.9	7.1	3.0	2.4		3.5		66	103		66	288	74	104		101
p-Diisopropylbenzene	483.3	676.2	2360	2.4	12.6	5.9	5.1	0.6	32.2	22.0	4.4	20.9	2.2	7.8	2.3	14.6	82	29	128	13	87	401	56	48	134	48
Dipropylene glycol	502.4	705.2	3380	21.8	45.7	26.3	1.2	4.9	14.0	78.4	54.9	28.6		51.9	46.0	44.1	307	691	89	150	203	696		473	50	210
gamma-Butyrolactone	477.5	732.5	5100				9.6	1.6		10.0	7.0			1.6	164.0				31	1442	398			237	361	
1,1-Ethanediol diacetate	442.0	618.2	2970	20.5	21.1	7.1	20.2	3.7	31.1		8.4	16.5		4.8	4.8		494	114	60		172	304		200	249	
Diethyl oxalate	458.8	645.8	3060	2.0	13.9	0.0	30.1	10.2	5.7	227.1	0.3	11.8	0.2	3.4	4.1	9.8	83	7	73	1260	33	132	6	82	39	3063
tert-Butyl acetate	371.2	541.2	3040	10.6	3.6	3.2	4.6	4.7	46.4	3.0	5.3	6.6	0.8	5.5	11.7		3	147	196	144	126	229	24	152	211	
1,3-Butanediol	481.8	692.4	5180	48.8	31.5	44.4	5.5	16.6	55.9	37.7	47.7	23.0		46.6	80.3	38.1	60	841	36	291	177	40		150	506	221
Oxazole	342.7	550.6	6770	5.2	0.7		121.6	2.9	20.2			1.9	16.0	1.2		1.4	745		513			238	786	149		106
N-Formylmorpholine	519.1	779.3	6080				15.2	5.9											57							
Dimethyl disulfide	382.6	607.8	5070	265.4	23.1	3.8	5.2	6.2	4.1	38.6	2.5	1.0	3.6	1.9	0.8	1.6	387	247	722		294	717	226	212	779	
Diglycolamine	496.3	721.2	4800	68.3	42.3	3.1	14.4	5.7	75.3	102.6	48.2	13.9	47.3	43.0	77.4	37.6	166	35	1420	124	439	125	587	172	456	160
Methyldiethanolamine	520.0	741.9	4160	57.2	49.5	31.1	18.3	29.2	64.1	96.7	64.8	28.9	64.5	62.1	46.1	53.1	686	457	27	706	284	135	533	191	664	151
2,2-Dimethyloxirane	323.2	499.9	4350			13.5	9.8	2.4		25.1	18.5	9.8		11.7				10	175	934	311	96		499		
Phenyl isocyanate	438.8	656.9	4000				4.1	24.2					5.9						383				498			
Naphthalene	491.3	750	4130	2.6	6.3	1.6	13.2	6.2	53.1	1.9	11.2	16.5	1.5	8.8	5.8		249	76	185	479	466	191	78	272	506	
2-Propen-1-ol	370.5	547.1	5640			7.4	6.2	3.1	28.8	3.9	7.8	1.4	12.2	5.6	26.5	2.0		7	5		17	151	77	320	712	343
1,6-Hexanediol	523.2	740.8	4080	47.8	46.2	31.7	24.2	27.6	65.0	98.3	61.7	31.3	24.4	59.6	70.8	61.6	40	243	328	833	473	252	53	222	636	99
1,3-Dihydroxybenzene	554.6	836	6240	144.2	8.6	15.6		26.6		28.1	90.7	49.0	19.0	17.6	72.8	13.6	293	1244	949	376	415	516	1192	1321	1109	905
2-Phenylethanol	492.7	723.5	3990	18.6	26.5	6.9	6.8	1.1	32.8	45.5	38.9	14.3	42.2	38.8	42.0	33.0	91	267	27	162	74	489	202	103	314	41
1-Phenyl-1-thiaethane	467.5	705.9	4050			3.5	4.7	1.0	28.6		4.8	12.4	3.4	6.9	2.6			36	265		8	689	39	156	74	
1-tert-Butoxy-2-propanol	425.2	600.7	2720		18.8	8.6	6.8	5.9	46.6	40.3	22.8	6.3		16.9	3.6	20.6	228	356	1	414	276	628		408	245	211
Piperazine	420.0	856.3	5420	36.0	9.3	8.3	1.3	4.7		38.4	17.0	3.7		3.5	47.8	9.4	614	909	380	773	113	887		372	485	580
n-Dodecyl mercaptan	549.9	733.7	1810	21.9	4.1	0.2	1.9	13.3	15.0	11.5	7.3	36.2	0.3	1.0	23.7	1.9	188	25	284		35	284	24	71	74	85
Sulfolane †	560.0	868.2	5060	405.6	17.1		23.9	13.3									733		1230							
5,6-Dithiodecane †	508.1	711	2470	151.6	15.2	2.7	18.1	16.9	1.8	66.7	4.8	31.2	2.7	0.2	7.8	3.0	68	0	66		16	330	4	154	59	
1,2-Dihydroxybenzene †	519.1	800	5740	108.2	11.2	32.1	50.5	40.7		0.0	102.4	88.0	35.3	34.0	38.8	23.7	293	1244	1099	248	415	516	1192	1321	1109	834
Triacontane †	726.1	843	636	52.2	1.2	16.8	4.9	1.1	16.8	120.8	55.5	5.8	16.8	50.9	6.8	84.4	14	198	9	103	202	305	198	41	28	30
				74.1	19.4	11.9	16.5	10.5	32.2	61.3	28.8	18.7	15.9	19.5	35.8	23.5	273.1	316.8	314.4	496.7	212.0	349.6	307.7	297.6	395.3	424.5
w/o extrapolated (last 4)				47.7	21.4	11.1	15.2	9.3	34.8	49.5	25.2	16.3	16.4	16.3	38.7	21.0	272.7	292.2	266.6	639.5	212.2	344.8	278.3	269.2	394.8	423.5

* Does not required Tb
† Experimental values were extrapolated

Table 7-34: Test set of experimental and estimated critical temperature [K] and pressure [kPa] for 28 compounds.

7.7.4 Overall Discussion

The proposed method employs a larger number of groups than most of the other methods. As the limited number of experimental data limits the applicability of the method to groups for which data are available, this does not hinder but improve the reliability of the model. If a certain group has a well known significant effect on physical properties, it should not be replaced by a more general group because no data are available to regress the more specific group contribution. It should rather be included in the method without a contribution value. This again stresses the argument that a group contribution method development should start with a property for which a large range of data is available (such as the normal boiling point). The larger amount of data will lead to knowledge about the required differentiation.

The limited experimental information can also limit the reliability of several group contributions. It has been discussed throughout this chapter that a few points or a single point is sufficient for a group parameter. However, the parameter value is then dependant on the quality of data. There is one means, though, to verify the group contribution value. This involves comparing the numerical value of the group to other groups that are of a similar chemical nature and which are based on a larger set of data. Thus, group contributions for which there is only a single or a few points were examined by reviewing the reference reporting the data. Table 7-35 lists all cases where the parameter values created serious doubt about their validity. The references listed in this table are either outdated or questionable with no further means of verification. For example, in the case of the OCN-OCN group interaction contribution (number 176), for the critical temperature all three data points were measured by the same author and the parameter value is physically very improbable (around four times greater than the OH-OH or Ester-Ester interaction).

Table 7-35: Questionable group contribution values.

Group ID	Group Name	GC[*]	NC[†]	Reference
Critical Temperature				
78	$B(O-)_3$	157.3401	1	Hansen & Hughes (1959)
103	-OCOO-	764.9595	1	Nesterov *et al.* (2000)
176	OCN - OCN	-1866.0970	3	Zhuravlev *et al.* (1991)
179	EtherO - Epox	707.4116	1	Steele *et al.* (1997a)
183	EtherO - Teth	-654.1363	1	Steele *et al.* (1993)
205	Teth - Teth	-861.1528	1	Steele *et al.* (1993)
Critical Pressure				
78	$B(O-)_3$	12.6786	1	Hansen & Hughes (1959)
103	-OCOO-	58.9190	1	Nesterov *et al.* (2000)
148	OH(a) - OH(a)	57.8350	1	Steele *et al.* (1997b)
179	EtherO - Epox	88.8752	1	Steele *et al.* (1997a)
205	Teth - Teth	43.9001	1	Steele *et al.* (1993)
Critical Volume				
179	EtherO - Epox	-329.5074	1	Steele *et al.* (1997a)
205	Teth - Teth	-403.1196	1	Steele *et al.* (1993)

In addition, the contributions of the groups (ID = 68 (T_c, P_c, V_c), 76 (T_c, P_c), 78 (T_c, P_c), 82 (T_c, P_c), 83 (T_c, P_c)) are based on data obtained from small molecules. As it was shown throughout his chapter, small molecules that are the first members in their homologous series deviate significantly from the trend in the series. Thus if a contribution is based on the data from only the smallest molecule, great caution must be taken when extrapolating.

Finally, three filters have been developed by differentiating all compounds with respect to the predominant type of intermolecular force.

Table 7-36 presents the results of all models for the different types of intermolecular forces for all critical properties. As expected, the strength of these forces (Table 5-2) is proportional to the average absolute deviation. For the critical volume, the limited number of components resulted in a lower deviation for the hydrogen bonding

---

[*] Denotes group contribution value

[†] Denotes number of components

components as compared to the other interaction types. The proposed method yields an excellent and consistent set of results for all types of interactions and properties as compared to the other methods.

Table 7-36: Critical property deviations for all models for the different types of intermolecular forces.

	Average Absolute Deviations (Number of components in Superscript)										
Interaction Type	**PR**	**JR**	**CG**	**MP**	**AB**	**CT**	**WQ**	**DB**	**LD**	**SJ**	**KR**
Critical Temperature (K)											
Non-Polar	3.1^{81}	5.3^{78}	7.6^{80}	7.8^{78}	2.5^{78}	8.5^{80}	3.6^{78}	16.7^{78}	6.4^{80}	5.5^{81}	5.8^{78}
Dipole-Dipole *	4.1^{380}	6.8^{338}	19.0^{349}	5.2^{255}	6.2^{323}	28.3^{376}	6.3^{304}	21.0^{272}	7.6^{350}	8.4^{347}	7.1^{342}
Hydrogen bond	6.6^{127}	16.5^{127}	18.3^{130}	13.2^{125}	7.6^{127}	23.7^{116}	14.2^{124}	34.7^{125}	21.7^{127}	11.1^{89}	11.1^{127}
Critical Pressure (kPa)											
Non-Polar	57^{83}	97^{80}	90^{80}	134^{80}	64^{78}	-	80^{80}	80^{77}	104^{82}	160^{83}	129^{80}
Dipole-Dipole *	102^{304}	268^{273}	240^{234}	200^{203}	287^{237}	-	200^{243}	296^{179}	232^{283}	338^{280}	255^{273}
Hydrogen bond	128^{99}	302^{99}	399^{98}	288^{96}	328^{97}	-	285^{85}	310^{96}	317^{99}	301^{75}	314^{98}
Critical Volume (%)											
Non-Polar	1.6^{58}	2.8^{57}	3.3^{57}	2.7^{57}	3.0^{57}	-	3.5^{57}	-	3.4^{58}	3.6^{58}	3.1^{57}
Dipole-Dipole *	1.9^{233}	3.9^{206}	6.3^{187}	3.6^{140}	4.1^{131}	-	5.9^{182}	-	6.3^{212}	4.3^{217}	4.1^{205}
Hydrogen bond	1.5^{67}	4.0^{67}	4.7^{63}	3.4^{51}	4.8^{64}	-	3.6^{66}	-	3.8^{67}	4.2^{32}	4.2^{67}

An overall analysis of the proposed method revealed large deviations for smaller components. As discussed throughout this chapter (together with examples), these components are among the first members in their homologous series. It is often the case that first members in a homologues series do not follow the trend of the series. Fortunately, experimental data are mostly available for these simple substances and thus there is no need for group contribution estimation.

Critical compressibility can be calculated using Equation 7-5. For a set of 290 components for which experimental T_c, P_c and V_c were available and Z_c could be calculated, the proposed method yielded a 3.25% average relative error. A histogram of the experimental and estimated critical compressibilities for the above data set is also

---

* Includes Dipole-Induced dipole interaction.

presented in Figure 7-9. These results compare favourably with the results presented in Table 7-33 and shows that the different parameters sets for T_c, P_c and V_c are consistent with each other.

$$Z_c = \frac{P_c V_c}{R T_c} \qquad (R = 8314.5\ \mathrm{kPa.cm^3.K^{-1}.mol^{-1}}) \qquad (7\text{-}5)$$

The methods proposed here should be further extended in the future. The basic parameters for groups present in many compounds (CH_3, CH_2, etc) can be considered final* and only special group contributions need to be revised or added.

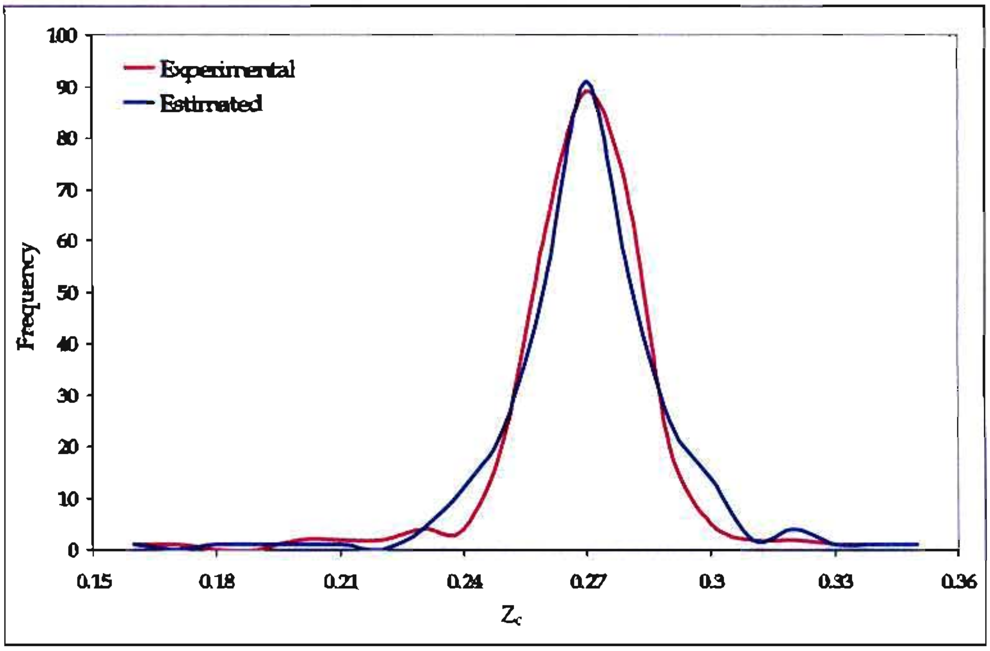


Figure 7-9: Histogram of the experimental (calculated via T_c, P_c and V_c) and estimated Z_c.

---

[*] This is similar as in the case of the Ambrose method, where the basic group increments regressed in 1978 and 1979 are still valid today and give a very good description of data published long after the publication of the method.

Chapter Eight

Estimation of the Liquid Vapour Pressure Curve: Development, Results and Discussion

8.1 Introduction

The correlation and prediction of vapour pressures has long since been a very significant problem in engineering thermodynamics and has been addressed by many researchers. In the beginning, work usually focused on the region between a few kilopascal and the critical pressure, which is required in unit operations such as distillation. Importance of vapour pressure data, in particular for high-boiling organic compounds became more evident over the last several decades with raising awareness of the environmental impact of pollutants.

The description of the temperature dependence of the vapour pressure between reduced temperatures of *0.8* and *1* is not trivial. This dependence is given by the well known Clausius-Clapeyron equation (Equation 3-15). When approaching the critical point, both the change in enthalpy and compressibility of vaporization exhibit a non-linear and strong change with temperature, which even modern volume translated equations of state find difficult to reproduce. One result of this behaviour is that the slope $d\ln P^S/d(1/T)$ shows a point of inflection due to a minimum in $\Delta H^V/\Delta Z^V$.

The correlation and estimation of vapour pressures up to the critical point is commonly achieved with the Wagner or the Riedel model (Section 3.3). Both models require the knowledge of the critical point and reduce the number of coefficients as well as their numeric range by employing physically meaningful constraints. While both models are adequate to correlate experimental vapour pressure data at high pressures, extrapolation into the low pressure range is usually unsatisfactory. Furthermore, the requirements for critical property data drastically reduce the range of applicability of these methods.

To avoid the complex dependence on temperature near the critical point and the limited information that is available for the near-critical temperature range, this work will focus on vapour pressures below the inflection point. Applicable correlations are those that are described in Section 3.3, of which the most popular is the Antoine equation (Equation 3-18).

The experimental determination of vapour pressure is relatively simple in the pressure range between *1* and *200 kPa*, which is sometimes denoted as the moderate pressure region. The majority of published data are in the range of *5* to *100 kPa*. The best experimental accuracy is usually found near the normal boiling point or atmospheric pressure. Measurements become difficult at low pressures ($P^S < 1\ kPa$) and are available only for a limited number of substances. Subsequently, the data is of a lower quality and often subject to large systematic errors. At higher pressures and temperatures, decomposition often limits the quality of experimental data.

The availability of group contribution estimation methods for liquid vapour pressures is rather limited (Section 3.4). Currently, a large amount of experimental data for common industrial components is available together with tabulated correlation parameters from many different sources that include books and databases. Due to the predominant influence of the vapour pressure on the vapour-liquid separation factor, one would also not rely on estimated data for this purpose.

This chapter will present a group contribution method for the estimation of liquid vapour pressures with special attention to the low pressure region. As current group contribution methods are nowhere near the accuracy required for use in engineering or that of correlative methods, this work will only employ the Antoine and DIPPR models for comparison.

8.2 Vapour Pressure Model

The estimation of the vapour-liquid equilibrium curve can be broken down into two parts. The first is the estimation of the normal boiling temperature which has been achieved in the work of Nannoolal (2004) & Nannoolal *et al.* (2004). This method gave an average absolute deviation of 6.52 K for just more than 2800 components. It is also the only method that can predict the boiling point of multi-functional compounds within a fair degree of accuracy. The second part will be presented in this chapter.

The difficulty in going from normal boiling point estimation to vapour pressure curve estimation lies in the fact that the latter property is a temperature dependant property. Most group contribution methods of temperature dependant properties employ simultaneous regressions of correlative parameters (Section 3.4 and 4.4). These types of parameters often show strong intercorrelation. Assumptions of simple linear dependence of these parameters on the number of structural groups are also in most cases not valid.

This work attempts to separate the absolute value (for example, normal boiling point) and the slope of the curve and represent each by only one parameter that can be estimated via group contribution. To achieve this, an analysis of the correlative models that are derived from the Clausius-Clapeyron equation must be undertaken. The goal is to find a two-parameter equation where separate parameters model the absolute value and slope and which at the same time is able to approximate the non-linearity in the $ln(P^S)$ vs. $1/T$ plot by the functional form without a third parameter.

The correlative models present an ideal foundation for the proposed development of group contribution estimation of liquid vapour pressures. Unluckily both the Kirchoff and DIPPR equations (Equations 3-23 and 3-24, respectively) cannot be written in a temperature explicit form. The Antoine equation is mathematically simpler and avoids this complication as well as being able to describe a very similar curvature as in the former two models in a limited temperature range of sufficient size.

The disadvantage of the Antoine equation is that there is a discontinuity at $T = C$. An examination of the value of C from the correlation of vapour pressure data for several hundred components was undertaken. It was found that the value of C can be directly related to the normal boiling point (as first suggested by Thompson (1946)). Hence, a simple correlation was established with the normal boiling point (Equation 8-1).

$$C-273.15\approx-\frac{T_b}{8} \qquad (8\text{-}1)$$

The above relationship is approximately valid for the temperature range from the inflection point to $T=0.5T_b$.

If Equation 8-1 is substituted into Equation 3-18, the number of parameters is reduced to two and the discontinuity is always in the range of $T_{rb}\approx 0.125$. At this reduced boiling temperature, the vapour pressure has very little importance in practical applications.

The vapour pressure model for this work was developed by firstly introducing a fixed vapour pressure point (P^s = 1 atm), which is the normal boiling temperature, and secondly by defining the reduced boiling temperature ($T_{rb}=T/T_b$), dB (Equation 8-2) and an adjustable correction function $f(T_{rb}, T)$. The final model is presented in Equation 8-3.

$$dB=B-4.1012 \qquad (8\text{-}2)$$

$$\log\left(\frac{P^S}{1atm}\right)=(4.1012+dB)\left(\frac{T_{rb}-1}{T_{rb}-\frac{1}{8}}\right)+f(T_{rb},T) \qquad (8\text{-}3)$$

Equation 8-3 is a vapour pressure equation that now has only two parameters. The constant 4.1012 was derived as a mean value from the correlation of vapour pressure data for several hundred components. In this form, the equation can also be applied approximately when using $dB=0$. Interestingly, dB is usually in the range [-0.5, 2.0] and close to zero for non-polar components. The value of dB can be estimated using a group contribution method that will be presented in this chapter.

The introduction of the normal boiling point has an advantage as it is a fixed point on the vapour pressure saturation curve. At the same time, a vast amount of experimental information is available for this auxiliary property. If there is no knowledge of the normal boiling point, the property can be estimated by the group contribution method of the previous work Nannoolal (2004) & Nannoolal *et al.* (2004). However, a safer option is, if there is experimental information for the vapour pressure at other temperatures, to calculate the normal boiling point from Equation 8-3. This calculation and subsequent estimation serves as a test set and will be presented later on.

The correction function $f(T_{rb}, T)$ can be introduced to allow the equation to be more suitable for data correlation. For example, higher order terms that are a function of temperature (as in the Wagner and Riedel equations) can be introduced to estimate vapour pressures close to the critical point. This is however not of interest in this work. Also, an additional term can be added to correlate solid vapour pressures (Chapter 11).

8.3 Software Platform for the Development of the Vapour Pressure Estimation Method

Prior to the proposed estimation method presented in this work and by Nannoolal (2004) & Nannoolal *et al.* (2004), the development of group contribution methods most often dealt with scalar properties (not temperature dependant). The reason for this is that for the development of estimation methods for non-scalar properties, more sophisticated data handling and analysis tools are required. When dealing with these properties, the amount of data is usually significantly higher. To be able to cope with these problems, a great deal of time and thought has been put into developing the technology employed in this work (some of which has already been presented in Chapter 6). The procedure used to develop the estimation method for *dB* values proceeded as follows:

- A *dB* value (approximately the slope of $ln(P^S)$ *vs.* $1/T$) can be calculated for each experimental data point using a predefined experimental normal boiling temperature from Equation 8-3. Close to the normal boiling point, *dB* values diverge due to experimental errors in the data point that affect the calculated slope over the small temperature difference. This was typically observed in the range of $T_b \pm 10$ K (sometimes this region was slightly larger but this was later detected during an analysis for each component). As two close data points carry only little information about the slope, these values were discarded. An alternative approach would have been to calculate slopes between any two data points more than a certain temperature apart. This idea was discarded after some tests as it was obvious that normal boiling points allowed additional verification of the data quality as they were extensively verified during the development of two previous estimation methods.

- Only data in the range from 10 K above the melting point to $1.2^* T_b$ were used. For components where there was no melting point information, a reasonable lower temperature limit was chosen.

- In order to avoid the need to process all experimental data in the group contribution regression, a mean *dB* value was regressed for each component. In the first step, this was limited to components for which there were more than 10 data points available. At a later step this criterion was removed in order to include components with fewer data points as well as single data points from the Beilstein data bank into the regression for groups where there were a few or no components.

- In the next step a group contribution method was developed to estimate *dB* based on the mean *dB* values. As in case of the previous methods, the behaviour in homologous series was carefully analysed. In this case, a simple linear relationship between the sum of the group contributions and the calculated *dB* values was sufficient (see Section 8.8).

- For further analysis of the regression results, calculated vapour pressure values were generated for each experimental data point using the experimental normal boiling point and estimated *dB*.

In order to obtain mean deviations for judging the quality of the regression, neither the absolute nor the relative deviation proved useful. The reason is that low pressure data usually contain a large relative and low absolute error while the opposite is true at high pressures.

Using reasonable estimates of experimental errors in temperature and pressure, a maximum likelihood approach would lead to a more meaningful error representation. In this case the error for each data point is normalised with respect to the probable error. Unluckily this procedure is strongly influenced by the error estimates. As an alternative, it proved to be useful to convert pressure errors into temperature errors using the estimated slope of the vapour pressure curve. Differentiating Equation 8-2 with respect to temperature (Equation 8-3) leads to:

$$\frac{dP^S}{dT} = 10^{(4.1012+dB)\left(\frac{T-T_b}{T-\frac{1}{8T_b}}\right)}\left[\frac{(4.1012+dB)}{(T-\frac{1}{8T_b})} - (4.1012+dB).\frac{(T-T_b)}{(T-\frac{1}{8T_b})^2}\right]\ln(10) \qquad (8\text{-}3)$$

Using Equations 8-4 and 8-5, the pressure deviation can now be converted into the corresponding temperature deviation.

$$\Delta P^s = P_{\exp} - P_{est} \qquad (8\text{-}4)$$

$$\Delta T = \frac{\Delta P^s}{\frac{dP^s}{dT}} \qquad (8\text{-}5)$$

For further analysis, separate average boiling temperature and relative pressure errors were calculated for two low pressure regions (< 0.001 kPa and 0.001 to 10 kPa), one moderate pressure region (10 to 500 kPa) and one high pressure (> 500 kPa) region. Separate deviations for these regions are also reported in the final results to assist the user in judging the quality of the method.

In addition, a graphical approach (using the Multiple Plot program described in Section 6.7) was employed for the final analysis.

After data verification and removal of questionable data, the entire procedure was repeated.

8.4 Data Verification

The verification of vapour pressure data was performed using similar criteria as presented in Section 7.2 for critical properties.

In the case of vapour pressures (or any other temperature dependant property), a graphical output is required to verify data. The multiple plot program presented previously has the disadvantage that individual points cannot be indexed. This means that a direct link from the data point in the diagram to the source of the numerical value is not available.

An alternate approach was implemented by designating an Excel worksheet for each component and inserting all data, deviations and plots into this worksheet. As an Excel workbook (document file) can only store up to 256 worksheets, several excel files were created to store the data for all components. A separate Excel file was used to store the VBA code for the creation and modification of the other files and to re-import the revised data and *dB* values into the central database. In order to be able to quickly access the worksheet for a specific component, a hyperlink to the sheet was stored in the database. A typical worksheet is shown in Figure 8-1.

When analysing the data and regression results, a phenomenon long known to experimental scientists and very clearly described by the famous physicist Feynman (1989) was observed:

"You see, it depended on one or two points at the very edge of the range of the data, and there's a principle that a point on the edge of the range of the data--the last point-- isn't very good, because if it was, they'd have another point further along."

As the measurement of vapour pressure usually employ different experimental setups for the different pressure regions, it is not unusual that the end points are close to or out of the optimum range of the equipment. It was therefore required to be able to identify the end points of individual data sets in the plots. In very few cases like in case of ethyl-tertbutyl-ether, one author obviously measured not only one but several data points far outside the range of the equipment.

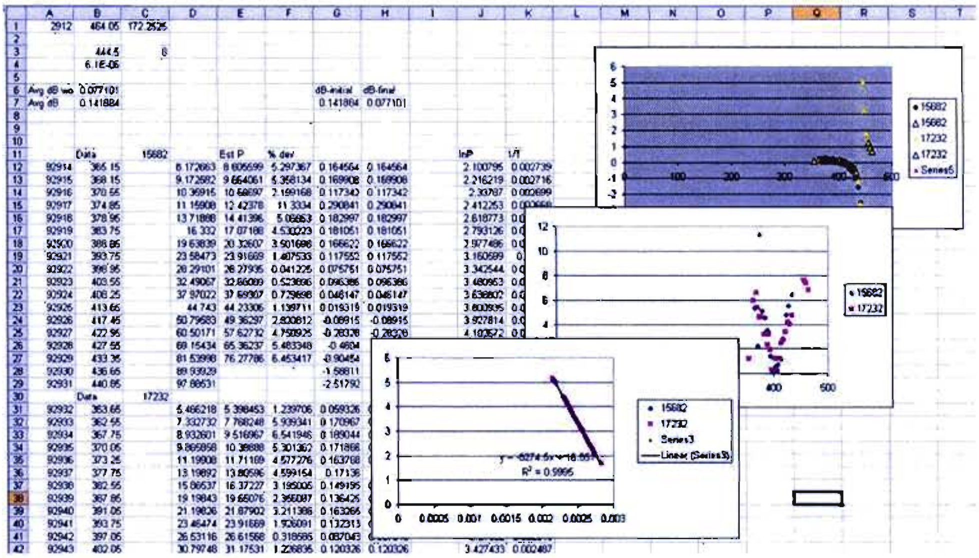


Figure 8-1: Screen shot of the MS-Excel worksheet employed for data verification.

8.5 Results and Discussion

8.5.1 Hydrocarbon Compounds

The strategy for the development of a group contribution estimation method for vapour pressures and further properties is similar to the strategy employed and described previously in the case of critical properties. At this point, little is known about the new parameter *dB*. Apart from the assumption that it should be related to the enthalpy of vaporisation of a component, it had to be verified whether or not the previous group definitions would be sufficient. Thus, as before, group contribution regression started with hydrocarbons and was slowly extended to further groups. The results are presented here in the same order.

As there is no comparable group contribution method for the estimation of vapour pressures, the proposed method will be compared to popular correlations such as:

- the Antoine equation with parameters regressed by DDBST GmbH (DDB (2006)).
- the DIPPR 101 equation with parameters regressed within the DIPPR 801 project (DIPPR (1992)).

In order to be able to judge the quality of the group contribution parameter regression, relative mean absolute deviations in pressure and average absolute deviations in boiling temperature are reported for the four different pressure ranges defined previously. In addition, the normal boiling point is included in the results.

The presentation of the results will focus on the different classes of compounds and more general observations will be summarised in the final section.

For the vapour pressure group contribution method, the group definition, description, identification number (ID), priority (PR) and examples, for first-order groups and second-order corrections can be found in Tables B-1 and B-2 in Appendix B, respectively. The groups are similar to those employed for critical properties. The group, correction and interaction contributions are presented in Tables C-10, C-11 and C-12 in Appendix C, respectively. For the proposed method, a detailed procedure is provided for the calculation of vapour pressure for one component in Table D-4 in Appendix D.

The development of the proposed group contribution model for the estimation of vapour pressures started with the regression of n-alkanes. In the first regression, data were verified to allow model development to start from a 'clean' set of data. Subsequent regressions produced an excellent representation of the dB parameter by a group contribution method.

A series plot for the vapour pressure estimation in case of n-alkanes is presented in Figure 8-2. For all compounds, the estimations from this work show an excellent representation of the temperature dependence. The only exceptions are the last three compounds which represent the highest molecular weight compounds in the data set. As the proposed model adequately reproduces the data for all other components, this source should be considered questionable. Data for these compounds, dotriacontane, tetratriacontane and hexatriacontane were all obtained from the same reference, Piacente *et al.* (1994).

A multiple plot for twelve cyclic alkane compounds is presented in Figure 8-3. The multiple plot is employed in this case as the components do not form a simple "linear" series as in case of n-alkanes. All data are adequately represented except for cis-1,3,5-trimethylcyclohexane. In this case, low pressure data were taken from a rather old reference (Dyke *et al.* (1959)), and might be of questionable quality. The slope of these data in the $ln\ (P)$ vs. $1/T$ plot matches the slope of the estimated curve, which could either be explained by an offset in the data or an error in the normal boiling point. As the estimation of the slope parameter dB is usually of high reliability, regression of T_b with fixed estimated dB should lead to a more reliable value of T_b than regressing both. This procedure should be used for a future extension of the normal boiling point estimation method to components where only low pressure data are available (this will be proposed in Chapter 11).

A multiple plot of twelve alkene and aromatic compounds is presented in Figures 8-4 and 8-6, respectively. A series plot of alkynes is presented in Figure 8-5. For a few components, deviations can be observed between the proposed method and experimental data at high pressures, for example in the case of naphthalene in Figure 8-6. This is usually the case above the inflection point and outside the range of the proposed method.

A detailed analysis of the results for the different types of hydrocarbons for the proposed method and the correlative models is presented in Tables 8-1 and 8-2, respectively. The proposed method yields a consistent and accurate set of results for the different classes of hydrocarbons for the different pressure ranges. The results of the proposed method compare well to the correlative models (direct correlation of experimental data).

For the DIPPR model, the lowest deviation is usually observed as five parameters are employed in the correlation. This includes a logarithmic and higher order term that will allow a more accurate fit but may lead to less reliable extrapolation outside the range of data.

Although the results of the Antoine and DIPPR models should not be compared to the proposed work, the advantage of employing this comparison is that the deviations reported for the correlative models give an indication about the scatter ("noise") of the data. Thus the difference between the deviations of estimation and correlation present a more "true" measure of the quality of the estimation.

Table 8-1: Vapour Pressure average absolute deviations of this work for the different types of hydrocarbons (number of data points as superscript).

		Average Absolute Deviation (%)					**Average Absolute Deviation (K)**				
	NC[*]	**ELP**	**LP**	**MP**	**HP**	**AV**	**ELP**	**LP**	**MP**	**HP**	**AV**
Hydrocarbons (HC)	424	29.1^{356}	6.7^{6550}	1.9^{11662}	4.1^{3637}	4.0^{21207}	2.7^{358}	1.2^{6550}	0.6^{11238}	2.2^{3637}	1.1^{20763}
Saturated HC	131	23.1^{113}	6.6^{2107}	1.9^{5347}	4.7^{2289}	3.8^{9856}	2.5^{113}	1.2^{2107}	0.5^{5216}	2.4^{2289}	1.1^{9725}
Non-aromatic HC	319	28.7^{150}	6.9^{2891}	2.0^{7669}	4.5^{2697}	3.8^{13407}	3.0^{150}	1.2^{2891}	0.6^{7350}	2.3^{2697}	1.1^{13088}
Unsaturated HC	188	45.8^{37}	7.5^{784}	2.2^{2322}	3.3^{408}	4.0^{3551}	4.4^{37}	1.3^{784}	0.7^{2134}	1.6^{408}	1.0^{3363}
n-Alkanes	26	24.5^{67}	7.9^{1136}	2.3^{2216}	5.6^{1289}	5.0^{4708}	2.7^{67}	1.5^{1136}	0.6^{2180}	2.7^{1259}	1.4^{4682}
Alkanes (non-cyclic)	73	24.3^{94}	7.4^{1546}	2.2^{3624}	5.0^{2030}	4.4^{7193}	2.6^{94}	1.3^{1545}	0.6^{3461}	2.5^{2030}	1.3^{7120}
Alkanes (cyclic)	58	17.6^{19}	4.6^{562}	1.4^{1623}	2.4^{259}	2.3^{2663}	1.7^{19}	0.8^{562}	0.4^{1765}	1.7^{259}	0.6^{2605}
Aromatic HC	105	29.4^{208}	6.6^{2659}	1.8^{3993}	3.0^{940}	4.3^{7800}	2.6^{208}	1.2^{2659}	0.6^{3838}	2.2^{940}	1.1^{7696}
Fused aromatic HC	31	33.9^{68}	6.1^{666}	1.9^{866}	3.8^{76}	4.9^{1677}	2.8^{68}	1.3^{666}	0.8^{837}	3.2^{75}	1.2^{1646}
Alkenes HC	139	45.8^{37}	7.9^{565}	2.1^{1606}	2.8^{372}	4.0^{2780}	4.4^{37}	1.4^{565}	0.7^{1667}	1.2^{372}	0.9^{2641}
Alkenes (cyclic HC)	39	22.4^{2}	8.9^{265}	2.4^{573}	2.4^{21}	4.5^{861}	1.8^{2}	1.6^{265}	0.8^{534}	1.8^{21}	1.1^{822}
Alkynes HC	32	-	6.2^{108}	2.5^{333}	9.5^{33}	3.8^{474}	-	0.9^{108}	0.7^{301}	6.1^{33}	1.1^{442}

---

[*] All abbreviations throughout this chapter will follow these definitions (will not be repeated again): NC - Number of components, ELP - P < 0.01 kPa, LP - 0.01 kPa >= P =< 10 kPa, MP - 10 kPa < P =< 500 kPa, HP - P > 500 kPa.

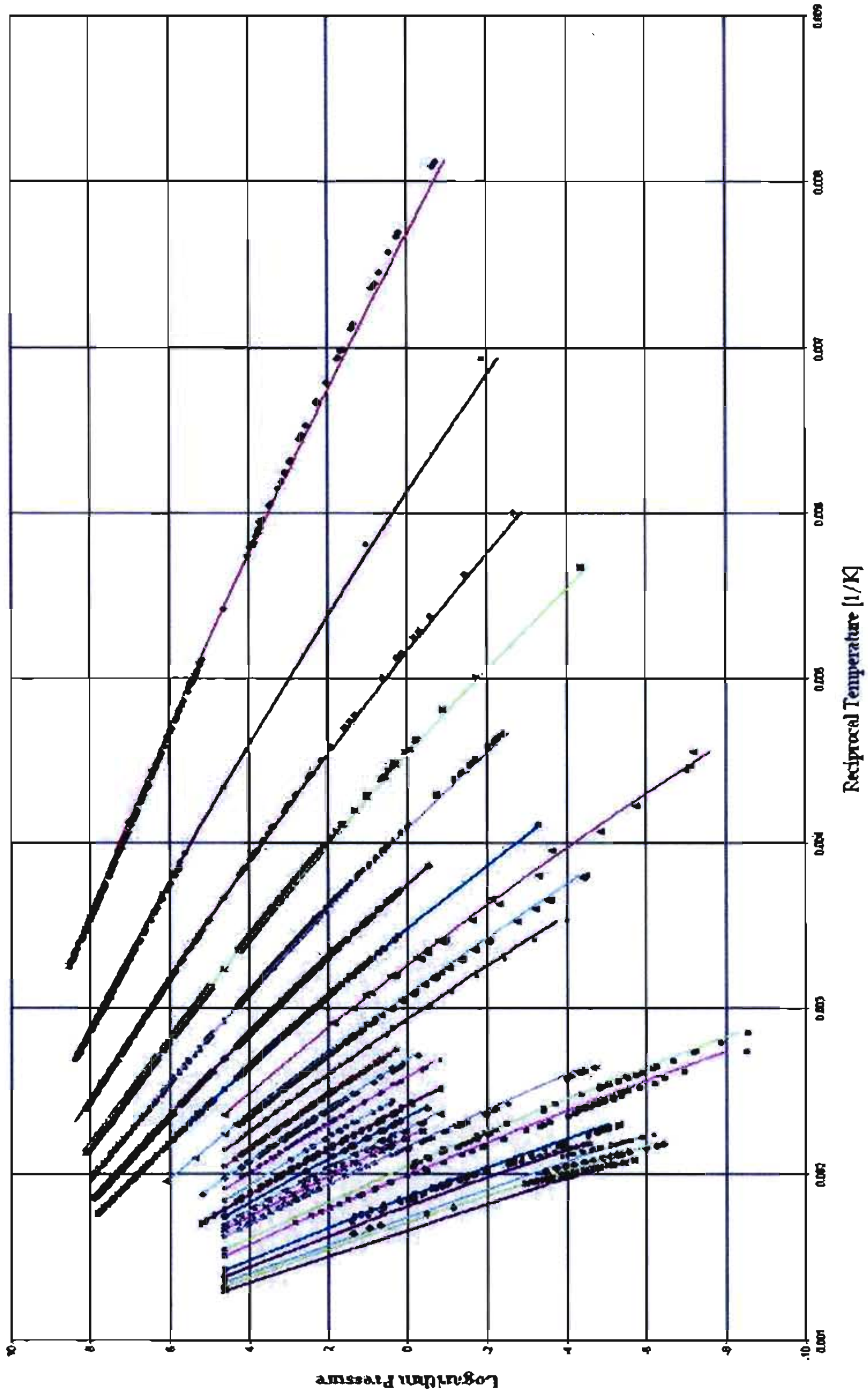


Figure 8-2: Series plot experimental and estimated liquid vapour pressures for n-alkanes.

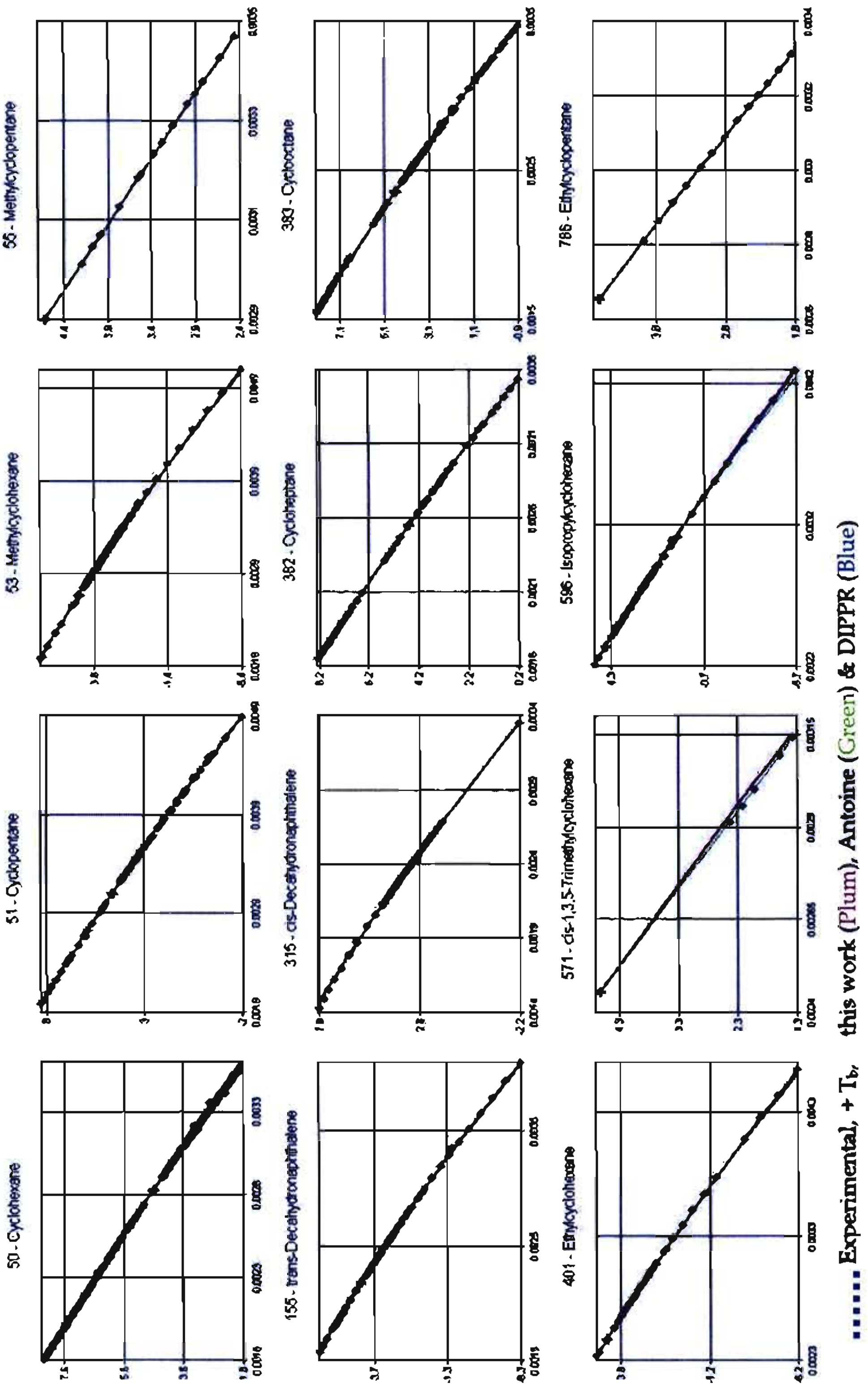


Figure 8-3: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for cyclic alkanes.

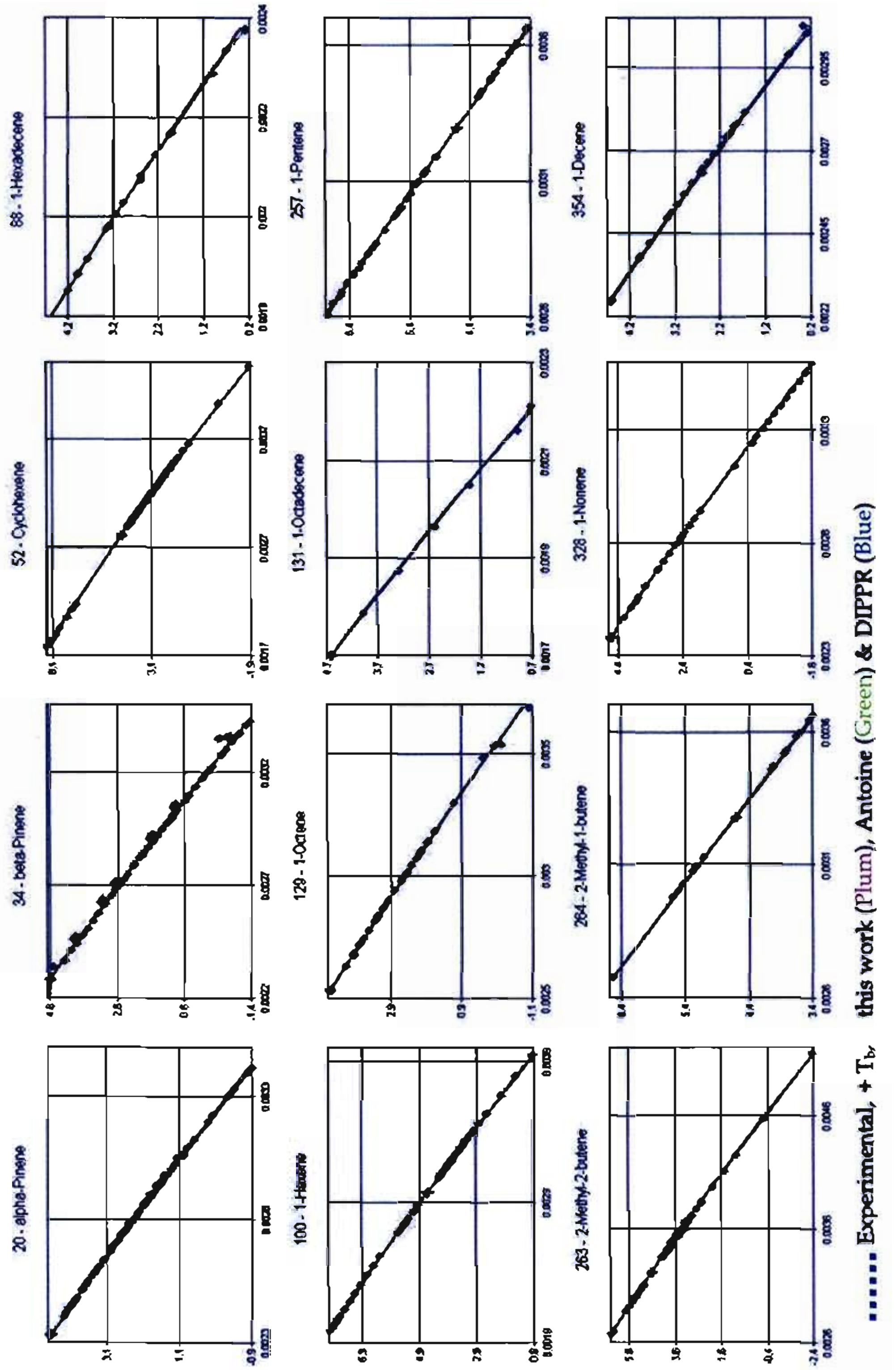


Figure 8-4: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for alkenes

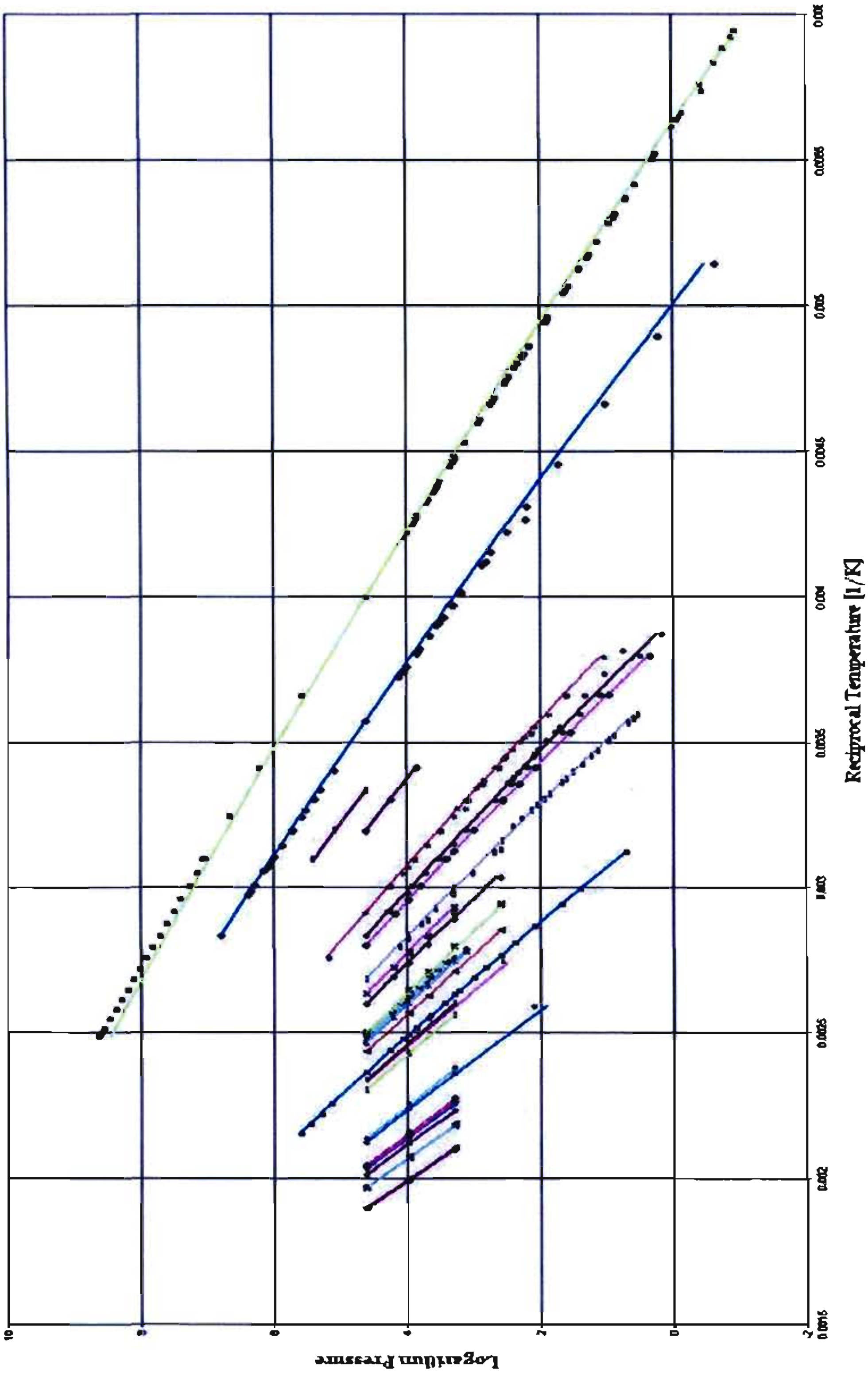


Figure 8-5: Series plot of experimental and estimated liquid vapour pressures for alkynes.

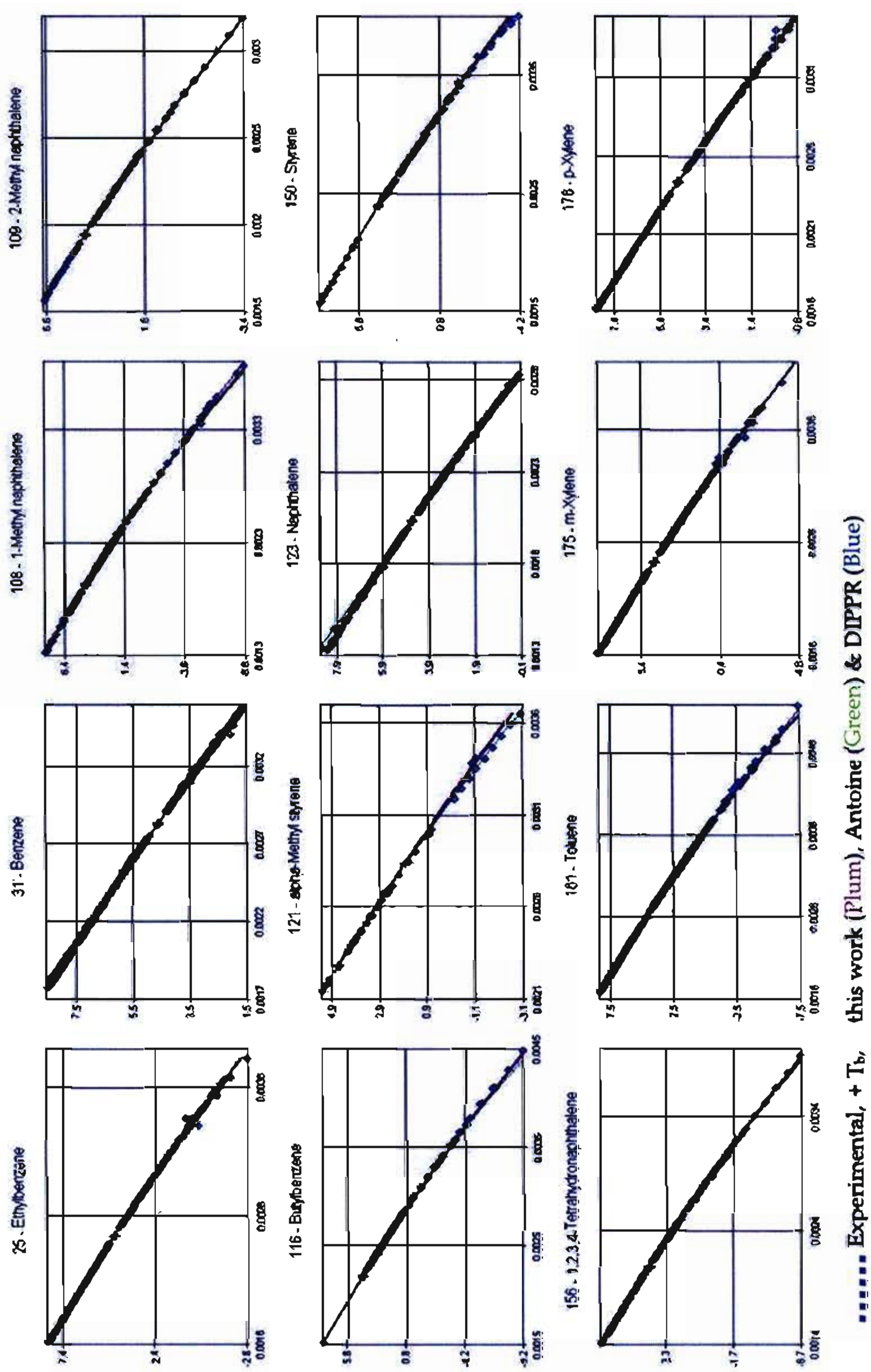


Figure 8-6: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for aromatic compounds.

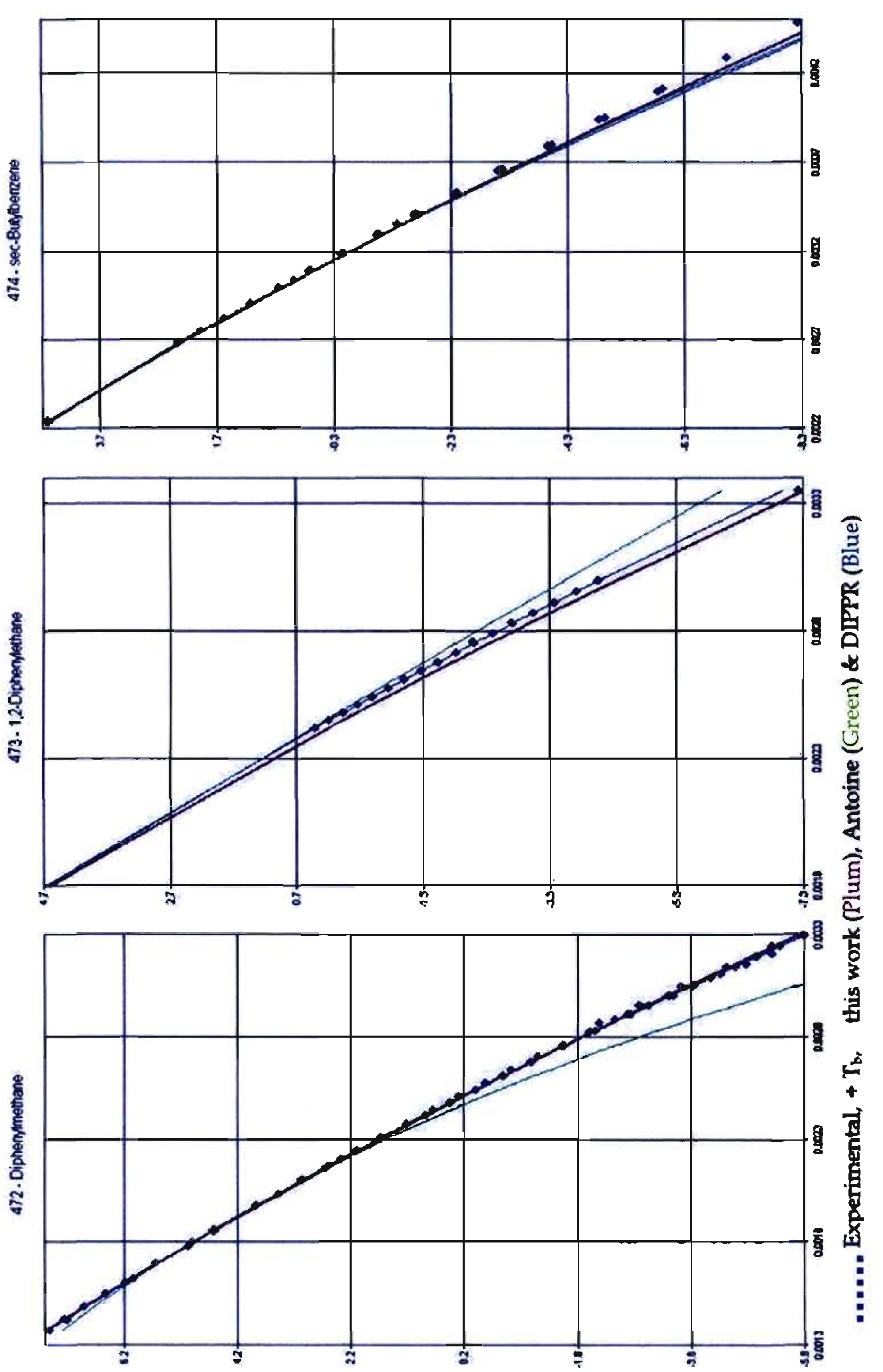


Figure 8-7: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for aromatic compounds.

Table 8-2: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for the different types of hydrocarbons (number of data points as superscript).

	Average Absolute Deviation (%)											
	Antoine						**DIPPR**					
	NC	**ELP**	**LP**	**MP**	**HP**	**AV**	**NC**	**ELP**	**LP**	**MP**	**HP**	**AV**
Hydrocarbons (HC)	415	40.3^{356}	5.9^{6512}	1.0^{11644}	3.7^{3636}	3.4^{21147}	255	19.9^{279}	3.6^{4795}	1.0^{10424}	1.0^{3637}	1.9^{19135}
Saturated HC	131	53.3^{113}	5.5^{2107}	0.6^{6347}	2.7^{2259}	2.7^{9656}	96	19.4^{62}	2.6^{1684}	0.7^{5032}	0.9^{2259}	1.3^{9287}
Non-aromatic HC	315	47.8^{150}	6.6^{2870}	0.6^{7663}	2.7^{2697}	2.7^{13386}	188	20.7^{119}	3.6^{2506}	1.0^{6862}	0.9^{2697}	1.7^{11984}
Unsaturated HC	184	31.0^{37}	5.9^{763}	1.4^{2318}	2.4^{408}	2.8^{3524}	92	23.7^{37}	6.7^{822}	1.7^{1630}	1.0^{408}	3.0^{2697}
n-Alkanes	26	64.8^{87}	7.0^{1136}	0.5^{2216}	2.6^{1269}	3.8^{4708}	23	22.7^{58}	3.0^{1075}	0.6^{2219}	0.8^{1269}	1.5^{4618}
Alkanes (non-cyclic)	73	61.7^{94}	6.7^{1545}	0.6^{3524}	2.7^{2030}	3.3^{7193}	63	22.7^{65}	2.6^{1434}	0.6^{3486}	0.8^{2030}	1.3^{7014}
Alkanes (cyclic)	58	11.8^{19}	2.0^{582}	0.5^{1823}	3.1^{259}	1.1^{2683}	33	6.7^{17}	2.6^{450}	1.0^{1547}	1.9^{259}	1.5^{2273}
Aromatic HC	100	34.8^{205}	6.2^{2642}	1.2^{3981}	6.5^{939}	4.5^{7767}	67	19.3^{160}	3.6^{2289}	0.9^{3782}	1.1^{940}	2.2^{7161}
Fused aromatic HC	31	31.3^{64}	10.4^{686}	2.4^{686}	18.9^{75}	7.5^{1677}	15	10.3^{34}	3.4^{415}	1.8^{785}	3.4^{75}	2.5^{1299}
Alkenes HC	136	31.0^{37}	6.8^{558}	1.4^{1803}	2.3^{372}	3.0^{2768}	70	23.7^{37}	7.6^{429}	1.8^{1269}	1.0^{372}	3.2^{2101}
Alkenes (cyclic HC)	38	47.5^{2}	9.0^{263}	2.0^{672}	4.3^{21}	4.3^{958}	13	77.6^{2}	12.4^{161}	3.4^{297}	2.1^{21}	6.5^{471}
Alkynes HC	32	-	5.7^{108}	1.4^{333}	3.9^{33}	2.6^{474}	9	-	7.7^{103}	1.8^{206}	0.5^{33}	3.4^{342}

Tables 8-3 and 8-4 present results for all components where steric corrections were used to account for cumulated branching and isomeric effects for the proposed method and the correlative models, respectively. According to Equation 5-1, the steric correction corrects the additional strain added to the change in enthalpy of vaporisation.

Table 8-3: Vapour Pressure average absolute deviations of this work for branched hydrocarbons (number of data points as superscript).

		Average Absolute Deviation (%)					Average Absolute Deviation (K)				
	NC	ELP	LP	MP	HP	AV	ELP	LP	MP	HP	AV
(C,C=)C-CC_3	9	16.6^{9}	7.7^{73}	1.7^{81}	-	5.2^{163}	1.8^{9}	1.3^{73}	0.6^{72}	-	1.0^{154}
C_2C-CC_2	47	18.4^{6}	6.5^{313}	1.7^{764}	2.7^{112}	3.2^{1165}	1.9^{6}	1.2^{313}	0.5^{707}	1.8^{112}	0.9^{1138}
C_3C-CC_2	20	-	5.4^{205}	3.0^{301}	1.5^{38}	3.8^{544}	-	1.1^{205}	1.0^{261}	1.1^{38}	1.1^{524}
C_3C-CC_3	4	-	6.4^{14}	2.7^{39}	-	3.7^{53}	-	1.6^{14}	0.9^{35}	-	1.1^{49}

Table 8-4: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for branched hydrocarbons (number of data points as superscript).

	Average Absolute Deviation (%)											
	Antoine						DIPPR					
	NC	ELP	LP	MP	HP	AV	NC	ELP	LP	MP	HP	AV
(C,C=)C-CC_3	9	42.3^{9}	8.3^{73}	0.8^{81}	-	8.4^{163}	5	14.8^{4}	3.7^{38}	0.4^{42}	-	2.6^{80}
C_2C-CC_2	47	6.8^{6}	7.6^{313}	1.3^{754}	2.7^{112}	3.1^{1185}	17	9.3^{6}	3.6^{149}	1.4^{422}	1.7^{107}	2.0^{684}
C_3C-CC_2	20	-	3.2^{205}	2.2^{301}	3.0^{38}	2.7^{544}	8	-	4.0^{115}	2.5^{192}	0.7^{39}	2.8^{346}
C_3C-CC_3	4	-	5.2^{14}	3.3^{39}	-	3.8^{53}	1	-	0.2^{2}	0.0^{12}	-	0.1^{14}

8.5.2 Mono-functional Compounds

8.5.2.1 Oxygen Compounds

For mono-functional alcohol compounds, a distinct deviation was observed at low pressures between the proposed method and experimental data. For this reason a correction was derived, Equation 8-6, which is only applicable to mono-functional alcohol compounds (i.e. a hydrocarbon compound with only one alcohol group). The pressure deviations for all these compounds with and without the correction are plotted in Figure 8-8. All parameters were fixed in Equation 8-6 to account for the trend depicted in Figure 8-8 for the deviations without the correction. The only exception was the parameter *a*, which was optimised by minimising the sum of squared errors.

$$f(T)=a\left[\frac{2}{1+\exp\left[\left(\frac{201}{T-91}\right)^{7}\right]}-1\right] \tag{8-6}$$

Where: $a = 0.37704$

The development of the correction was solely based on the error obtained from the proposed method. In theory, strong associating compounds that exhibit hydrogen bonding could dimerise even at low pressures. The change in slope and subsequent deviation for these types of compounds could be a result of dimerisation. However, this type of behaviour was not observed for other strongly associating compounds such as alkane diols and carboxylic acids. The correction was not applicable or did not improve the estimations for these compounds. The correction was therefore only applied to mono-functional alcohols.

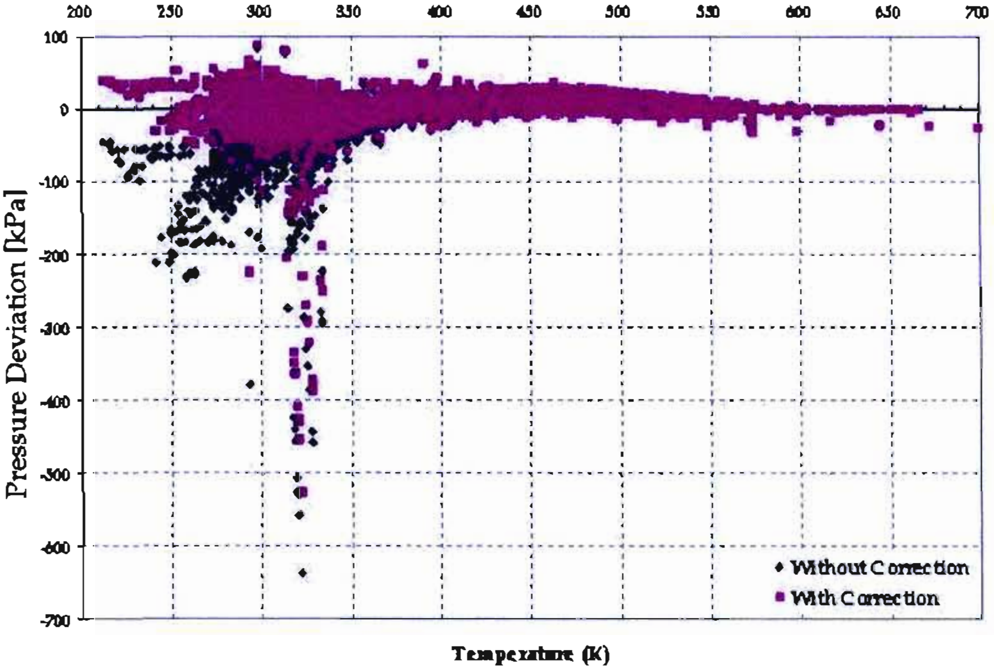


Figure 8-8: Pressure deviation for mono-functional alcohols.

The inclusion of the correction improved the vapour pressure estimation for data at low pressures. However, it did have a drawback as to alter the estimations at moderate pressures. This drawback meant that the estimation especially in the case of the smaller molecules vapour pressures at the normal boiling point was not exactly atmospheric pressure. For most cases the estimation at this point is acceptable, however, for smaller molecules (compounds with five carbons or less) there is an observable deviation. For example, ethanol and tert-butanol had estimated the vapour pressures at the normal boiling point of 94.4 and 95.2 kPa, respectively. These were the worst case estimations. Adjustment of the fixed parameters in Equation 8-6 worsened the estimation at low pressures. Thus, this minor disadvantage of using this correction was accepted for the overall improvement of the method.

Multiple plots of ten 1-alcohol, twelve secondary alcohol, tertiary alcohol, aromatic alcohol and alkane diol and triol compounds are presented in Figures 8-10 to 8-13, respectively. From all plots, it is evident that the experimental data is rather more scattered than for the case of hydrocarbon compounds. It is the usual problem with strongly associating compounds that the quality of experimental data is poor, especially in the low pressure region where systematic errors are more common.

Overall, the proposed method yields a good agreement with experimental data as well as with the correlative models. The inclusion of the correction function also improves the estimation in the low pressure region, where a large amount of data is available for alcohol compounds.

In several cases, data from different sources are in disagreement. For example, for 3-methyl-3-pentanol in Figure 8-11, two sets of data, Hovorka *et al.* (1940) and Kulikov *et al.* (2001), with two different slopes are available with the latter reference containing the lower pressure data. The correlative parameters are based on the earlier reference, which is outdated and questionable. However, the proposed method employs many chemically similar compounds and predicts a slope similar to the latter reference.

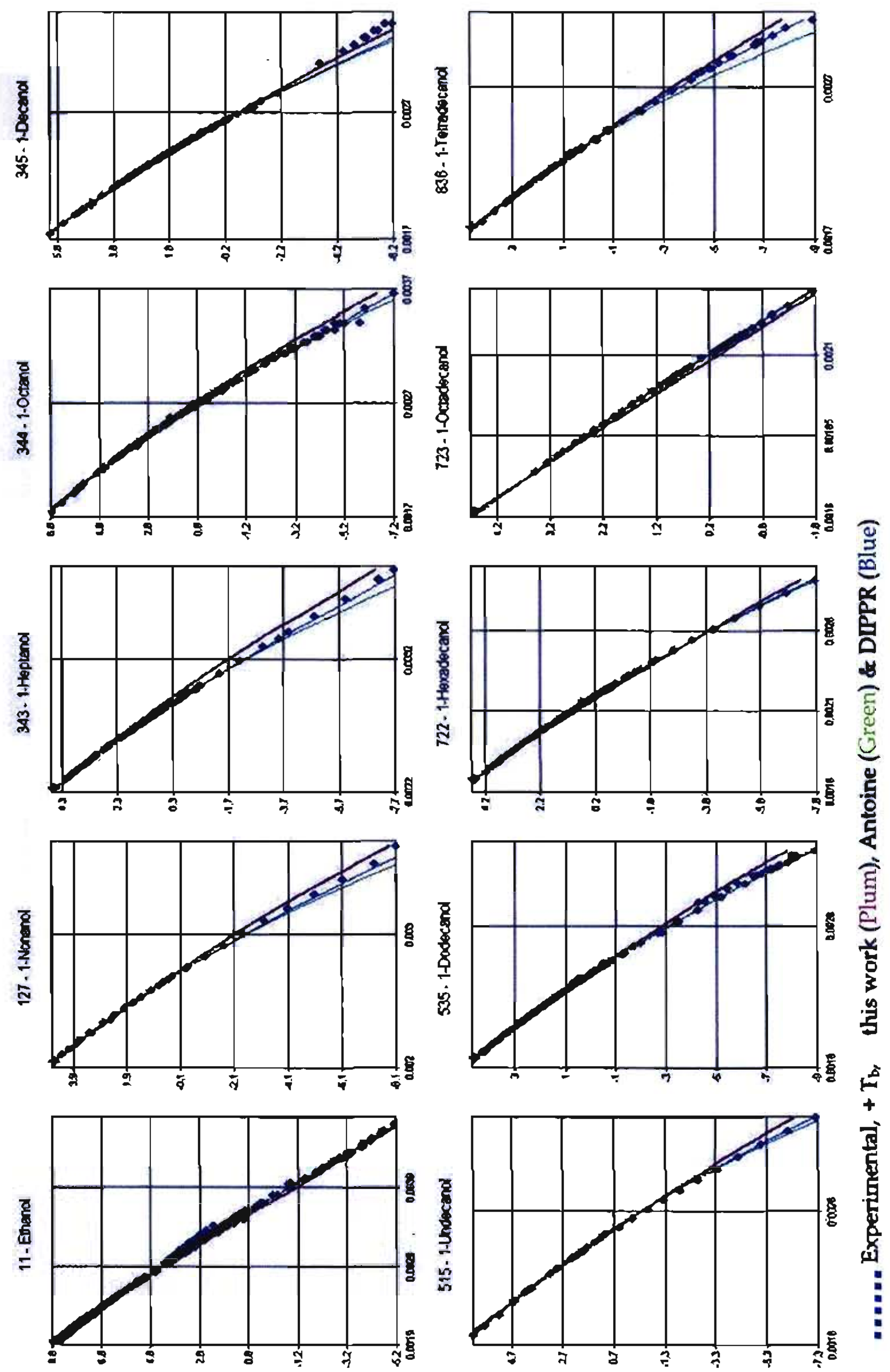


Figure 8-9: Multiple plot (Ln(P) vs. 1/T K^{-1}) of experimental and estimated liquid vapour pressures for 1-alcohols.

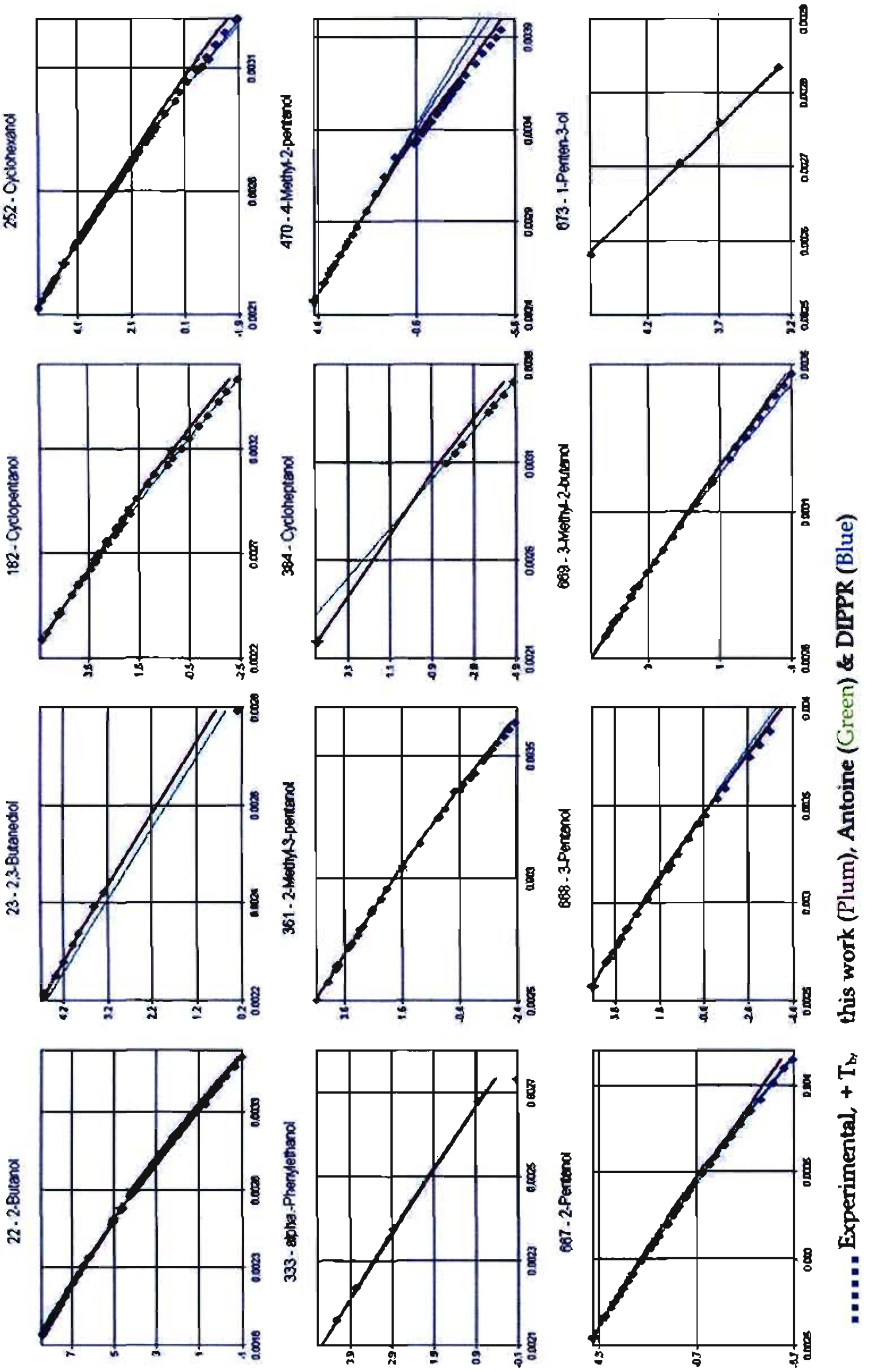


Figure 8-10: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for secondary alcohols.

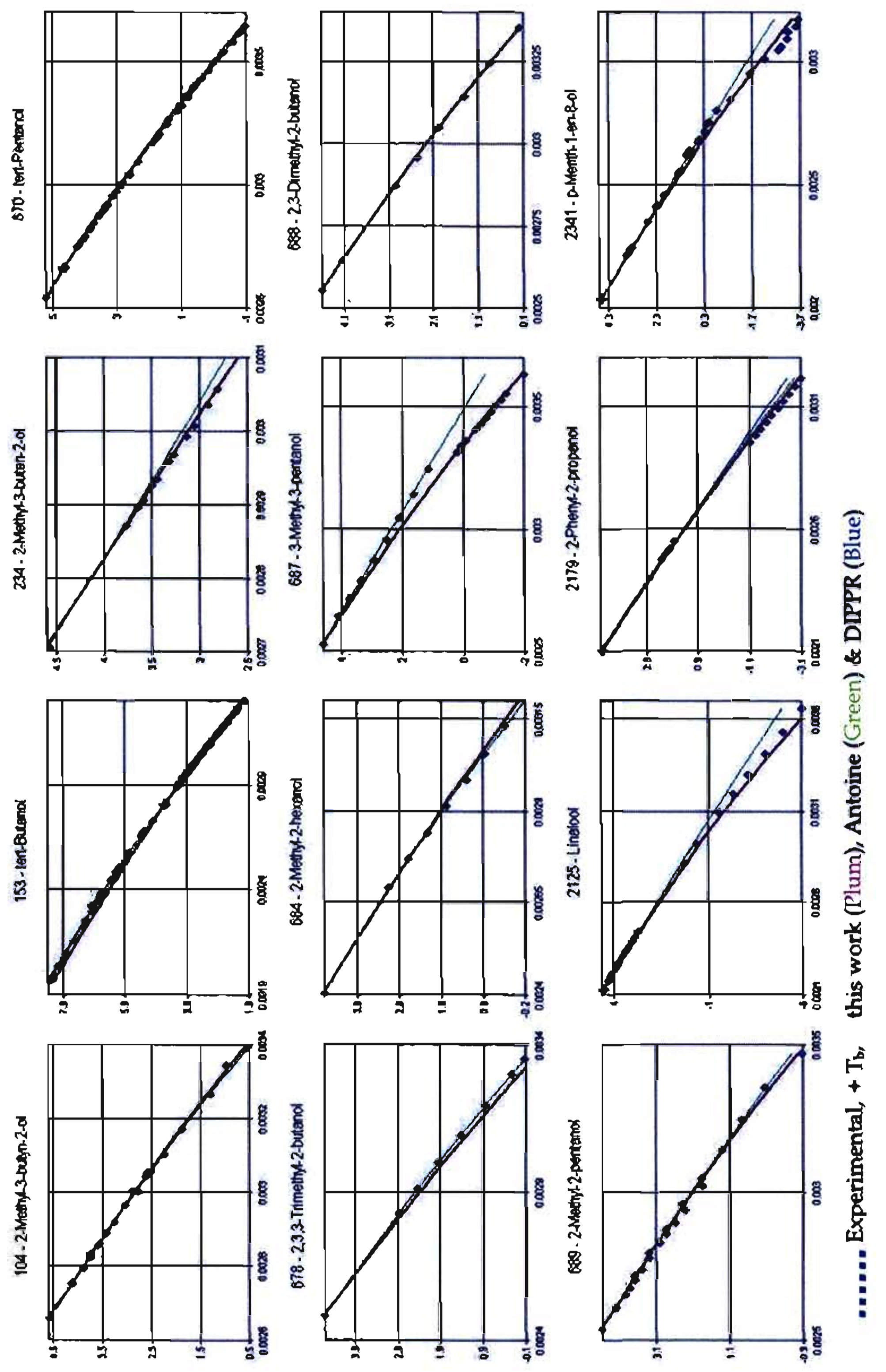


Figure 8-11: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for tertiary alcohols.

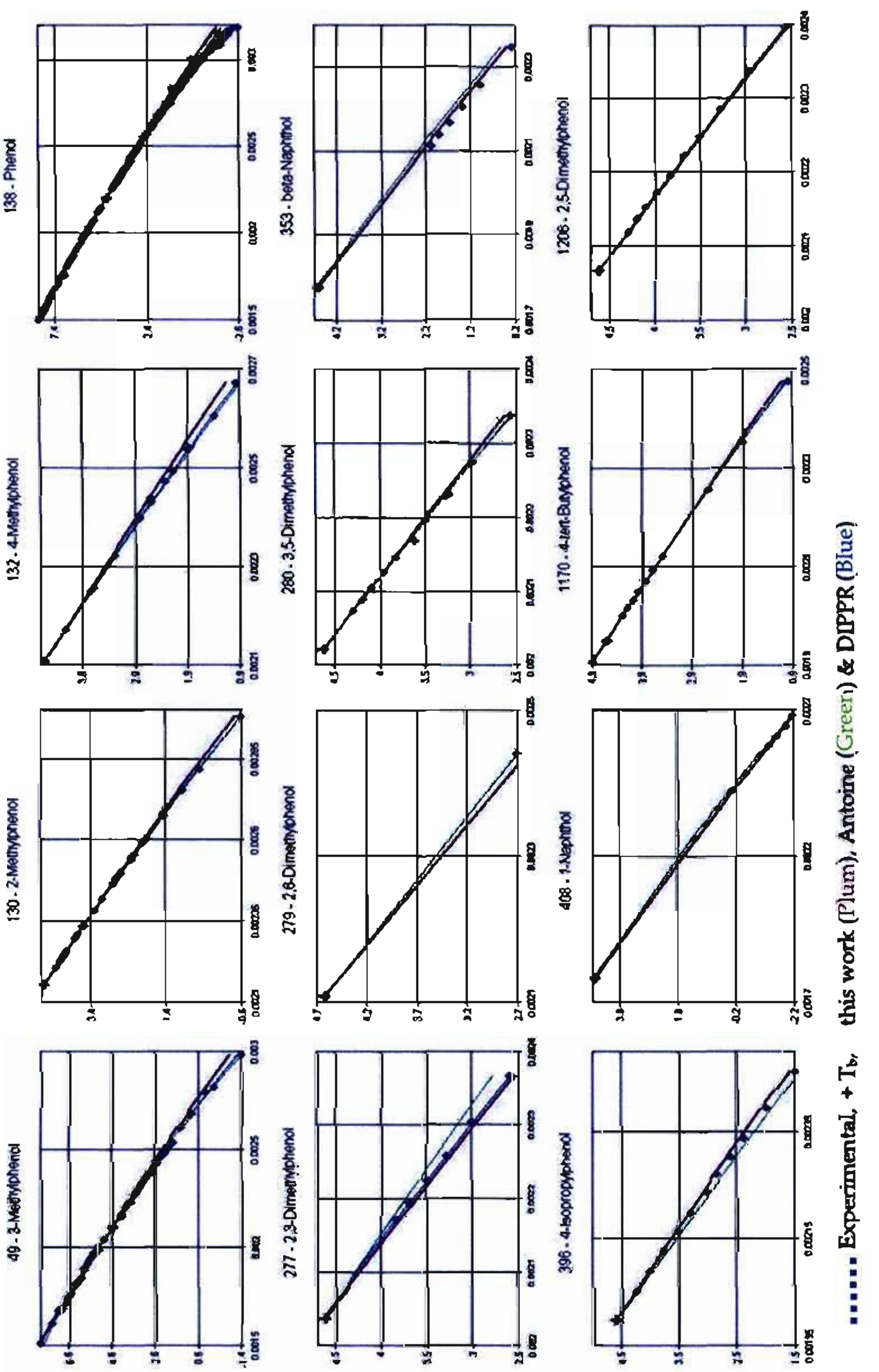


Figure 8-12: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for aromatic alcohols.

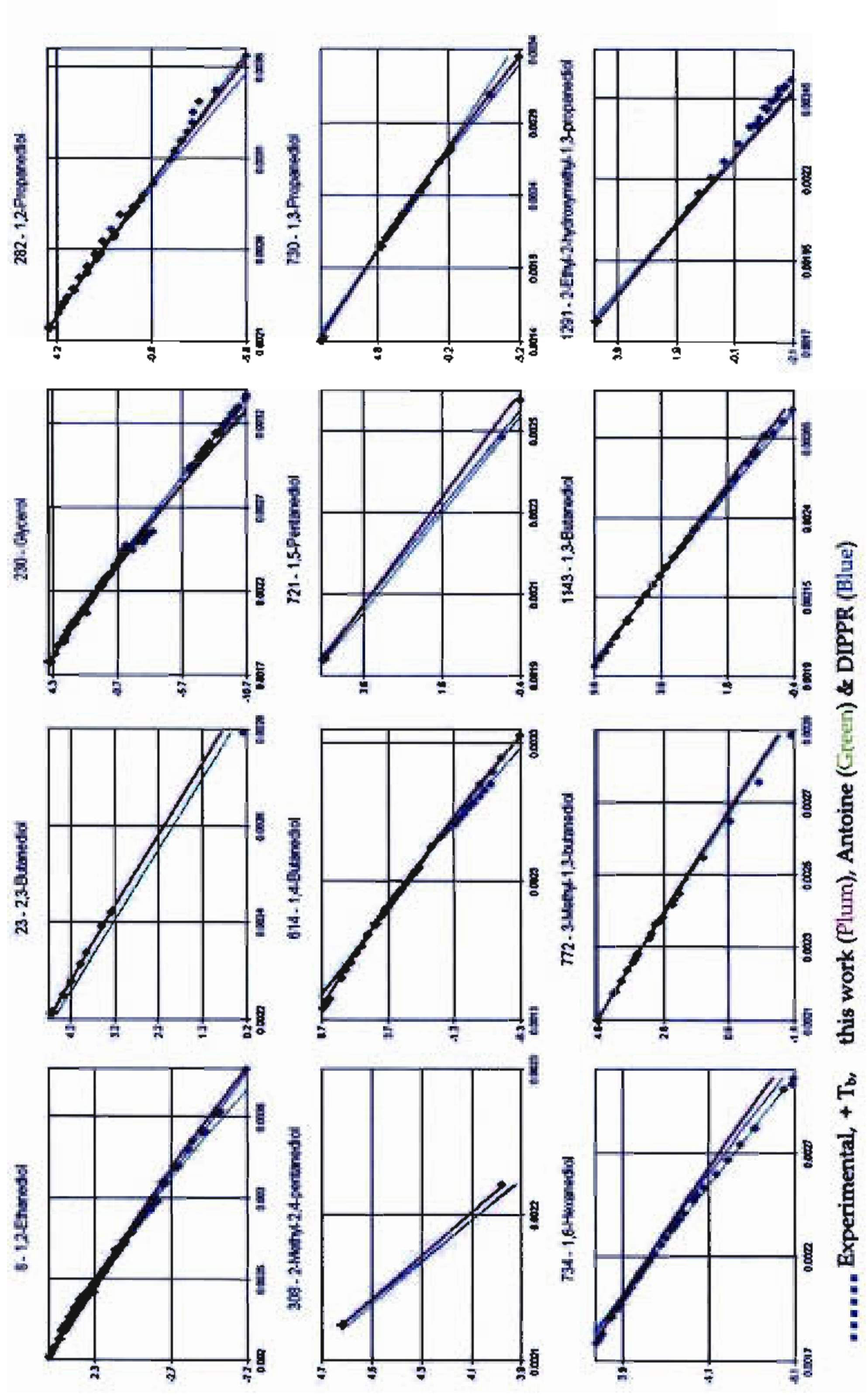


Figure 8-13: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for alkane diols and triols.

Detailed results for the different types of alcohol compounds for the proposed method and both the correlative models are presented in Tables 8-5 and 8-6, respectively. Large deviations were observed for the low pressure region (< 0.01 kPa), in many cases caused by unreliable data.

Table 8-5: Vapour Pressure average absolute deviations of this work for the different types of alcohol compounds (number of data points as superscript).

		Average Absolute Deviation (%)					**Average Absolute Deviation (K)**				
	NC	**ELP**	**LP**	**MP**	**HP**	**AV**	**ELP**	**LP**	**MP**	**HP**	**AV**
1-Alcohols	11	82.8^{98}	16.6^{764}	5.4^{629}	22.7^{136}	15.5^{1627}	4.6^{98}	2.6^{764}	1.6^{618}	15.5^{136}	3.2^{1616}
Alcohols '	177	55.2^{260}	19.1^{3002}	5.5^{3934}	16.5^{444}	13.3^{7640}	4.1^{260}	2.8^{3002}	1.6^{3657}	9.5^{444}	2.8^{7363}
Primary alcohols	31	71.0^{122}	18.1^{1275}	5.6^{1554}	19.0^{177}	14.0^{3128}	4.0^{122}	2.5^{1275}	1.5^{1523}	12.9^{177}	2.7^{3097}
Secondary alcohols	30	50.9^{13}	19.4^{398}	3.8^{488}	6.0^{26}	11.2^{925}	3.2^{13}	2.3^{398}	0.9^{458}	3.3^{26}	1.6^{896}
Tertiary alcohols	20	33.5^{2}	12.7^{153}	4.1^{321}	13.8^{18}	7.2^{494}	4.6^{2}	2.4^{153}	1.1^{301}	7.8^{18}	1.8^{474}
Aromatic alcohols	20	31.9^{13}	34.4^{264}	3.5^{340}	2.2^{48}	16.7^{665}	2.5^{13}	4.2^{264}	1.1^{320}	1.4^{48}	2.4^{645}
Alkane Diols, Triols	14	55.2^{61}	24.9^{265}	6.3^{261}	13.8^{34}	19.5^{621}	5.9^{61}	4.1^{265}	2.1^{247}	8.4^{34}	3.7^{607}

Table 8-6: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for the different types of alcohol compounds (number of data points as superscript)

	Average Absolute Deviation (%)											
	Antoine						**DIPPR**					
	NC	**ELP**	**LP**	**MP**	**HP**	**AV**	**NC**	**ELP**	**LP**	**MP**	**HP**	**AV**
1-Alcohols	11	39.0^{98}	4.7^{764}	1.6^{829}	8.2^{136}	5.4^{1827}	11	22.3^{98}	4.0^{764}	1.4^{629}	1.5^{136}	3.7^{1627}
Alcohols '	171	47.9^{259}	10.7^{2971}	3.8^{3823}	18.1^{444}	8.9^{7497}	88	25.4^{216}	9.6^{2495}	3.2^{3044}	8.6^{323}	6.9^{6078}
Primary alcohols	31	37.7^{122}	6.0^{1275}	2.2^{1554}	17.1^{177}	6.0^{3128}	21	25.3^{117}	5.4^{1228}	1.5^{1497}	1.3^{177}	4.0^{3019}
Secondary alcohols	30	129.2^{13}	19.2^{398}	2.2^{488}	13.2^{26}	11.6^{925}	10	93.1^{8}	12.6^{246}	1.8^{377}	0.8^{26}	6.7^{657}
Tertiary alcohols	20	161.6^{2}	25.2^{153}	2.0^{321}	5.5^{18}	9.9^{494}	4	-	15.8^{80}	5.9^{161}	3.2^{18}	8.0^{259}
Aromatic alcohols	20	44.7^{13}	9.0^{264}	1.7^{340}	6.3^{48}	5.8^{665}	12	-	13.4^{237}	1.4^{285}	1.8^{48}	6.5^{570}
Alkane Diols, Triols	14	44.1^{61}	14.2^{265}	7.8^{261}	77.3^{34}	17.9^{621}	11	15.3^{61}	15.9^{250}	8.3^{208}	68.2^{31}	15.9^{550}

' Includes multi-functional compounds

A detailed analysis of the results for the different types of oxygenated compounds (except alcohols) for the proposed method and the both correlative models are presented in Tables 8-7 and 8-8, respectively. A multiple plot of twelve ether and ester compounds is presented in Figures 8-14 and 8-15. The estimations from this work are in excellent agreement with the experimental data in both plots. The plots for the other types of oxygenated compounds listed in Table 8-7 are also in similar agreement, but will not be presented here.

For carboxylic acids, a larger average absolute percentage deviation was observed, especially for the low pressure data. A multiple plot of twelve carboxylic acids is presented in Figure 8-16. From the plot, it is evident that the larger deviations are the result of the conflicting experimental data of different authors, especially in the cases of butyric, pentanoic and hexanoic acids. For these components, the departure of experimental data from the general trend (encircled in Figure 8-16) is the result of an outdated reference, Kahlbaum (1894). A correction was temporarily introduced as was employed in the case of mono-functional alcohol compounds, but the correction had produced no improvement as the majority of data did not show this type of behaviour. Thus, it can be concluded that the inclusion of the outdated reference resulted in the higher deviations observed for carboxylic acids and, in future, should be removed from the training set. Apart from this data, the proposed method is in excellent agreement with the experimental data.

For lactone compounds, an inconsistency in the experimental data resulted in the higher deviations listed, which is also presented for the correlative models. For aromatic oxygenated compounds, the higher deviations listed for the correlative models were from the poor extrapolation to low pressure data.

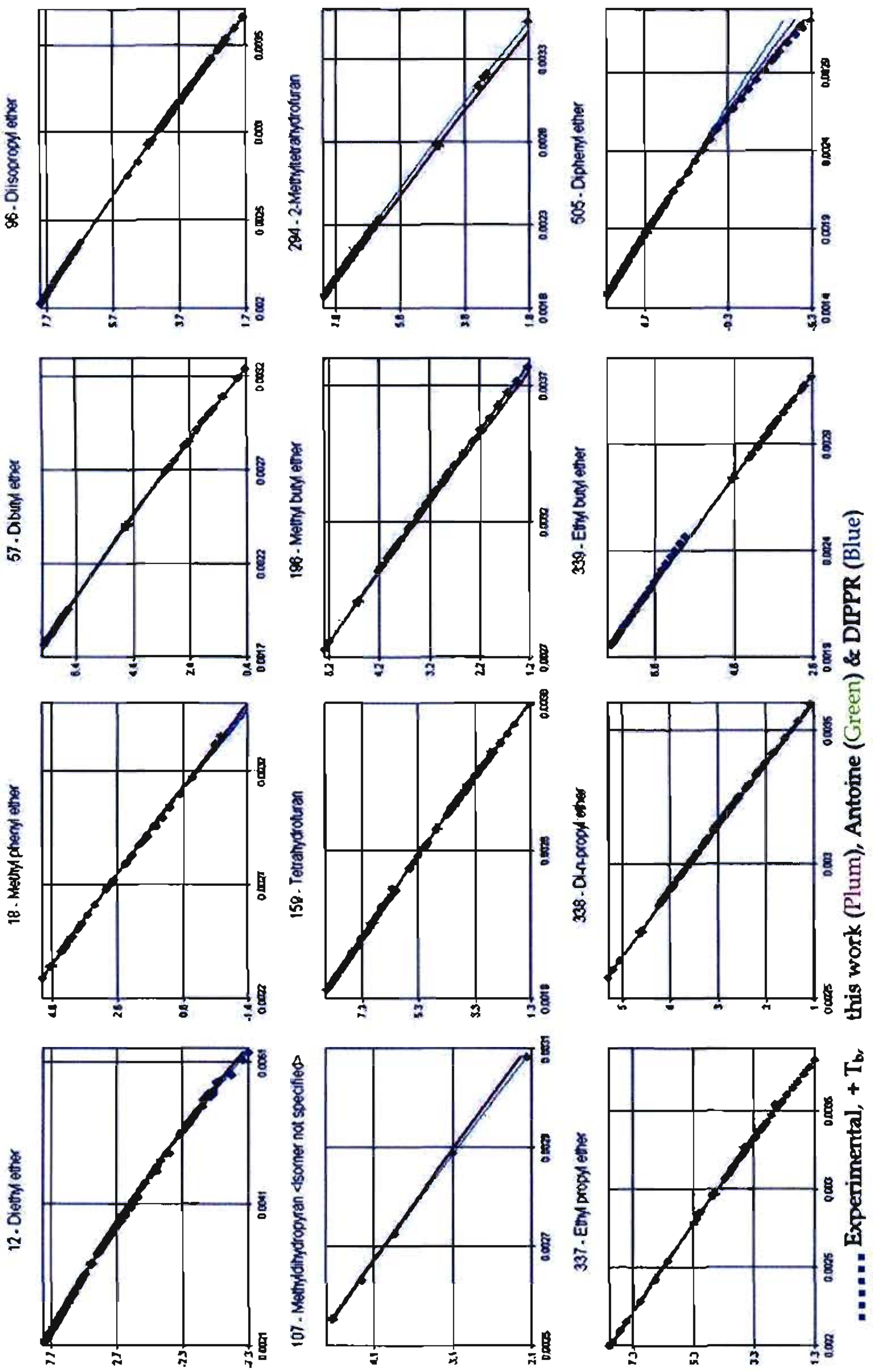


Figure 8-14: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for ethers.

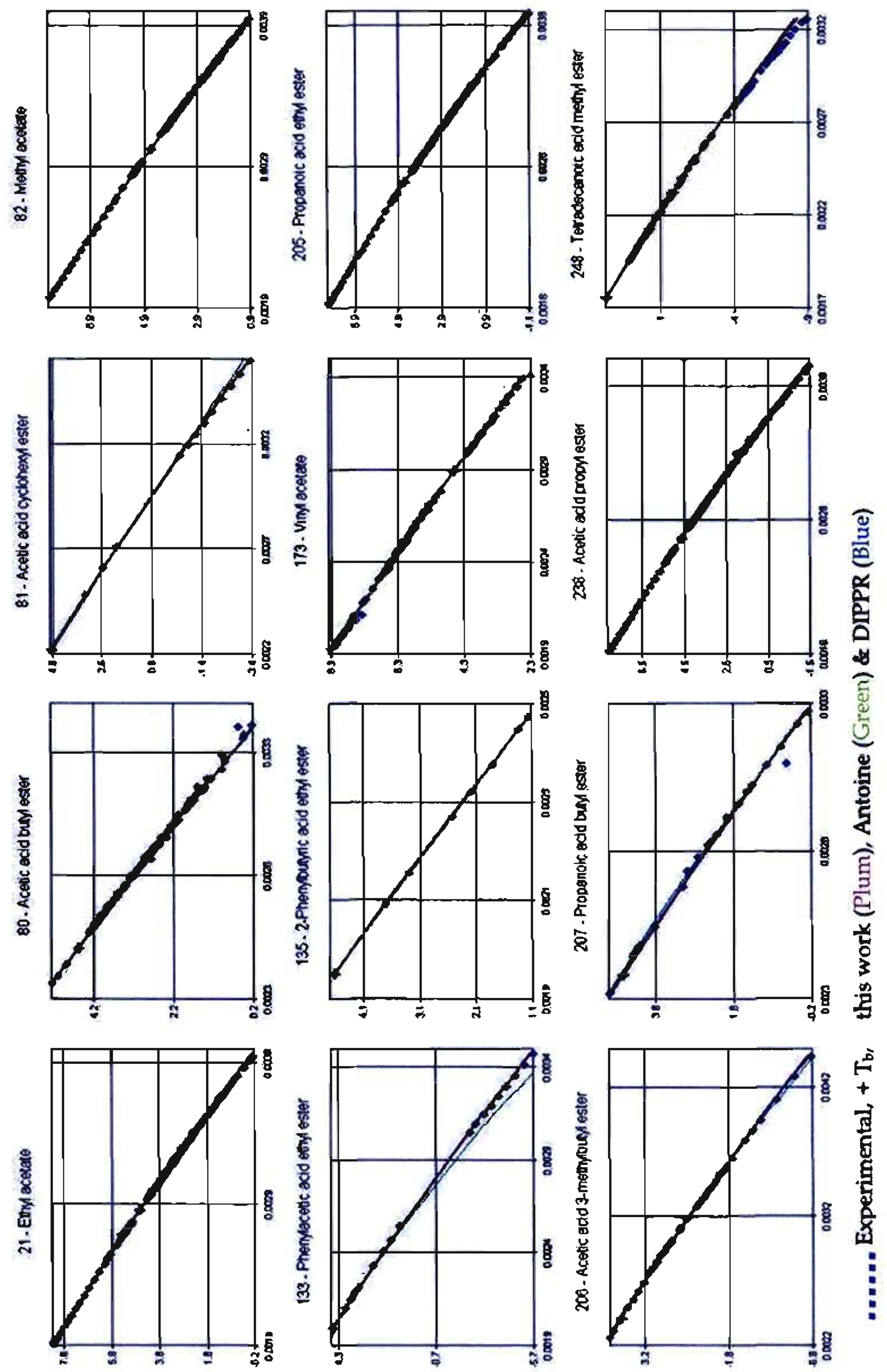


Figure 8-15: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for esters.

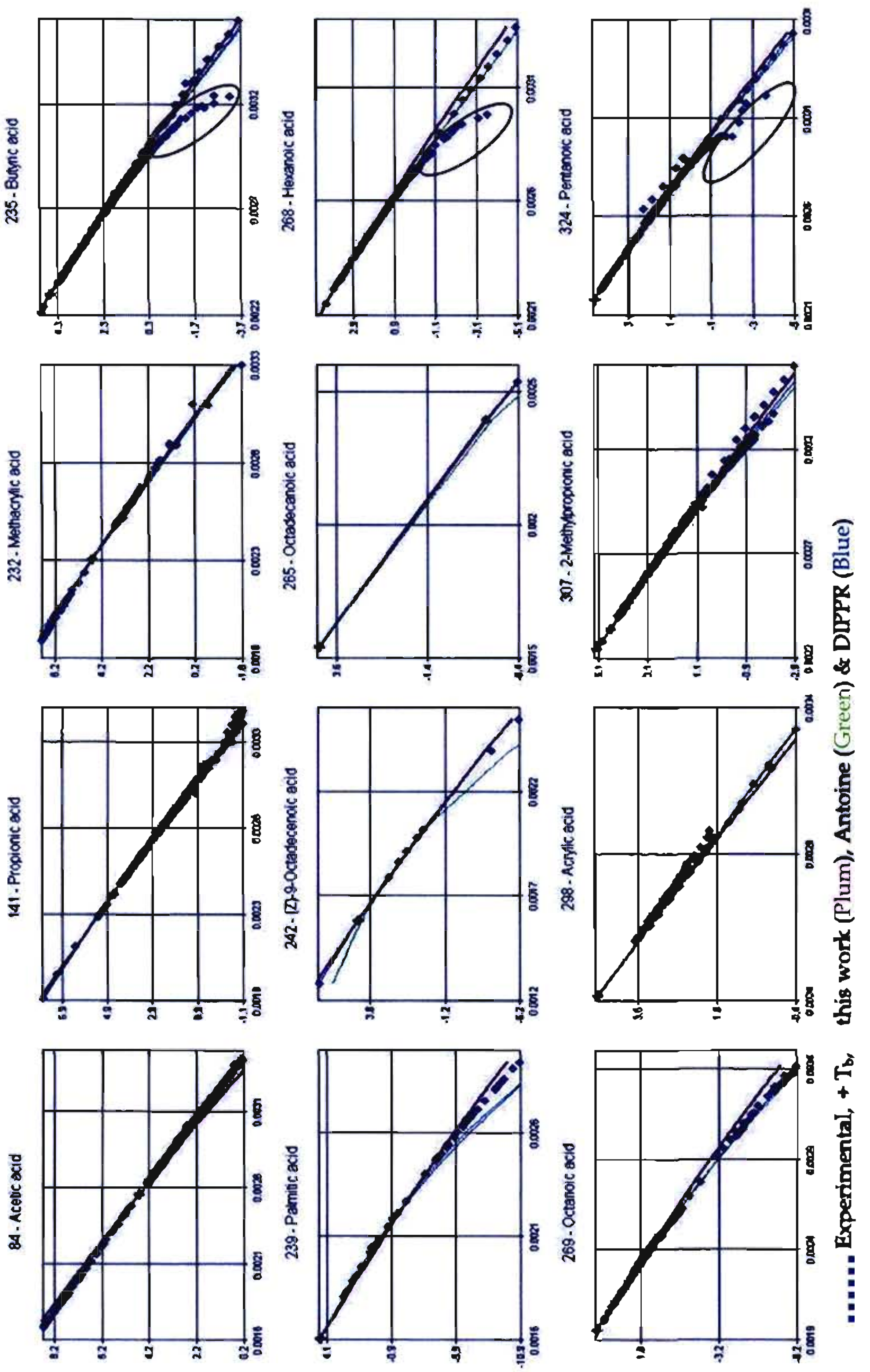


Figure 8-16: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for carboxylic acids.

Table 8-7: Vapour Pressure average absolute deviations of this work for the different types of oxygen (except alcohol) compounds (number of data points as superscript).

	Average Absolute Deviation (%)						Average Absolute Deviation (K)				
	NC	ELP	LP	MP	HP	AV	ELP	LP	MP	HP	AV
Ethers	47	29.5^{16}	6.4^{317}	2.0^{1648}	4.0^{446}	3.1^{2427}	1.9^{16}	1.0^{317}	0.6^{1601}	2.3^{446}	1.0^{2380}
Epoxides	8	-	9.3^{23}	2.6^{171}	2.1^{37}	3.2^{231}	-	1.5^{23}	0.7^{163}	1.3^{37}	0.9^{223}
Aldehydes	22	20.9^{4}	10.9^{292}	2.6^{403}	5.2^{20}	6.2^{719}	1.9^{4}	1.8^{292}	0.8^{381}	2.4^{20}	1.3^{687}
Ketones	50	43.8^{37}	8.8^{620}	2.2^{1463}	5.9^{263}	5.0^{2383}	3.1^{37}	1.4^{620}	0.7^{1413}	3.9^{263}	1.3^{2333}
Non-cyclic carbonates	4	33.4^{1}	12.8^{144}	2.1^{249}	14.0^{10}	6.3^{404}	5.6^{1}	2.9^{144}	0.7^{245}	11.5^{10}	1.7^{400}
Carboxylic acids	27	85.9^{97}	18.1^{1602}	6.3^{839}	24.0^{145}	16.9^{2963}	4.8^{97}	3.1^{1602}	1.8^{912}	10.8^{145}	3.1^{2858}
Esters	78	23.2^{50}	9.6^{1209}	2.5^{2134}	6.0^{287}	5.4^{3680}	1.9^{50}	1.6^{1209}	0.8^{2058}	3.5^{287}	1.3^{3582}
Formic acids esters	12	-	4.6^{81}	1.6^{418}	3.4^{61}	2.2^{560}	-	0.9^{81}	0.4^{408}	1.9^{51}	0.7^{538}
Lactones	2	-	13.5^{47}	8.5^{44}	16.8^{1}	11.2^{92}	-	2.7^{47}	3.6^{42}	11.0^{1}	3.2^{90}
Anhydride chains	3	-	9.8^{28}	2.9^{34}	-	6.0^{62}	-	1.7^{28}	0.9^{31}	-	1.3^{59}
Anhydride cyclic	2	-	3.4^{35}	4.0^{7}	-	3.5^{42}	-	0.6^{35}	2.1^{5}	-	0.8^{40}
Aromatic oxygen	4	8.7^{1}	7.5^{67}	4.3^{70}	4.9^{49}	6.6^{187}	1.0^{1}	2.0^{67}	1.8^{66}	3.3^{49}	2.3^{163}
All (w/o alcohols) *	457	42.3^{353}	12.3^{6130}	3.2^{9612}	7.0^{1920}	7.6^{18015}	3.0^{353}	2.2^{6130}	1.0^{9155}	3.7^{1920}	1.7^{17558}

8.5.2.2 Nitrogen Compounds

A detailed analysis of the results for the different types of nitrogen compounds for the proposed method and both the correlative models are presented in Tables 8-9 and 8-10, respectively. For amine compounds, a slightly higher deviation is observed which can be attributed to the larger scatter in the experimental data. Some of the results for amine components are shown in a multiple plot, Figure 8-17.

A series plot of tertiary amines is presented in Figure 8-18. For tributylamine, N,N-dimethylaniline and N,N-diethylaniline (encircled), a large scatter in the data can be observed. In this case, there were many contradictory results from different authors that will not be listed here in detail.

---

* Includes multi-functional compounds

Multiple plots are employed for the presentation of nine nitrous or nitrite and twelve cyanide compounds in Figures 8-19 and 8-20, respectively. Considering the complex nature of these compounds, the proposed method shows an excellent agreement with experimental data.

Table 8-8: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for the different types of oxygen (except alcohol) compounds (number of data points as superscript).

	Average Absolute Deviation (%)											
	Antoine						DIPPR					
	NC	ELP	LP	MP	HP	AV	NC	ELP	LP	MP	HP	AV
Ethers	45	63.9^{16}	9.7^{316}	0.9^{1637}	5.6^{448}	3.3^{2409}	27	42.5^{10}	7.4^{230}	1.1^{1432}	1.6^{426}	2.1^{2098}
Epoxides	7	-	7.1^{23}	1.4^{169}	4.0^{37}	2.4^{229}	3	-	11.8^{13}	1.7^{112}	2.5^{35}	2.7^{160}
Aldehydes	22	37.6^{4}	15.2^{292}	1.9^{403}	6.2^{20}	7.6^{719}	15	41.6^{4}	11.4^{257}	2.5^{304}	4.2^{20}	6.7^{585}
Ketones	48	22.5^{37}	5.1^{615}	2.1^{1461}	7.7^{263}	3.8^{2376}	26	71.1^{32}	8.3^{486}	1.6^{1237}	3.6^{245}	4.6^{2000}
Non-cyclic carbonates	4	28.8^{1}	0.7^{144}	1.0^{249}	11.6^{10}	1.2^{404}	2	-	4.1^{76}	3.2^{44}	-	3.8^{120}
Carboxylic acids	26	39.2^{97}	9.1^{1796}	3.3^{924}	5.0^{145}	8.1^{2962}	23	40.0^{97}	8.6^{1721}	2.7^{914}	1.0^{145}	7.4^{2877}
Esters	71	60.6^{48}	6.8^{1143}	2.2^{2093}	8.2^{266}	5.0^{3550}	44	20.5^{18}	4.7^{788}	1.7^{1876}	2.0^{217}	2.7^{2900}
Formic acids esters	12	-	3.4^{81}	2.5^{418}	7.0^{51}	3.0^{550}	7	-	3.3^{67}	1.2^{376}	0.4^{49}	1.4^{492}
Lactones	1	-	19.0^{22}	8.5^{41}	12.0^{1}	12.2^{64}	2	-	12.3^{47}	8.9^{44}	7.6^{1}	10.6^{92}
Anhydride chains	2	-	6.3^{24}	2.9^{42}	-	4.4^{66}	3	-	7.2^{28}	3.9^{34}	-	5.4^{62}
Anhydride cyclic	2	-	5.4^{35}	0.7^{7}	-	4.6^{42}	2	-	3.1^{35}	4.3^{7}	-	3.3^{42}
Aromatic oxygen	4	112.1^{1}	39.2^{67}	4.8^{70}	4.7^{49}	17.7^{187}	3	600.4^{1}	76.1^{65}	10.6^{39}	1.1^{25}	46.1^{130}
All (w/o alcohols) *	432	45.7^{347}	6.5^{5676}	2.7^{9495}	8.1^{1919}	6.1^{17737}	228	36.6^{273}	9.4^{4784}	2.3^{7505}	2.2^{1346}	5.4^{14000}

---

* Includes multi-functional compounds

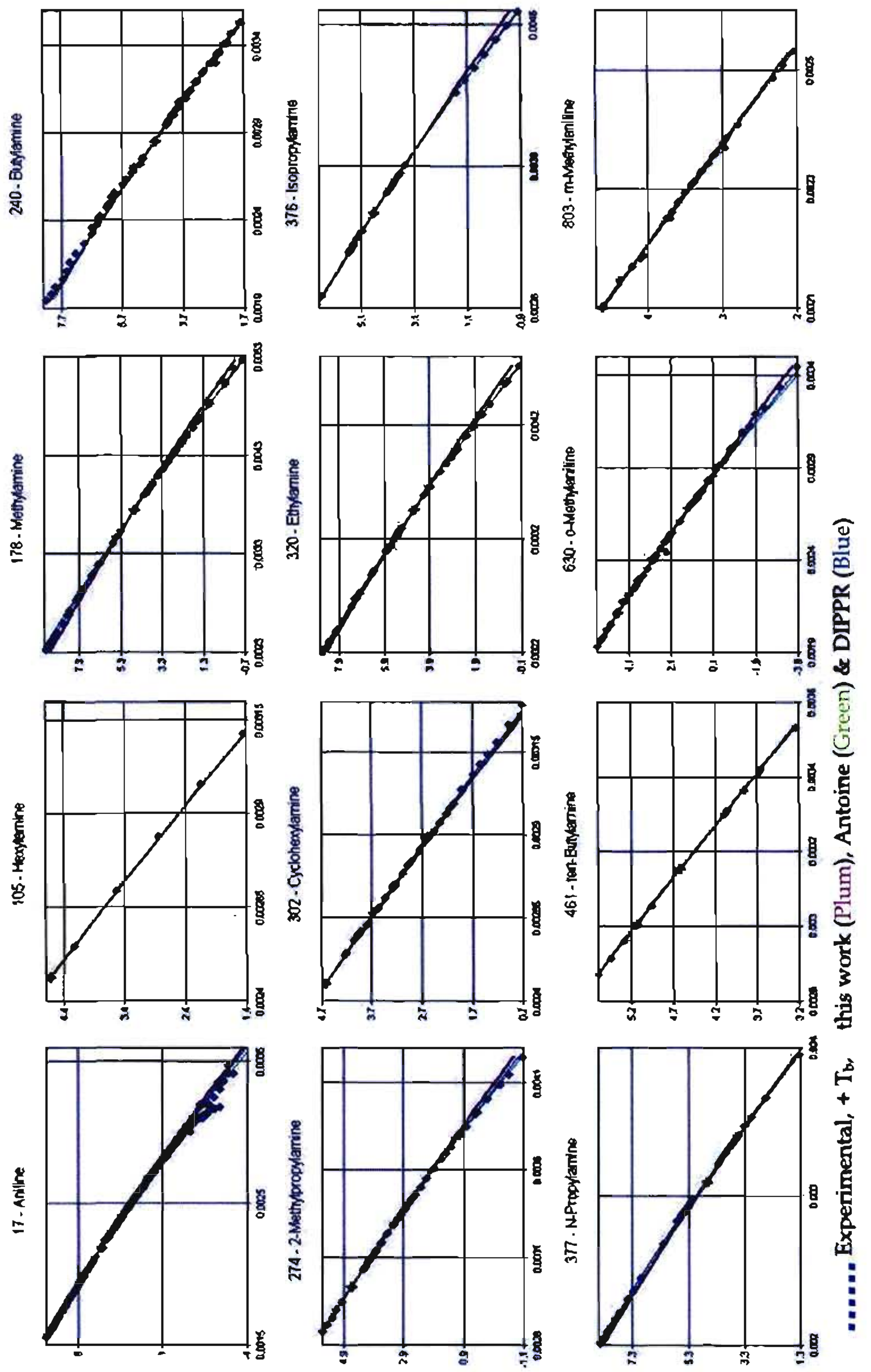


Figure 8-17: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for primary amines.

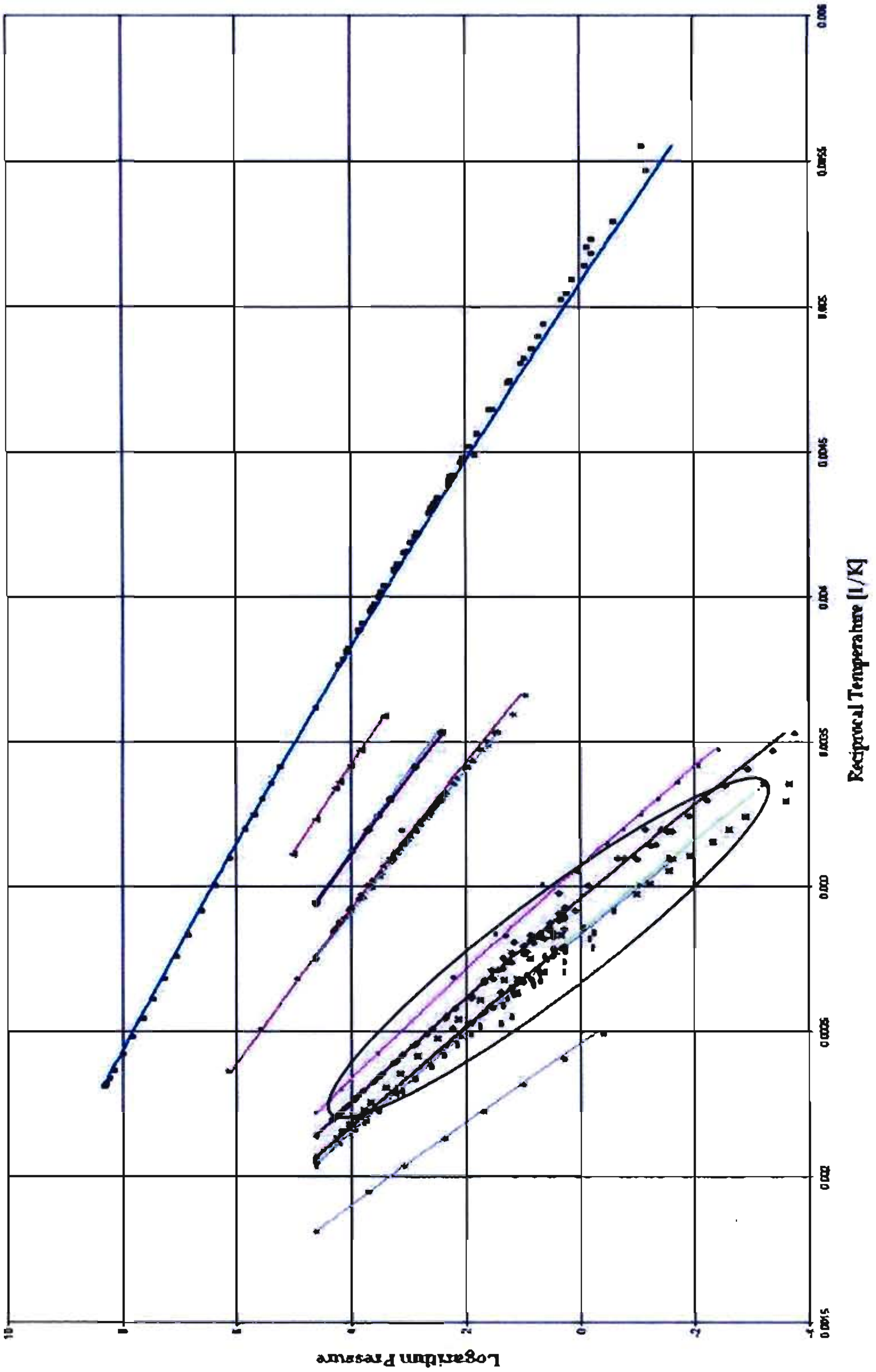


Figure 8-18: Series plot of experimental and estimated liquid vapour pressures for tertiary amines from this work.

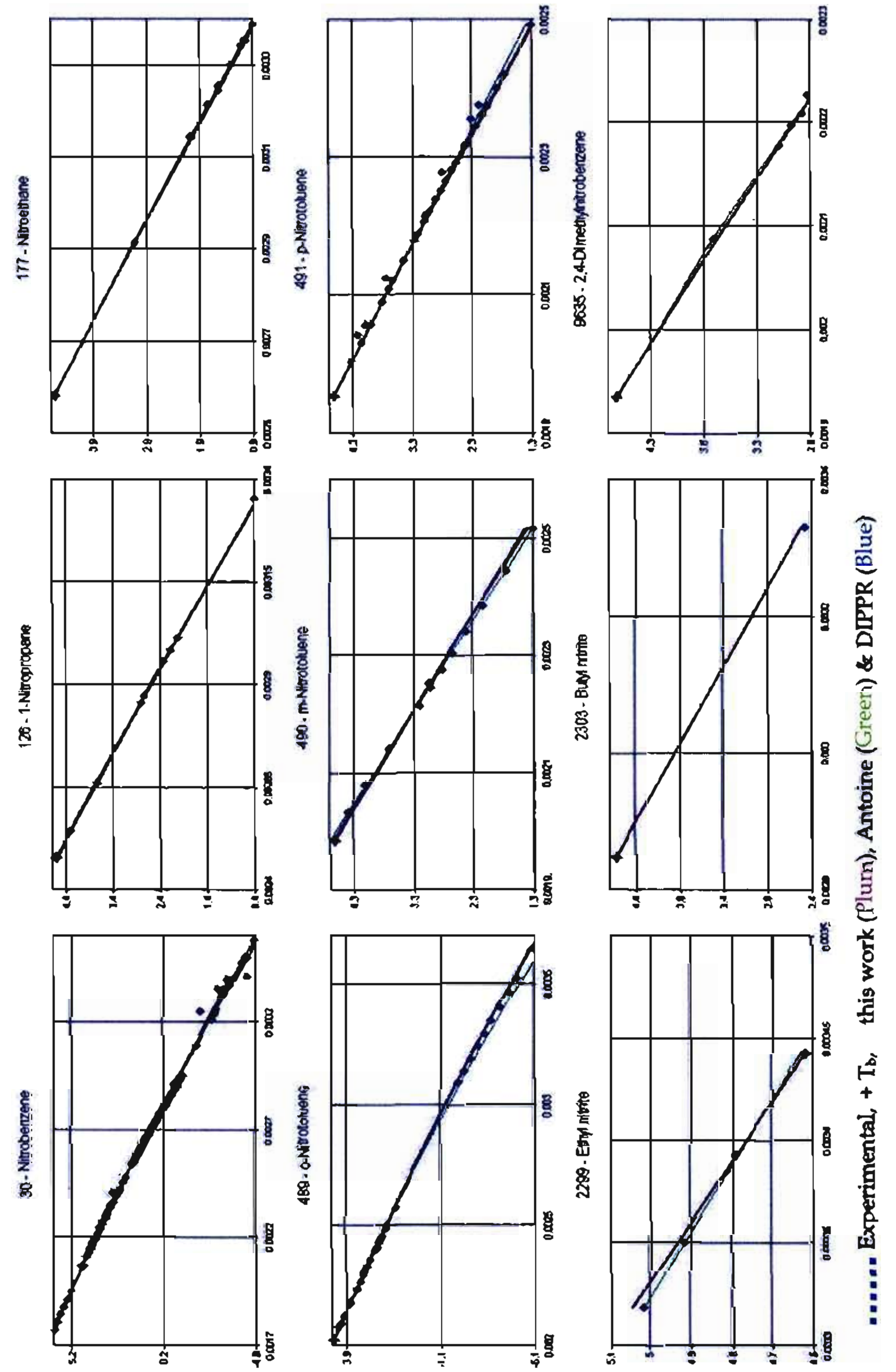


Figure 8-19: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for nitrous and nitrite compounds.

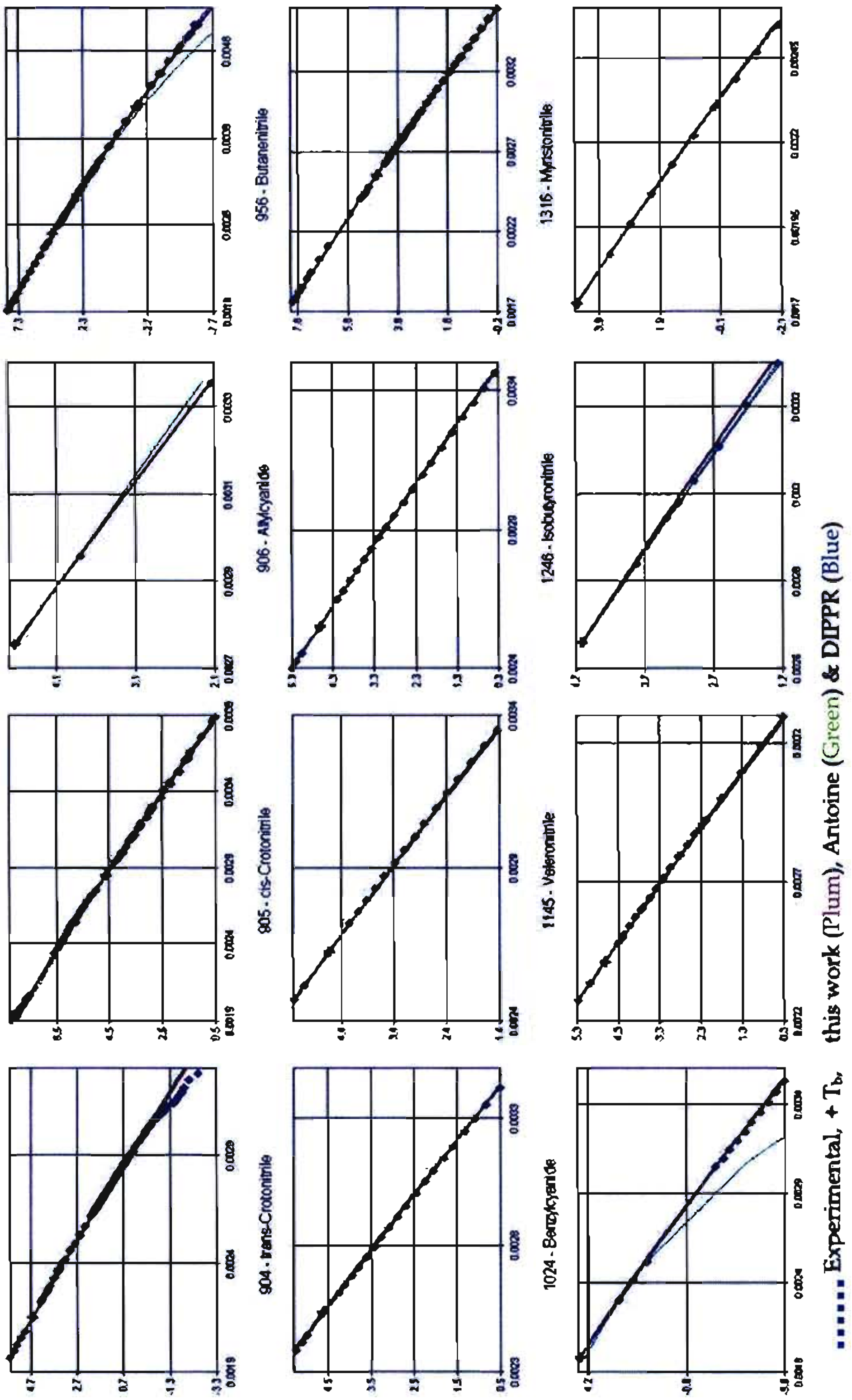


Figure 8-20: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for cyanide compounds.

Table 8-9: Vapour Pressure average absolute deviations of this work for the different types of nitrogen compounds (number of data points as superscript).

		Average Absolute Deviation (%)					Average Absolute Deviation (K)				
	NC	ELP	LP	MP	HP	AV	ELP	LP	MP	HP	AV
Primary amines	36	24.6^{2}	16.3^{485}	3.3^{652}	10.5^{103}	9.0^{1242}	2.6^{2}	2.2^{485}	1.0^{616}	6.7^{103}	2.0^{1206}
Secondary amines	22	-	10.9^{165}	2.8^{463}	5.3^{115}	5.0^{743}	-	1.6^{165}	0.8^{441}	3.2^{115}	1.4^{721}
Tertiary amines	12	-	14.4^{215}	4.5^{274}	3.5^{29}	8.6^{518}	-	2.5^{215}	1.2^{262}	1.8^{29}	1.8^{506}
Amines[*]	109	30.2^{29}	14.5^{1235}	4.0^{1891}	9.7^{300}	8.4^{3455}	2.2^{29}	2.4^{1236}	1.2^{1782}	6.8^{300}	2.1^{3346}
N in 5-membered rings	8	-	18.6^{104}	6.1^{179}	7.3^{15}	10.5^{298}	-	3.6^{104}	2.3^{171}	4.6^{15}	2.9^{290}
N in 6-membered rings	25	-	4.8^{425}	1.6^{888}	3.2^{67}	2.7^{1380}	-	0.9^{426}	0.6^{863}	2.6^{67}	0.8^{1356}
Cyanides	25	15.8^{15}	6.8^{405}	2.5^{378}	5.2^{31}	4.9^{829}	1.5^{15}	1.1^{405}	0.8^{353}	3.8^{31}	1.1^{804}
Amides	1	-	3.0^{5}	0.0^{1}	-	2.5^{6}	-	0.6^{5}	-	-	0.6^{5}
Mono amides	4	-	9.1^{185}	5.8^{91}	1.1^{2}	8.0^{278}	-	1.9^{185}	2.1^{87}	0.7^{2}	2.0^{274}
Di amides	7	14.6^{1}	12.4^{316}	3.5^{283}	-	8.2^{600}	1.7^{1}	2.1^{316}	1.1^{276}	-	1.6^{593}
Isocyanates	9	-	19.1^{46}	5.3^{75}	-	10.6^{121}	-	3.6^{46}	1.5^{66}	-	2.4^{112}
Oximes	6	13.4^{2}	4.0^{56}	1.9^{40}	-	3.3^{98}	1.5^{2}	0.7^{56}	0.6^{34}	-	0.7^{92}
Nitrous and nitrites	9	9.9^{4}	7.3^{185}	3.0^{136}	-	5.5^{325}	1.0^{4}	1.3^{185}	1.2^{127}	-	1.2^{316}
Nitrates	3	-	16.0^{16}	6.5^{14}	-	11.6^{30}	-	3.2^{16}	2.0^{11}	-	2.7^{27}
N-$(C)_4$	3	-	11.1^{10}	6.6^{16}	-	8.3^{26}	-	3.0^{10}	2.4^{13}	-	2.7^{23}
All (w/o amines)[*]	120	28.7^{23}	8.5^{1874}	3.0^{2174}	4.3^{116}	6.1^{4186}	2.2^{23}	1.7^{1874}	1.0^{2054}	3.2^{116}	1.4^{4066}

8.5.2.3 Sulphur Compounds

A detailed analysis of the results for the different types of sulphur compounds for the proposed method and both the correlative models are presented in Tables 8-11 and 8-12, respectively. Due to the smaller number of sulphur components, the graphical presentation was slightly modified. In this case, three multiple plots of various mono-functional sulphur compounds are presented in Figures 8-21, 8-22 and 8-23. For all thirty six compounds, the proposed method is in excellent agreement with experimental data. Similar results were obtained for compounds not shown in this plot.

---

[*] Includes multi-functional compounds

Table 8-10: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for the different types of nitrogen compounds (number of data points as superscript).

	Average Absolute Deviation (%)											
	Antoine						DIPPR					
	NC	ELP	LP	MP	HP	AV	NC	ELP	LP	MP	HP	AV
Primary amines	35	186.8^{1}	8.0^{479}	1.9^{651}	11.3^{109}	6.2^{1234}	25	33.4^{1}	8.2^{405}	2.1^{555}	3.0^{103}	4.5^{1064}
Secondary amines	22	-	4.4^{165}	1.3^{463}	4.9^{115}	2.6^{743}	12	-	6.5^{136}	1.3^{381}	1.6^{115}	2.5^{632}
Tertiary amines	12	-	11.4^{215}	2.0^{274}	6.6^{29}	6.1^{518}	5	-	13.8^{187}	2.7^{237}	1.6^{29}	7.2^{453}
Amines *	104	56.0^{26}	10.7^{1224}	2.2^{1868}	8.2^{300}	6.1^{3417}	60	19.8^{25}	11.4^{1031}	3.3^{1489}	7.1^{300}	6.7^{2845}
N in 5-membered rings	7	-	2.3^{66}	0.7^{167}	2.0^{16}	1.3^{263}	4	-	3.9^{53}	1.0^{117}	3.6^{15}	2.1^{185}
N in 6-membered rings	25	-	4.4^{425}	1.1^{868}	4.2^{67}	2.3^{1360}	10	-	4.5^{290}	0.9^{622}	1.4^{87}	2.0^{882}
Cyanides	25	86.0^{15}	8.9^{405}	1.6^{379}	14.7^{31}	7.3^{829}	12	10.9^{16}	6.7^{279}	1.6^{254}	3.9^{31}	4.4^{579}
Amides	1	-	5.6^{5}	0.0^{1}	-	4.7^{6}	1	-	6.9^{5}	1.4^{1}	-	7.7^{6}
Mono amides	4	-	5.9^{185}	3.0^{91}	20.0^{2}	5.0^{278}	4	-	10.3^{185}	9.1^{91}	1.8^{2}	9.9^{278}
Di amides	7	0.0^{1}	6.1^{316}	3.4^{283}	-	5.9^{600}	3	-	10.3^{253}	4.2^{201}	-	7.6^{454}
Isocyanates	9	-	9.0^{46}	4.5^{75}	-	6.2^{121}	3	-	8.4^{25}	3.1^{43}	-	5.1^{68}
Oximes	6	12.1^{2}	3.8^{58}	1.0^{40}	-	2.8^{100}	1	-	46.5^{31}	16.3^{16}	-	36.2^{47}
Nitrous and nitrites	8	31.2^{4}	6.6^{165}	2.3^{134}	-	6.1^{303}	6	20.3^{4}	6.3^{165}	3.0^{123}	-	5.2^{312}
Nitrates	3	-	1.1^{16}	0.3^{14}	-	0.7^{30}		-	-	-	-	-
N-(C)$_4$	3	-	5.9^{10}	2.3^{16}	-	3.7^{26}		-	-	-	-	-
All (w/o amines) *	116	66.6^{23}	6.7^{1839}	1.9^{2137}	7.0^{115}	4.5^{4114}	45	10.6^{19}	8.4^{1256}	2.7^{1376}	2.4^{116}	5.3^{2766}

As mentioned previously, the proposed method estimates the slope by regressing groups belonging to compounds of a similar chemical nature. Thus, it has a direct advantage over correlative models which are entirely dependant on the data for any single component. Some examples where the estimated slope probably leads to a more reliable result than experimental data are sulfolane, 3-methyl sulfolane and dimethyl sulphate in Figure 8-21. There are also no cases where the method fails substantially.

---

* Includes multi-functional compounds

Table 8-11: Vapour Pressure average absolute deviations of this work for the different types of sulphur compounds (number of data points as superscript).

		Average Absolute Deviation (%)					Average Absolute Deviation (K)				
	NC	ELP	LP	MP	HP	AV	ELP	LP	MP	HP	AV
Disulfides	4	-	2.5^{74}	1.7^{130}	-	2.0^{204}	-	0.5^{74}	0.5^{126}	-	0.5^{200}
Thiols	30	89.0^{4}	4.5^{64}	2.3^{574}	10.3^{64}	3.8^{726}	4.5^{4}	0.8^{64}	0.7^{544}	7.8^{64}	1.4^{698}
Thioether	14	-	9.2^{58}	1.3^{304}	5.2^{22}	2.7^{384}	-	1.6^{58}	0.4^{290}	4.0^{22}	0.6^{370}
Aromatic thioether	7	-	9.6^{104}	3.1^{199}	6.9^{35}	5.5^{338}	-	1.7^{104}	0.9^{192}	5.9^{35}	1.7^{331}
Sulfolane (O=S=O)	2	32.6^{5}	9.4^{22}	0.6^{13}	-	9.4^{40}	5.7^{5}	1.6^{22}	0.3^{11}	-	1.8^{38}
Isothiocyanates	3	-	4.0^{48}	2.6^{5}	-	3.9^{53}	-	0.7^{48}	1.7^{2}	-	0.8^{50}
Sulfates, sulfon amides & sulfoxides	5	-	9.1^{38}	0.0^{5}	-	8.0^{43}	-	2.1^{34}	-	-	2.1^{36}
Sulphur compounds *	99	40.4^{21}	9.0^{581}	2.1^{1624}	8.4^{121}	4.6^{2347}	3.2^{21}	1.6^{581}	0.7^{1525}	6.6^{121}	1.2^{2248}

Table 8-12: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for the different types of sulphur compounds (number of data points as superscript).

	Average Absolute Deviation (%)											
	Antoine						DIPPR					
	NC	ELP	LP	MP	HP	AV	NC	ELP	LP	MP	HP	AV
Disulfides	4	-	0.9^{74}	0.2^{130}	-	0.5^{204}	3	-	0.5^{74}	0.3^{116}	-	0.4^{190}
Thiols	29	0.6^{1}	1.2^{64}	0.4^{573}	2.8^{64}	0.7^{722}	17	44.2^{3}	4.0^{55}	1.1^{408}	3.0^{64}	1.8^{530}
Thioether	14	-	5.6^{58}	0.7^{304}	5.9^{22}	1.7^{384}	6	-	5.4^{23}	0.9^{180}	2.8^{22}	1.5^{225}
Aromatic thioether	7	-	4.3^{104}	1.2^{199}	3.9^{35}	2.6^{338}	5	-	5.8^{102}	1.2^{181}	2.3^{35}	2.8^{318}
Sulfolane (O=S=O)	1	30.4^{5}	7.0^{20}	1.7^{12}	-	8.5^{37}	2	56.3^{5}	19.4^{22}	4.0^{13}	-	19.3^{40}
Isothiocyanates	3	-	1.2^{48}	10.4^{5}	-	2.0^{53}		-	-	-	-	-
Sulfates, sulfon amides & sulfoxides	2	-	11.9^{13}	3.4^{2}	-	10.8^{15}	2	-	8.6^{20}	1.5^{2}	-	8.9^{22}
Sulphur compounds *	94	16.7^{18}	4.0^{564}	0.7^{1619}	3.7^{121}	1.8^{2317}	37	29.6^{17}	6.2^{315}	1.0^{970}	2.8^{121}	2.4^{1423}

---

* Includes multi-functional compounds

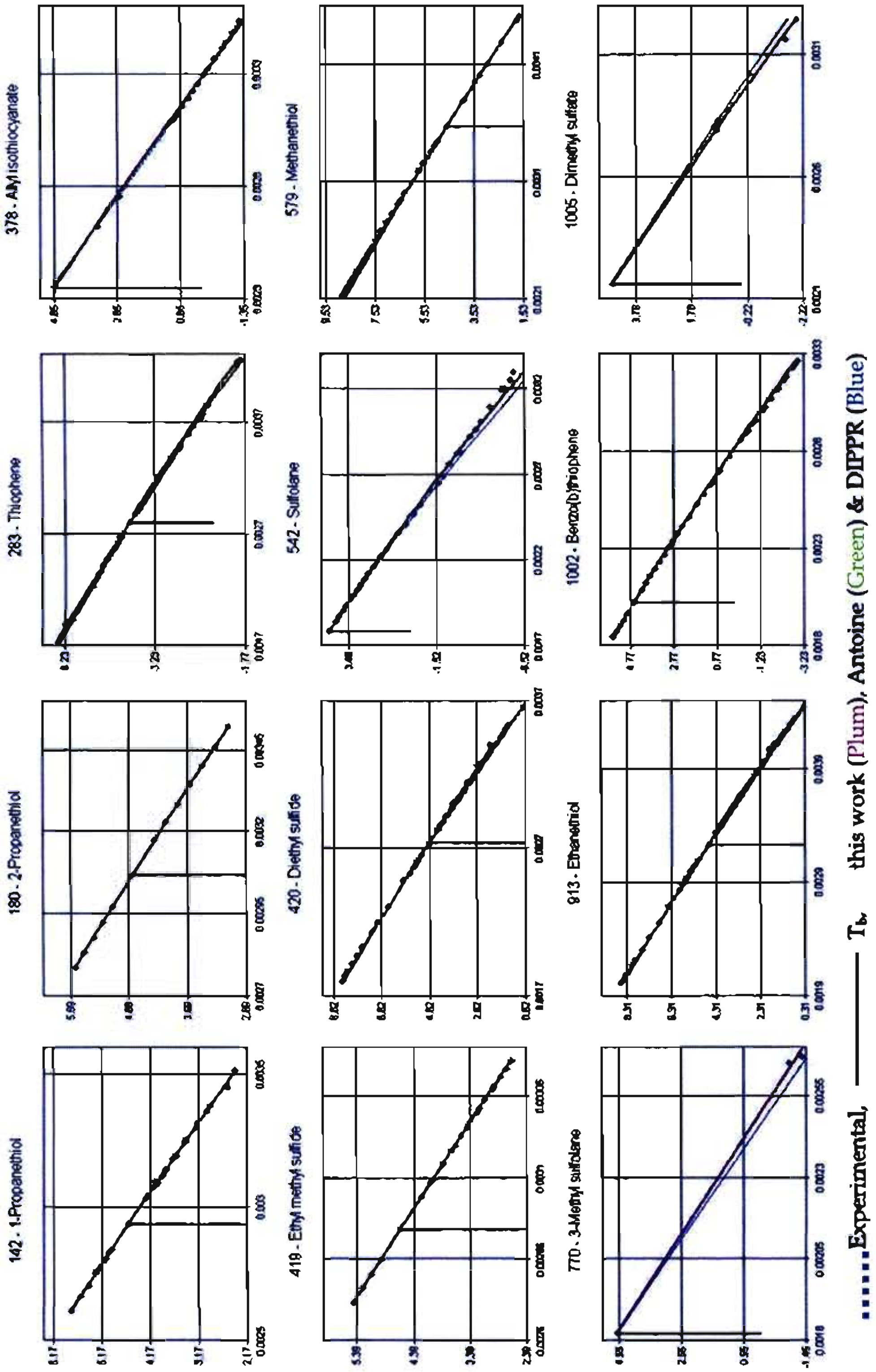


Figure 8-21: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for sulphur compounds.

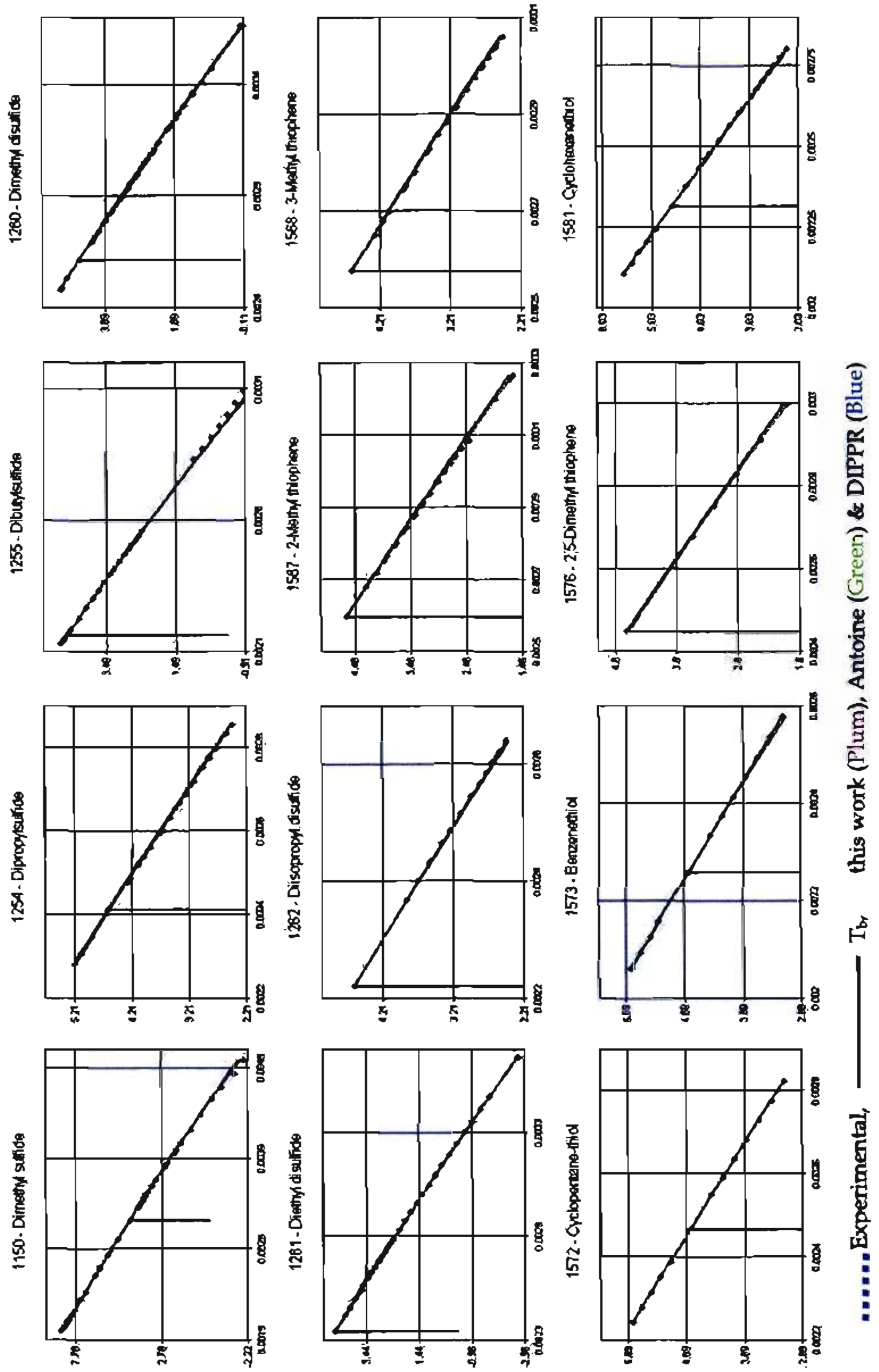


Figure 8-22: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for sulphur compounds.

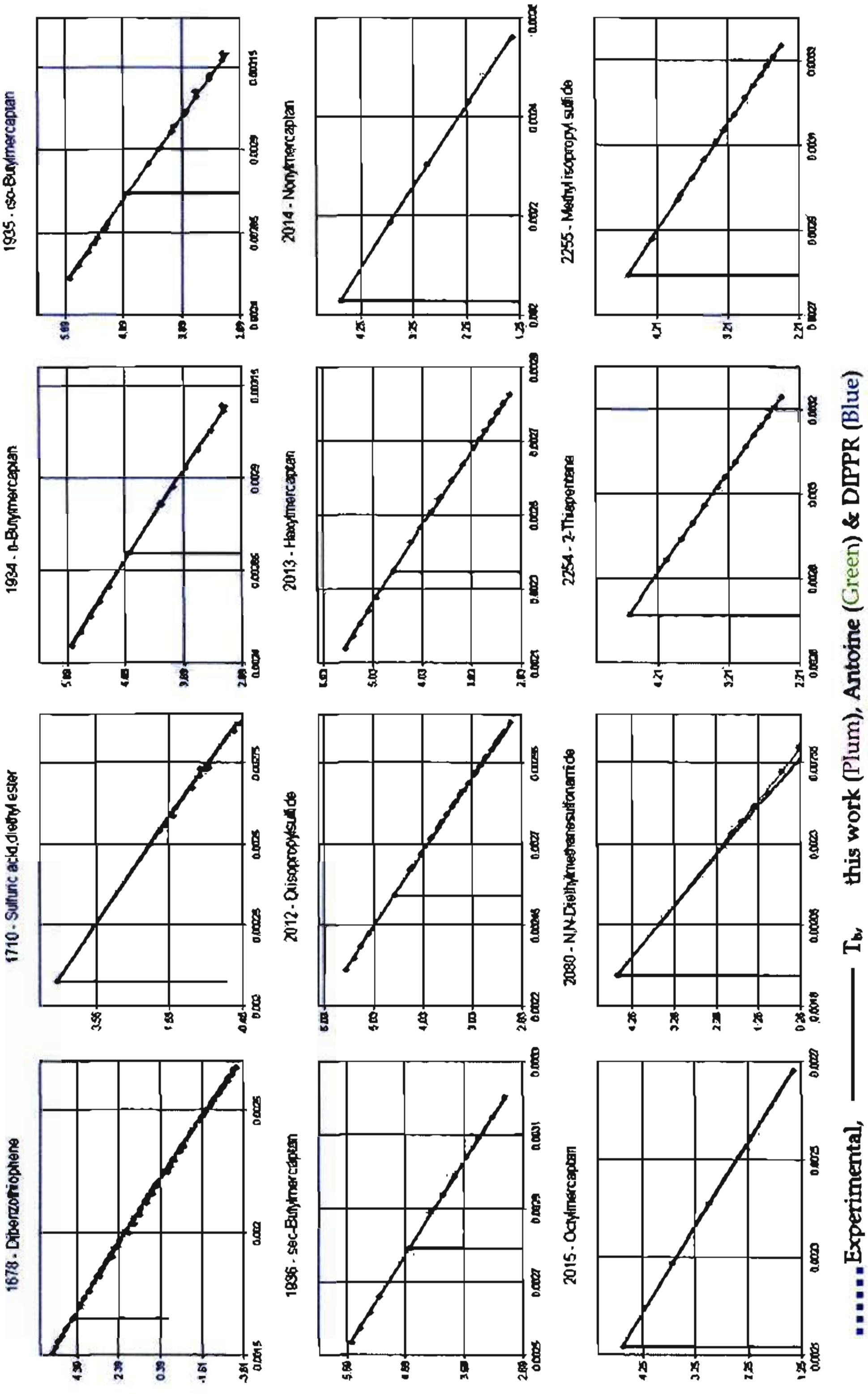


Figure 8-23: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for sulphur compounds.

8.5.2.4 Halogen Compounds

Multiple plots of fluorine, chlorine, bromine and iodine compounds are presented in Figures 8-24 to 8-27, respectively. From Figure 8-24, it can be seen that there are a few components with only high pressure data and where the estimation from the proposed method shows a slight discrepancy with respect to experimental data. For these components it is noticeable that the estimated curve is almost parallel to the data. This would mean that either the data or normal boiling point is in error. For example, for perfluoropropylene, the data was obtained from three different references (Feng *et al.* (1986), Li *et al.* (1996) and Whipple (1952)), all of whom show good agreement. The interpolation (as there were data below the normal boiling point but those were removed from the *dB* regression due to the divergence at and close to this point) of the vapour pressure at the experimental normal boiling point from the Antoine equation leads to a pressure of 112.2 kPa instead of 101.3 kPa. Also, the T_b regressed from Equation 8-3 was much lower than the experimental value. In conclusion, the proposed method estimates the slope of perfluoropropylene accurately while the deviation arises from the error in the experimental normal boiling point. Thus, the proposed method can also be employed to verify normal boiling point data using vapour pressure data at other temperatures.

From the graphical representations of the data for fluorine compounds as well as the results from Table 8-13, it is evident that there is a lack of experimental data at low pressures. Extrapolations in this temperature range from correlative models will prove to be erroneous as seen in the case of 1,1,2-trichloroethane, 1,2-dibromoethane as well as many other cases observed in this chapter. Thus, this case presents a typical example for which the proposed method leads to better results than the correlative models.

For all plots, the proposed method shows a good representation of the temperature dependence, even for highly halogenated compounds such as perfluoro compounds. Similar trends are also observed for other halogen compounds not shown in the plots. There were slight deviations for 1-bromo-2,2-dimethylpropane, 1-bromopentane and 3-bromopentane in case of a few low vapour pressure data points. However, all these data were reported by Kreibich *et al.* (1970) and as the estimation in case of other bromine compounds at even lower pressures is accurate, it can be assumed that the few experimental points for the above three compounds are questionable. Also, the deviations in the case of multi-functional halogen compounds are similar to that of the mono-functional components. Unlike strongly associating or hydrogen bonding groups, halogen groups obey additivity.

Results for the different types of halogen compounds for the proposed method and both the correlative models are presented in Tables 8-13 and 8-14, respectively. There were no especially large deviations between the experimental data and the proposed method.

Table 8-13: Vapour Pressure average absolute deviations of this work for the different types of halogen compounds (number of data points as superscript).

		Average Absolute Deviation (%)					**Average Absolute Deviation (K)**				
	NC	**ELP**	**LP**	**MP**	**HP**	**AV**	**ELP**	**LP**	**MP**	**HP**	**AV**
Saturated fluorine	54	-	8.7^{245}	2.3^{1578}	6.3^{2738}	5.1^{4561}	-	1.0^{245}	0.6^{1524}	3.3^{2738}	2.3^{4507}
Fluorinated	75	-	7.2^{361}	2.4^{2153}	6.0^{2993}	4.7^{5507}	-	0.9^{361}	0.6^{2078}	3.2^{2993}	2.1^{5432}
Saturated chlorine	49	16.4^{4}	6.9^{361}	2.5^{1574}	6.9^{468}	4.0^{2407}	1.5^{4}	1.2^{361}	0.7^{1525}	6.3^{468}	1.7^{2358}
Chlorinated	81	10.5^{11}	6.8^{733}	2.5^{2471}	6.0^{579}	3.9^{3794}	1.0^{11}	1.2^{733}	0.7^{2390}	4.5^{579}	1.4^{3713}
Saturated bromine	18	21.0^{10}	8.5^{150}	2.6^{194}	-	5.6^{354}	2.0^{10}	1.6^{150}	0.8^{176}	-	1.2^{336}
Brominated	31	32.5^{16}	9.1^{357}	2.4^{441}	2.2^{15}	5.9^{829}	2.8^{16}	1.6^{357}	0.8^{410}	1.4^{16}	1.2^{799}
Iodinated	10	-	7.6^{110}	2.1^{153}	3.8^{5}	4.4^{268}	-	1.4^{110}	0.8^{143}	2.2^{5}	1.1^{258}
Halogenated Compounds*	353	28.0^{34}	9.1^{2401}	2.7^{7456}	5.5^{5570}	4.7^{15461}	2.3^{34}	1.5^{2401}	0.8^{7103}	3.0^{5570}	1.7^{15108}

---

* Includes multi-functional compounds

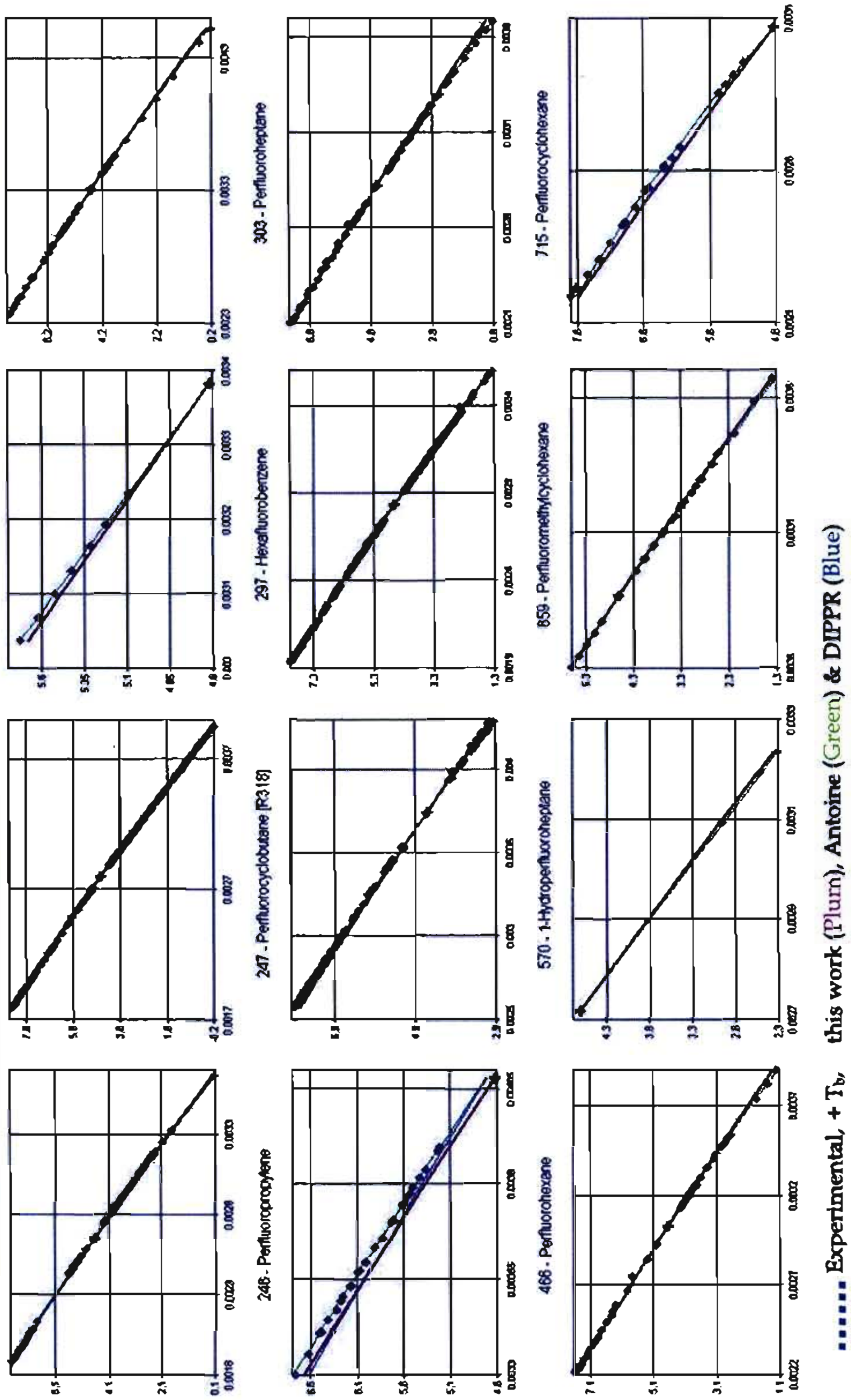


Figure 8-24: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for fluorine compounds.

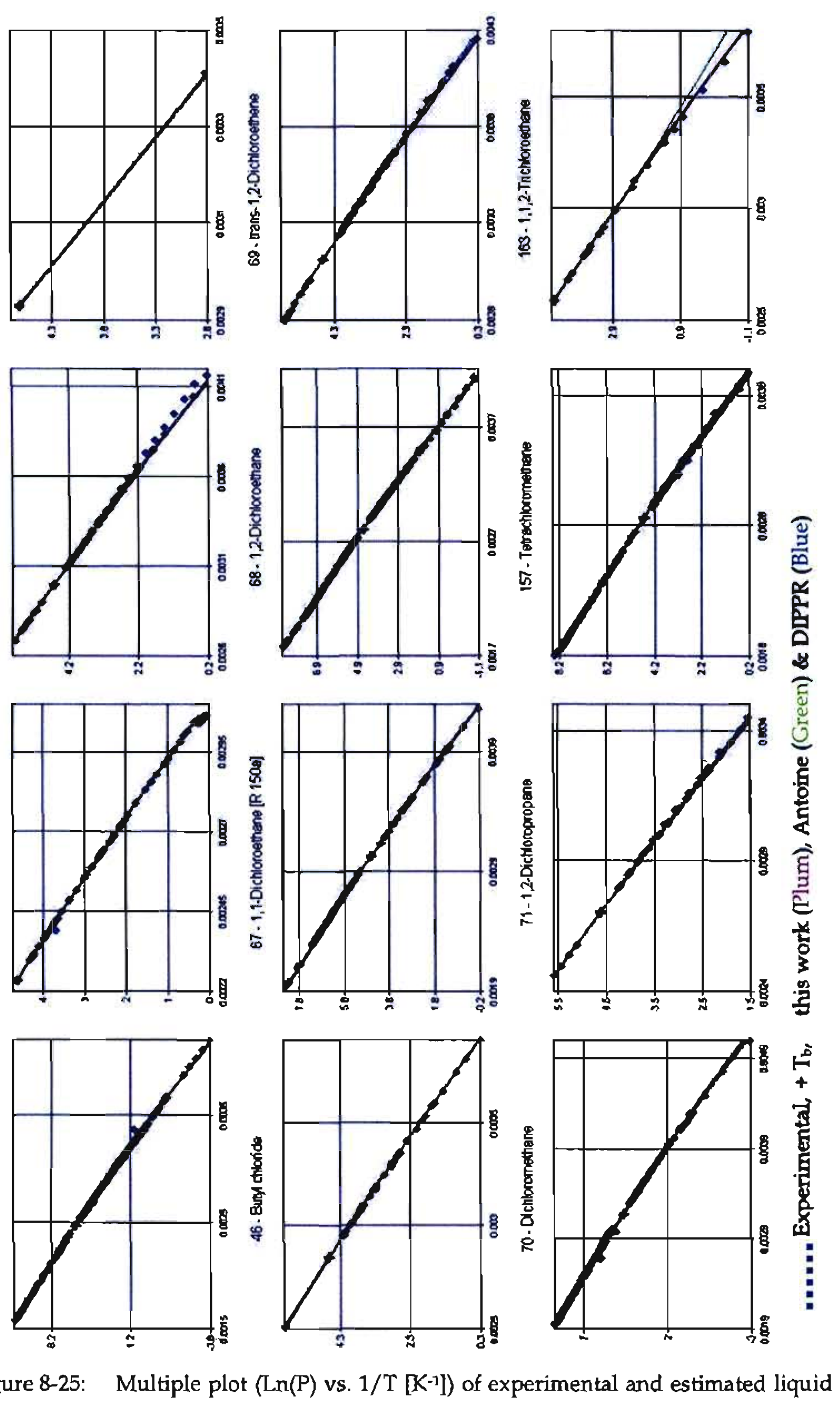


Figure 8-25: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for chlorine compounds.

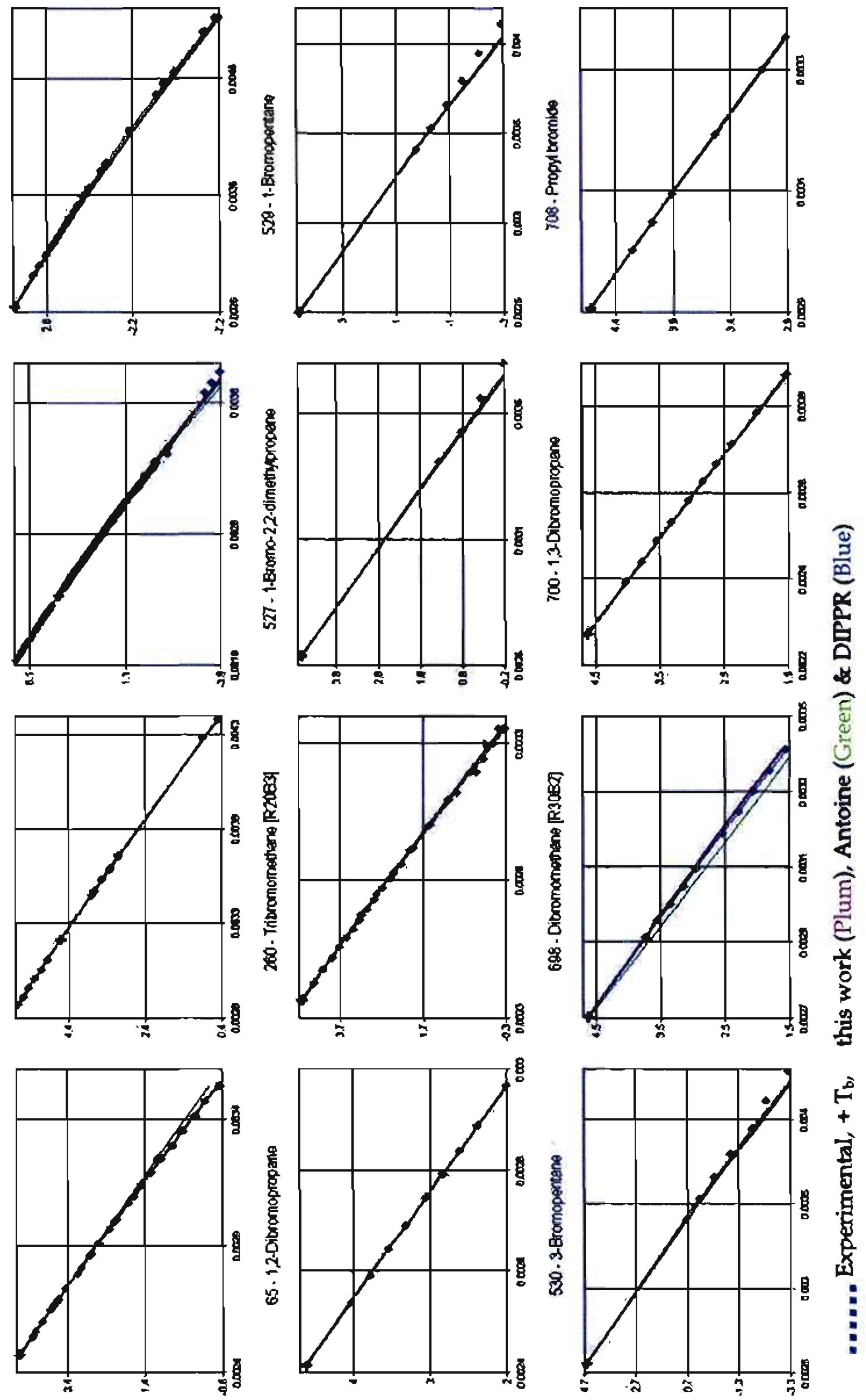


Figure 8-26: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for bromine compounds.

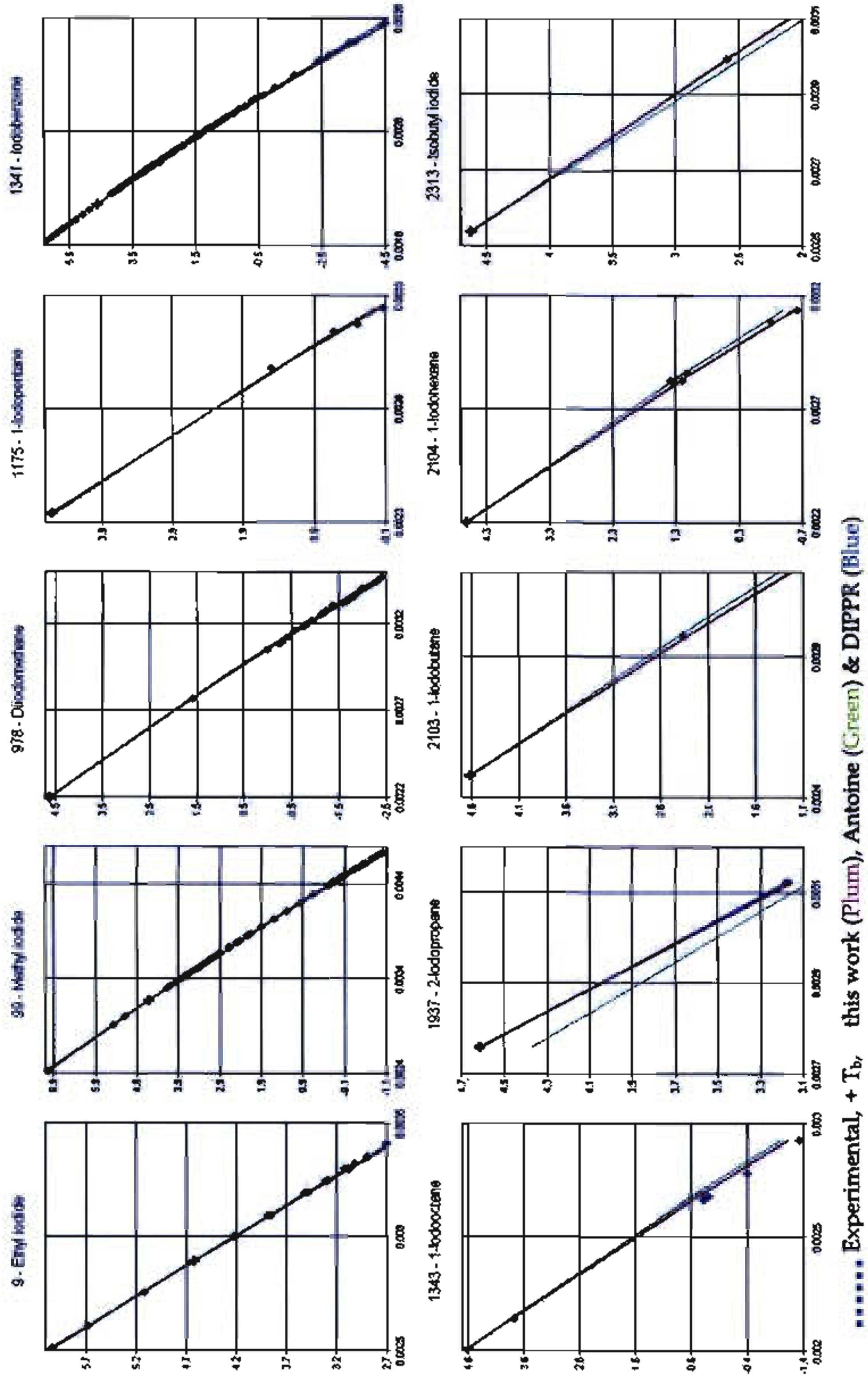


Figure 8-27: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for iodine compounds.

Table 8-14: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for the different types of halogen compounds (number of data points as superscript).

	Average Absolute Deviation (%)											
	Antoine						DIPPR					
	NC	ELP	LP	MP	HP	AV	NC	ELP	LP	MP	HP	AV
Saturated fluorine	53	-	6.5^{244}	1.5^{1577}	2.0^{2738}	2.1^{4559}	14	-	3.6^{161}	2.2^{855}	1.8^{2206}	2.0^{3222}
Fluorinated	74	-	4.9^{360}	1.3^{2182}	2.4^{2993}	2.1^{5535}	20	-	2.9^{221}	1.9^{1187}	1.8^{2371}	1.9^{3779}
Saturated chlorine	49	60.2^{4}	6.3^{361}	1.5^{1574}	4.7^{468}	2.9^{2407}	24	-	4.7^{257}	1.5^{1379}	2.4^{449}	2.1^{2085}
Chlorinated	80	33.3^{11}	5.3^{732}	1.5^{2470}	4.5^{579}	2.8^{3792}	45	21.4^{7}	5.0^{601}	1.5^{2195}	2.3^{560}	2.3^{3363}
Saturated bromine	18	5.9^{10}	5.1^{160}	2.2^{184}	-	3.6^{354}	8	6.5^{10}	7.3^{110}	1.6^{119}	-	4.4^{239}
Brominated	30	35.1^{16}	6.4^{355}	3.2^{430}	2.9^{15}	5.2^{816}	11	9.4^{15}	6.6^{287}	1.7^{305}	1.9^{15}	3.7^{622}
Iodinated	10	-	4.6^{110}	1.4^{153}	2.3^{5}	2.7^{268}	5	-	2.2^{94}	0.7^{145}	0.4^{5}	1.3^{244}
Halogenated Compounds *	343	33.7^{34}	7.7^{2368}	1.8^{7425}	3.7^{5569}	3.6^{15396}	131	14.6^{28}	6.8^{1652}	1.7^{5004}	1.6^{4301}	2.6^{10985}

8.5.2.5 Various Other Compounds

Tables 8-15 and 8-16 present results for various other compounds for the proposed method and both the correlative models. A slightly larger deviation was observed in the case of phosphate compounds (Figure 8-28). The estimation of the slope is in all cases acceptable and deviations arise from only a few outlying data points.

For arsine compounds, a multiple plot is presented in Figure 8-29. The unusual curvature for arsenic sec-butyl dichloride does not appear for any of the other five similar compounds. Consequently, it can be assumed that these data are questionable.

Multiple plots for boron and silicon compounds are presented in Figures 8-30 and 8-31, respectively. A deviation was observed for boric acid trimethyl ester where the low pressure data were obtained from a rather old source, Wiberg & Suetterlin (1931).

---

* Includes multi-functional compounds

Table 8-15: Vapour Pressure average absolute deviations of this work for various other types of compounds (number of data points as superscript).

		Average Absolute Deviation (%)					**Average Absolute Deviation (K)**				
	NC	**ELP**	**LP**	**MP**	**HP**	**AV**	**ELP**	**LP**	**MP**	**HP**	**AV**
Phosphates	3	15.8^{7}	18.6^{8}	5.6^{8}	-	13.2^{23}	1.2^{7}	4.6^{6}	2.9^{6}	-	3.0^{20}
Arsine	6	-	10.8^{15}	2.1^{22}	-	5.6^{37}	-	1.7^{15}	1.0^{16}	-	1.3^{31}
Germanium	1	-	8.5^{22}	1.7^{13}	-	5.9^{35}	-	1.1^{22}	0.4^{12}	-	0.9^{34}
Germanium (-Cl)3	3	-	1.1^{33}	0.6^{26}	-	0.9^{59}	-	0.2^{33}	0.2^{23}	-	0.2^{56}
Tin	3	-	1.7^{55}	0.5^{90}	2.0^{14}	1.0^{159}	-	0.3^{55}	0.1^{87}	1.4^{14}	0.3^{156}
Boron	6	-	8.0^{26}	3.3^{69}	-	4.6^{95}	-	1.5^{26}	0.9^{63}	-	1.1^{89}
Silicon	23	-	6.7^{123}	2.4^{258}	1.7^{28}	3.7^{409}	-	1.4^{123}	0.8^{235}	1.0^{28}	1.0^{386}
Silicon (*en* [*])	65	-	11.2^{272}	2.7^{631}	2.7^{140}	4.9^{1043}	-	2.0^{272}	0.8^{566}	2.0^{140}	1.3^{978}
Acid chloride	2	-	15.6^{67}	6.9^{9}	-	14.6^{76}	-	4.0^{67}	2.2^{7}	-	3.8^{74}
Urea	1	-	1.4^{14}	0.7^{13}	-	1.0^{27}	-	0.3^{14}	0.2^{12}	-	0.2^{26}
Selenium	1	-	-	1.6^{28}	-	1.6^{28}	-	-	0.4^{27}	-	0.4^{27}
Aluminium	1	-	3.8^{20}	1.0^{14}	-	2.7^{34}	-	0.7^{20}	0.3^{13}	-	0.5^{33}

8.5.3 Multi-functional compounds

Up to this point, results have only been presented for mono-functional compounds (and in only a few cases for multi-functional compounds where all groups obey additivity). The estimation of the *dB* parameter was shown to be accurate with no cases where the method has failed substantially.

In case of strongly associating and hydrogen bonding groups, the estimation of the *dB* parameter for multi-functional compounds employs interaction groups in the same way as in the case of critical properties. The details of the calculation are not repeated here.

Results for multi-functional compounds for the proposed method and the correlative models are presented in Tables 8-17 and 8-18, respectively. Five multiple plots of multi-

---

[*] Denotes silicon connected to any electronegative neighbour. This filter also includes all multi-functional compounds.

functional compounds that contain various different interaction groups are also presented in Figures 8-32 to 8-36. From all plots, the scatter or inconsistency in experimental data is evident and it can be assumed that experimental measurements usually encounter a higher experimental error for these strongly associating compounds. For this reason, deviations listed in the table are slightly higher for the proposed method as well as the correlative models.

Table 8-16: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for various other types of compounds (number of data points as superscript).

	Average Absolute Deviation (%)											
	Antoine						DIPPR					
	NC	ELP	LP	MP	HP	AV	NC	ELP	LP	MP	HP	AV
Phosphates	3	9.6^{7}	6.1^{8}	2.0^{8}	-	5.7^{23}	-	-	-	-	-	-
Arsine	6	-	22.3^{15}	1.5^{22}	-	9.9^{37}	-	-	-	-	-	-
Germanium	1	-	4.8^{22}	3.0^{13}	-	4.1^{35}	-	-	-	-	-	-
Germanium (-Cl)$_3$	1	-	1.2^{15}	0.2^{8}	-	0.9^{23}	-	-	-	-	-	-
Tin	3	-	1.5^{55}	0.6^{90}	7.2^{14}	1.5^{159}	-	-	-	-	-	-
Boron	6	-	6.6^{26}	2.5^{69}	-	3.7^{95}	1	-	159.8^{1}	37.2^{9}	-	49.4^{10}
Silicon	21	-	1.7^{115}	0.6^{256}	1.7^{24}	1.0^{395}	3	-	2.8^{11}	0.8^{26}	1.1^{28}	1.2^{65}
Silicon (*en* *)	66	-	6.3^{272}	1.7^{631}	11.9^{140}	4.3^{1043}	15	-	9.3^{68}	1.9^{231}	0.7^{102}	2.8^{401}
Acid chloride	2	-	3.6^{67}	30.5^{9}	-	6.8^{76}	2	-	1.1^{67}	3.3^{9}	-	1.3^{76}
Urea	1	-	0.6^{14}	0.9^{13}	-	0.6^{27}	-	-	-	-	-	-
Selenium	1	-	-	1.8^{26}	-	1.8^{26}	-	-	-	-	-	-
Aluminium	1	-	0.3^{20}	0.1^{14}	-	0.2^{34}	1	-	4.0^{20}	0.3^{14}	-	2.5^{34}

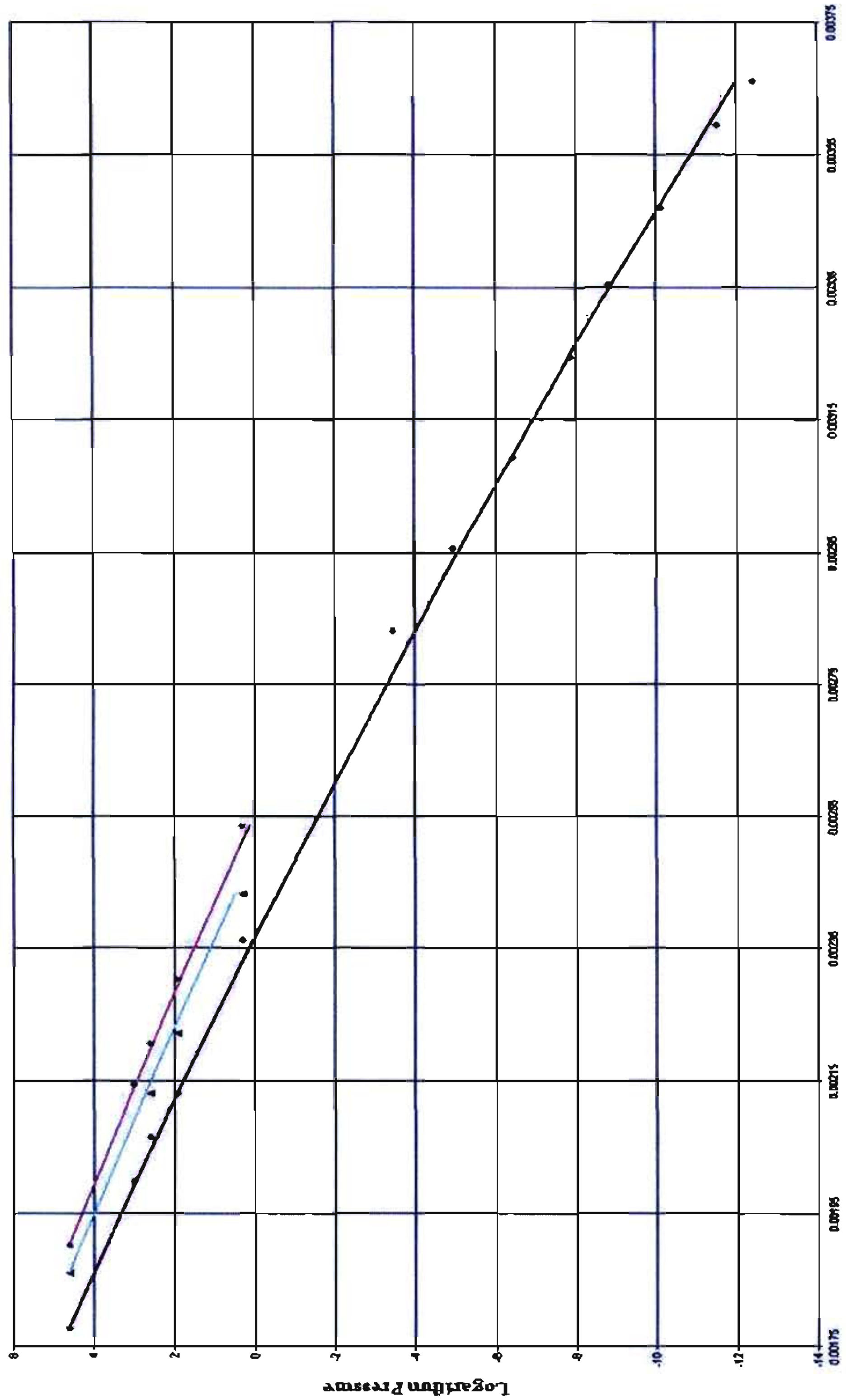


Figure 8-28: Series plot of experimental and estimated liquid vapour pressures for phosphate compounds from this work.

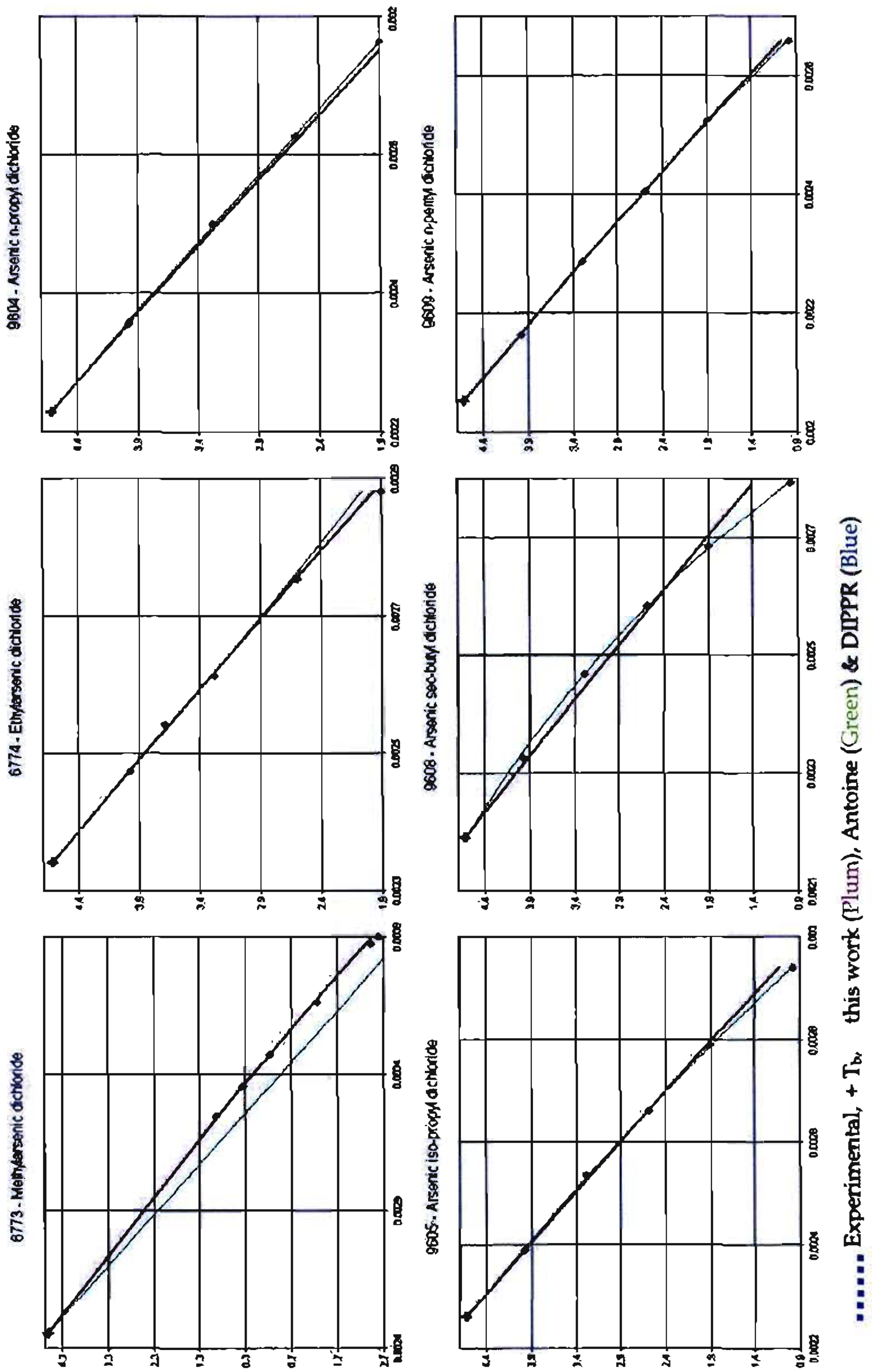


Figure 8-29: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for arsine compounds.

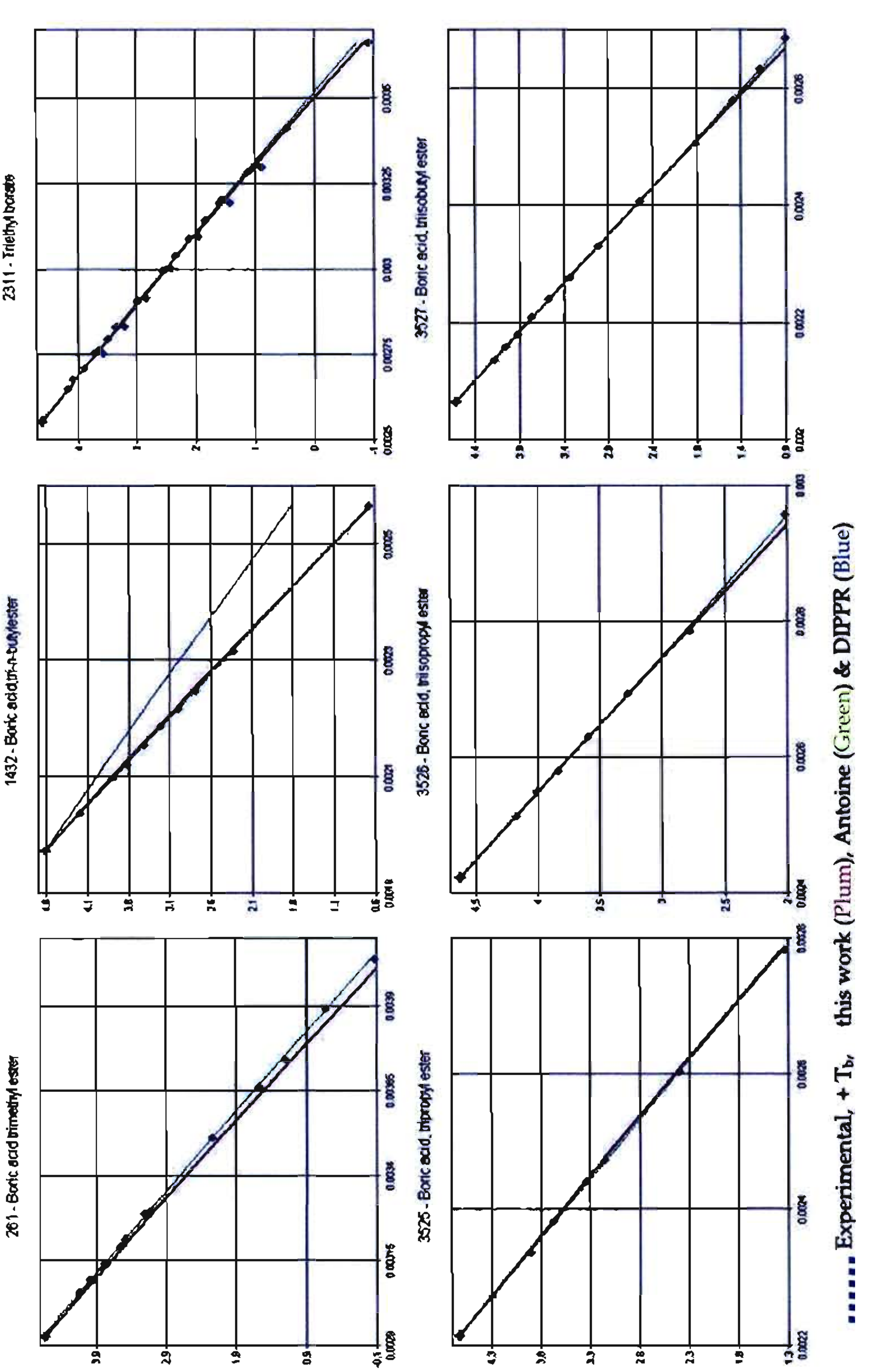


Figure 8-30: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for boron compounds.

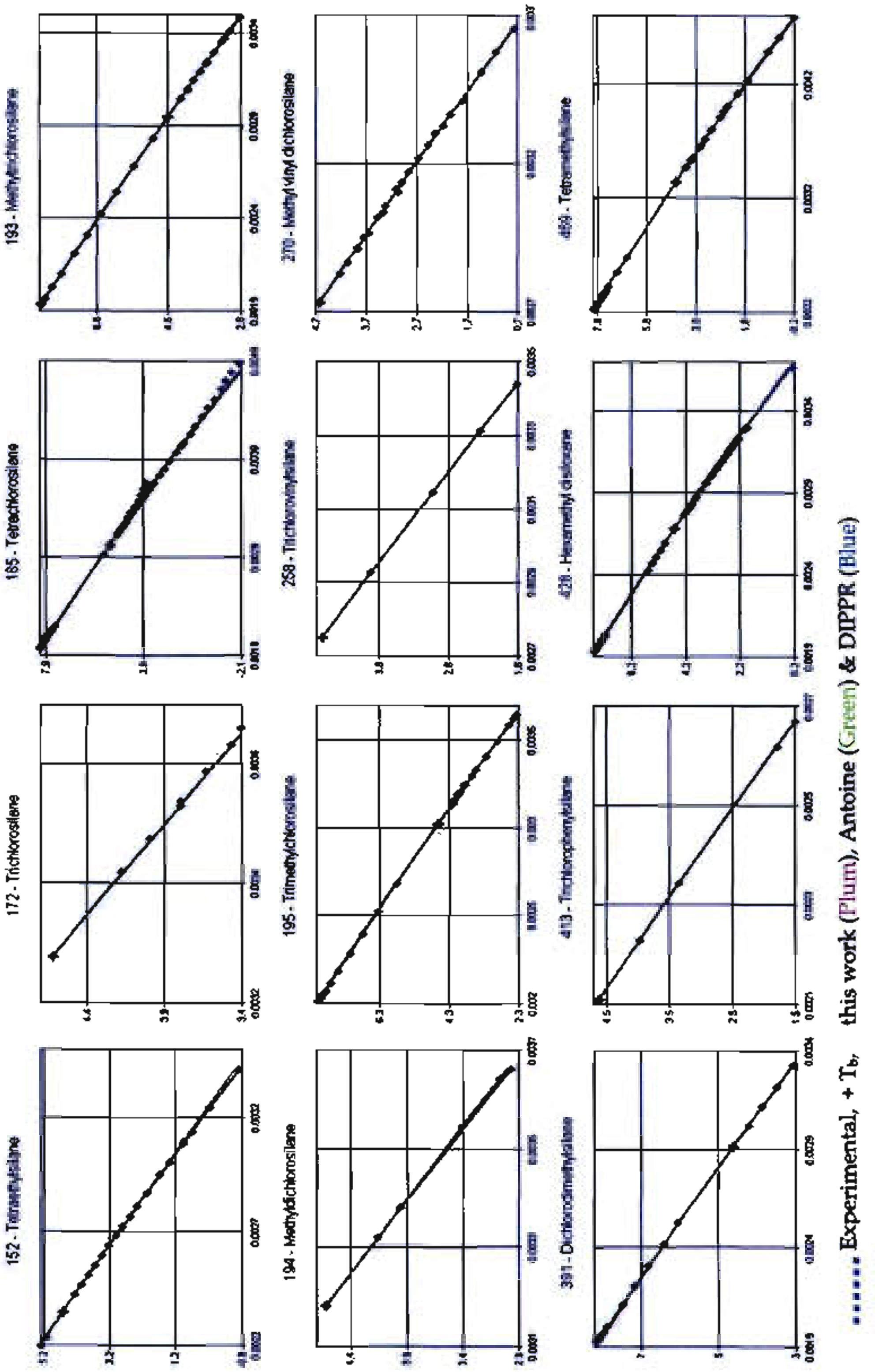


Figure 8-31: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for silicon compounds.

There are no cases of high prediction failures for these complex molecules. There are, though, a few cases where a slight deviation is observed between the estimated values and experimental data at low pressures. This range of data is usually of lower quality especially for these complex molecules. In addition, there are a number of cases where estimated and experimental curves are parallel, for example in the case of methylene diacetate in Figure 8-34. As discussed earlier, this is a result of an error in the normal boiling point. Overall though, even for complex multi-functional compounds the proposed method yields a deviation not significantly different from the correlative models.

Table 8-17: Vapour Pressure average absolute deviations of this work for multi-functional compounds (number of data points as superscript).

		Average Absolute Deviation (%)					**Average Absolute Deviation (K)**				
	NC	**ELP**	**LP**	**MP**	**HP**	**AV**	**ELP**	**LP**	**MP**	**HP**	**AV**
OH	54	47.1^{94}	17.3^{752}	8.7^{817}	19.1^{57}	13.9^{1720}	5.0^{94}	3.1^{752}	2.3^{763}	10.2^{57}	3.1^{1666}
OH(a)	6	7.3^{16}	5.7^{35}	1.9^{24}	-	4.8^{75}	0.8^{16}	1.2^{35}	0.8^{18}	-	1.0^{69}
NH_2	14	4.9^{3}	11.0^{144}	6.4^{259}	20.0^{53}	9.4^{459}	0.6^{3}	2.2^{144}	1.9^{245}	11.2^{53}	3.1^{445}
NH	8	51.8^{14}	16.3^{109}	2.6^{154}	20.0^{27}	11.3^{304}	3.4^{14}	3.2^{109}	0.8^{146}	14.0^{27}	3.0^{296}
SH	10	-	9.5^{13}	2.1^{28}	-	4.5^{41}	-	1.9^{13}	1.0^{18}	-	1.4^{31}
COOH	3	-	3.8^{7}	0.3^{5}	-	2.4^{12}	-	0.9^{7}	0.2^{2}	-	0.8^{9}
OCN	3	92.9^{2}	17.5^{36}	4.8^{27}	-	14.6^{65}	5.9^{2}	4.8^{36}	2.0^{24}	-	3.8^{62}
Ether	91	13.0^{31}	9.1^{697}	3.9^{1169}	8.1^{182}	6.2^{2079}	2.2^{31}	1.7^{697}	1.3^{1078}	4.1^{182}	1.7^{1988}
Epoxide	3	-	3.7^{31}	1.7^{15}	-	3.0^{46}	-	0.8^{31}	0.5^{12}	-	0.7^{43}
Ester	40	24.2^{116}	16.0^{370}	7.5^{383}	14.6^{79}	13.5^{948}	2.4^{116}	3.1^{370}	2.7^{343}	8.0^{79}	3.3^{908}
Ketone	11	2.1^{2}	10.0^{64}	6.9^{129}	16.1^{42}	9.3^{237}	0.3^{2}	2.1^{64}	2.8^{118}	9.7^{42}	3.9^{226}
Aldehyde	3	-	7.5^{53}	1.7^{50}	0.7^{2}	4.6^{105}	-	1.3^{53}	0.5^{47}	0.4^{2}	0.9^{102}
Nitro, AtS, CN, AO, AN5, AN6	20	89.8^{2}	11.5^{219}	3.7^{177}	0.7^{2}	8.4^{400}	5.4^{2}	1.8^{219}	1.5^{157}	0.4^{2}	1.7^{380}
All GI Components	199	32.9^{232}	13.9^{1642}	5.2^{2385}	13.0^{353}	10.4^{4612}	3.3^{232}	2.6^{1642}	1.8^{2186}	7.1^{353}	2.6^{4613}

Table 8-18: Vapour Pressure average absolute deviations (%) of the Antoine and DIPPR models for multi-functional compounds (number of data points as superscript).

	Average Absolute Deviation (%)											
	Antoine						DIPPR					
	NC	ELP	LP	MP	HP	AV	NC	ELP	LP	MP	HP	AV
OH	51	48.3^{93}	11.4^{745}	8.8^{814}	51.9^{57}	13.5^{1709}	34	21.1^{93}	14.4^{678}	7.6^{664}	44.1^{54}	12.9^{1489}
OH(a)	6	45.4^{16}	26.2^{35}	28.3^{24}	-	31.0^{75}	3	-	4.8^{30}	2.1^{21}	-	3.7^{51}
NH_2	12	-	8.8^{139}	4.2^{256}	9.6^{53}	6.3^{448}	11	-	9.5^{135}	7.7^{247}	29.1^{53}	10.9^{436}
NH	5	51.4^{14}	11.3^{108}	1.6^{133}	9.1^{27}	8.5^{282}	6	17.5^{14}	14.5^{108}	2.9^{146}	50.7^{27}	12.1^{295}
SH	10	-	0.2^{13}	0.6^{28}	-	0.5^{41}	1	-	1.2^{4}	3.5^{10}	-	2.8^{14}
COOH	3	-	7.4^{7}	2.0^{5}	-	5.1^{12}	3	-	6.7^{7}	3.0^{5}	-	5.2^{12}
OCN	3	38.6^{2}	5.0^{36}	6.6^{27}	-	6.7^{65}	2	2.9^{2}	4.0^{32}	10.1^{17}	-	6.0^{51}
Ether	65	62.4^{30}	8.9^{676}	5.1^{1141}	10.1^{162}	7.5^{2026}	34	56.2^{12}	9.5^{486}	4.4^{682}	4.3^{114}	6.8^{1294}
Epoxide	3	-	3.9^{31}	2.7^{15}	-	3.5^{46}	-	-	-	-	-	-
Ester	36	46.0^{113}	9.9^{357}	6.1^{369}	11.6^{79}	13.2^{918}	19	15.6^{98}	17.9^{263}	7.6^{236}	11.4^{40}	13.4^{637}
Ketone	11	37.3^{2}	9.6^{64}	5.9^{129}	15.7^{42}	8.9^{237}	7	-	23.0^{53}	6.4^{115}	2.8^{42}	9.9^{210}
Aldehyde	3	-	6.0^{53}	2.6^{50}	11.9^{2}	4.5^{105}	1	-	11.0^{27}	1.6^{45}	1.2^{2}	5.0^{74}
Nitro, AtS, CN, AO, AN5, AN6	17	5.2^{2}	8.4^{202}	3.1^{157}	11.9^{2}	6.1^{363}	11	16.7^{2}	11.2^{164}	12.9^{112}	1.2^{2}	11.8^{280}
All GI Components	185	47.6^{226}	9.6^{1799}	5.4^{2320}	17.4^{353}	10.1^{4700}	93	18.3^{195}	13.3^{1390}	6.1^{1696}	17.7^{243}	10.6^{3424}

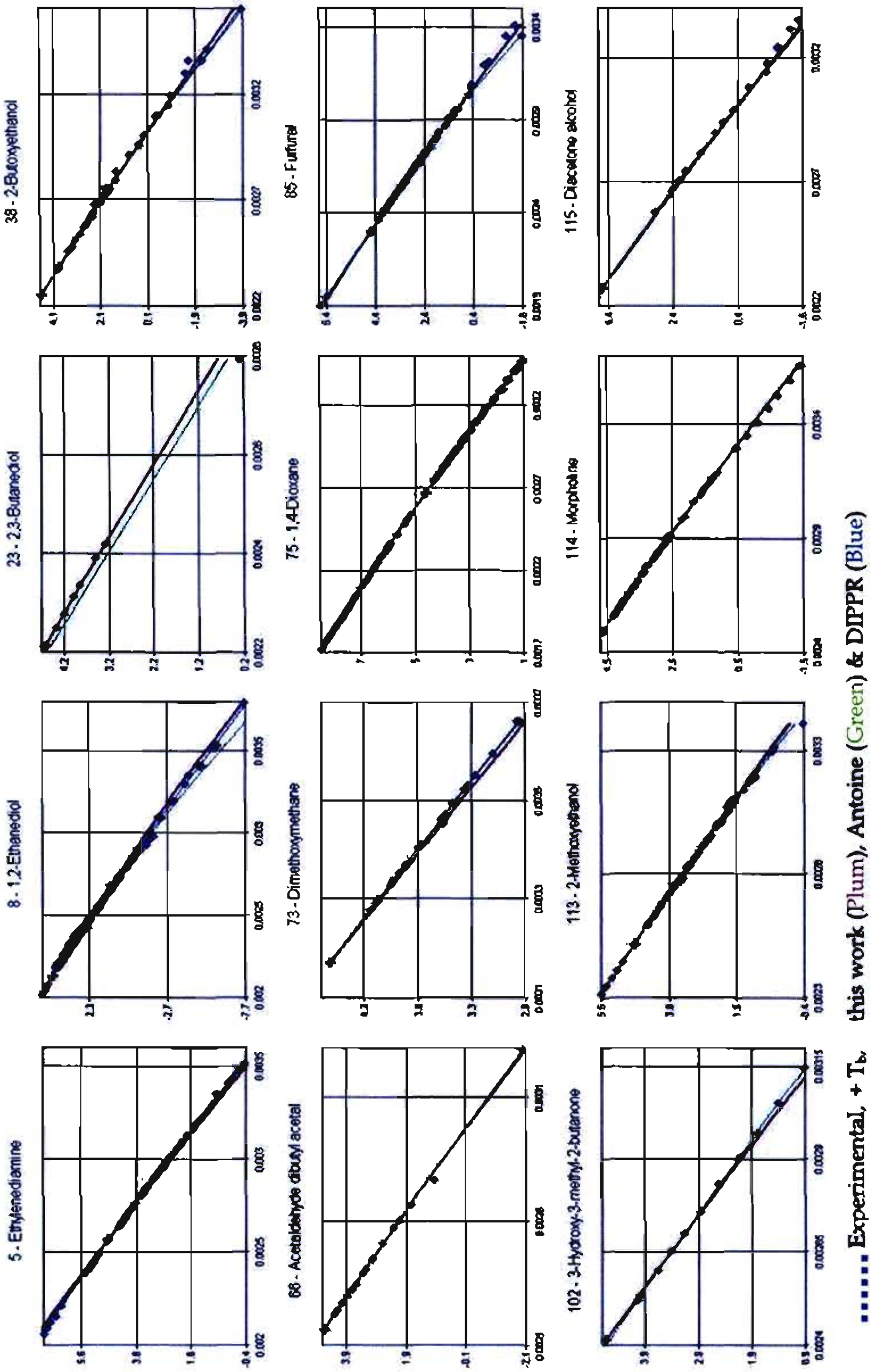


Figure 8-32: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for multi-functional compounds.

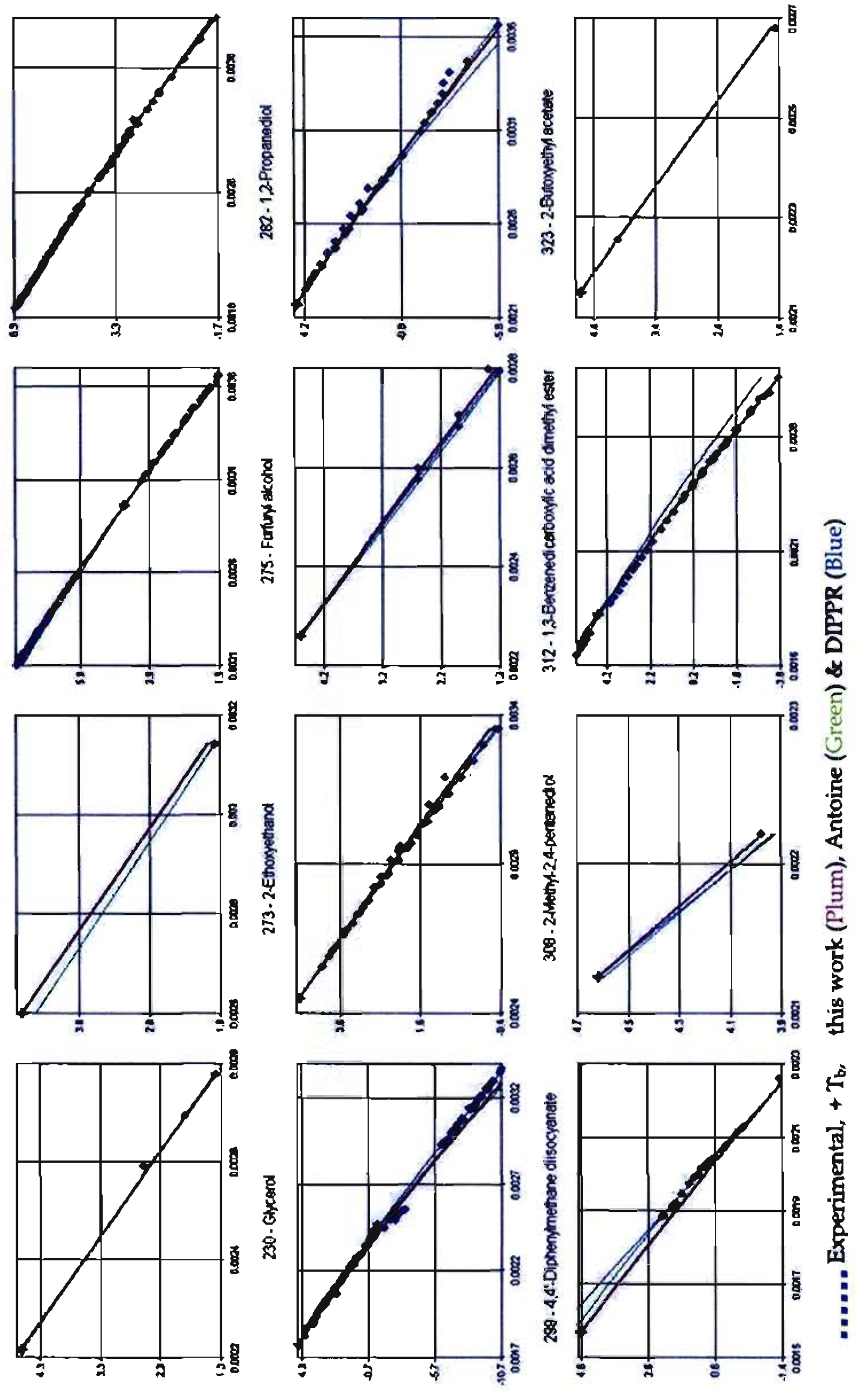


Figure 8-33: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for multi-functional compounds.

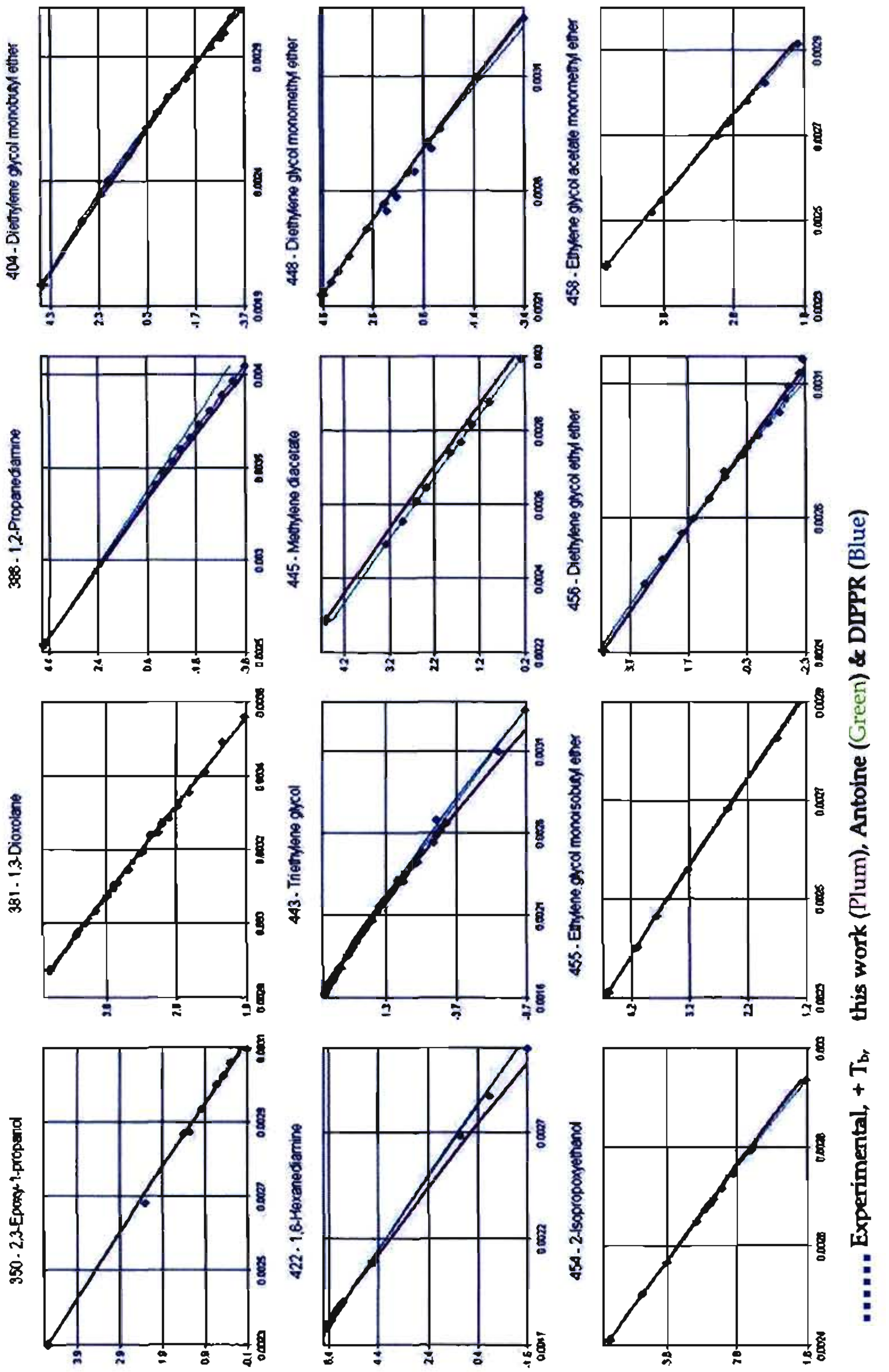


Figure 8-34: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for multi-functional compounds.

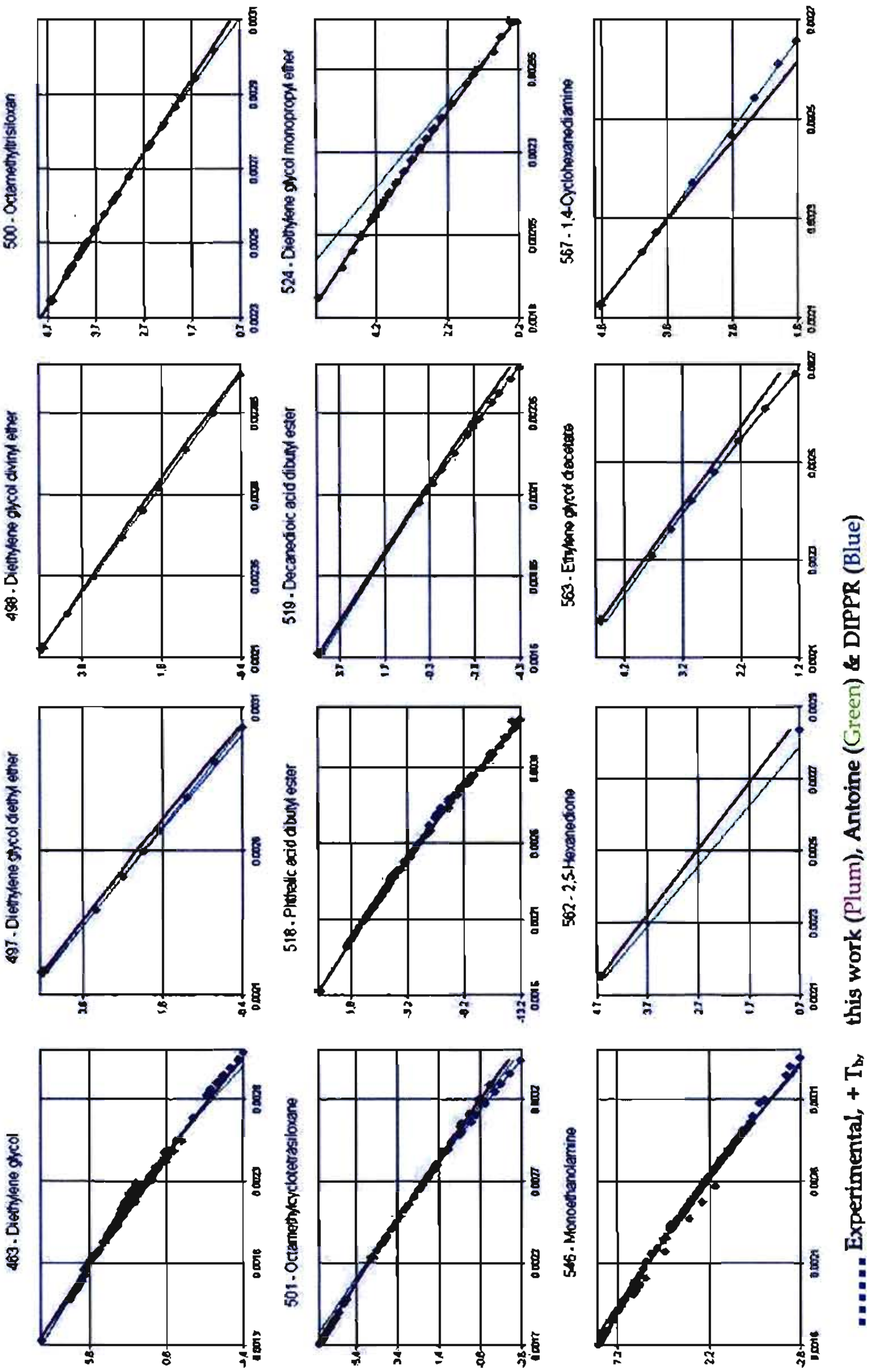


Figure 8-35: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for multi-functional compounds.

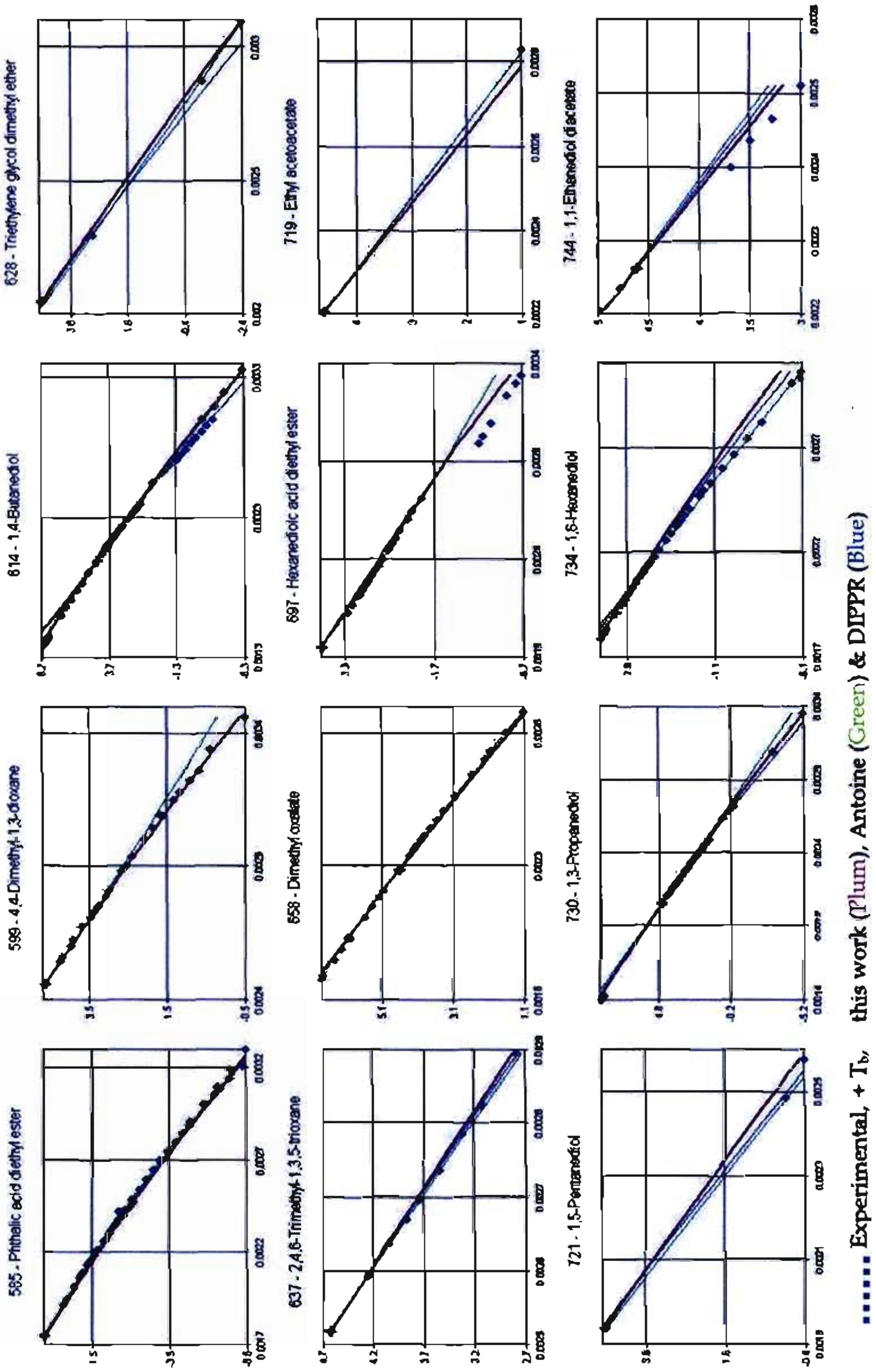


Figure 8-36: Multiple plot (Ln(P) vs. 1/T [K^{-1}]) of experimental and estimated liquid vapour pressures for multi-functional compounds.

8.5.4 Model Development

The development of a property prediction equation for the *dB* parameter led to a very simple result. Various other models were examined, but the linear model (Equation 8-8) proved to be the most accurate.

$$dB = \sum_{i}^{m} N_i C(dB)_i - 0.176055 \tag{8-8}$$

The reason is that there is a nearly linear relationship between the *dB* parameter and the heat of vaporisation or the total enthalpic interaction in the liquid phase. Except in the case of non-additive groups, this interaction depends more or less linearly on the number and type of interacting groups.

For the group contribution estimation of *dB*, the proposed method reported mean absolute percentage error of 112% for 1663 components. As *dB* represents only a small correction to the slope parameter *B*, Equation 8-2, the mean absolute percentage error of the B parameter is only 2.1%. This means that when estimating the vapour pressure of for example acetone, at a temperature 50 K below the normal boiling point, an error of only ±2.1% has to be expected. No high deviations (> 13%) were observed.

8.6 Overall Discussion

8.6.1 Overall Results

The most important feature of Equation 8-3 is that the parameters show very little intercorrelation. The new parameter *dB* (which describes the slope of the vapour pressure curve) does not depend significantly on the normal boiling point and on the pressure unit used. The value of *dB* only depends on the size and type of molecule. It is also directly related to the strength of the intermolecular forces between the molecules. The group contribution approach employed in this work has been shown to adequately estimate this parameter; while significant failures have not been observed.

The results for the estimation of vapour pressures for all data points from this work and correlative models are presented in Table 8-19. Overall, the proposed method yields results that are only slightly worse than the correlative models (direct correlation).

Table 8-19: Vapour pressure average absolute deviations of this work and correlative models for all compounds.

		Average Absolute Deviation (Number of data points as Superscript)				
	NC	**ELP**	**LP**	**MP**	**HP**	**AV**
This work (% kPa)	1663	40.4^{1030}	11.0^{20243}	2.8^{37615}	5.7^{11610}	6.2^{70498}
This work (K)	1663	3.1^{1030}	1.8^{20243}	0.8^{35952}	3.2^{11610}	1.6^{68835}
Antoine (% kPa)	1603	43.7^{1017}	7.6^{19929}	1.8^{37374}	4.8^{11607}	4.5^{69927}
DIPPR (% kPa)	818	26.1^{823}	7.2^{15904}	1.8^{28512}	1.9^{10143}	3.7^{55382}

8.6.2 Test of the Predictive Capability

To test the predictive capability of the vapour pressure estimation method, two test sets of data not used in the regression were prepared. Due to the inclusion of the model correction for mono-functional alcohol compounds, six components were removed from the regression set. These components constituted part of the first test set. From a total of 1982 data points from the different vapour pressure regions, the proposed method yielded an average relative deviation of 12.1% in the vapour pressure. This compares favourably with the deviation of all mono-functional alcohols listed in Table 8-5.

The second test set consisted of 396 components with a total of 1978 data points. This test set primarily consisted of components for which there were only a few data points usually in the low pressure region. Because of the insufficient means to verify these data, they were not added to the regression set except for functional groups where there were only a few or no components. For this set of components, the proposed method yielded an average relative deviation of 7.0% in the vapour pressure. This also compares favourably with the overall deviation listed in Table 8-19.

Both test sets yielded excellent results and the potential uncertainty that may arise from the extrapolation was shown to be minimal. The plots also presented in this chapter illustrate an excellent agreement between estimated and experimental vapour pressures. Even the worst cases showed only slight discrepancies in the slope.

The large number of vapour pressure data available in the DDB allowed regressing contributions for nearly all functional groups. However, a potential uncertainty for the proposed method may arise for groups for which there is only a single component and data from one source. As discussed in Chapter 7, a single point is sufficient for a group parameter, however, the parameter value is dependant on the quality of data.

A means to verify the group contribution value involves comparing the numerical value of the contribution to that for other groups that are of a similar chemical nature and which are based on a larger set of data. An analysis was performed on all these groups and most were found to be acceptable. For example, Germane with four carbon neighbours (ID - 86) has a value of 0.0485 which is quite similar to its stronger associating sister group Germane attached to three chlorines and one carbon (ID - 85 and value of 0.1869). However, two groups, a secondary amine (chain) attached to a carbon (or silicon) via double bond (ID - 91) and an interaction group Epox - Epox (ID - 187) revealed improbable contribution values. The parameters for these groups add some higher uncertainty when extrapolating, thus caution should be taken when estimating the vapour pressure curve, especially over a large temperature range.

The interaction parameters have on average a slightly higher contribution value than the first-order groups. In the case of missing interaction contributions, a value of zero may be used but larger errors may be observed when extrapolating over a large temperature range.

8.6.3 Normal Boiling Point Omission

Estimation of the vapour pressure curve using the proposed method requires estimation of the dB parameter and the availability and reliability of the normal boiling point. For an accurate estimation, the fixed point is of great importance; however this absolute value does not always have to be at the normal boiling point. From any single vapour pressure point, the normal boiling point can easily be calculated using Equation 8-3.

For the regression set of components employed in this work, the back calculation of the normal boiling point produced an average absolute deviation of 8.9 K for extremely low vapour pressures (*ELP*), 2.8 K for low vapour pressures (*LP*), 1.2 K for moderate pressures (*MP*), 2.7 K for high pressures (*HP*) and 2.1 K for all points. With the exception of the extremely low vapour pressure data, the reported deviation for the back calculation of the normal boiling temperature is well within the deviations in temperature presented in Table 8-19. Thus, a single vapour pressure point will be sufficient for the proposed estimation method.

The slightly higher deviations reported from estimation of vapour pressures, as well as the back calculation of the normal boiling point for extremely low vapour pressures (< 0.01 kPa) is mostly due to the lower quality of these data points. In this region measurements are subjected to higher systematic errors. It is also common for higher molecular weight or strong associating components to have vapour pressure points available only for this pressure region (no normal boiling points). As mentioned earlier, extrapolation from correlative models where the parameters are regressed for points within this region is often very unreliable. For example, the regression of Antoine parameters to five low vapour pressure points (0.00019 to 0.0067 kPa) for 1-methly naphthalene produced a vapour pressure at the normal boiling point (518.3 K) of 4 kPa. In fact, atmospheric pressure was attained at a temperature of 1980.0 K. When compared to the proposed method, the calculation of the normal boiling point by averaging the values obtained from the above low vapour pressure points reported an average absolute error of only 4.3 K.

If no experimental information is available, the normal boiling point can be estimated from the previous work, Nannoolal (2004) & Nannoolal *et al.* (2004). This method gave an average absolute deviation of 6.52 K for just more than 2800 components. Employing an estimated value instead of experimental will produce an offset error directly related to the estimation error. For this reason, a statistical analysis was not presented for the estimation of both the fixed point and slope.

If the estimated normal boiling point was employed for the current data set of 1663 components or 68835 data points, an average relative error of 27% was obtained. This estimation is based on only the molecular structure of the compound and currently no estimation method is available which can achieve these results and range of applicability.

8.6.4 Enthalpy of Vaporisation

The enthalpy of vaporisation can be calculated by differentiating Equation 8-3 with respect to the reciprocal temperature and substituting ΔH^V from Equation 3-15. Assuming $f\,(T, T_{rb}) = 0$, this leads to:

$$\Delta H^V = -(4.1012 + dB)\left[\frac{56T_b}{\left(\frac{T_b}{T} - 8\right)^2}\right] R\Delta Z^V \ln(10) \tag{8-9}$$

Note that since assuming $f\,(T, T_{rb}) = 0$, the above equation does not apply to mono-functional alcohols. ΔZ^V can be calculated via a corresponding states method using the critical temperature and pressure (Equation 8-10 (Haggenmacher (1946))).

$$\Delta Z^V = \left[1 - \frac{\frac{P}{P_c}}{\left(\frac{T}{T_c}\right)^3}\right]^{0.5} \tag{8-10}$$

For a set of 261 components or 2576 experimental data points obtained from the DDB, using Equation 8-9 with ΔZ^V from Equation 8-10, an average relative error of 2.5% in ΔH^V was found. This set of components does not include mono-functional alcohols and carboxylic acids. The latter type of compounds has a much lower ΔZ^V due to strong dimerisation in the vapour phase and the Haggenmacher corresponding states estimation of ΔZ^V cannot be used.

Assuming ΔZ^V=1, the proposed method can calculate ΔH^V usually up to the normal boiling point. For this calculation, an average relative error of 3.6% in ΔH^V for 1845 data points was found. An example calculation of ΔH^V was performed for acetone and the results are shown in Figure 8-37.

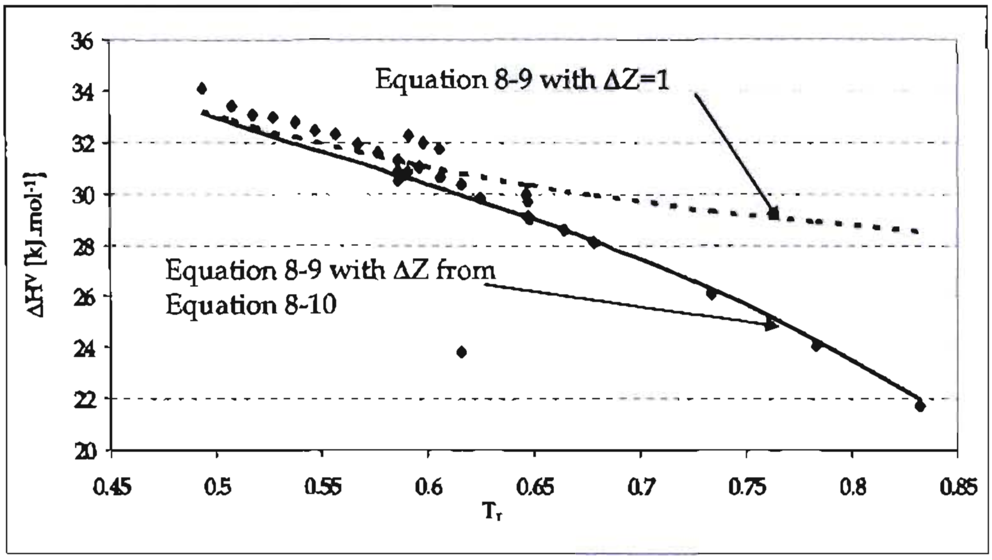


Figure 8-37: Plot of experimental and estimated ΔH^v for acetone.

8.6.5 Final Discussion

The DIPPR equation with 5 parameters yields the lowest average absolute deviation of all models in this comparison. However, the application of the model is limited as a minimum of five points is required to regress all parameters. If there are not enough data points of sufficient quality available to justify this number of parameters, some may be set to standard values.

As in the case of correlative models where data for only a single component are considered, the quality of the results depends strongly on the quality of the data for this component. This especially holds for the temperature dependence of vapour pressure. If data are only available in a limited temperature range and/or are of limited reliability, the regressed parameters can lead to large errors when extrapolating far outside the range of the data.

The method developed here is based on experimental data for a large number of components and was shown to reliably predict the temperature dependence of the pure component vapour pressure curve. Though a lower deviation is usually obtained from regression of single component data, use of the estimated slope together with experimental absolute values (vapour pressure data points) provides the most reliable results in most cases. This is supported by the good results for the estimation of heat of vaporisation data which were never used during the development of the method.

The basic parameters for example, CH_3 and CH_2, can be considered very reliable. Parameters for special groups which are based on only a few data points should be revised as soon as more experimental information becomes available. Missing group contributions can be added on future without the need to refit the existing parameters.

A further development of the method towards more complex molecules should proceed in a way similar to that developed for the liquid viscosity in Chapter 9. This would lead to the possibility to greatly extend both the boiling point and vapour pressure estimation methods using low vapour pressure data for liquids and solids. The latter data can be approximately corrected to hypothetical sub-cooled liquid vapour pressures using the melting temperature and heat of fusion[*].

---

[*] In case of data points far below the melting temperature, the difference in the heat capacities of subcooled liquid and solid as well as transition points need to be taken into account.

Chapter Nine

Estimation of the Saturated Liquid Viscosity Curve: Development, Results and Discussion

9.1 Introduction

Due to the importance of reliable information on liquid viscosity for many practical applications, many researchers have worked on this subject. The literature concerning liquid viscosity is therefore quite extensive. Many attempts have been made to correlate and estimate the viscosity of saturated or compressed liquids as function of temperature, pressure, and chemical constitution. As described in more detail in Chapter 4, theoretical approaches have not been successful and at present there is no theory available that allows the estimation of liquid viscosity within the required accuracy.

In addition, the various theoretical approaches described in Chapter 4 do not sufficiently link liquid viscosity to a set of molecular properties in a similar way as for example gas viscosity is linked to molecular cross-section, which itself can be expressed as function of collision energy (temperature). These approaches are therefore out of the scope of this work and will not be discussed any further. Besides an introduction to theoretical approaches, a detailed review of existing correlation methods as well as semi-empirical or empirical estimation approaches was also presented in the same chapter. Based on this knowledge, an improved approach to the estimation of liquid viscosity will be developed here.

Even though the mechanisms governing these properties are dissimilar, there are several similarities between the liquid viscosity and vapour pressure of a component:

- The energy required to remove a component from the liquid phase into the vapour phase or to break an existing structure of the liquid (in order to move liquid layers in opposite directions or with different velocity) is to a great part dependant on intermolecular attraction.

- The energy required for evaporation or displacement of liquid layers is supplied by the available thermal energy *RT*. Thus, both vapour pressure and viscosity approximately obey an equation of the form $f(T)=exp(A-B/T)$.

With increasing temperature, the vapour pressure increases while viscosity decreases. Thus volatility (vapour pressure) would better compare to fluidity (the reciprocal of viscosity).

Major dissimilarities affecting the development of estimation methods between liquid viscosity and vapour pressure lie in the availability and type of experimental information for both properties:

- For the temperature range employed in this work, there is less than a third of the amount of experimental data available for liquid viscosity as compared to vapour pressure. As a result, it was an advantage to develop a vapour pressure model before starting on liquid viscosity. Consequently, knowledge obtained from the development of the vapour pressure estimation method in the previous chapter will be important in this chapter. It was assumed that the same molecular properties determine, in different ways, vapour pressure and viscosity. Therefore, the exact same differentiation of structural groups that was required for vapour pressure estimation was also required for viscosity estimation.
- A large amount of vapour pressure data is available at a reference pressure of *1 atm* (the normal boiling temperature) providing a convenient reference point. Viscosity data are often available at 25°C. After several unsuccessful developments within this work it had to be concluded that a varying viscosity value at a fixed temperature is not a useful reference.

Vapour pressure data are needed for a variety of chemical engineering and thermodynamic calculations. These data are the main factor determining the distribution of a component between the liquid and vapour phase and therefore the key property for the design of distillation columns. Liquid viscosity data are needed for the design of fluid transport and mixing processes (pipes, pumps, stirred reactors, etc) which requires less accuracy of the calculated viscosity. Both the amount and quality of liquid viscosity data in literature is lower than for the case of vapour pressures. Available estimation methods for liquid viscosity are generally of poor quality.

This chapter will present the development of a new group contribution method for the estimation of liquid viscosity. The results will be compared to correlative models and in some cases, other group-contribution estimation methods.

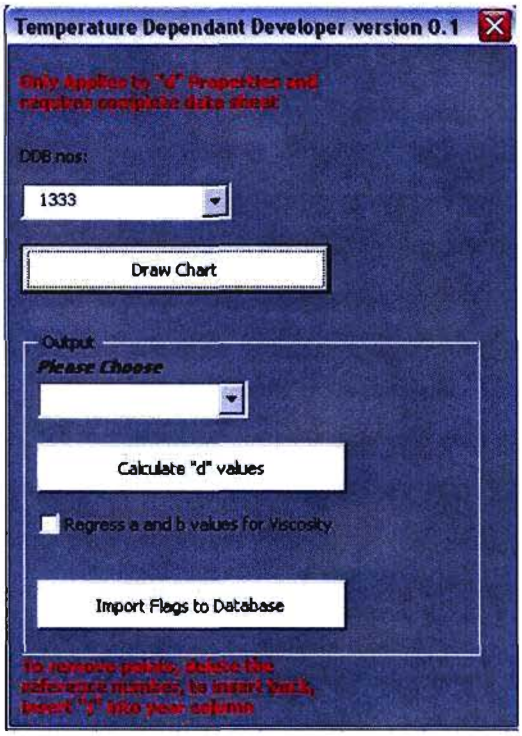
9.2 Data Verification

In the case of vapour pressures, data verification and reduction was the most tedious and time consuming part of the work. For liquid viscosity, the technique employed to verify data is identical to that used for vapour pressure (Section 8.4), but based on the experiences gained previously, the software was completely re-designed.

- Instead of storing the data and regression results for each component in a separate MS-Excel worksheet requiring several MS-Excel workbooks with up to 256 worksheets each, data sheets were always generated "on-the-fly" from data and regression results stored in a relational database (MS-Access).
- More extensive use of SQL (standard query language) for data retrieval, filtering and manipulation allowed more simple automation, flexibility and efficiency and at the same time less complex program code.
- MS-Excel was kept for the software "front-end" as it allows simple presentation of the data in tables and diagrams. Database features were accessed via DAO 3.6 (data access objects).

In the case of the new software, the results for each component are exported into an MS-Excel worksheet upon request for presentation and analysis (Figure 6-10). This is achieved by ticking the checkbox in the form presented in Figure 6-9. The advantage of this implementation is that the software is completely located in one MS-Excel file (which is the design file) and modifications can be implemented quite easily. The software can also be employed for the development of estimation methods for other temperature dependant properties.

The printout of each data point contains information about its reference. Another form has been designed to analyse these results, Figure 9-1. The form loads the component identification numbers (DDB ID) of all components for which data are available on start-up. By choosing a component, the command ('Draw Chart') filters out all data belonging to this component and groups them with respect to their references. A chart is then plotted with each reference having its own series (marker symbol). With the help of this chart, the data can be verified and flagged if found to be unreliable. The command ('Import Flags to Database') then stores the flags in the database using a unique index number for each point. Together with the multiple plot program which can be additionally employed to detect unreliable data, this method of data verification is more efficient as compared to the previous design (Section 8.4).


Temperature Dependant Developer version 0.1

Only Applies to "d" Properties and requires complete data sheet

DDB nos: 1333

Output

Please Choose

☐ Regress a and b values for Viscosity

To remove points, delete the reference number, to insert back, insert "y" into year column

Figure 9-1: Screen shot of the form employed to manage data verification.

9.3 Development of a Group Contribution Method for Estimating the Viscosity of Saturated Liquids

As discussed before, the development of the group contribution method for liquid viscosity data estimation is performed in a similar way as the in case of the vapour pressure estimation method.

9.3.1 First Approach: Group Contribution Regression of Andrade Parameters

For the vapour pressure estimation method, the first step was to develop a method for the normal boiling point. In the case of liquid viscosity data, no large data base with temperatures for a given viscosity value is available. A solution to this problem was the individual regression of the data for each component using suitable correlation equations with two parameters *A* and *B* representing the temperature at a reference viscosity and the slope of the $ln(\mu/\mu^r)$ vs. $ln(P/P^r)$ or $1/T$ curve. These parameters could then serve as a database for the development of the group contribution estimation method.

Following this idea, a first approach was to test a similar procedure as used by previous group contribution methods. This consisted of a group contribution estimation of the *A* and *B* parameters in Equations 4-8 (liquid viscosity as a function of vapour pressure) and 4-12 (liquid viscosity as a function of temperature). The regression employed was the multi-linear least squares fit for a simultaneous regression of both parameters, by substituting Equations 9-1 and 9-2 into the above two equations.

$$A = \sum_{i}^{m} v_i a_i \tag{9-1}$$

$$B = \sum_{i}^{m} v_i b_i \tag{9-2}$$

As with the previous methods in this work, model development involved regressing group contributions for the different structural groups, group interactions and corrections. But it became clearly evident after regressions of a few homologous series that this approach was not feasible. In the case of Equation 4-8 the parameters did not correlate well with the functional groups. This can also be observed in Figures 4-11 and 4-12. For Equation 4-12, an improved correlation of the parameters with respect to chemical constitution was observed. However, the estimation of the liquid viscosity only proved to be accurate for a few homologous series (such as n-alkanes). This was also observed for the Van Velzen method (Van Velzen *et al.* (1972)) where the parameters intercorrelated and difficult to regress by group contribution.

Due to this strong intercorrelation, it was difficult to gain reliable information about the behaviour of A and B within a homologous series. The assumption of linearity (Equations 9-1 and 9-2) is probably not valid and was a further reason for the failure of this approach.

The main reason lies quite obviously in the generally low quality of the data and the need to extrapolate to a reference viscosity temperature. Small errors in the slope resulted in a huge scatter of the regressed temperatures.

9.3.2 Evaluation of Alternatives

For the development of a group contribution estimation method, three alternative approaches were evaluated:

1. Simultaneous regression of all group contributions to all experimental data. While this procedure requires the least effort, it has the disadvantage that low quality or erroneous data are difficult to identify.
2. Group contribution regression of the reference temperatures from the individual regressions. Regression of only the slope for each component using the estimated reference temperature for all components. Group contribution regression of the newly regressed slopes.
3. Group contribution regression of the slopes from the individual regressions. Regression of only the reference temperature for each component using the

estimated slope for all components. Group contribution regression of the newly regressed reference temperature.

It can be expected that similar to the case of vapour pressures slopes (the change with temperature) can be more reliably estimated than the absolute value (reference temperature). For this reason procedure (3) should be safer than procedure (2).

An additional complication is caused by the fact that the logarithm of the viscosity vs. reciprocal temperature does not obey a strictly linear relationship and in most cases the data quality does not justify the use of a third parameter. Therefore the first regression of the data for each component was performed using a simple linear function if extrapolation of the reference temperature was required.

Instead of the simple Andrade equation, a modified equation with a more convenient reference point was used. By introducing a reference viscosity point, $\mu_v = 1cP$ and the viscosity reference temperature (T_v) at this point into the Andrade equation (Equation 4-5) Equation 9-3 was derived. This equation is identical to that employed by Van Velzen *et al.* (1972) ($B = dBv$ (slope parameter)).

$$\ln\frac{\mu}{\mu_v} = dBv\left[\frac{1}{T} - \frac{1}{T_v}\right] \qquad (9\text{-}3)$$

9.3.3 Model Development

The procedure used for the development of the final method is given in Figure 9-2. In the first step, a regression of the experimental data using a suitable equation was performed in order to find a reliable reference temperature. The reference viscosity was arbitrarily set to a value of $\mu_v = 1.3\ cP$, which is close to the mean value of all available experimental data.

If the reference viscosity value was within the temperature range of data, either the Andrade or Vogel equations were employed for interpolating. If the reference viscosity value was outside the temperature range of the available data, extrapolation was required. As the Vogel equation often extrapolated poorly, Equation 9-3 was usually employed. The Vogel equation was only used in cases where the extrapolation yielded a realistic value.

It became apparent that for a better representation of liquid viscosities, a slight curvature would have to be modelled. As for the case of vapour pressures, the Vogel Equation 4-6 (having the same form as the Antoine equation) was used and the third parameter was linked to the reference temperature as a convenient reference point:

$$C \approx -\frac{T_v}{s} \qquad (9\text{-}4)$$

with T_v - viscosity reference temperature (K)

In case of vapour pressure estimation, a value of *s=8* was used. From the numerous investigations and optimisations of the viscosity model, a value of *s=16* produced the most accurate result. Rearranging the Vogel equation with the third parameter from Equation 9-4 into a similar form as Equation 9-3 yields the following expression:

$$\ln\left(\frac{\mu}{1.3cP}\right) = -dBv\left(\frac{T - T_v}{T - \frac{T_v}{16}}\right) \qquad (9\text{-}5)$$

Equation 9-5 is the final model employed in this work to estimate the liquid viscosity.

Equations 8-3 and 9-5 are similar and in the case of the former model, the slope parameter varied only slightly with the size and type of the molecule.

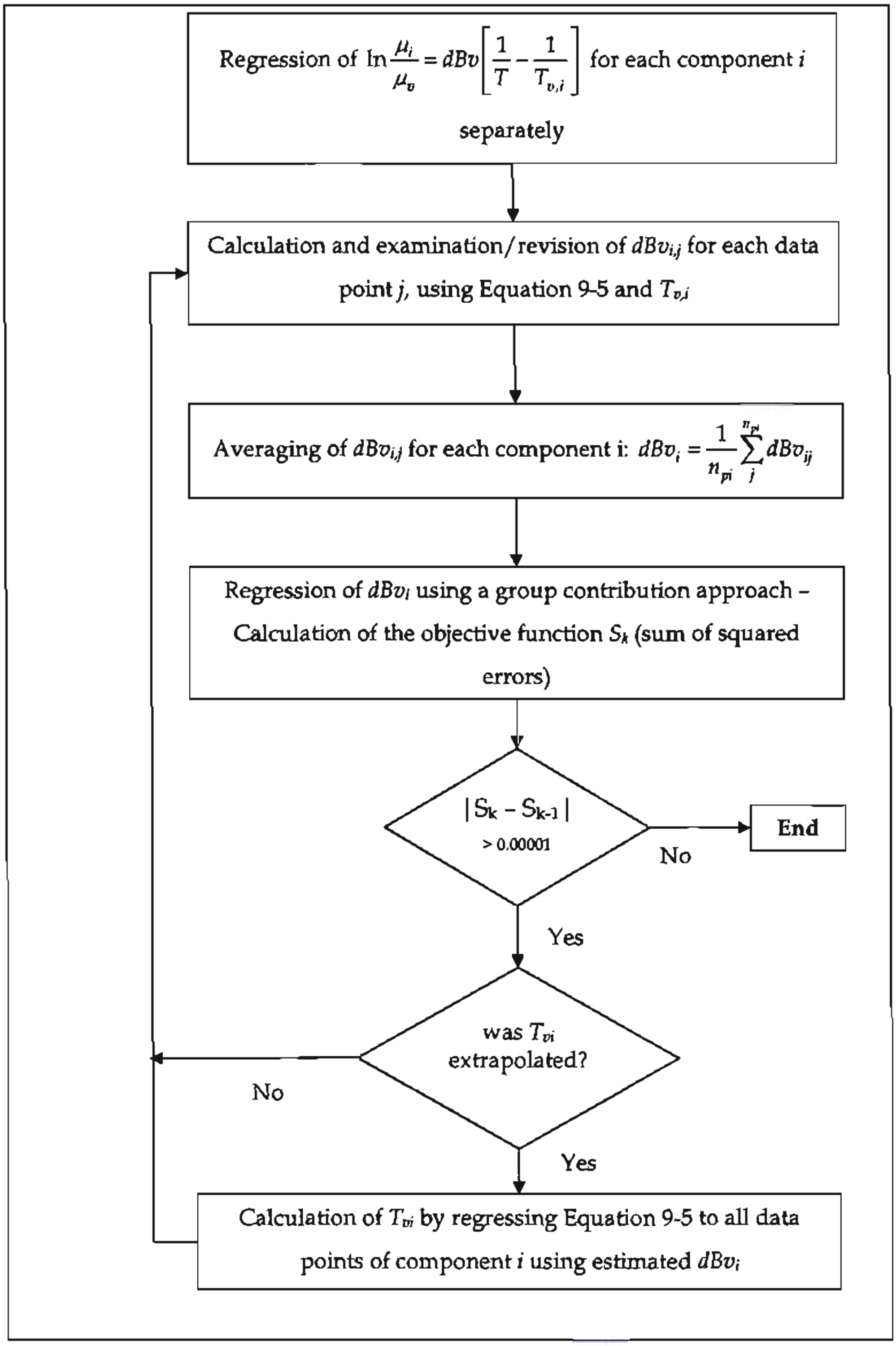


Figure 9-2: Flow diagram of the procedure employed to manage data verification.

Using the reference temperatures derived for each component, *dBv* values were calculated for each data point and carefully examined and revised. The reliable *dBv* values for each component were then averaged and regressed using the group contribution approach:

$$dBv = \frac{\sum_{i}^{m} N_i C(dBv)_i}{n^a + b} + c \qquad (9\text{-}6)$$

The values of *a*, *b* and *c* were optimised by nonlinear regression minimising the sum of squared errors (RMSD).

In cases where extrapolation was required, the reference temperatures were again derived from the experimental data by regression using Equation 9-5. In this case, the fitting routine employed extremely small step widths in *dBv* while also crucially constraining and damping the parameter after consecutive iterations. The idea behind this is to have the starting value of *dBv* for the regression of T_v estimated by group contribution. After consecutive iterations the damping was reduced, otherwise the regression would lead to the same values.

Using the new reference temperatures, new *dBv* values could be calculated for each data point. Averaging and regression of group contribution parameters lead to a significantly improved estimation method. This procedure was repeated until no significant change in the group contributions was observed between consecutive iterations. The final values of the constants for Equation 9-6 are:

$a = -2.5635$
$b = 0.0685$
$c = 3.7777$

In the last step, a group contribution method for the estimation of reference temperatures was developed.

Out of the many functional relationships evaluated to calculate the reference temperature from the sum of group contributions, one proved especially successful. It employs the sum of group contributions $\sum_{i}^{m} N_i C(T_v)_i$, the normal boiling temperature T_b and the number of atoms in the molecule (except hydrogen) *n*, Equation 9-7.

$$T_v = aT_b^{0.5} + \frac{\left(\sum_{i}^{m} N_i C(T_v)_i\right)^b \cdot 1K}{n^c + d} - e \tag{9-7}$$

with a = 21.8444 $K^{½}$
b = 0.9315
c = 0.6577
d = 4.9259
e = 231.1361 K

In Equation 9-7 the first two terms show a strong intercorrelation. For this reason, Equation 9-8 was regressed first to obtain the parameter *a* and the exponent for the normal boiling point term. These values were then set constant in the regression of the parameters in Equation 9-7. After successful regression of the constants and group contributions a further regression was performed varying also the value of a. This final regression led to another slight improvement.

$$T_v = aT_b^b + c \tag{9-8}$$

When estimating liquid viscosities, estimation of the reference temperature should only be used if no reliable data point for a component is available. Otherwise the reference temperature can be calculated from the experimental data and the estimated value of *dBv*. The latter property estimation method is generally more reliable than the estimation of T_v.

9.4 Results and Discussion

9.4.1 Hydrocarbon Compounds

Previous group contribution methods for the estimation of liquid viscosities required knowledge of only the molecular structure and have proven to be of low reliability. For this reason, the proposed method will be compared to correlative models such as the Andrade and Vogel models instead. The latter two models are almost always employed to estimate and correlate viscosity data for the applicable temperature range employed in this work.

As with the vapour pressure method, the calculated viscosity reference temperature is included as a point in the results for all models. The correlation values for the Vogel equation were taken from DDB (parameters were regressed where no values were available). However, as the Andrade parameters were important in the early part of this development, the Andrade correlative parameters were regressed to the current data set.

Results are, as in the preceding chapter, presented mainly in graphical form. A plot for a particular component includes the estimated slope and calculated reference temperature as well as the correlative models. In addition, another curve was included where both slope and reference temperature was estimated.

In order to be able to judge the quality of the group contribution parameter regression, relative mean deviations in liquid viscosity are reported for the different pressure ranges defined in Chapter 8. In this case, the temperature of a viscosity point is converted to the corresponding vapour pressure by means of the method presented in Chapter 8. Since there were only a few points at high vapour pressures (> 500 kPa), this range (HP employed in the previous chapter) has been merged into the moderate pressure range (MP).

For the group contribution estimation of the *dBv* parameter and the viscosity reference temperature, the group definition, description, identification number (ID), priority (PR) and examples, for first-order groups and second-order corrections can be found in

Tables B-1 and B-2 in Appendix B, respectively. The groups employed are the same as for critical properties and vapour pressure. A quality analysis, which will be shown in the following sections, showed that no changes in the structural groups were required. The group, correction and interaction contributions are presented in Tables C-13, C-14 and C-15 for *dBv* and Tables C-16, C-17 and C-18 for the viscosity reference temperature in Appendix C. For the proposed method, a detailed procedure is provided for the calculation of liquid viscosity for one component in Tables D-5 in Appendix D.

The development of the proposed group contribution model for the estimation of liquid viscosities started with the regression of n-alkane viscosities. In the first regression, data were verified to allow model development to start from a 'clean' set of data. Subsequent regressions revealed an excellent representation of the *dBv* parameter by group contribution. A series plot for the liquid viscosity estimation in case of n-alkanes is presented in Figure 9-3. For all compounds, the estimations from this work are in excellent agreement with the experimental data. The estimation of the slope shows no variance with increasing molecular weight and can be assumed to extrapolate correctly with respect to chemical constitution. The close proximity of the higher molecular weight curves also suggest that the change in viscosity between consecutive members in the series is decreasing.

A multiple plot of twelve cyclic alkane compounds is presented in Figure 9-4. The proposed method yielded an excellent representation of the temperature dependence. This means that the difference between the experimental and estimated curves is more or less independent of temperature and a convenient measure of the deviation could be:

- The approximately constant ratio of estimated and calculated viscosities or the difference in the logarithms.
- The difference in reference temperature.

Due to the similarities between the viscosity and vapour pressure discussed previously, as in the case of vapour pressure estimation, the mean temperature difference between experiment and estimation for the same experimental viscosities is reported with each diagram. It can be expected that mean temperature errors for both properties should be of similar magnitude.

Higher deviations were observed for cyclohexane and cis-decahydronaphthalene. These deviations are not untypical for smaller molecules like cyclohexane consisting solely of one type of structural group. In the case of cis-decahydronaphthalene, this component shows a very peculiar structure compared to the trans- form and the method contains no correction for the cis- and trans- forms. Nevertheless, even these deviations are well below 20 K.

As smaller compounds do not follow the trend of other members in a homologous series, ethane and benzene were removed from the regression set.

A multiple plot for twelve alkene and twelve aromatic compounds is presented in Figures 9-5 and 9-6, respectively. The proposed method yielded an excellent representation of the experimental data, also in case of components where the reference temperature was optimised (1-octene in Figure 9-5). This confirms the validity of the optimisation procedure described earlier. Furthermore, the correlative models sometimes yield erroneous extrapolations especially in the case of the Vogel equation.

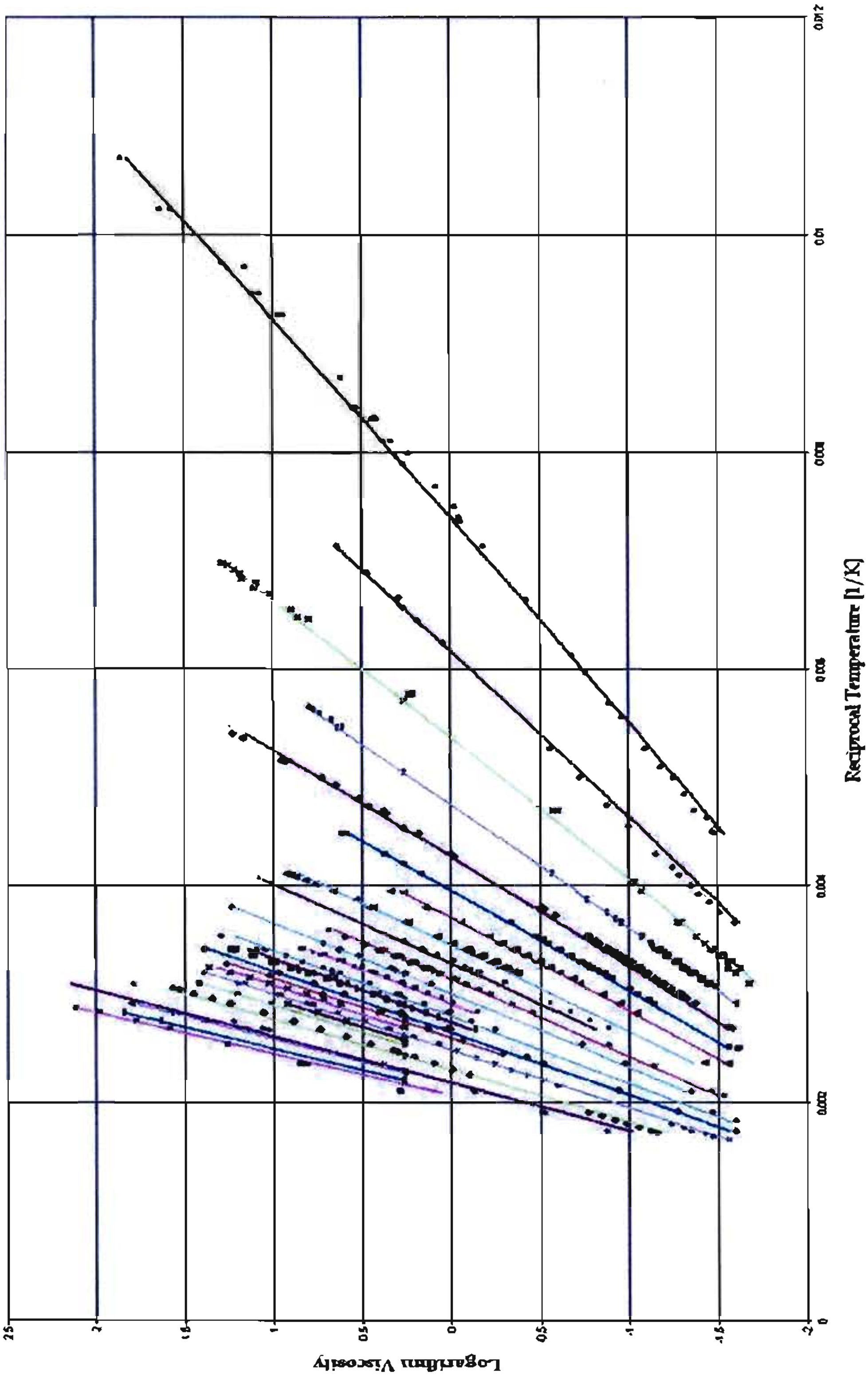


Figure 9-3: Series plot of experimental and estimated liquid viscosities for n-alkanes using adjusted reference temperatures.

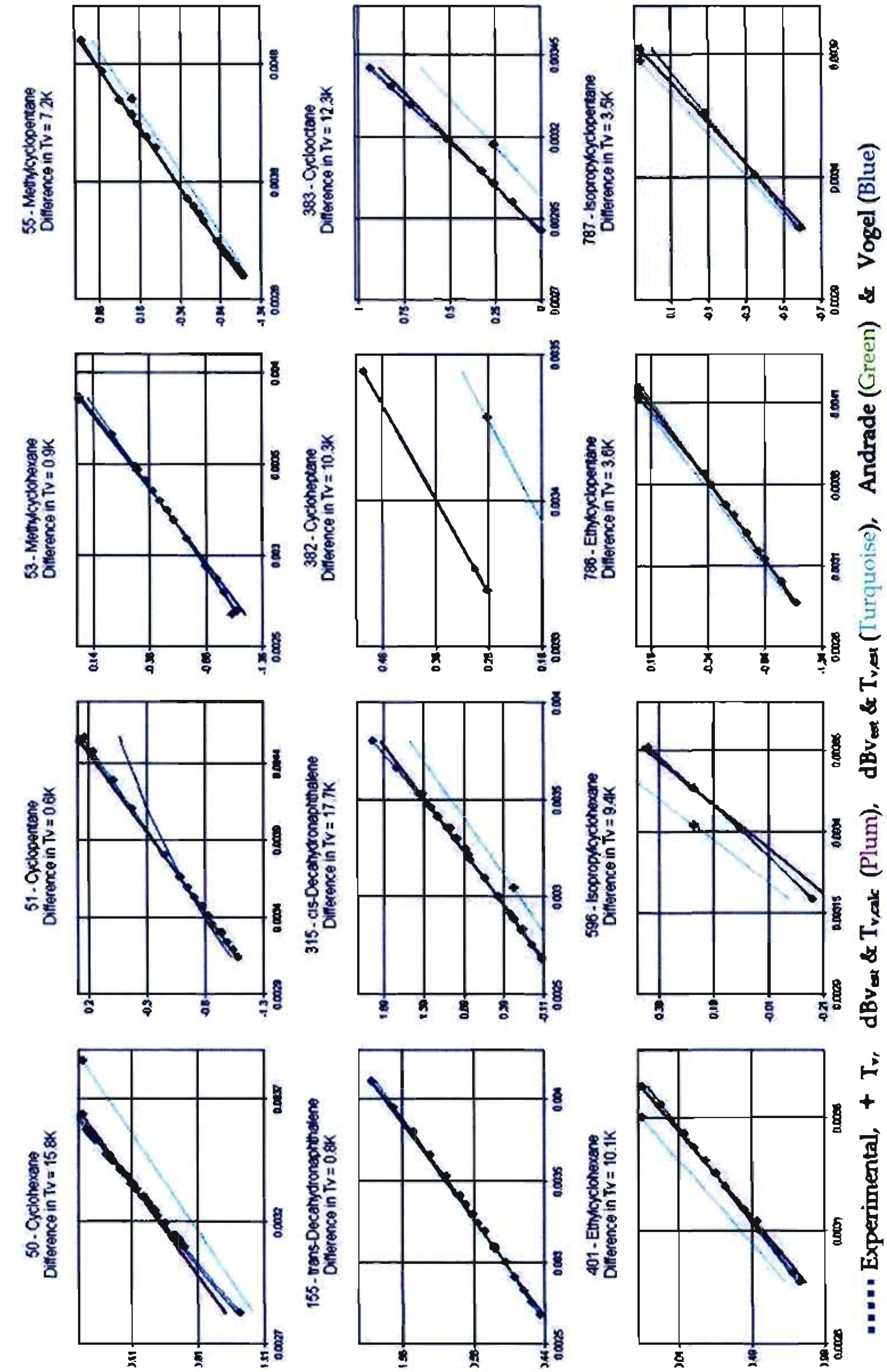


Figure 9-4: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for cyclic alkanes.

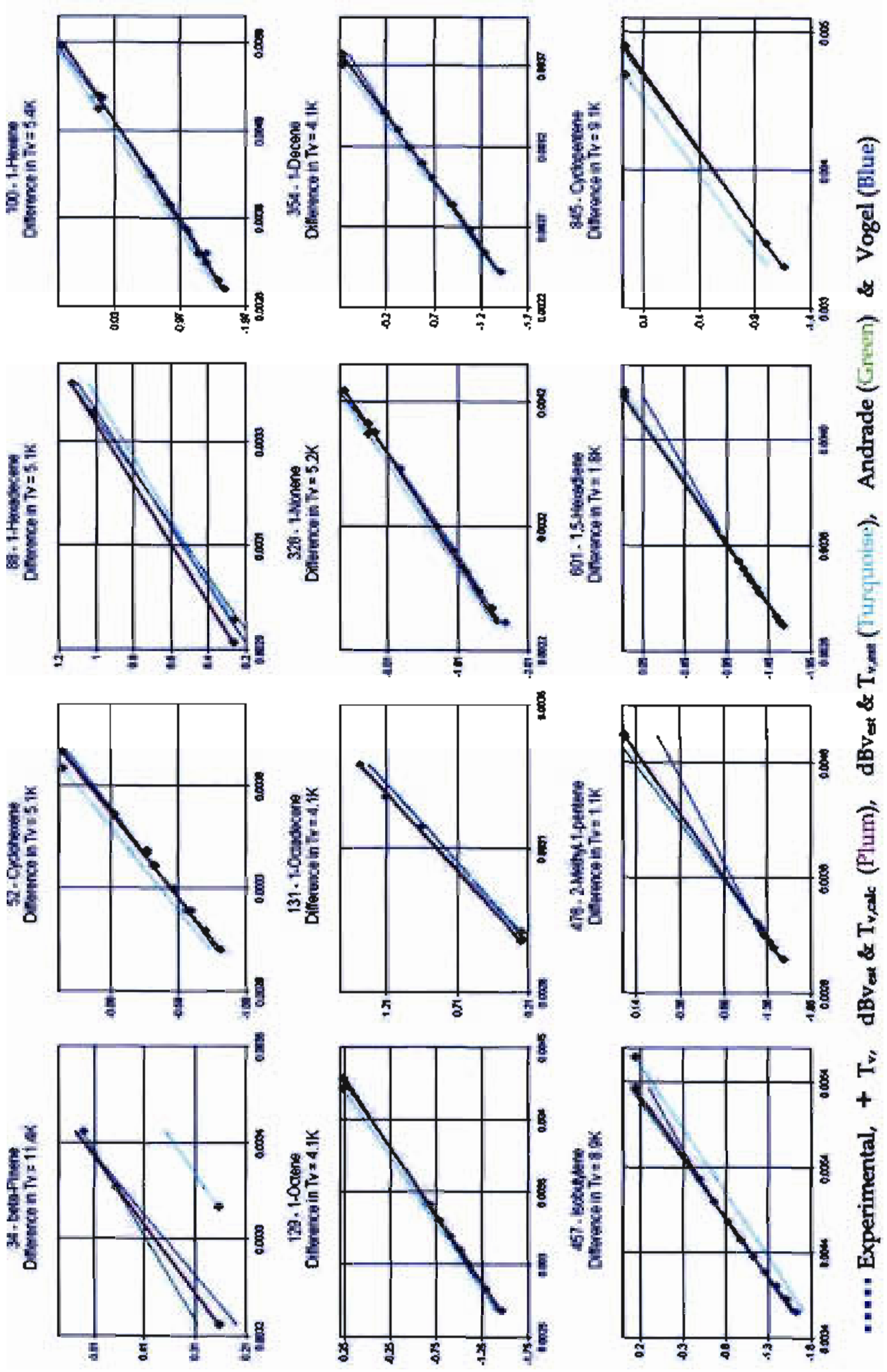


Figure 9-5: Multiple plot (Ln (μ) vs. 1/T [K⁻¹]) of experimental and estimated liquid viscosities for alkenes

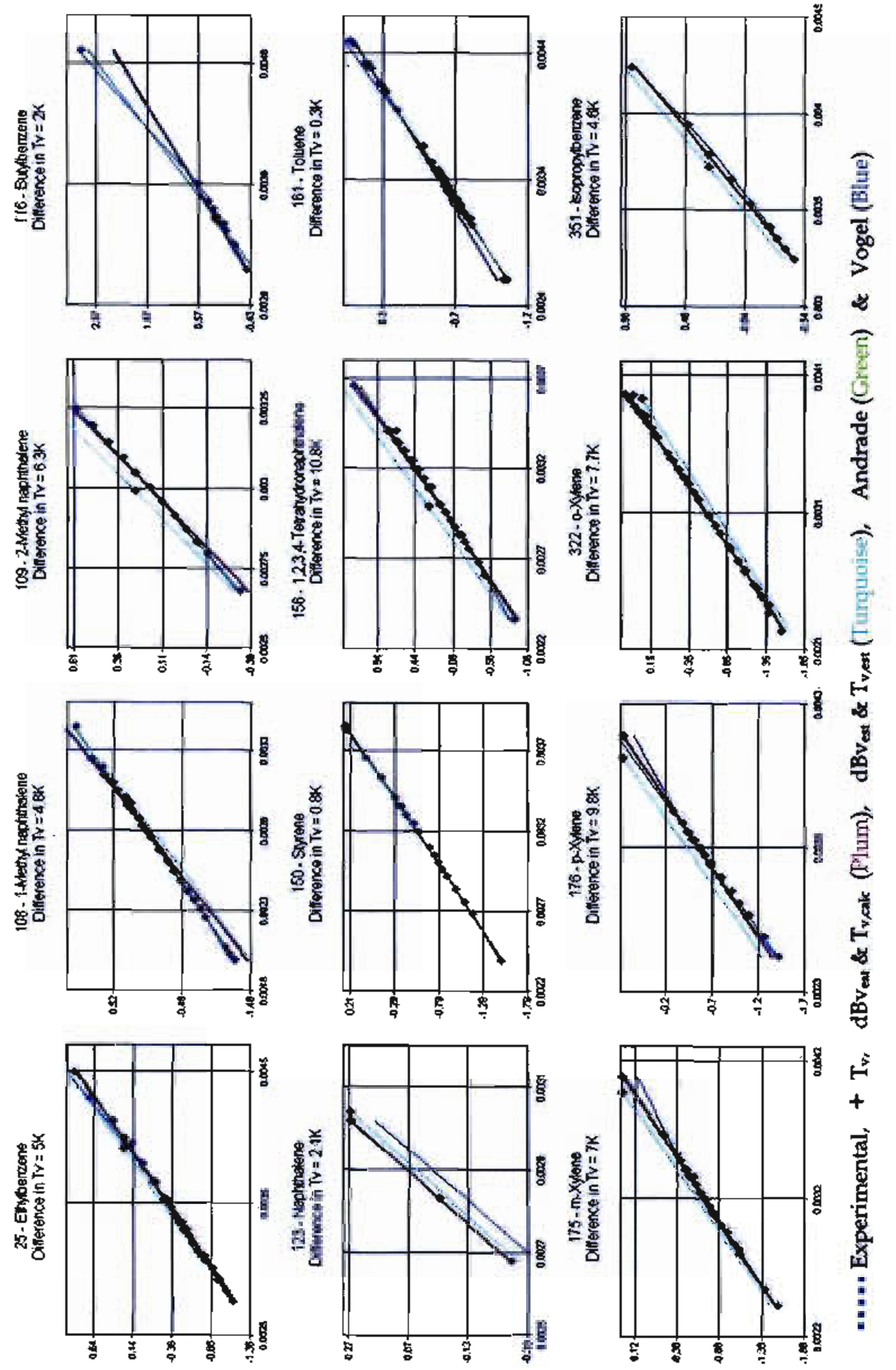


Figure 9-6: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for aromatic compounds

Detailed results for the different types of hydrocarbons for both the proposed method and the correlative models are presented in Tables 9-1 and 9-2, respectively. The proposed method yields consistent and accurate set of results for the different classes of hydrocarbons and only slightly higher deviations than the direct correlation.

For n-alkanes, a plot of the 'experimental' (interpolated or adjusted) and estimated viscosity reference temperature is presented in Figure 9-7. Larger errors are observed for the smaller molecules which do not follow the trend of the other members of the series. However, the proposed method demonstrates an excellent representation of the data and can be assumed to extrapolate correctly. For all hydrocarbon compounds, there were no deviations larger than 20K.

Table 9-1: Viscosity average absolute deviations of this work for the different types of hydrocarbons (number of data points as superscript).

		Average Absolute Deviation (%)				**T_v**		
	NC[*]	**ELP**	**LP**	**MP**	**AV**	**NC**	**AAD**	**MAPE**
Hydrocarbons (HC)	147	5.1^{320}	3.0^{1662}	2.7^{877}	3.1^{2859}	147	6.3	2.4
Saturated HC	91	4.9^{280}	2.5^{930}	2.7^{628}	3.0^{1838}	91	6.5	2.5
Non-aromatic HC	113	4.8^{289}	2.5^{983}	2.6^{739}	2.8^{2011}	113	6.3	2.5
Unsaturated HC	22	1.5^{9}	2.1^{53}	1.6^{111}	1.7^{173}	22	5.6	2.7
n-Alkanes	25	4.2^{251}	2.4^{536}	1.7^{277}	2.6^{1064}	25	4.2	1.5
Alkanes (non-cyclic)	63	4.9^{276}	2.7^{714}	3.3^{434}	3.3^{1424}	63	5.7	2.3
Alkanes (cyclic)	28	6.7^{4}	2.0^{216}	1.4^{194}	1.7^{414}	28	8.3	3.0
Aromatic HC	34	7.9^{31}	3.6^{679}	3.5^{138}	3.8^{848}	34	6.4	2.0
Fused aromatic HC	8	11.2^{2}	2.8^{93}	4.2^{64}	3.5^{159}	8	5.3	1.4
Alkenes HC	18	1.5^{9}	1.6^{45}	1.8^{81}	1.7^{135}	18	6.1	2.9
Alkenes (cyclic HC)	3	-	1.7^{7}	0.7^{13}	1.0^{20}	3	11.1	5.1
Alkynes HC	2	-	5.6^{7}	1.5^{7}	3.6^{14}	2	5.7	2.4

---

[*] All abbreviations throughout this chapter will follow these definitions (will not be repeated again): NC - Number of components, ELP (extremely low pressure) - P < 0.01kPa, LP (low pressure) - 0.01kPa >= P =< 10kPa, MP (medium to higher pressure) - P > 10kPa, AAD - Average absolute deviation (K), MAPE - Mean absolute percentage error (%).

Table 9-2: Viscosity average absolute deviations (%) of the Andrade and Vogel models for the different types of hydrocarbons (number of data points as superscript).

	Average Absolute Deviation (%)									
	Andrade					Vogel				
	NC	ELP	LP	MP	AV	NC	ELP	LP	MP	AV
Hydrocarbons (HC)	147	2.6^{320}	1.1^{1662}	1.5^{877}	1.4^{2859}	147	4.6^{320}	3.3^{1662}	3.4^{877}	3.5^{2859}
Saturated HC	91	2.4^{280}	1.0^{930}	1.5^{628}	1.4^{1838}	91	2.7^{280}	3.5^{930}	3.4^{628}	3.4^{1838}
Non-aromatic HC	113	2.4^{289}	1.0^{983}	1.5^{739}	1.4^{2011}	113	2.9^{289}	3.4^{983}	3.5^{739}	3.4^{2011}
Unsaturated HC	22	1.5^{9}	0.8^{53}	1.9^{111}	1.5^{173}	22	7.1^{9}	2.2^{53}	4.3^{111}	3.8^{173}
n-Alkanes	25	2.2^{251}	1.0^{536}	1.2^{277}	1.3^{1064}	25	2.9^{251}	1.9^{536}	3.8^{277}	2.6^{1064}
Alkanes (non-cyclic)	63	2.3^{276}	1.0^{714}	1.7^{434}	1.5^{1424}	63	2.8^{276}	3.8^{714}	4.2^{434}	3.7^{1424}
Alkanes (cyclic)	28	7.5^{4}	1.0^{216}	0.9^{194}	1.0^{414}	28	0.4^{4}	2.4^{216}	1.7^{194}	2.1^{414}
Aromatic HC	34	4.7^{31}	1.3^{679}	1.7^{138}	1.5^{848}	34	20.5^{31}	3.0^{679}	2.8^{138}	3.6^{848}
Fused aromatic HC	8	7.3^{2}	1.7^{93}	1.8^{64}	1.8^{159}	8	11.3^{2}	2.8^{93}	2.5^{64}	2.8^{159}
Alkenes HC	18	1.5^{9}	0.8^{45}	2.0^{81}	1.6^{136}	18	7.1^{9}	2.5^{45}	5.3^{81}	4.5^{135}
Alkenes (cyclic HC)	3	-	1.2^{7}	1.9^{13}	1.6^{20}	3	-	1.2^{7}	7.7^{13}	5.4^{20}
Alkynes HC	2	-	0.6^{7}	4.0^{7}	2.3^{14}	2	-	0.4^{7}	0.9^{7}	0.7^{14}

The results reported for the viscosity reference temperature show higher deviations for cyclic alkanes, aromatics and the smaller molecules. Thus, some mention must be made about the molecular rotational symmetry number of a compound.

The molecular symmetry number is the number of ways a molecule can be oriented by rotating about its centre of mass up to 360° in each of the two spherical angles. By arbitrarily denoting one position as a reference orientation, the number of orientations that are identical to the reference orientation is the rotational symmetry number. This number is a prominent factor for properties of solid compounds. This is because molecules in this phase are restricted to a single conformation but can adopt a variety of conformations in the liquid. This will be discussed more in detail in Chapter 11.

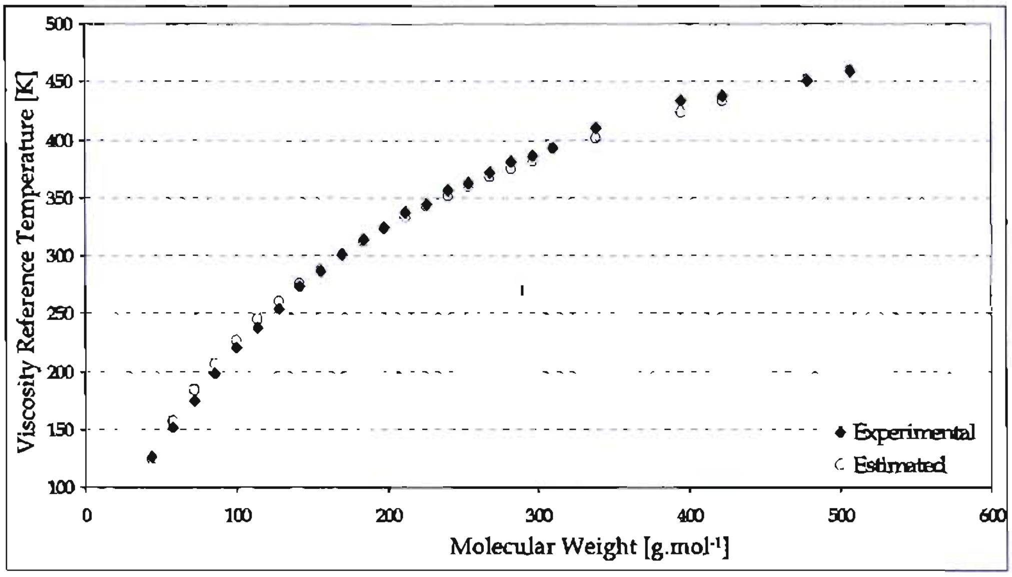


Figure 9-7: Plot of adjusted and estimated viscosity reference temperatures for n-alkanes.

Cyclooctane has a viscosity reference temperature of 327.0 K with a rotational symmetry of 8. Eleven isomers of this compound have an average reference temperature of 264.8 K with a highest rotational symmetry of 2. In addition, the difference between the reference temperature for cyclooctane and the isomer with the highest temperature is 33.7 K. Cyclohexane and methylcyclopentane with a rotational symmetry of 6 and 1, respectively, show a difference of 46.2 K with the former compound having the higher reference temperature.

A possible interpretation of this behaviour could be that higher symmetry of the molecules decreases the entropy difference between disordered liquid and larger crystal-like associations and thus favours the existence of these associates. This would lead to the observed increase in viscosity.

Due to the difficulties in deriving the symmetry of molecules from the molecular structure by an automated algorithm, this effect was not included in the current estimation method for liquid viscosity.

The results for components where steric corrections were used to account for cumulated branching and isomeric effects for the proposed method and the correlative models are presented in Tables 9-3 and 9-4, respectively. As with vapour pressures, the added strain, to some extent, influences the activation energy of the molecules. There were no data to regress for the $C_3C\text{-}CC_3$ steric.

Table 9-3: Viscosity absolute average deviations of this work for the branched hydrocarbons (number of data points as superscript).

	Average Absolute Deviation (%)					**T_v**		
	NC	**ELP**	**LP**	**MP**	**AV**	**NC**	**AAD**	**MAPE**
$(C,C=)C\text{-}CC_3$	3	-	5.6^{11}	2.9^{5}	4.7^{16}	3	9.1	2.3
$C_2C\text{-}CC_2$	18	6.7^{4}	3.6^{139}	0.7^{24}	3.3^{167}	18	8.3	2.8
$C_3C\text{-}CC_2$	4	-	1.1^{15}	0.6^{10}	0.9^{25}	4	9.6	3.6

Table 9-4: Viscosity absolute average deviations (%) of the Andrade and Vogel models for branched hydrocarbons (number of data points as superscript).

	Average Absolute Deviation (%)									
	Andrade					**Vogel**				
	NC	**ELP**	**LP**	**MP**	**AV**	**NC**	**ELP**	**LP**	**MP**	**AV**
$(C,C=)C\text{-}CC_3$	3	-	1.6^{11}	3.7^{5}	2.2^{16}	3	-	0.9^{11}	4.0^{5}	1.9^{16}
$C_2C\text{-}CC_2$	18	7.5^{4}	2.2^{139}	4.0^{24}	2.6^{167}	17	0.4^{4}	1.5^{132}	7.0^{23}	2.3^{159}
$C_3C\text{-}CC_2$	4	-	0.2^{15}	2.3^{10}	1.0^{25}	4	-	0.4^{15}	2.6^{10}	1.3^{25}

9.4.2 Mono-functional Compounds

9.4.2.1 Oxygen Compounds

Results for the different types of alcohol compounds for both the proposed method and the correlative models are presented in Tables 9-5 and 9-6, respectively. All deviations are in a similar order of magnitude as in case of the vapour pressure estimation method.

For alkane diols, the results from the graphical analysis also confirm the reference temperature estimation algorithm presented earlier. For all compounds, the viscosity reference temperature was optimised and there is a good agreement between estimated and experimental data.

Table 9-5: Viscosity average absolute deviations of this work for the different types of oxygen compounds (number of data points as superscript).

	Average Absolute Deviation (%)					T_v		
	NC	ELP	LP	MP	AV	NC	AAD	MAPE
1-Alcohols	16	4.8^{133}	6.4^{610}	2.1^{94}	5.7^{837}	15	8.3	2.2
Alcohols[*]	123	7.7^{317}	6.6^{1849}	3.3^{440}	6.2^{2606}	119	10.8	3.0
Primary alcohols	29	5.1^{136}	6.7^{821}	3.2^{136}	6.1^{1093}	27	10.4	3.0
Secondary alcohols	29	21.2^{4}	7.5^{259}	1.8^{129}	5.8^{392}	29	7.1	2.1
Tertiary alcohols	8	-	10.2^{55}	7.9^{65}	8.9^{120}	7	8.1	2.5
Aromatic alcohols	6	-	8.9^{129}	4.2^{10}	8.5^{139}	6	7.2	1.9
Alkane Diols, Triols	13	10.7^{61}	5.1^{264}	0.0^{13}	5.9^{338}	12	9.2	2.3

There were large deviations for the smaller compounds in the estimation of the viscosity reference temperature. The smaller molecules have a more spherical shape and thus a high rotational symmetry number (and sometimes infinite values). For example, the largest deviations for alcohols were observed for 2-methyl-1-butanol (26.4 K), tert-butanol (24.4 K) and 1-pentanol (18.0 K). Although there are smaller molecular weight compounds, the above compounds are among the smallest compounds in their respective group (separate contributions are used for alcohols groups on a carbon chain with four or less and five and more carbon atoms). As data is usually available for these compounds, there is no need for group contribution estimation. Even if there is only a single point for these compounds, the back calculation of the reference temperature is more reliable. Thus, these compounds were removed from the data set as they hinder the estimation of higher molecular weight compounds, and consequently, the extrapolation capability of the method. Also, data for 1,2-ethanediol were removed (21.0 K) which is the first compound in an alkane diol series. The errors reported here for the removed compounds were from a regression of

---

[*] Includes multi-functional compounds

all components, but the final regression did not include them. No deviations greater than 22 K for mono-functional alcohol compounds were observed.

Table 9-6: Viscosity average absolute deviations (%) of the Andrade and Vogel models for the different types of oxygen compounds (number of data points as superscript).

	Average Absolute Deviation (%)									
	Andrade					**Vogel**				
	NC	**ELP**	**LP**	**MP**	**AV**	**NC**	**ELP**	**LP**	**MP**	**AV**
1-Alcohols	16	2.4^{133}	1.8^{610}	2.0^{94}	1.9^{837}	16	3.3^{133}	2.7^{610}	3.6^{94}	2.9^{837}
Alcohols[*]	123	3.9^{317}	2.8^{1849}	3.9^{440}	3.2^{2606}	111	4.4^{304}	3.7^{1777}	5.8^{424}	4.1^{2505}
Primary alcohols	29	2.5^{136}	2.1^{821}	2.3^{136}	2.2^{1093}	27	3.3^{136}	2.7^{813}	3.3^{130}	2.9^{1079}
Secondary alcohols	29	4.3^{4}	4.4^{259}	3.8^{129}	4.2^{392}	29	0.7^{4}	3.3^{259}	2.9^{129}	3.1^{392}
Tertiary alcohols	8	-	5.1^{56}	3.4^{65}	4.2^{120}	7	-	2.1^{50}	2.0^{64}	2.1^{114}
Aromatic alcohols	6	-	4.6^{129}	6.5^{10}	4.8^{139}	6	-	3.0^{129}	2.8^{10}	3.0^{139}
Alkane Diols, Triols	13	4.1^{61}	2.5^{264}	14.4^{13}	3.2^{338}	11	10.0^{55}	9.4^{240}	56.9^{11}	11.2^{306}

The results for the different types of oxygen (except alcohol) compounds for the proposed method and the correlative models are presented in Tables 9-7 and 9-8, respectively. The proposed method yields a consistent and accurate set of results for the different classes of oxygenated compounds which is in comparable accuracy to the correlative models. Even at low temperature, there were no exceptionally high deviations.

---

[*] Includes multi-functional compounds

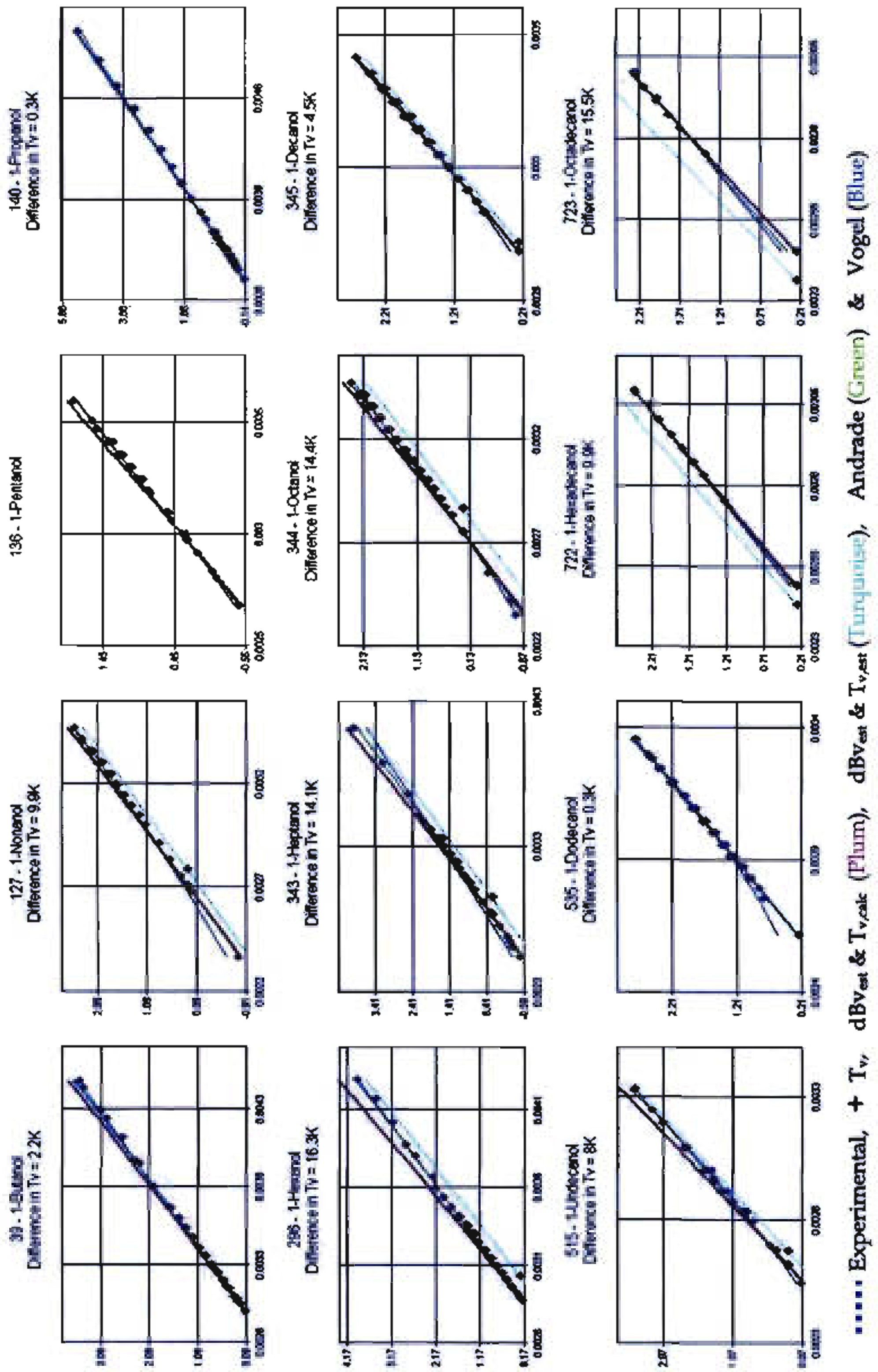


Figure 9-8: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for 1-alcohols.

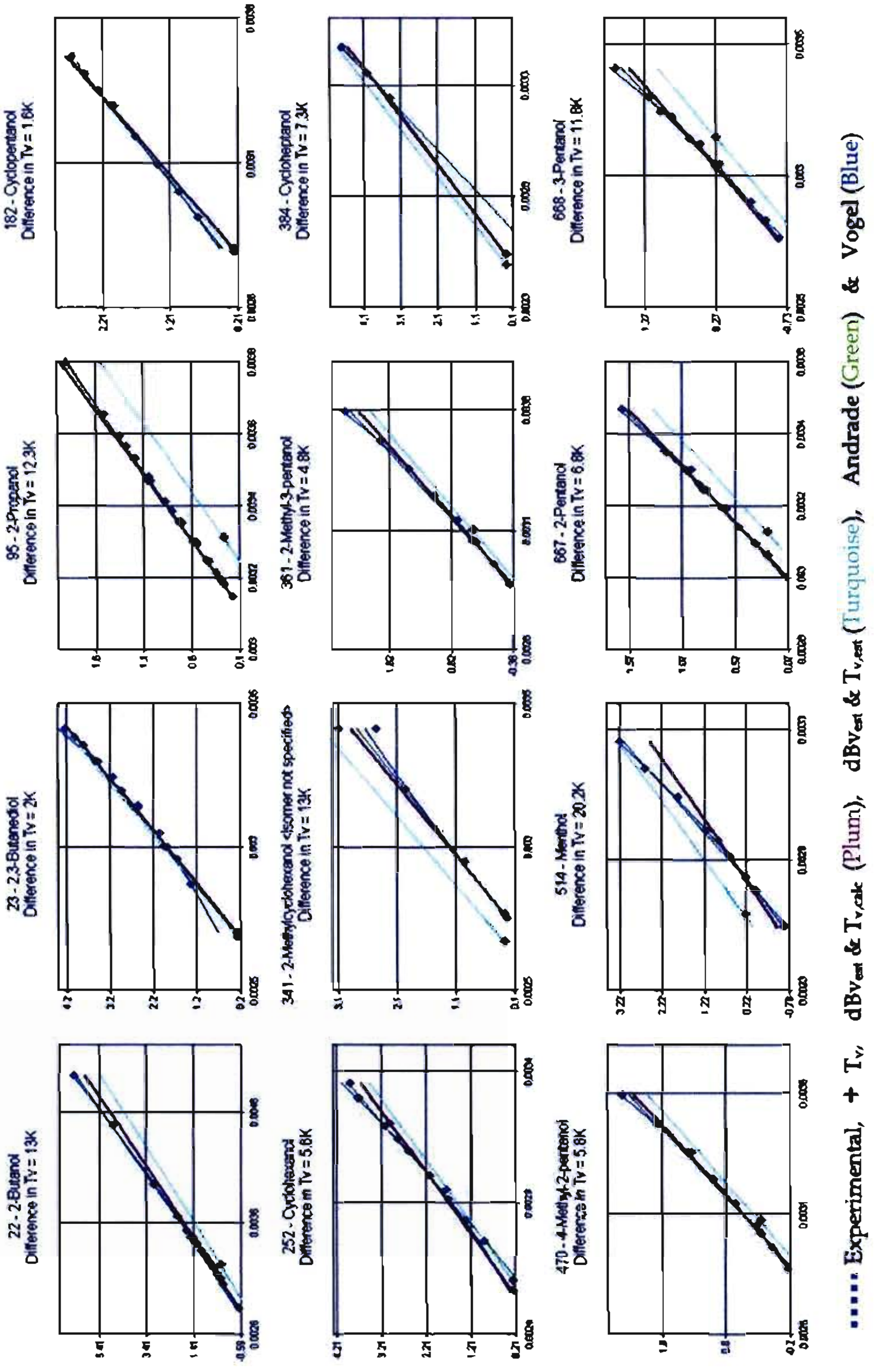


Figure 9-9: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for secondary alcohols.

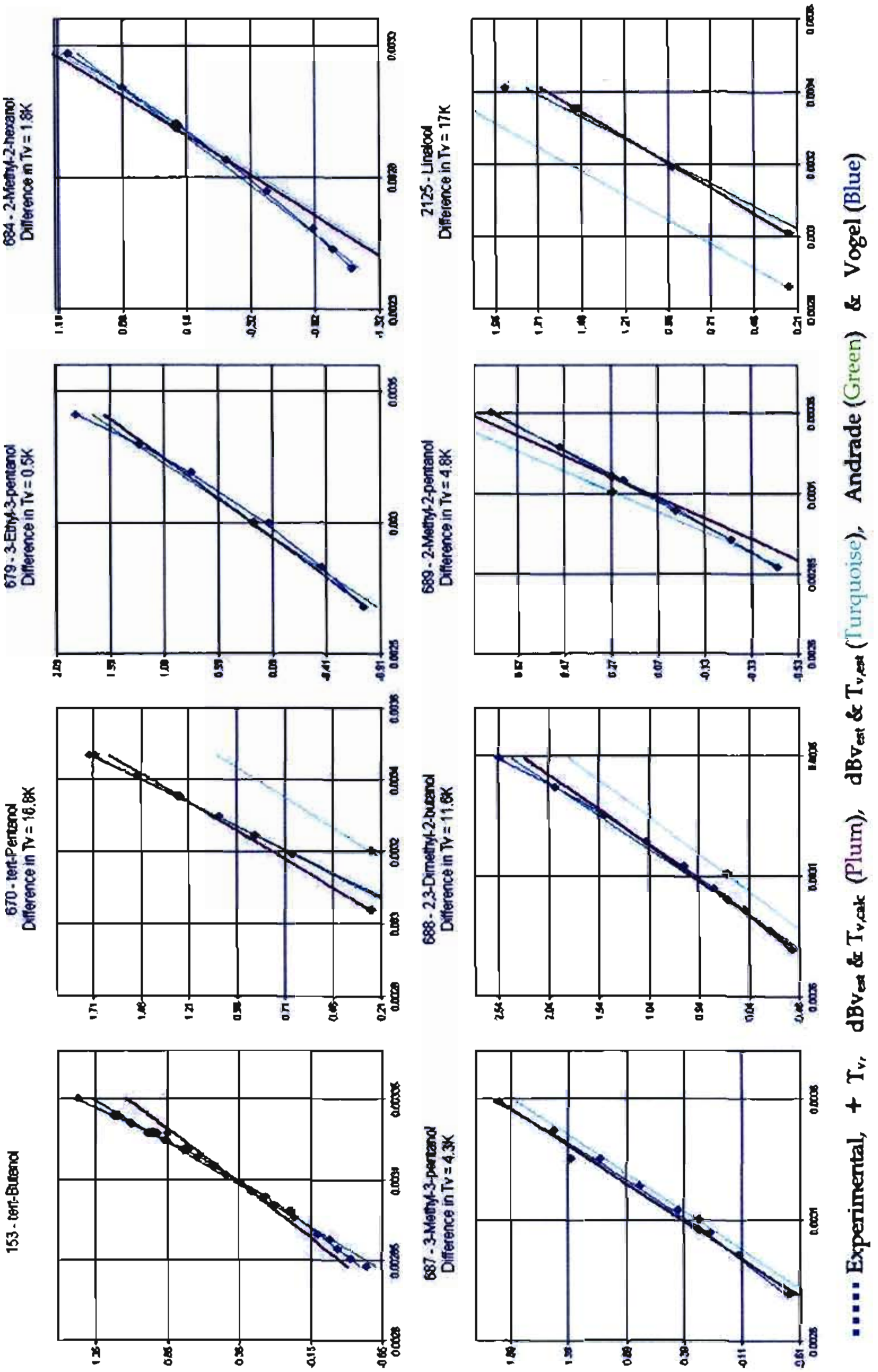


Figure 9-10: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for tertiary alcohols.

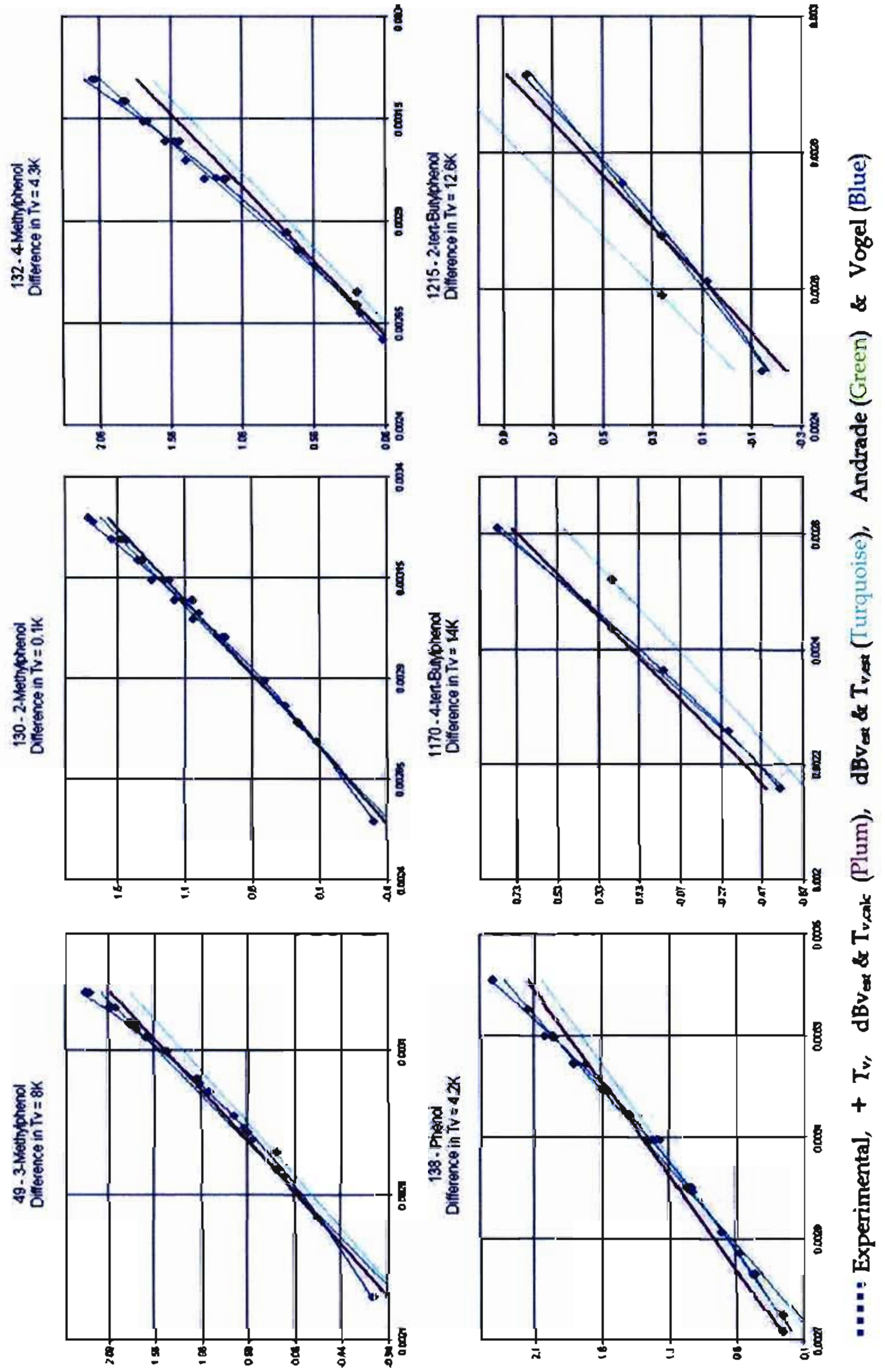


Figure 9-11: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for aromatic alcohols.

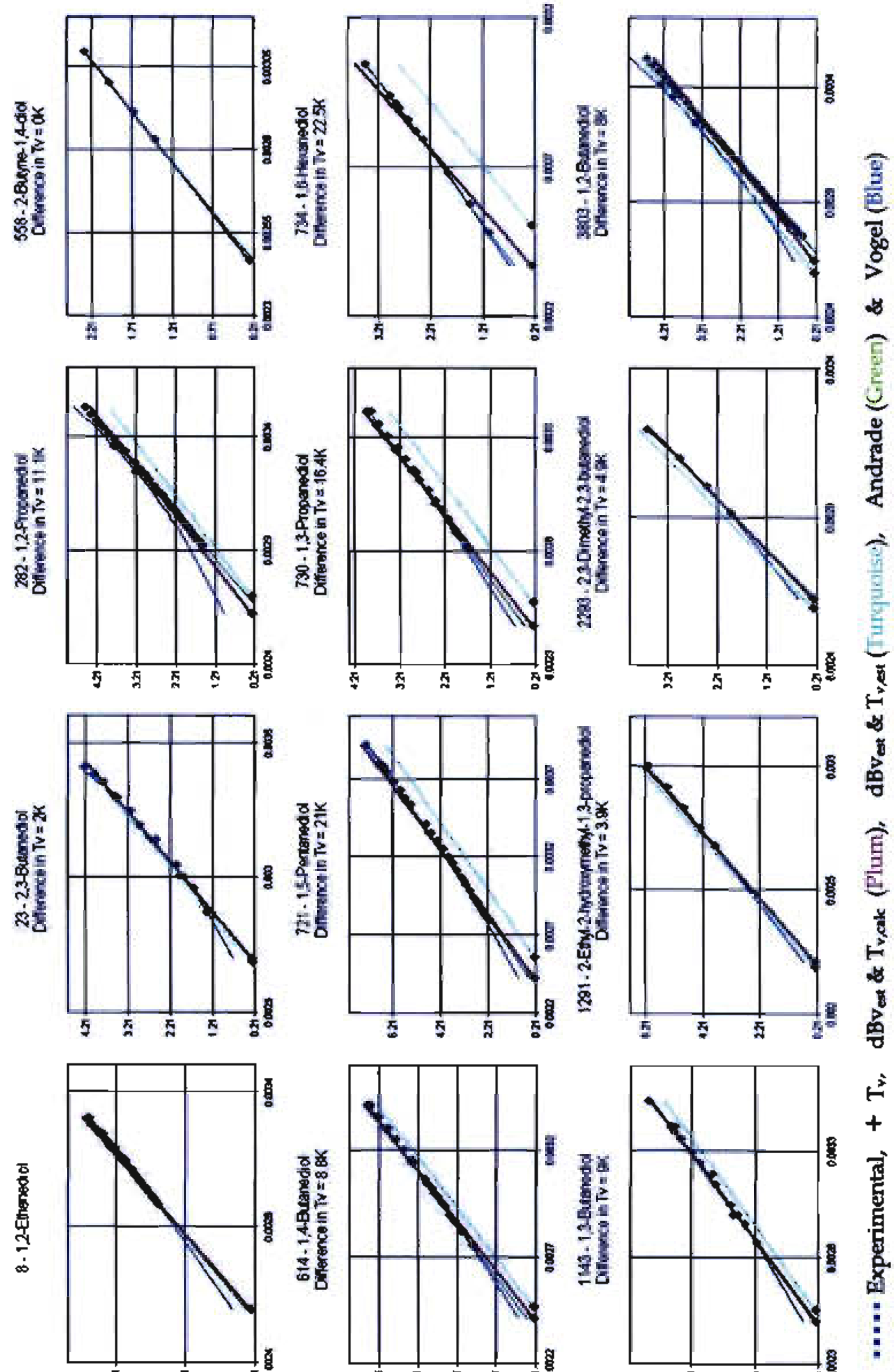


Figure 9-12: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for alkane diols.

Multiple plots of ether, ester and carboxylic acid compounds are presented in Figures 9-13, 9-14 and 9-15, respectively. Discrepancies are observed for smaller compounds at higher temperatures. For example, the data obtained at high temperatures for propionic acid in Figure 9-15 were from a rather outdated source, Thorpe & Rodger (1894). This reference contributed data for 56 other components to this work.

Table 9-7: Viscosity average absolute deviations of this work for the different types of oxygen (except alcohol) compounds (number of data points as superscript).

	Average Absolute Deviation (%)					**T_v**		
	NC	**ELP**	**LP**	**MP**	**AV**	**NC**	**AAD**	**MAPE**
Ethers	27	8.8^{10}	3.1^{208}	2.8^{215}	3.1^{433}	26	4.2	1.8
Epoxides	2	-	0.4^{5}	0.7^{13}	0.6^{18}	2	4.3	2.3
Aldehydes	8	-	0.6^{21}	0.8^{44}	0.8^{65}	7	5.2	2.3
Ketones	23	12.6^{13}	2.5^{237}	2.9^{188}	3.0^{438}	23	7.9	2.8
Non-cyclic carbonates	3	1.8^{56}	0.9^{24}	1.5^{10}	1.5^{90}	3	3.7	1.5
Carboxylic acids	22	4.6^{148}	1.9^{194}	3.8^{44}	3.1^{386}	18	14.6	3.9
Esters	49	3.7^{42}	1.9^{468}	1.5^{276}	1.8^{786}	49	5.2	1.9
Formic acids esters	9	-	2.3^{31}	1.5^{91}	1.7^{122}	9	3.4	1.4
Lactones	1	2.1^{8}	1.2^{20}	0.0^{1}	1.4^{29}	1	0.0	0.0
Anhydride chains	4	-	0.9^{47}	0.5^{15}	0.8^{62}	4	2.0	0.7
Anhydride cyclic	2	-	3.9^{5}	0.0^{2}	2.8^{7}	2	12.2	3.2
Aromatic oxygen	1	-	-	0.0^{5}	0.0^{5}	1	0.0	0.0
All (w/o alcohols) [*]	254	5.4^{472}	2.5^{1878}	2.2^{1145}	2.8^{3495}	248	7.8	2.5

---

[*] Includes multi-functional compounds

Table 9-8: Viscosity average absolute deviations (%) of the Andrade and Vogel models for the different types of oxygen (except alcohol) compounds (number of data points as superscript).

	Average Absolute Deviation (%)									
	Andrade					**Vogel**				
	NC	**ELP**	**LP**	**MP**	**AV**	**NC**	**ELP**	**LP**	**MP**	**AV**
Ethers	27	1.8^{10}	1.4^{208}	1.2^{215}	1.3^{433}	26	1.6^{10}	1.6^{206}	1.8^{214}	1.7^{430}
Epoxides	2	-	0.4^{5}	1.2^{13}	0.9^{18}	2	-	0.4^{5}	5.3^{13}	4.0^{18}
Aldehydes	8	-	0.6^{21}	1.7^{44}	1.4^{65}	7	-	0.6^{19}	14.5^{43}	10.2^{62}
Ketones	23	2.3^{13}	1.6^{237}	1.5^{188}	1.5^{438}	20	1.5^{13}	1.7^{224}	2.1^{185}	1.9^{422}
Non-cyclic carbonates	3	2.0^{56}	0.7^{24}	2.2^{10}	1.6^{90}	3	0.9^{56}	0.8^{24}	64.7^{10}	7.9^{90}
Carboxylic acids	22	1.1^{148}	0.9^{194}	5.8^{44}	1.6^{386}	21	1.4^{148}	1.5^{192}	5.5^{43}	1.9^{383}
Esters	49	2.1^{42}	1.0^{468}	1.3^{276}	1.2^{786}	42	1.5^{41}	1.5^{455}	2.5^{261}	1.9^{757}
Formic acids esters	9	-	1.0^{31}	1.2^{91}	1.1^{122}	9	-	4.0^{31}	5.9^{91}	5.4^{122}
Lactones	1	2.4^{8}	1.2^{20}	0.0^{1}	1.5^{29}	1	1.8^{8}	0.8^{20}	3.7^{1}	1.2^{29}
Anhydride chains	4	-	1.0^{47}	0.4^{15}	0.8^{62}	3	-	0.9^{45}	0.5^{14}	0.9^{59}
Anhydride cyclic	2	-	0.2^{5}	12.6^{2}	3.7^{7}	2	-	0.4^{5}	11.9^{2}	3.7^{7}
Aromatic oxygen	1	-	-	0.4^{5}	0.4^{5}	1	-	-	0.4^{5}	0.4^{5}
All (w/o alcohols) [*]	254	2.6^{472}	1.3^{1878}	2.0^{1145}	1.7^{3495}	207	2.0^{454}	1.7^{1745}	3.9^{1063}	2.4^{3262}

For the viscosity reference temperature large deviations were observed for the smaller compounds. These compounds, acetic acid (23.3 K), propionic acid (43.2 K), butyric acid (32 K), 2-methylpropionic acid (37.8 K), 2-methyltetrahydrofuran (27.9 K) and acetaldehyde (14.7 K) were removed from the regression set. Even with the removal of the above compounds, there were still large deviations for the smaller carboxylic acids up to hexanioc acid. Apart from these compounds, overall there were no large deviations for all mono-functional oxygen compounds (except alcohols) greater than 17 K.

---

[*] Includes multi-functional compounds

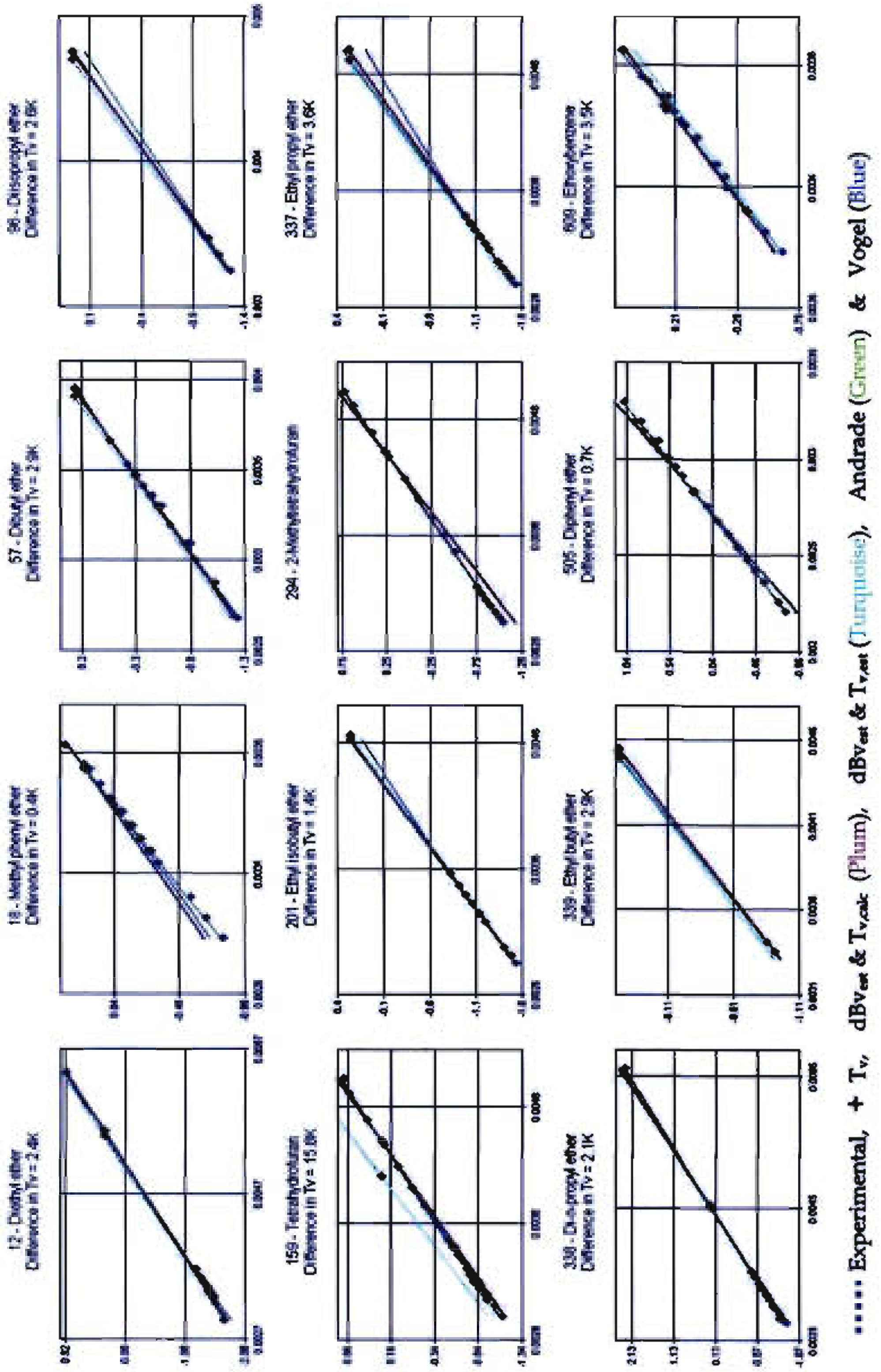


Figure 9-13: Multiple plot (Ln (μ) vs. 1/T [K-1]) of experimental and estimated liquid viscosities for ethers.

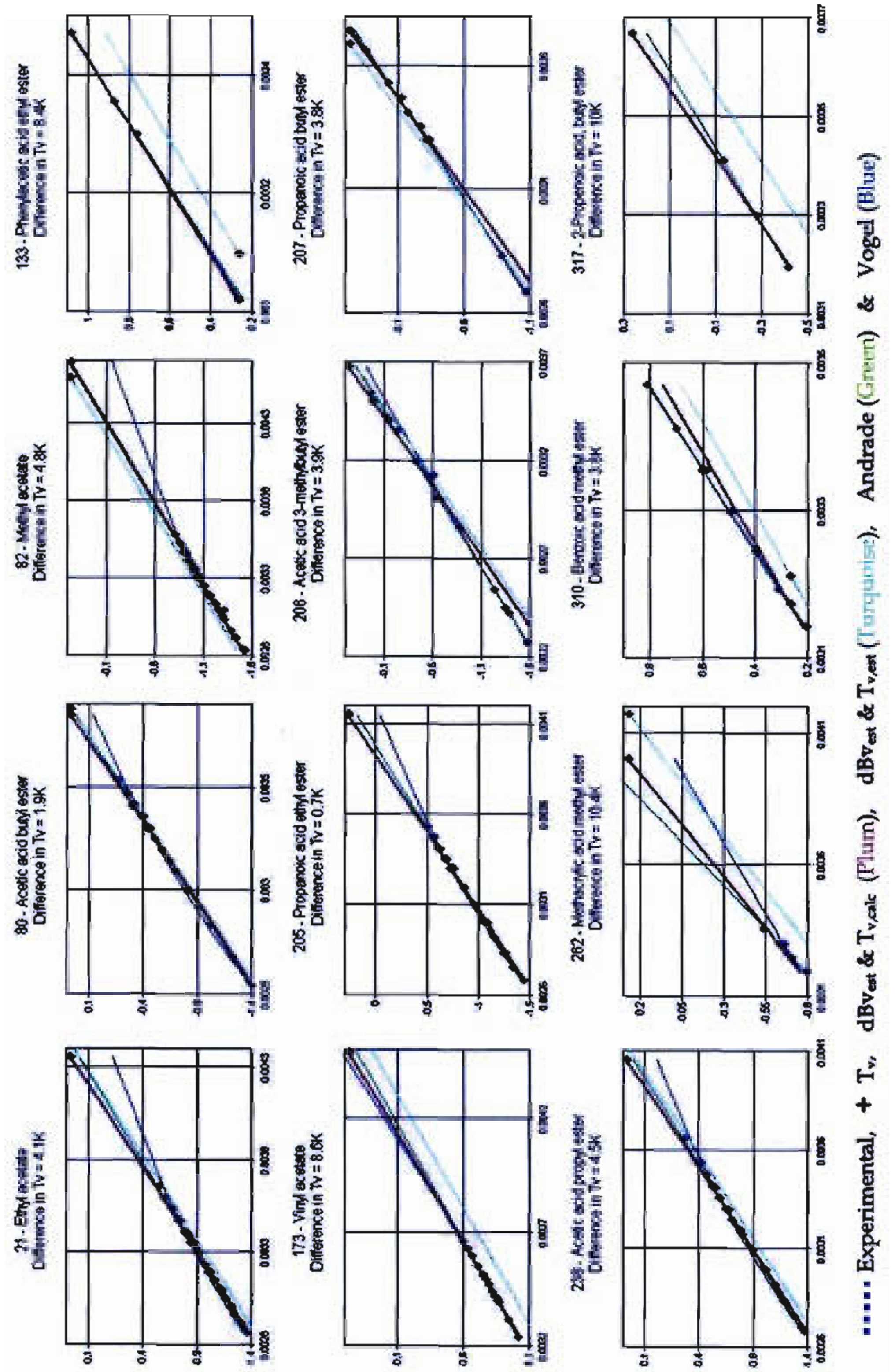


Figure 9-14: Multiple plot (Ln (μ) vs. $1/T$ [K^{-1}]) of experimental and estimated liquid viscosities for esters.

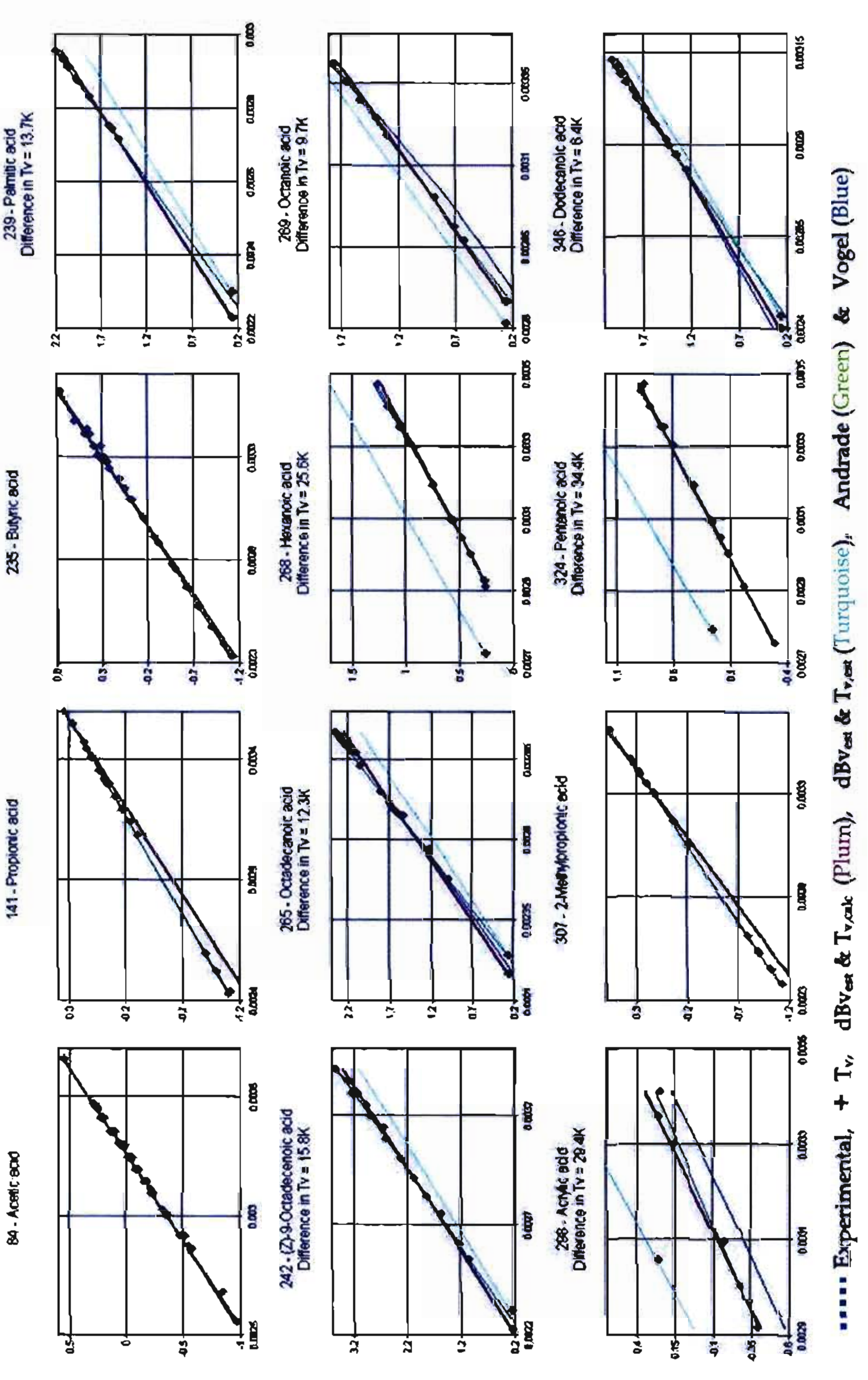


Figure 9-15: Multiple plot (Ln (μ) vs. 1/T [K⁻¹]) of experimental and estimated liquid viscosities for carboxylic acids.

9.4.2.2 Nitrogen Compounds

Results for the different types of nitrogen compounds for the proposed method and both the correlative models are presented in Tables 9-9 and 9-10, respectively. There were no relatively large deviations observed at low temperatures.

Multiple plots of primary amines, cyanides and nitrous or nitrates compounds are presented in Figures 9-16, 9-17 and 9-18, respectively. The proposed method yielded an excellent agreement between estimated and experimental data. In case of the smaller compounds which are the first members in its series such as aniline, methylamine and nitromethane, larger deviations were observed.

For these compounds a unique observation is made concerning the error in the optimised viscosity reference temperature. The error is the result of the estimated *dBv* being employed in the optimisation procedure. But, the reasoning for using this technique is because of the estimation of the slope employing chemically similar groups (discussed in Chapter 8). For many components where the optimisation procedure is evident, it is observed that the results are exceptional. Thus, the optimisation procedure was not modified for these special cases and the results are accepted.

For other nitrogen compounds not shown in the plots, similar or significantly better results are obtained. Usually, the multiple plots presented in this work start with the smaller molecular compounds which usually incur slightly higher errors. To confirm this argument, a plot of the remaining primary amines is presented in Figure 9-19. All components reveal an excellent agreement between estimated and experimental data for the proposed method. For alpha-aminotoluene the higher temperature data was obtained from an old reference, Friend & Hargreaves (1944). For 1-naphthylamine, only two points were available which were obtained from two references, Mussell *et al.* (1912) & Thole *et al.* (1913). As chemically similar compounds of the two above components show better results, it can be assumed that the data are questionable.

Table 9-9: Viscosity average absolute deviations of this work for the different types of nitrogen compounds (number of date points as superscript).

	Average Absolute Deviation (%)					T_v		
	NC	ELP	LP	MP	AV	NC	AAD	MAPE
Primary amines	22	16.8^{2}	4.0^{277}	2.6^{152}	3.5^{431}	21	5.1	1.8
Secondary amines	15	8.8^{10}	3.6^{137}	3.1^{51}	3.7^{198}	15	2.2	0.7
Tertiary amines	6	8.6^{4}	2.3^{124}	2.9^{43}	2.6^{171}	6	7.0	2.4
Amines*	59	11.6^{65}	4.6^{570}	3.0^{271}	4.6^{906}	58	5.9	1.8
N in 5-membered rings	2	-	2.3^{31}	0.0^{2}	2.1^{33}	2	1.2	0.4
N in 6-membered rings	16	6.3^{16}	3.4^{213}	3.9^{32}	3.6^{261}	16	2.7	0.9
Cyanides	15	4.2^{7}	2.1^{142}	1.7^{174}	2.0^{323}	14	6.5	2.5
Amides	3	-	2.8^{59}	0.4^{4}	2.6^{63}	2	1.2	0.3
Mono amides	3	6.4^{11}	6.6^{59}	0.0^{3}	6.3^{73}	2	8.8	2.4
Di amides	5	6.8^{6}	1.3^{160}	0.0^{6}	1.5^{171}	5	8.0	2.8
Isocyanates	4	-	4.5^{15}	2.7^{16}	3.6^{31}	4	9.6	4.2
Oximes	1	-	0.0^{2}	0.0^{1}	0.0^{3}	1	0.0	0.0
Nitrous and nitrites	14	4.0^{12}	2.4^{158}	4.0^{73}	3.0^{243}	14	4.7	1.7
Nitrates	1	-	0.0^{2}	0.0^{1}	0.0^{3}	1	0.0	0.0
All (w/o Amines)*	62	5.5^{61}	2.7^{745}	1.9^{254}	2.7^{1060}	59	5.0	1.8

For tert-butylamine and acryloamine in Figure 9-16 and 9-17, respectively, a disastrous extrapolation is observed for the Vogel model. For the correlative models the extrapolative capabilities decline with decreasing temperature ranges of the data. An example was also shown for the extrapolation of the Antoine equation in Section 8.6.3.

For the viscosity reference temperature, the proposed method yields a consistent set of results for the different classes of nitrogen compounds. For all nitrogen compounds (including multi-functional compounds), an average absolute error of 1.8% is tabulated which is satisfactory considering the errors that may arise from the calculation of this point. N-methylformamide (26.9 K), formamide (26.5 K), methylamine (17.6 K) and acetonnitrile (13.5 K) which are the first compounds in its series were removed from

---

* Includes multi-functional compounds

the regression set. For all mono-functional nitrogen compounds, there were no deviations greater than 20 K.

Table 9-10: Viscosity average absolute deviations (%) of the Andrade and Vogel models for the different types of nitrogen compounds (number of date points as superscript).

	Average Absolute Deviation (%)									
	Andrade					**Vogel**				
	NC	**ELP**	**LP**	**MP**	**AV**	**NC**	**ELP**	**LP**	**MP**	**AV**
Primary amines	22	13.2^{2}	2.1^{277}	1.8^{162}	2.1^{431}	20	2.3^{2}	1.4^{275}	6.6^{144}	3.2^{421}
Secondary amines	15	3.4^{10}	2.7^{137}	3.9^{51}	3.0^{198}	13	2.3^{9}	2.1^{133}	5.0^{49}	2.8^{191}
Tertiary amines	6	4.2^{4}	1.8^{124}	1.3^{43}	1.7^{171}	6	3.2^{4}	1.7^{124}	1.6^{43}	1.7^{171}
Amines[*]	59	4.8^{66}	2.6^{570}	2.6^{271}	2.7^{906}	49	2.9^{60}	1.8^{529}	7.0^{246}	3.4^{835}
N in 5-membered rings	2	-	2.3^{31}	1.5^{2}	2.3^{33}	2	-	2.3^{31}	1.9^{2}	2.3^{33}
N in 6-membered rings	16	3.1^{16}	1.1^{213}	2.3^{32}	1.4^{261}	15	2.8^{16}	1.5^{211}	3.3^{31}	1.8^{258}
Cyanides	15	3.4^{7}	1.2^{142}	1.8^{174}	1.6^{323}	11	3.6^{4}	1.1^{137}	19.7^{170}	11.3^{311}
Amides	3	-	1.6^{59}	4.0^{4}	1.7^{63}	3	-	2.5^{59}	3.8^{4}	2.6^{63}
Mono amides	3	1.0^{11}	1.7^{59}	14.3^{3}	2.1^{73}	3	1.2^{11}	1.6^{59}	4.9^{3}	1.7^{73}
Di amides	5	0.6^{6}	0.9^{160}	2.0^{5}	0.9^{171}	4	0.5^{5}	0.9^{157}	0.7^{4}	0.9^{166}
Isocyanates	4	-	0.4^{15}	5.2^{16}	2.9^{31}	2	-	0.3^{8}	2.9^{7}	1.5^{15}
Oximes	1	-	0.0^{2}	3.3^{1}	1.1^{3}	-	-	-	-	-
Nitrous and nitrites	14	1.2^{12}	1.1^{158}	1.2^{73}	1.1^{243}	14	0.8^{12}	1.5^{158}	2.1^{73}	1.6^{243}
Nitrates	1	-	0.0^{2}	1.1^{1}	0.4^{3}	-	-	-	-	-
All (w/o Amines)[*]	62	1.9^{51}	1.2^{745}	2.4^{254}	1.5^{1050}	50	1.9^{47}	1.4^{714}	15.2^{235}	4.7^{996}

---

[*] Includes multi-functional compounds

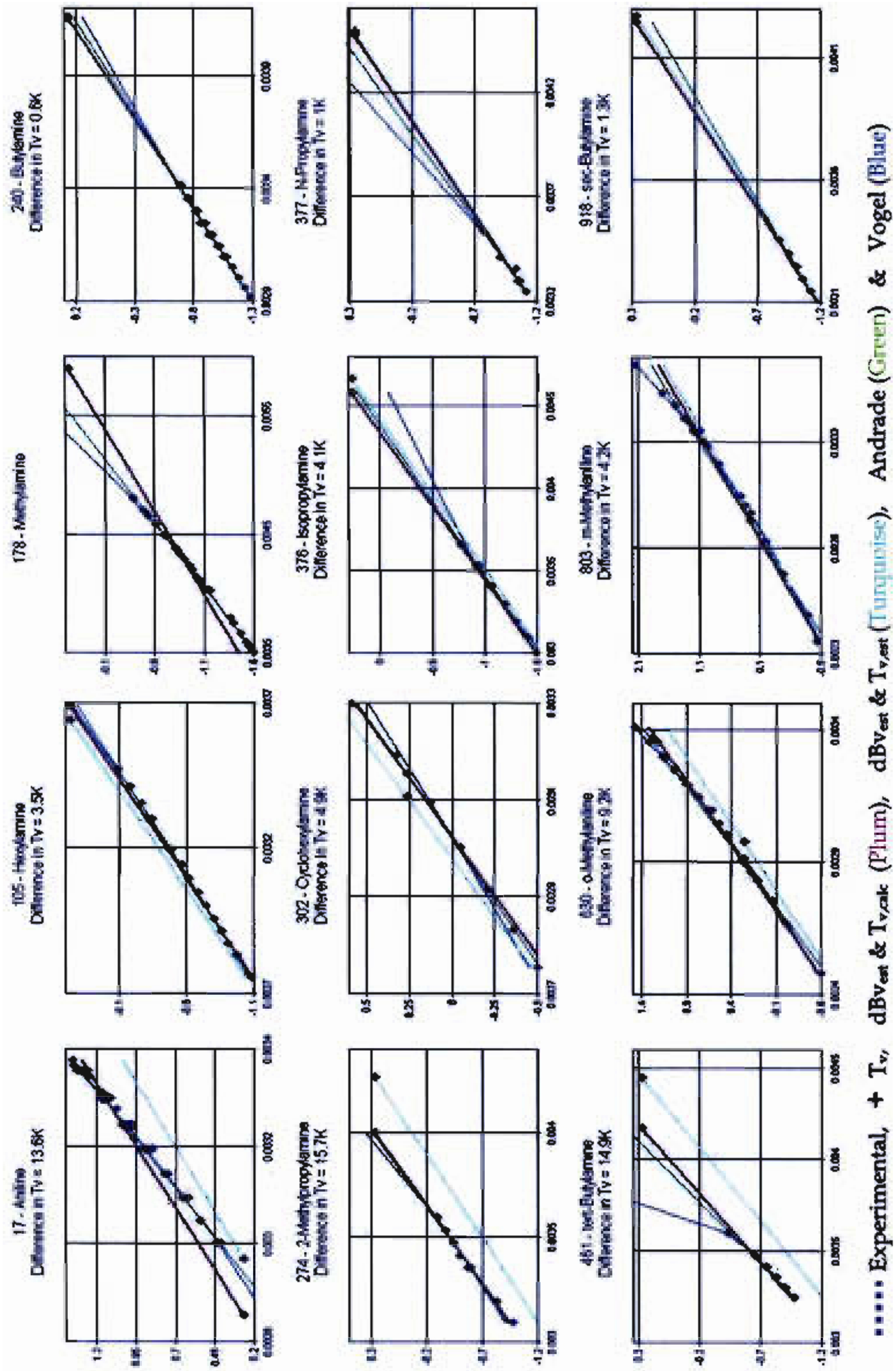


Figure 9-16: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for primary amines

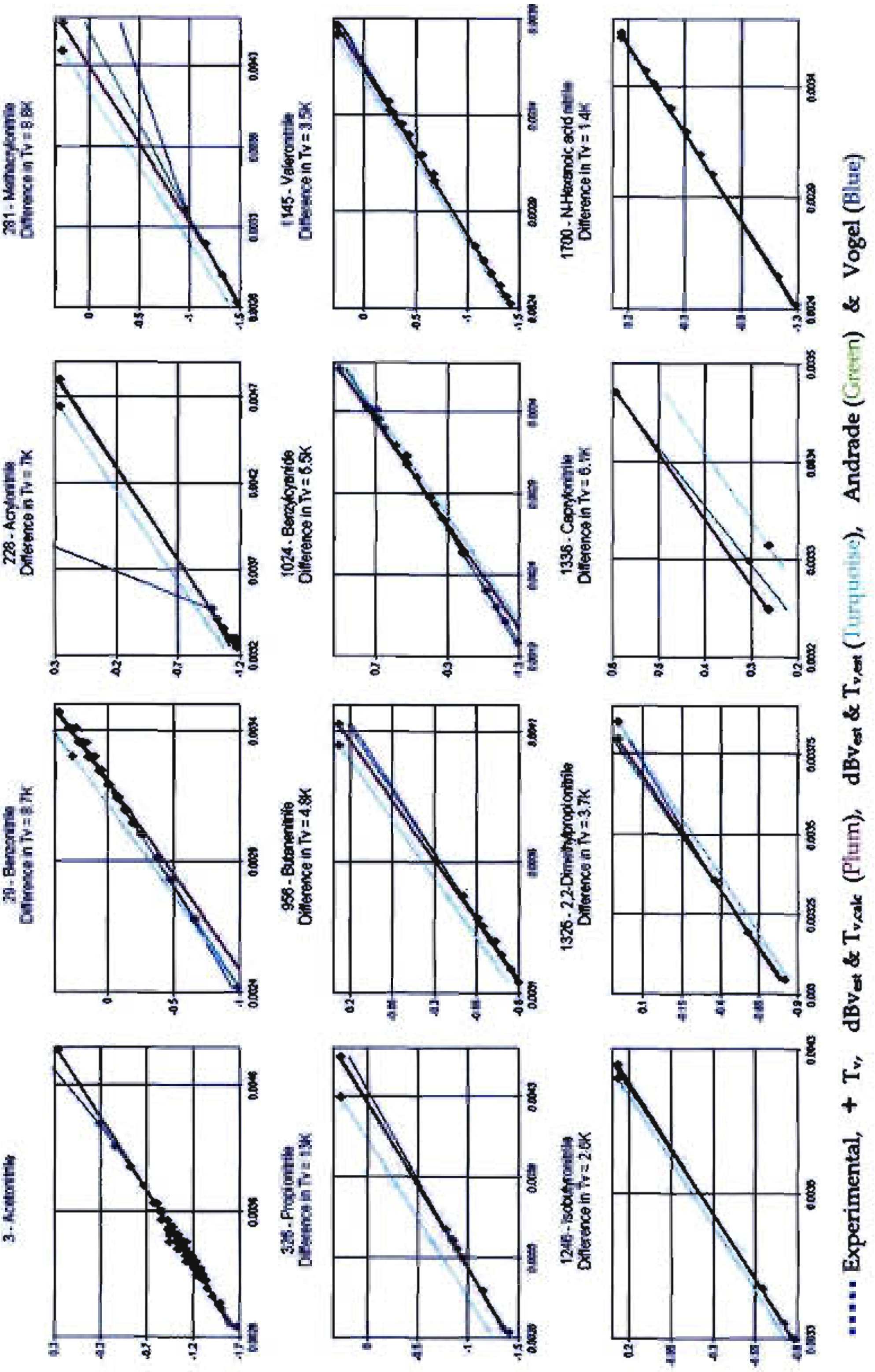


Figure 9-17: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for cyanides

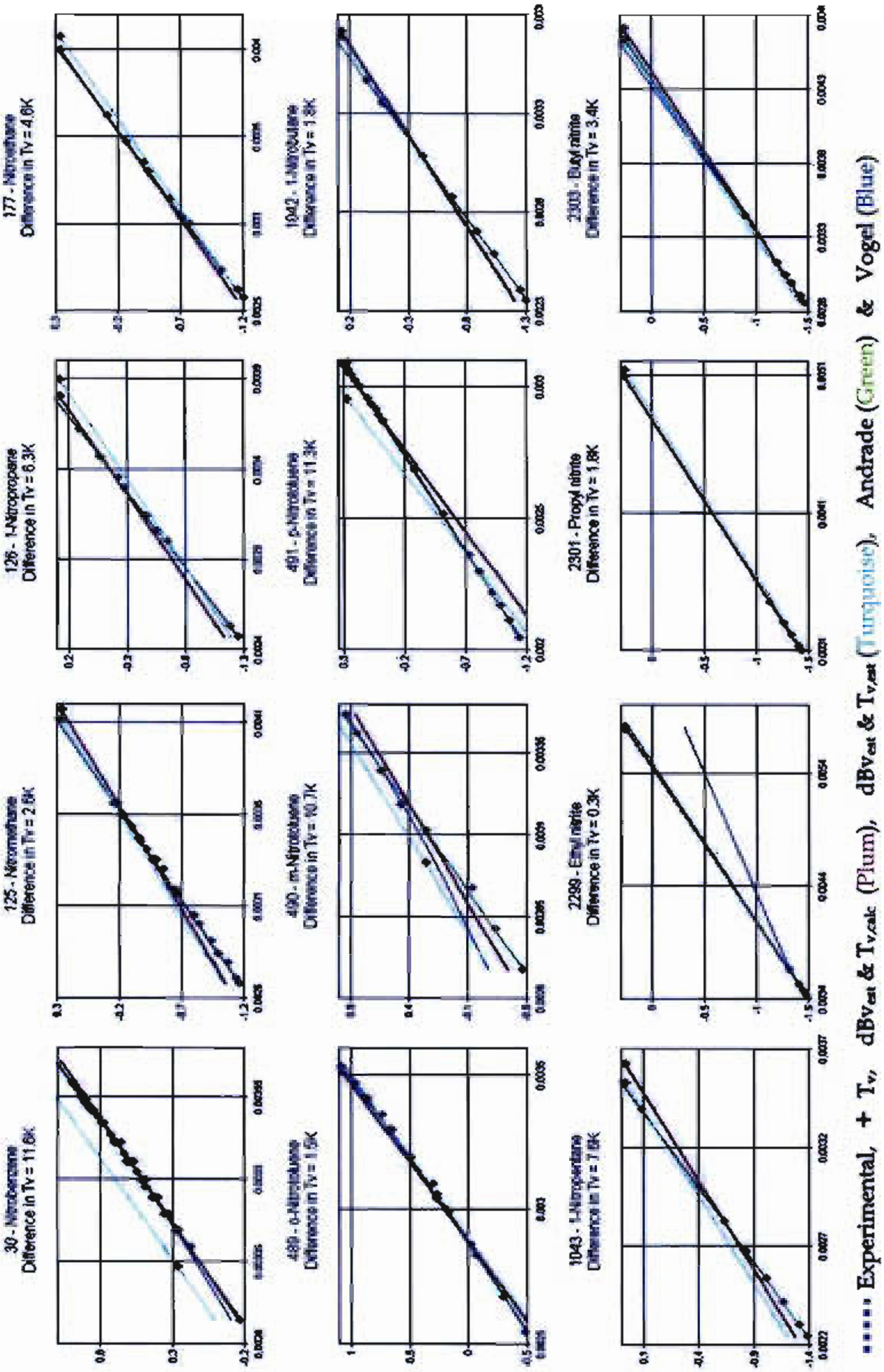


Figure 9-18: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for nitrous or nitrate compounds

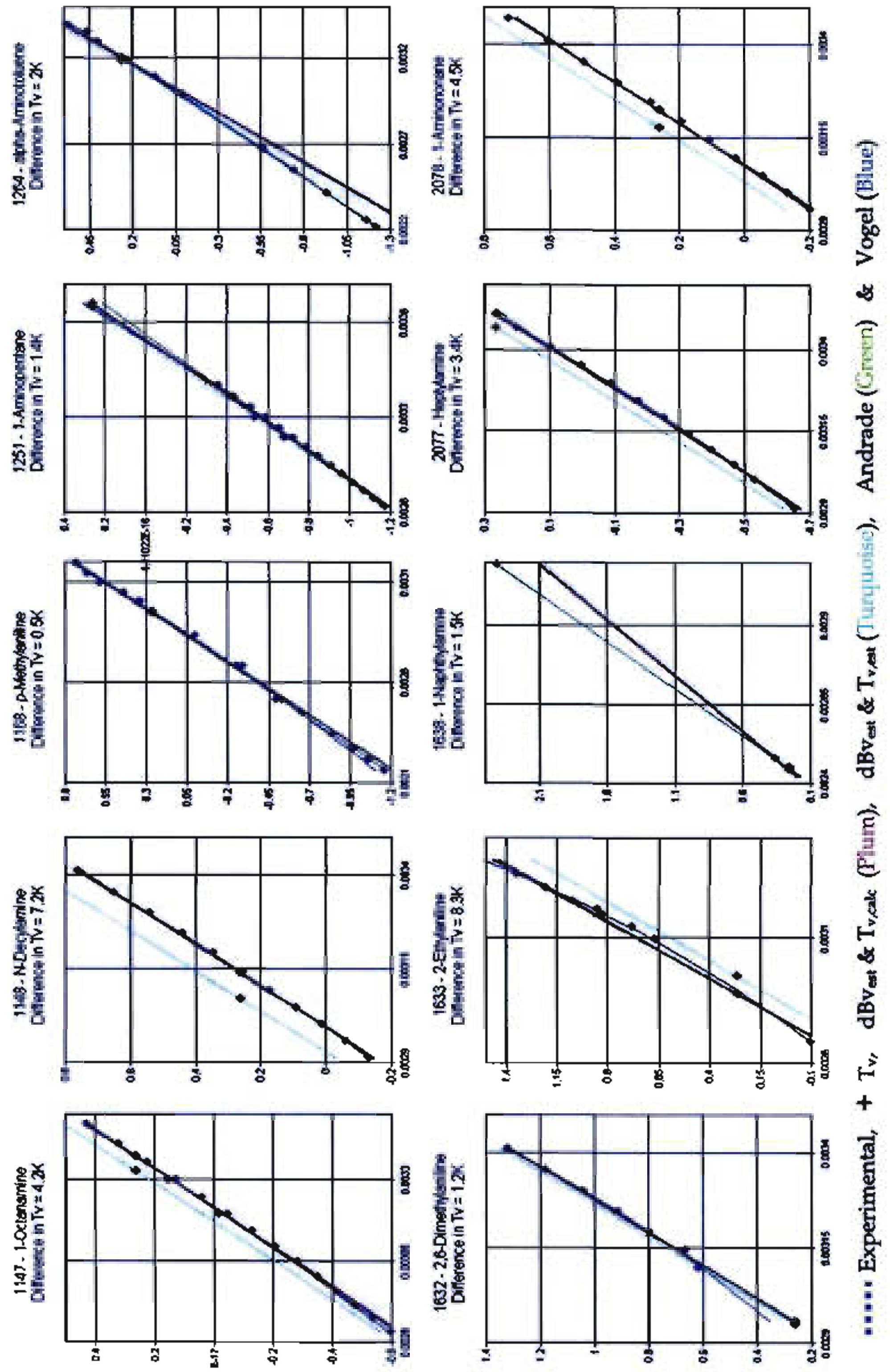


Figure 9-19: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for primary amines

9.4.2.3 Sulphur Compounds

Results for the different types of sulphur compounds for the proposed method and both the correlative models are presented in Tables 9-11 and 9-12, respectively. There were no exceptionally large deviations observed from the estimation of the slope for all sulphur compounds over the entire temperature range.

Multiple plots of sulphur compounds are presented in Figures 9-20, 9-21 and 9-22. The three plots include all mono-functional sulphur compounds and show an excellent agreement between estimated and experimental data for the proposed method.

Table 9-11: Viscosity average absolute deviations of this work for the different types of sulphur compounds (number of data points as superscript).

	Average Absolute Deviation (%)					T_v		
	NC	**ELP**	**LP**	**MP**	**AV**	**NC**	**AAD**	**MAPE**
Disulfides	2	-	0.1^{6}	0.0^{2}	0.1^{8}	2	2.6	1.0
Thiols	12	-	1.5^{39}	1.7^{36}	1.6^{75}	12	7.2	2.9
Thioether	8	-	0.9^{29}	0.6^{27}	0.8^{56}	8	6.2	2.6
Aromatic thioether	3	-	0.8^{17}	1.2^{19}	1.0^{36}	3	1.5	0.6
Sulfolane (O=S=O)	3	1.3^{51}	4.9^{10}	0.0^{3}	1.8^{64}	3	6.6	1.6
Isothiocyanates	2	-	1.6^{9}	0.0^{2}	1.3^{11}	2	0.9	0.4
Sulfates, sulfon amides & sulfoxides	6	4.1^{15}	1.8^{10}	0.0^{6}	2.6^{31}	6	3.8	1.1
Sulphur compounds[*]	41	2.0^{66}	1.4^{138}	1.0^{102}	1.4^{306}	41	6.1	2.2

There are also many components where the extrapolated viscosity reference temperature produced excellent results. For dimethly sulfide in Figure 9-20, the one low temperature point which is further away from the other data would have produced a slightly different reference temperature if extrapolated. However, with the extrapolated reference temperature the slope of the curve is in excellent agreement

---

[*] Includes multi-functional compounds

with the experimental slope. This suggests, together with the outdated reference of Waller (1934), that the reliability of the point is questionable.

Table 9-12: Viscosity average absolute deviations of the Andrade and Vogel models for the different types of sulphur compounds (number of data points as superscript).

	Average Absolute Deviation (%)									
	Andrade					**Vogel**				
	NC	**ELP**	**LP**	**MP**	**AV**	**NC**	**ELP**	**LP**	**MP**	**AV**
Disulfides	2	-	0.0^{6}	1.1^{2}	0.3^{8}	2	-	0.0^{6}	19.2^{2}	4.8^{8}
Thiols	12	-	0.6^{39}	2.3^{36}	1.4^{75}	12	-	2.0^{39}	7.2^{36}	4.5^{75}
Thioether	8	-	0.5^{29}	1.8^{27}	1.1^{56}	8	-	0.5^{29}	5.1^{27}	2.7^{56}
Aromatic thioether	3	-	0.6^{17}	0.9^{19}	0.8^{36}	3	-	0.6^{17}	0.8^{19}	0.7^{36}
Sulfolane (O=S=O)	3	0.7^{51}	1.6^{10}	10.6^{3}	1.3^{64}	3	1.0^{51}	0.7^{10}	20.6^{3}	1.8^{64}
Isothiocyanates	2	-	0.8^{9}	6.0^{2}	1.8^{11}	2	-	0.8^{9}	15.1^{2}	3.4^{11}
Sulfates, sulfon amides & sulfoxides	6	2.1^{15}	1.8^{10}	5.9^{6}	2.7^{31}	1	4.2^{3}	0.7^{5}	0.9^{1}	1.9^{9}
Sulphur compounds[*]	41	1.0^{66}	0.7^{138}	2.4^{102}	1.3^{306}	35	1.1^{54}	1^{131}	5.9^{96}	2.7^{281}

For the viscosity reference temperature, the proposed method yields a consistent set of results for the different classes of sulphur compounds. For all mono-functional sulphur compounds, there were no deviations greater than 18 K. Compared to oxygen and nitrogen, sulphur is a weaker hydrogen bonding acceptor. This implies that the influence of the intermolecular force is weaker on smaller sulphur compounds. Thus, no compounds were removed from the regression set.

---

[*] Includes multi-functional compounds

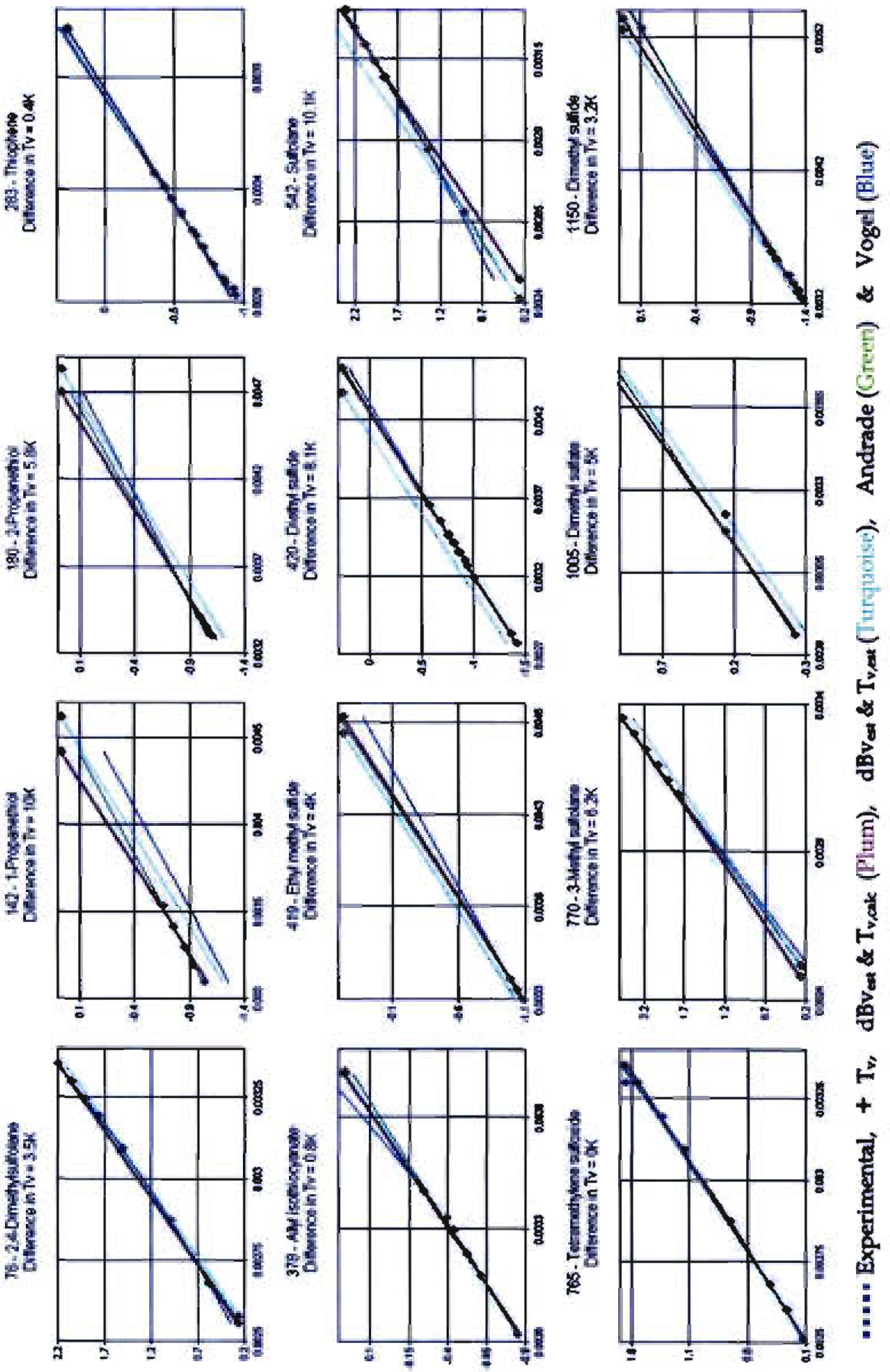


Figure 9-20: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for sulphur compounds

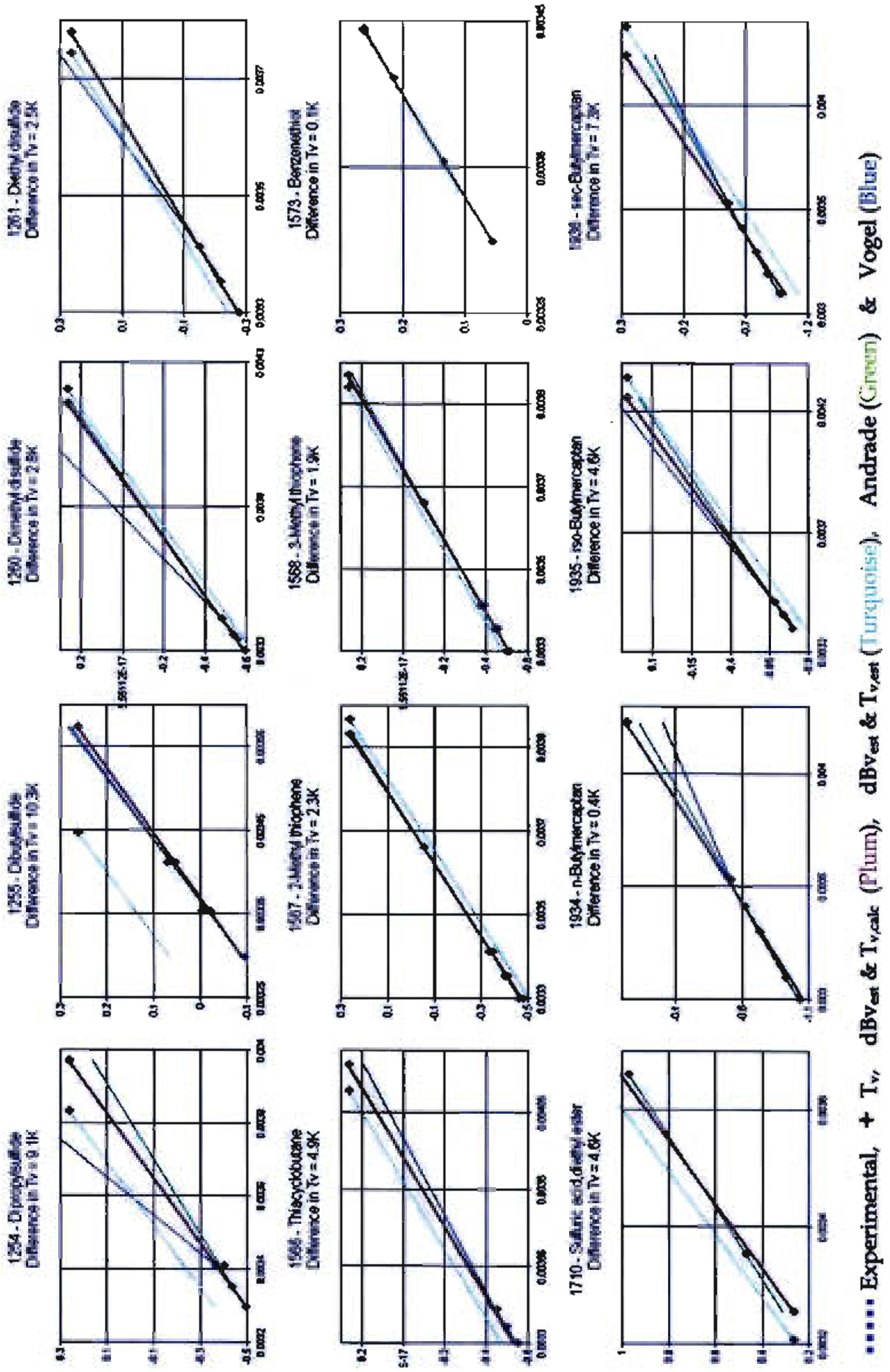


Figure 9-21: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for sulphur compounds

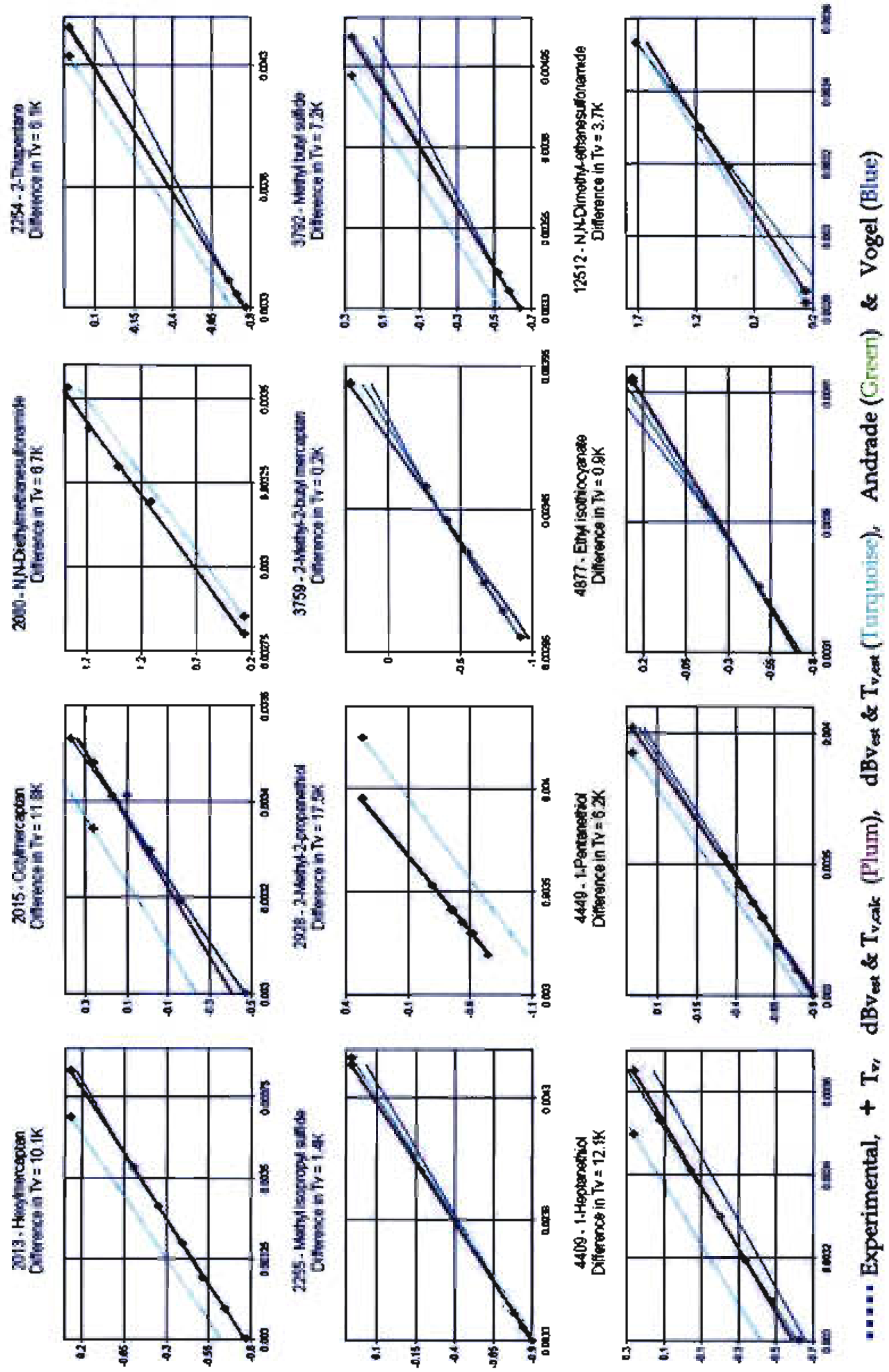


Figure 9-22: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for sulphur compounds

9.4.2.4 Halogen Compounds

Results for the different types of halogen compounds for the proposed method and both the correlative models are presented in Tables 9-13 and 9-14, respectively. There were no exceptionally large deviations observed from the estimation of the slope for halogen compounds over the entire temperature range.

Table 9-13: Viscosity average absolute deviations of this work for the different types of halogen compounds (number of data points as superscript).

	Average Absolute Deviation (%)					T_v		
	NC	ELP	LP	MP	AV	NC	AAD	MAPE
Saturated fluorine	13	-	3.3^{28}	4.2^{151}	4.1^{179}	13	6.1	3.1
Fluorinated	20	-	2.3^{54}	3.5^{198}	3.3^{252}	20	8.0	3.7
Saturated chlorine	34	4.5^{6}	1.6^{161}	2.6^{439}	2.4^{606}	34	7.3	2.9
Chlorinated	50	2.3^{15}	1.4^{357}	2.6^{540}	2.1^{912}	50	7.4	2.9
Saturated bromine	21	-	1.6^{231}	1.7^{143}	1.6^{374}	21	6.6	2.2
Brominated	28	4.3^{3}	1.7^{317}	1.8^{155}	1.8^{475}	28	6.4	2.1
Iodinated	14	9.5^{13}	2.2^{79}	2.3^{60}	2.9^{152}	13	3.8	1.4
Halogenated Compounds *	182	7.8^{69}	2.3^{1210}	2.6^{1385}	2.6^{2664}	179	7.1	2.8

Multiple plots of fluorine, chlorine, bromine and iodine compounds are presented in Figures 9-23, 9-24, 9-25 and 9-26, respectively. The proposed method yielded an excellent agreement between estimated and experimental data. Similar results are also observed for other halogenated compounds not plotted. For chloroform, Figure 9-24, the single low temperature point was obtained from Waller (1934), which is the same reference as for dimethyl sulphide with the same argument holding here as well. For dibromomethane, Figure 9-25, there is a distinct disparity between the experimental and estimated data. This compound is the first in its series and the data were reported by Friend & Hargreaves (1943), who also presented data for alpha-aminotoluene (shown earlier). At the same time, better results are observed for tribromomethane for which data from ten different references were available including the above reference.

---

* Includes multi-functional compounds

The reference was removed for the latter component because of its questionable quality, but included for dibromomethane due to lack of data. For methyl iodide in Figure 9-26, a similar argument holds as for chloroform where the single low temperature point is also obtained from the same unreliable source.

Table 9-14: Viscosity average absolute deviations of the Andrade and Vogel models for the different types of halogen compounds (number of data points as superscript).

	Average Absolute Deviation (%)									
	Andrade					**Vogel**				
	NC	**ELP**	**LP**	**MP**	**AV**	**NC**	**ELP**	**LP**	**MP**	**AV**
Saturated fluorine	13	-	1.4^{28}	1.6^{151}	1.5^{179}	12	-	1.5^{28}	2.5^{146}	2.4^{174}
Fluorinated	20	-	1.0^{54}	1.6^{198}	1.5^{252}	19	-	1.0^{54}	2.3^{193}	2.0^{247}
Saturated chlorine	34	0.9^{6}	0.9^{161}	0.9^{439}	0.9^{606}	29	0.3^{6}	1.7^{155}	2.0^{423}	1.9^{584}
Chlorinated	50	0.6^{15}	0.8^{357}	0.9^{540}	0.8^{912}	45	1.8^{15}	1.2^{351}	1.9^{524}	1.6^{890}
Saturated bromine	21	-	0.9^{231}	0.9^{143}	0.9^{374}	20	-	1.1^{229}	1.7^{142}	1.3^{371}
Brominated	28	0.5^{3}	0.9^{317}	1.2^{155}	1.0^{475}	26	26.2^{1}	1.3^{315}	2.3^{153}	1.7^{469}
Iodinated	14	3.6^{13}	2.1^{79}	1.3^{60}	1.9^{152}	12	4.0^{12}	2.4^{76}	1.9^{58}	2.4^{146}
Halogenated Compounds[*]	182	2.5^{69}	1.3^{1210}	1.1^{1385}	1.3^{2664}	154	4.1^{62}	1.6^{1135}	2.1^{1309}	1.9^{2506}

For the viscosity reference temperature, the proposed method yielded a consistent set of results for the different classes of halogen compounds. For all mono-functional (modified definition) halogenated compounds, there were no deviations greater than 17 K. For multi-functional halogenated compounds, there were large deviations for halogenated silicon compounds. These components will be discussed in the next section. Overall, large deviations were only observed for diiodomethane (20 K) and tribromofluoromethane (26.8 K) and since these are the first in their respective series, they were removed from the regression set. Caution should always be taken when estimating the viscosity of highly halogenated methane and to some degree ethane compounds.

---

[*] Includes multi-functional compounds

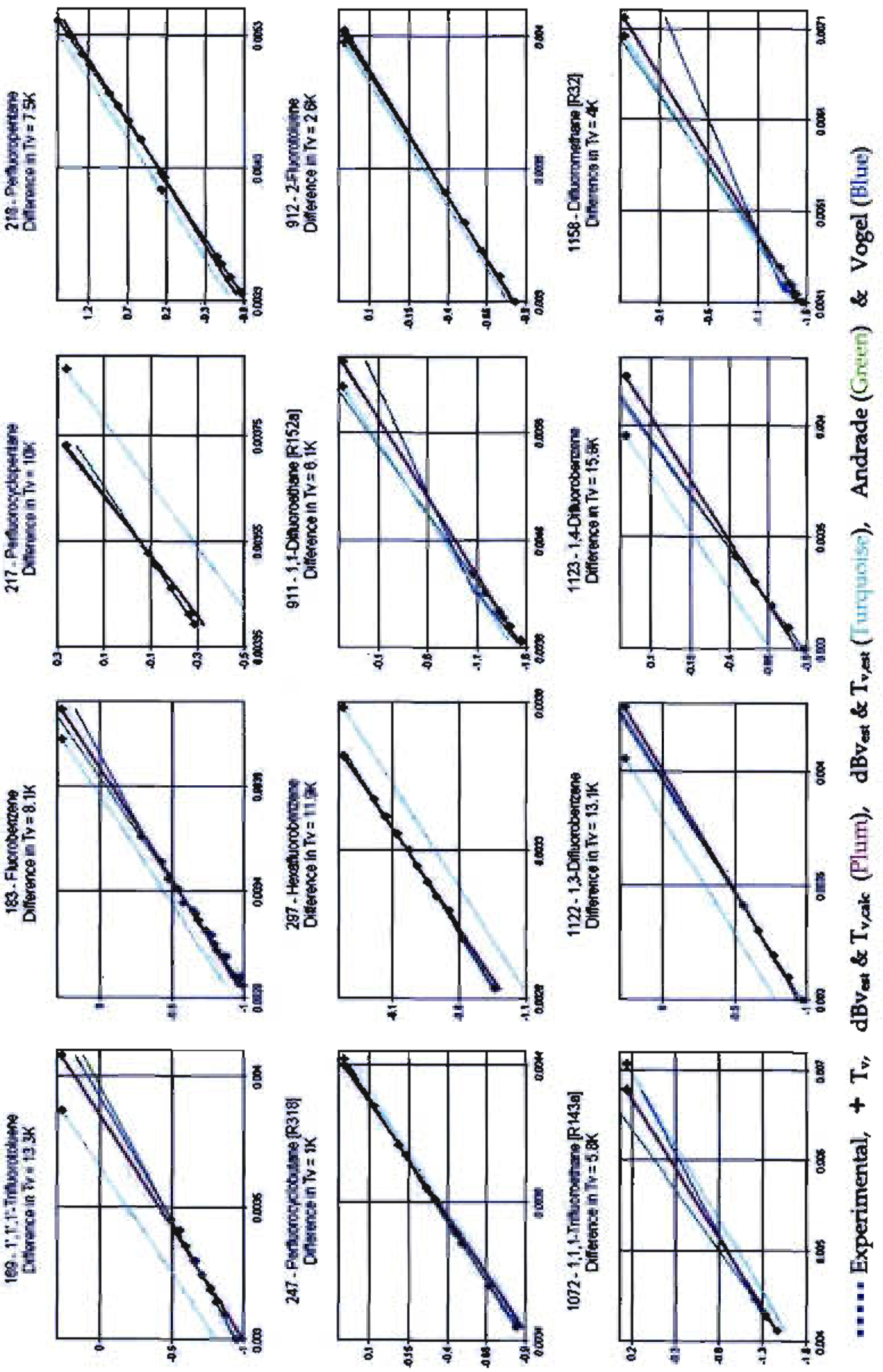


Figure 9-23: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for fluorines.

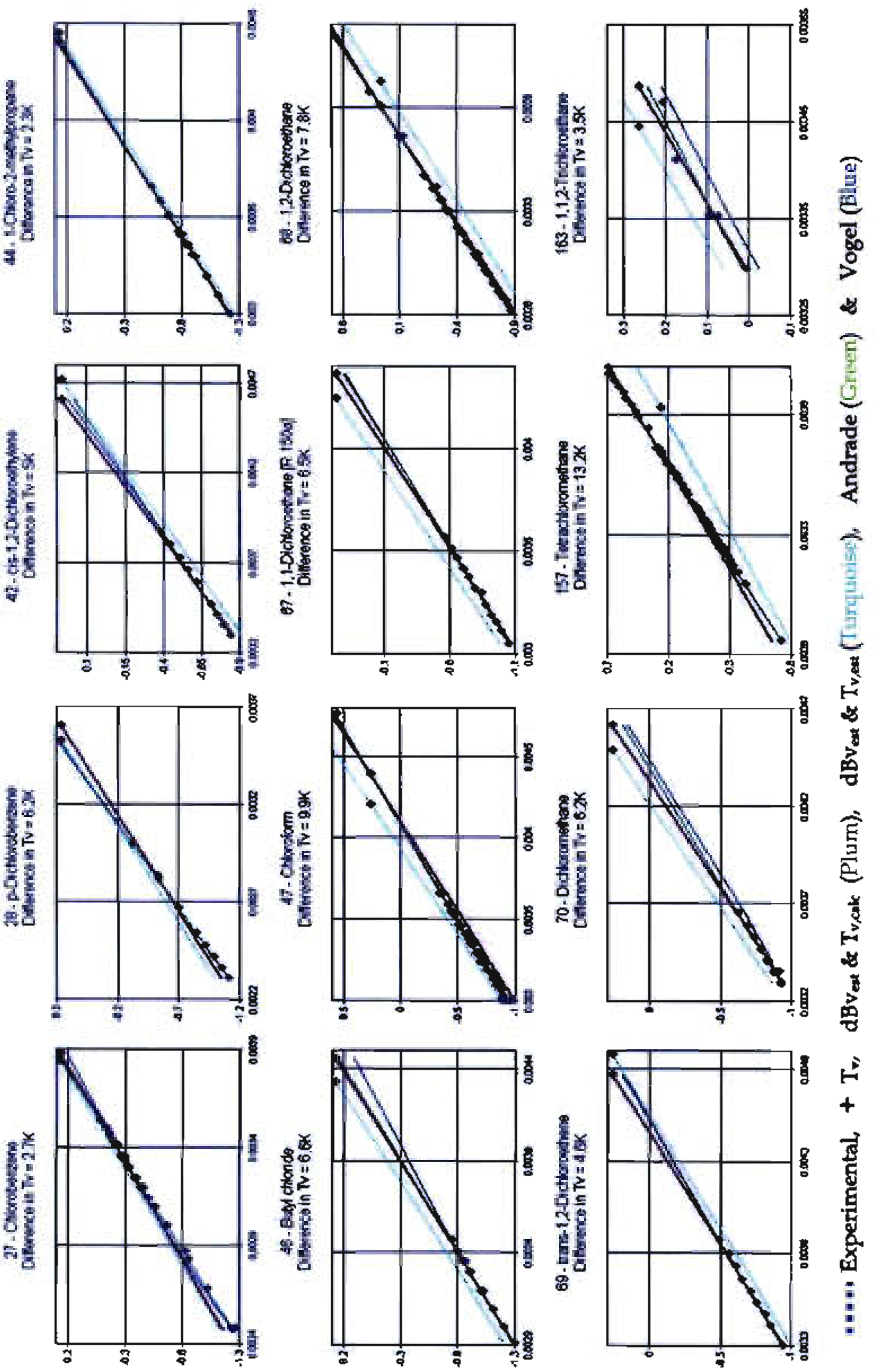


Figure 9-24: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for chlorines.

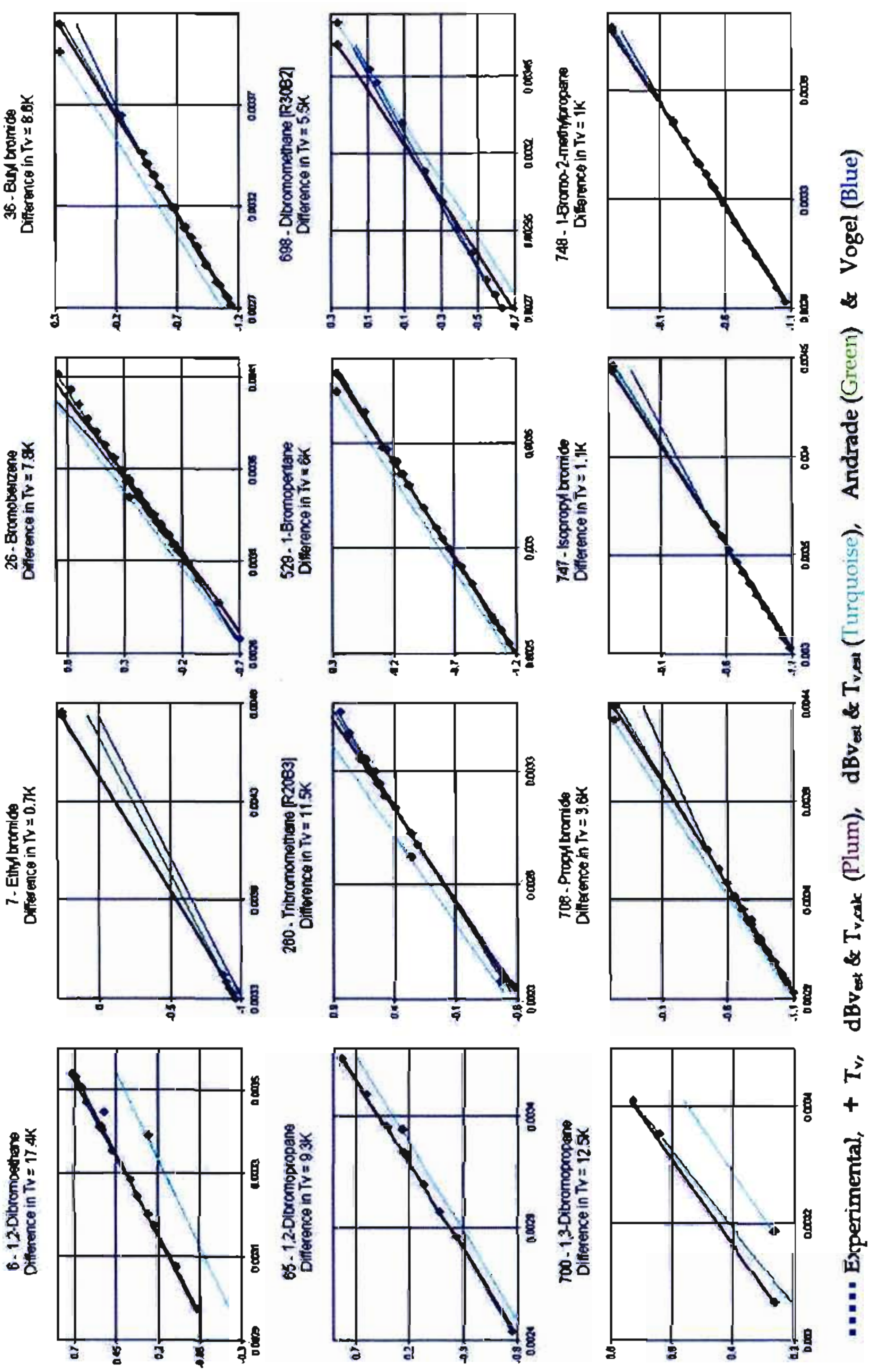


Figure 9-25: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for bromines.

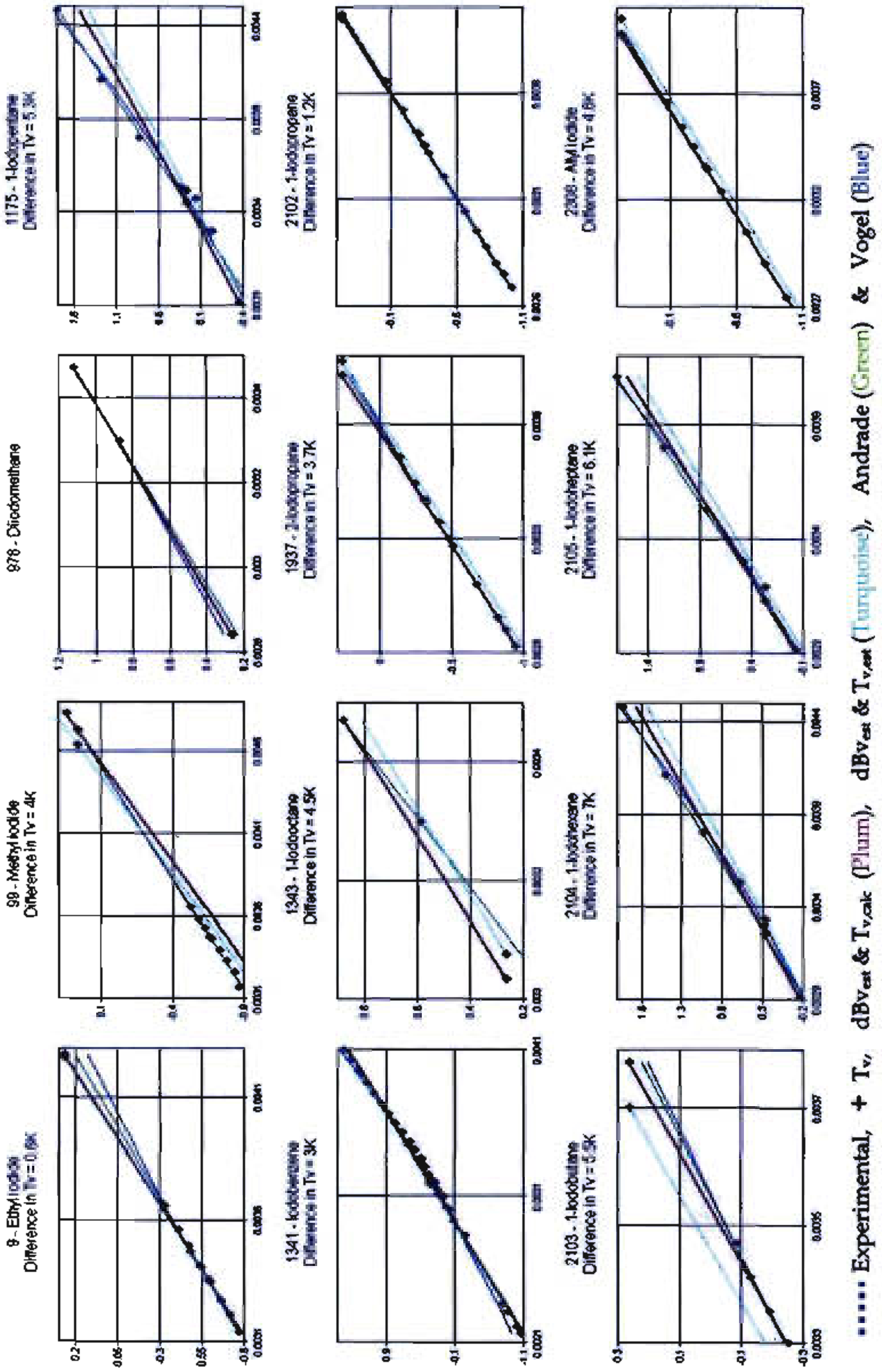


Figure 9-26: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for iodines.

9.4.2.5 Various Other Compounds

Results for the various other types of compounds for the proposed method and both the correlative models are presented in Tables 9-15 and 9-16, respectively. There were also no especially large deviations from the estimation of the slope for these compounds over the entire temperature range.

Table 9-15: Viscosity average absolute deviations of this work for the various other types of compounds (number of data points as superscript).

	Average Absolute Deviation (%)					T_v		
	NC	ELP	LP	MP	AV	NC	AAD	MAPE
Phosphates	4	3.8^{106}	5.2^{2}	0.0^{4}	3.7^{112}	4	17.0	4.6
Germanium	1	-	-	0.1^{7}	0.1^{7}	1	0.0	0.0
Boron	6	0.5^{2}	1.3^{30}	2.0^{29}	1.6^{61}	6	9.8	4.2
Silicon	2	-	0.5^{5}	0.0^{2}	0.4^{7}	2	9.8	3.9
Silicon (*en* [*])	23	4.5^{18}	2.8^{79}	2.2^{73}	2.7^{170}	22	17.7	6.2
Acid chloride	5	-	1.6^{7}	1.1^{24}	1.2^{31}	5	1.8	0.8
Urea	1	-	0.3^{9}	0.0^{1}	0.3^{10}	1	0.0	0.0

Multiple plots of phosphate, boron, silicon and acid chloride compounds are presented in Figures 9-27, 9-28, 9-29 and 9-30, respectively. The proposed method yielded an excellent agreement between estimated and experimental data and similar results are observed for the other compounds not plotted. For phosphate compounds, a slightly odd curvature of the trends from experimental data is observed for the latter three compounds in the plot. All data for these components were reported in the same publication. For boron compounds, a difference in the slope between the experimental and estimated trends is observed only for boric acid trimethyl ester which is also the smallest compound. However, estimations of the slope from other boron compounds show a better agreement. For silicon compounds, a slight disparity is observed for several compounds with data from only one source of data, such as trimethylchlorosilane and hexamethyldisiloxane.

---

[*] Denotes silicon connected to any electronegative neighbour. This filter also includes all multi-functional compounds.

Table 9-16: Viscosity average absolute deviations (%) of the Andrade and Vogel models for various other types of compounds (number of data points as superscript).

	Average Absolute Deviation (%)									
	Andrade					**Vogel**				
	NC	**ELP**	**LP**	**MP**	**AV**	**NC**	**ELP**	**LP**	**MP**	**AV**
Phosphates	4	2.1^{106}	4.8^{2}	10.9^{4}	2.5^{112}	4	5.2^{106}	3.3^{2}	17.3^{4}	5.6^{112}
Germanium	1	-	-	0.3^{7}	0.3^{7}	1	-	-	0.8^{7}	0.8^{7}
Boron	6	1.2^{2}	0.8^{30}	2.5^{29}	1.6^{61}	6	0.3^{2}	0.6^{30}	3.4^{29}	1.9^{61}
Silicon	2	-	0.0^{6}	0.9^{2}	0.3^{7}	-	-	-	-	-
Silicon (*en* [·])	23	1.1^{18}	1.3^{79}	2.6^{73}	1.9^{170}	19	0.8^{15}	1.2^{76}	8.0^{67}	4.0^{158}
Acid chloride	5	-	0.2^{7}	1.7^{24}	1.4^{31}	4	-	0.3^{5}	2.7^{23}	2.3^{28}
Urea	1	-	0.2^{9}	0.0^{1}	0.2^{10}	1	-	0.8^{9}	1.0^{1}	0.8^{10}

For the viscosity reference temperature, a large error was only observed for triphenyl phosphate (30.8 K). Phosphate triester is the only phosphate compound in the training set where the oxygen atoms are connected to an aromatic carbon. Usually, a distinction is required here; however, this distinction was not observed for the estimation of the normal boiling point of these compounds (an estimation error of 4 K was reported). Considering the questionable nature of the data and since there is only one component, a new group was not added in this case.

[·] Denotes silicon connected to any electronegative neighbour. This filter also includes all multi-functional compounds.

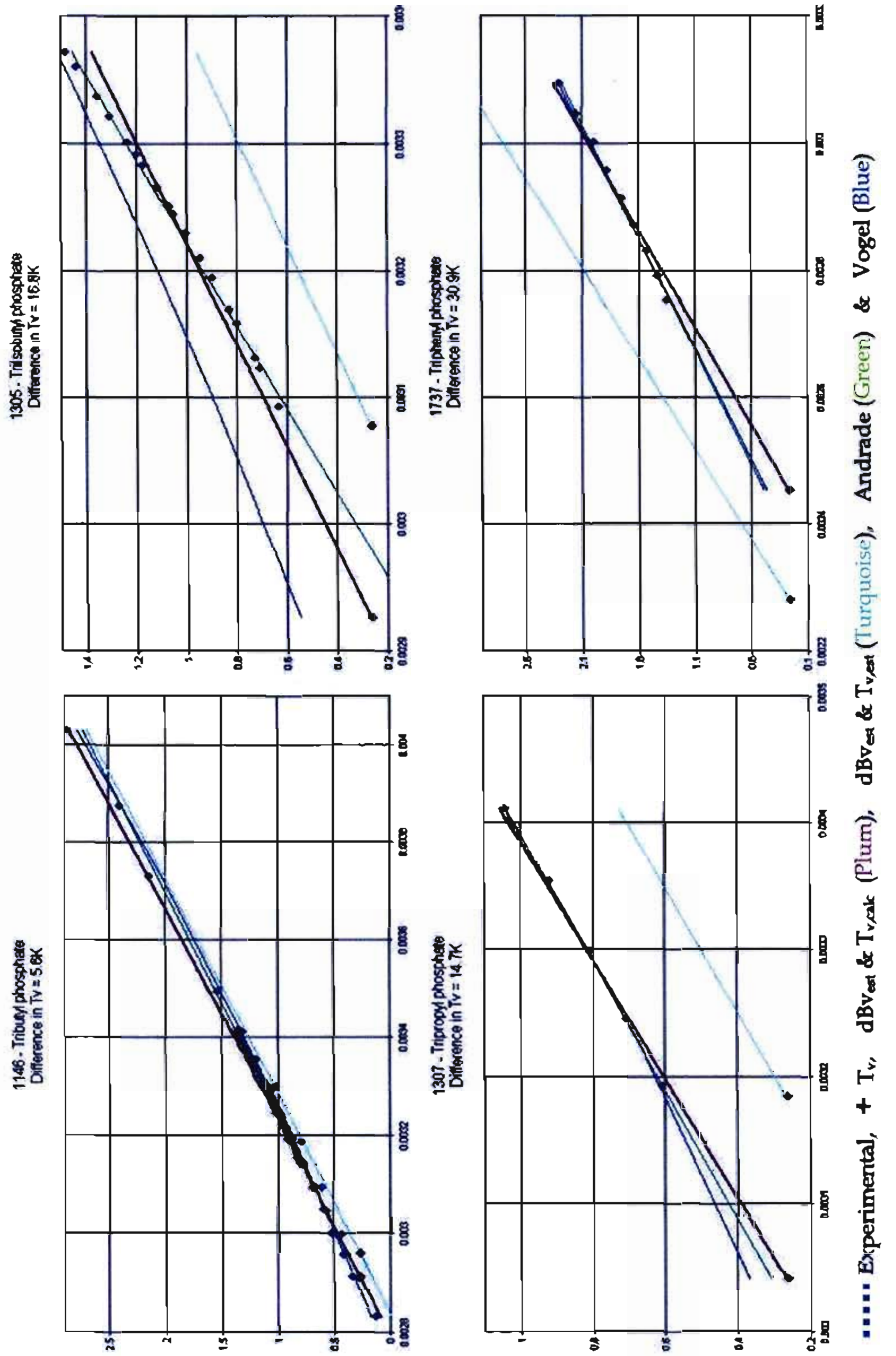


Figure 9-27: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for phosphates.

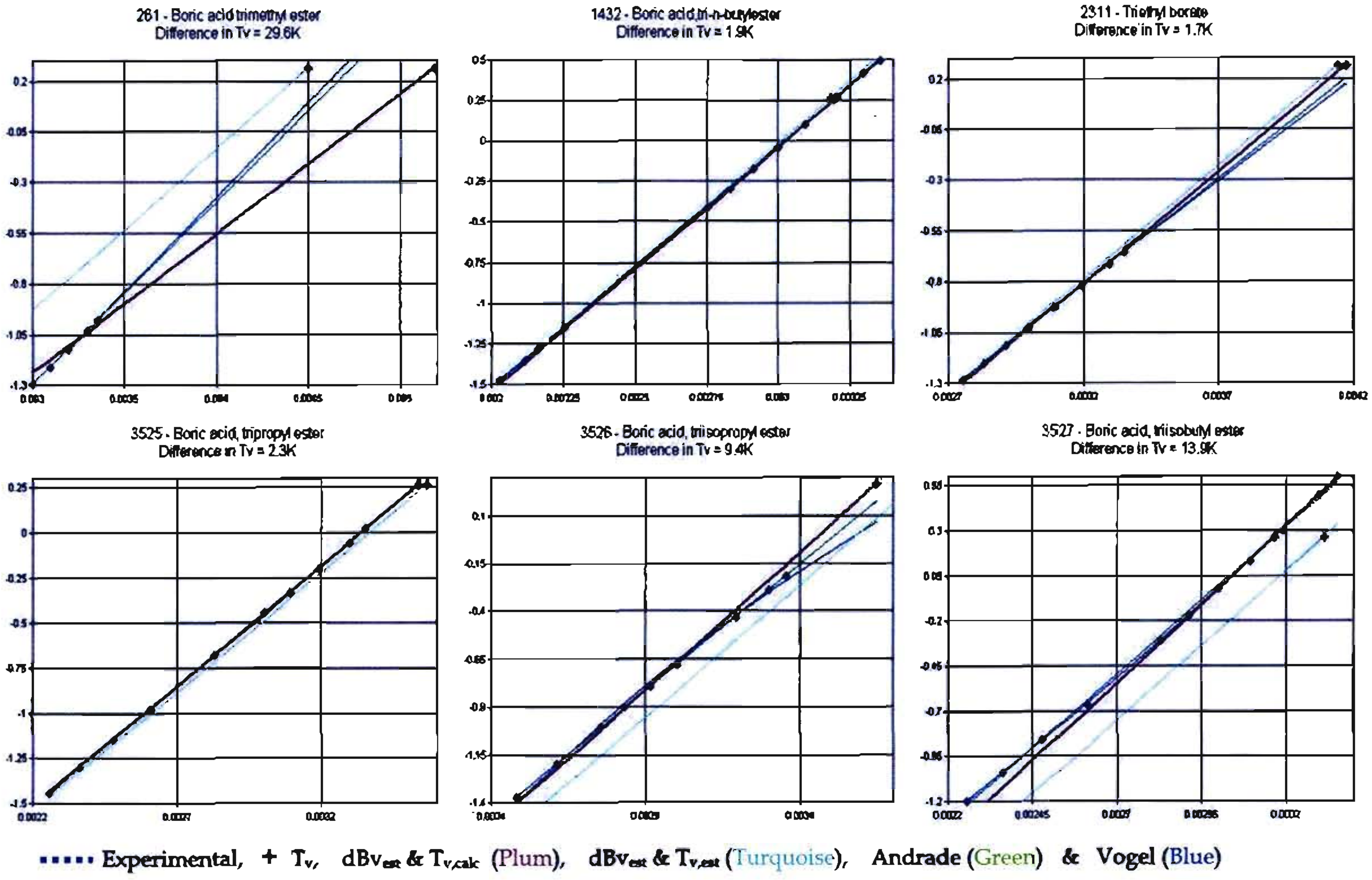


Figure 9-28: Multiple plot (Ln (μ) vs. 1/T [K⁻¹]) of experimental and estimated liquid viscosities for boron compounds.

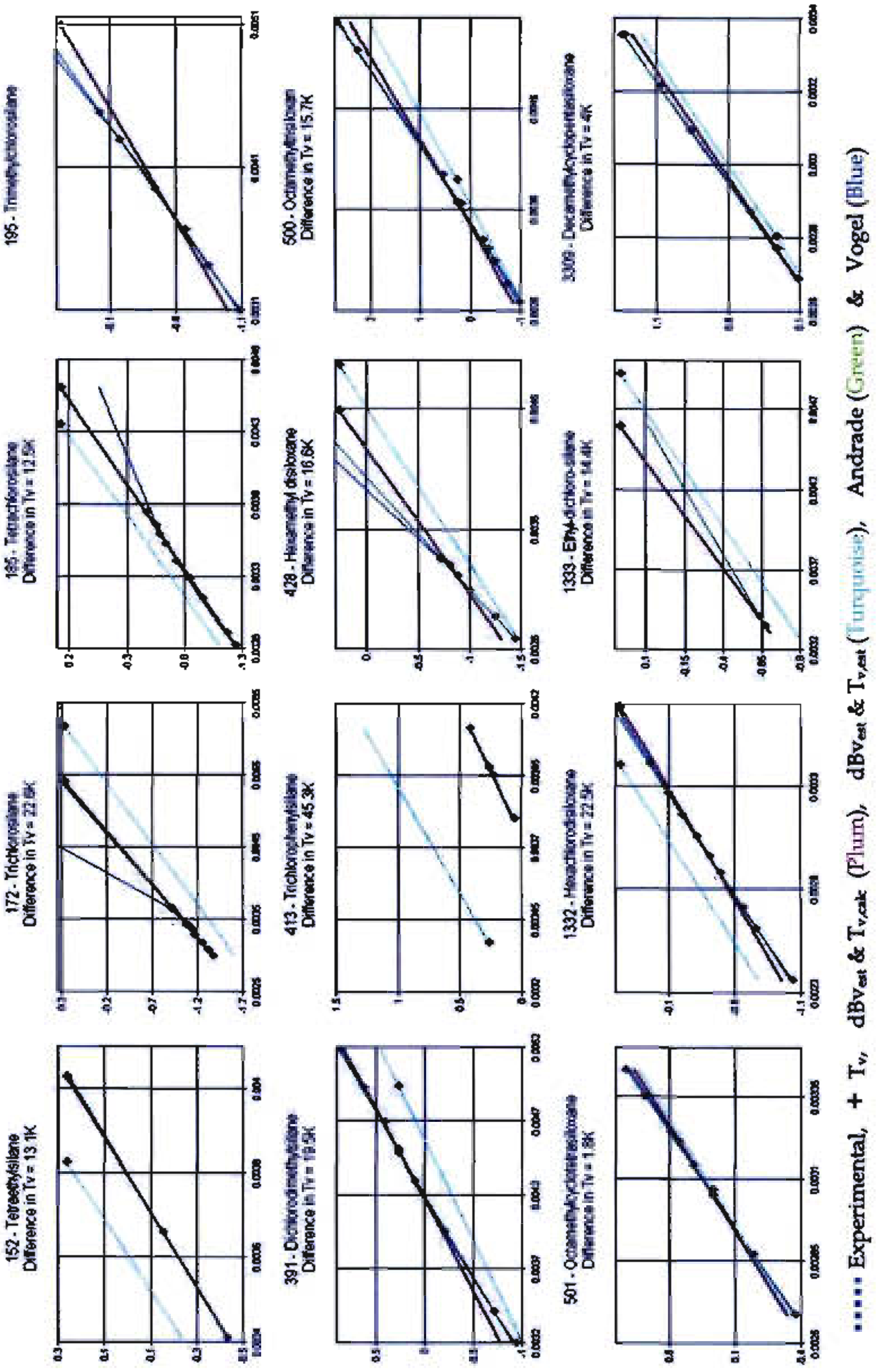


Figure 9-29: Multiple plot (Ln (μ) vs. 1/T [K⁻¹]) of experimental and estimated liquid viscosities for silicon compounds.

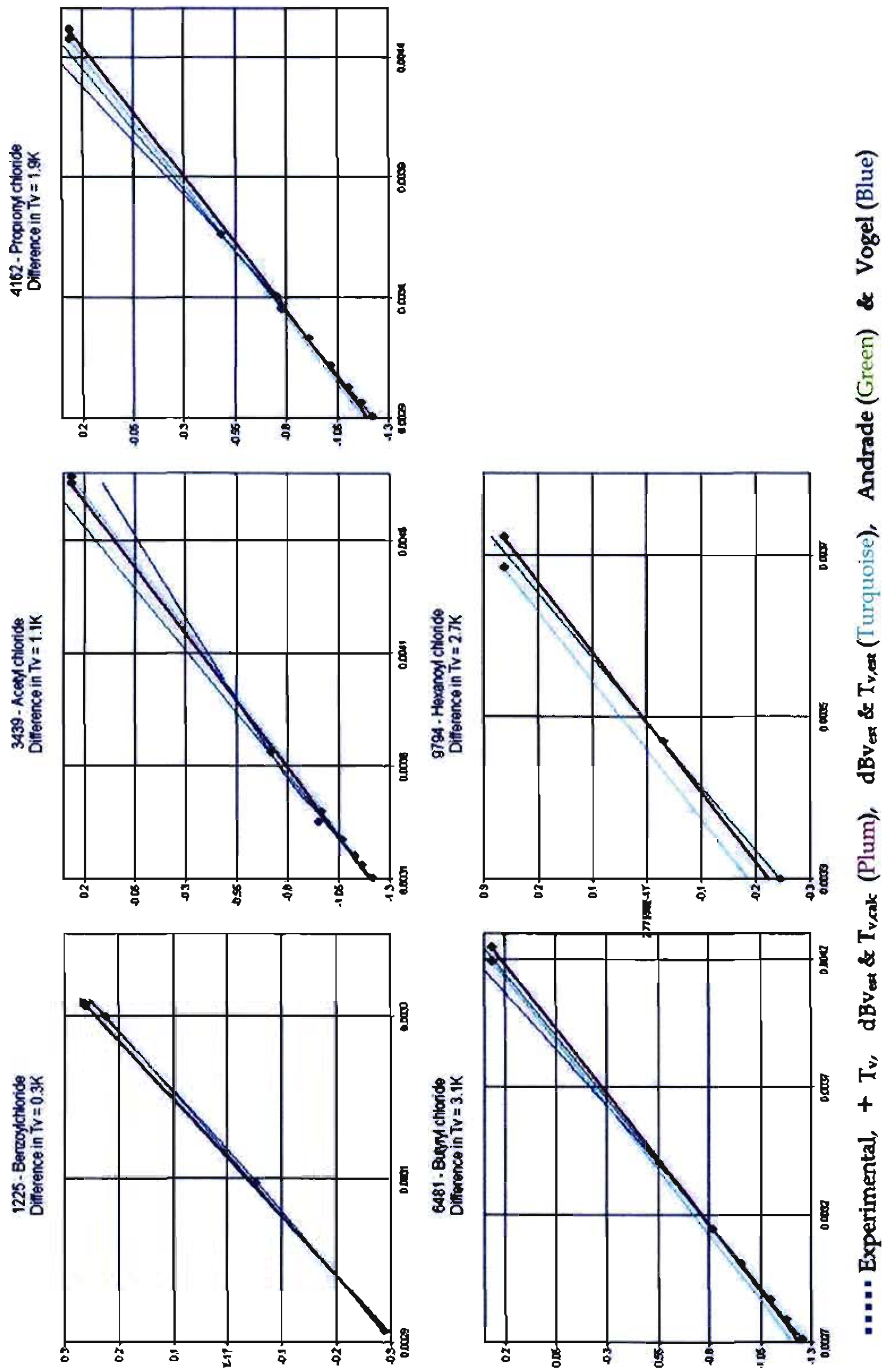


Figure 9-30: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for acid chlorides.

There were also large deviations observed for silicon compounds, especially for smaller highly halogenated or oxygenated compounds. The largest deviations reported were for trichlorophenylsilane (45.0 K), octadecamethyloctasiloxane (35.0 K) and trimethylchlororsilane (30.0 K). For these compounds, the greater steric strain and subsequent change in polarizability, especially in the case of smaller compounds leads to larger deviations. With increasing molecular weight, the estimation improves and extrapolates correctly as shown in Figure 9-31. Trimethylchlororsilan was also the first compound in its series and was removed from the regression set.

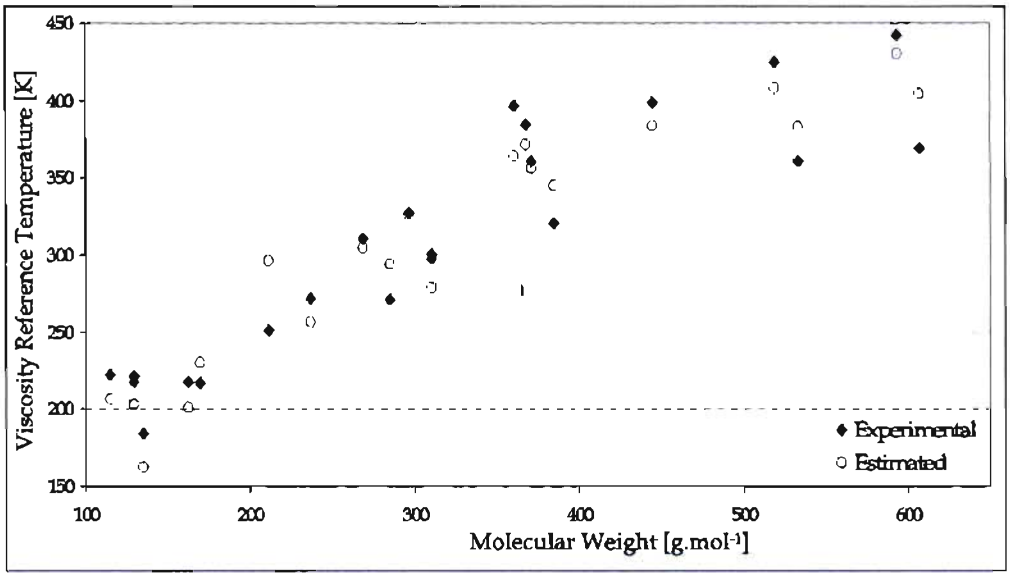


Figure 9-31: Plot of adjusted ('experimental') and estimated viscosity reference temperatures for silicon compounds connected to electronegative atoms.

There was also a large deviation reported for boric acid trimethyl ester (29.6 K) for which the data maybe of questionable accuracy (Figure 9-28). For other boron compounds, no deviations greater than 13 K were found.

9.4.3 Multi-functional Compounds

Results for multi-functional compounds for the proposed method and both the correlative models are presented in Tables 9-17 and 9-18, respectively. Slightly larger average errors should be expected as the experimental information is often of low quality for these molecules. However, there were no cases of extreme deviations for all classes of compounds over the whole temperature ranges.

Multiple plots for multi-functional compounds are presented in Figures 9-32 to 9-35. The proposed method yielded an excellent agreement between estimated and experimental data and similar results are observed for the other compounds not plotted.

The lower quality of the data in many cases leads to a scatter of the data points. In the case of ethylenediamine, Figure 9-32, two different sources of data (Friend & Hargreaves (1944) and Kapadi *et al.* (2003)) show two different temperature trends. The former reference covers the higher temperature range and was also cited and questioned earlier in the case of alpha-aminotoluene. The latter reference is a recent measurement and shows a good agreement with the proposed method. The error between the unreliable reference and the proposed method increased the average deviation while correlative models produce a more accurate fit. There are also components where dissimilar viscosity values are reported for the same temperature. For example, for 1,4-dioxane (Figure 9-32), four different viscosity values at the same temperature from four different references are shown. Unfortunately, none of these data points could be verified. Overall, as mentioned in this and the previous chapter, the estimation is based on chemically similar compounds and the method can to a certain extent be employed to verify data.

Compounds with amine interaction groups usually showed the largest disparity and a higher deviation in Table 9-17. Most of the data were reported by Friend and Hargreaves who published questionable values in several other cases. Overall, the proposed method reports satisfactory results, even for components where the viscosity reference temperature was extrapolated.

Table 9-17: Viscosity average absolute deviations of this work for multi-functional compounds (number of data points as superscript).

	Average Absolute Deviation (%)					T_v		
	NC	ELP	LP	MP	AV	NC	AAD	MAPE
OH	36	9.4^{171}	5.2^{478}	0.8^{37}	6.0^{686}	35	13.3	3.6
OH(a)	8	10.6^{6}	4.9^{66}	3.8^{30}	4.9^{102}	8	20.9	5.4
NH_2	10	15.6^{2}	9.3^{78}	2.0^{12}	8.5^{92}	10	7.0	1.9
NH	3	7.3^{18}	3.3^{26}	0.0^{3}	4.6^{46}	3	6.5	1.6
Ether	64	7.0^{93}	3.2^{494}	2.9^{149}	3.6^{736}	64	10.8	3.3
Ester	16	6.8^{101}	3.5^{40}	0.0^{16}	5.3^{157}	16	7.2	2.0
Ketone	5	-	0.3^{14}	1.1^{7}	0.6^{21}	5	1.5	0.4
Aldehyde	2	3.6^{1}	0.3^{3}	0.0^{2}	0.7^{6}	2	0.0	0.0
Nitro, CN, AO, AN6	11	2.1^{8}	3.2^{85}	1.4^{15}	2.9^{108}	11	9.3	2.4
All GI components	111	8.1^{312}	4.1^{948}	2.3^{205}	4.7^{1463}	110	10.3	2.9

Table 9-18: Viscosity average absolute deviations (%) of the Andrade and Vogel models for multi-functional compounds (number of data points as superscript).

	Average Absolute Deviation (%)									
	Andrade					Vogel				
	NC	ELP	LP	MP	AV	NC	ELP	LP	MP	AV
OH	36	4.8^{171}	2.4^{478}	11.9^{37}	3.5^{686}	27	5.6^{158}	6.7^{419}	49.7^{28}	8.4^{605}
OH(a)	8	11.3^{6}	3.3^{66}	3.3^{30}	3.8^{102}	8	1.0^{6}	1.8^{66}	2.7^{30}	2.0^{102}
NH_2	10	7.9^{2}	5.1^{78}	10.8^{12}	5.9^{92}	8	0.4^{1}	3.4^{72}	9.7^{10}	4.1^{83}
NH	3	4.4^{18}	2.3^{25}	8.6^{3}	3.5^{46}	2	3.0^{18}	1.6^{16}	60.6^{2}	5.6^{36}
Ether	64	5.1^{93}	1.8^{494}	2.9^{149}	2.4^{736}	41	3.9^{79}	2.0^{419}	6.8^{101}	3.1^{599}
Ester	16	3.1^{101}	0.8^{40}	13.2^{16}	3.6^{157}	13	2.1^{98}	1.4^{35}	21.4^{13}	3.7^{146}
Ketone	5	-	0.3^{14}	1.4^{7}	0.7^{21}	1	-	0.2^{6}	0.0^{1}	0.2^{7}
Aldehyde	2	0.0^{1}	0.0^{3}	0.1^{2}	0.0^{6}	1	-	3.5^{2}	9.1^{1}	5.4^{3}
Nitro, CN, AO, AN6	11	2.9^{8}	1.7^{85}	2.2^{15}	1.9^{108}	10	1.9^{8}	1.8^{76}	5.0^{14}	2.2^{98}
All GI components	111	4.1^{312}	2.1^{948}	5.0^{205}	2.9^{1463}	80	4.2^{289}	4.2^{822}	14.2^{149}	5.4^{1260}

The estimation of the viscosity reference temperature for multi-functional compounds employs interaction groups as in the case of other properties. However, the increase in the number of strongly associating groups resulted in a larger change in temperature as compared to the previous properties. Thus, the calculation of GI was modified by squaring the individual interaction group's frequency (Equation 9-6). This modification for the viscosity reference temperature is the only change in the group contribution approach employed in this work. In other words, the previous properties employ the exact same group definitions, etc.

$$GI = \frac{1}{n}\sum_{i=1}^{m}\sum_{j=1}^{m}\left(\frac{C_{i-j}}{m-1}\right)^2 \qquad \text{(Where } C_{i-j} = C_{j-i}\text{)} \qquad (9\text{-}6)$$

As described earlier, C_{i-j} is the group interaction contribution between group i and group j (where $C_{i-i} = 0$), n is the number of atoms (except hydrogen) and m is the total number of interaction groups in the molecule.

For the viscosity reference temperature, the proposed method yields reliable results in all cases. Higher deviations should be expected for these types of compounds mainly due to the poor quality of the data.

All methodology involving the estimation of multi-functional compounds for critical properties in Section 7.5 also applies here. This includes special cases for where the estimation should not be carried out. Overall, large deviations were observed for components which exhibit special behaviour like strong mesomeric or inductive interactions with an aromatic system. For example, the largest deviation was for o-nitrophenol (51.6 K) and its isomers, p-nitrophenol (35.5 K) and m-nitrophenol (15.0 K). However, an astonishing 99.4 K difference in the viscosity reference is reported for the former two compounds whereas the difference is only 19.6 K for the normal boiling point.

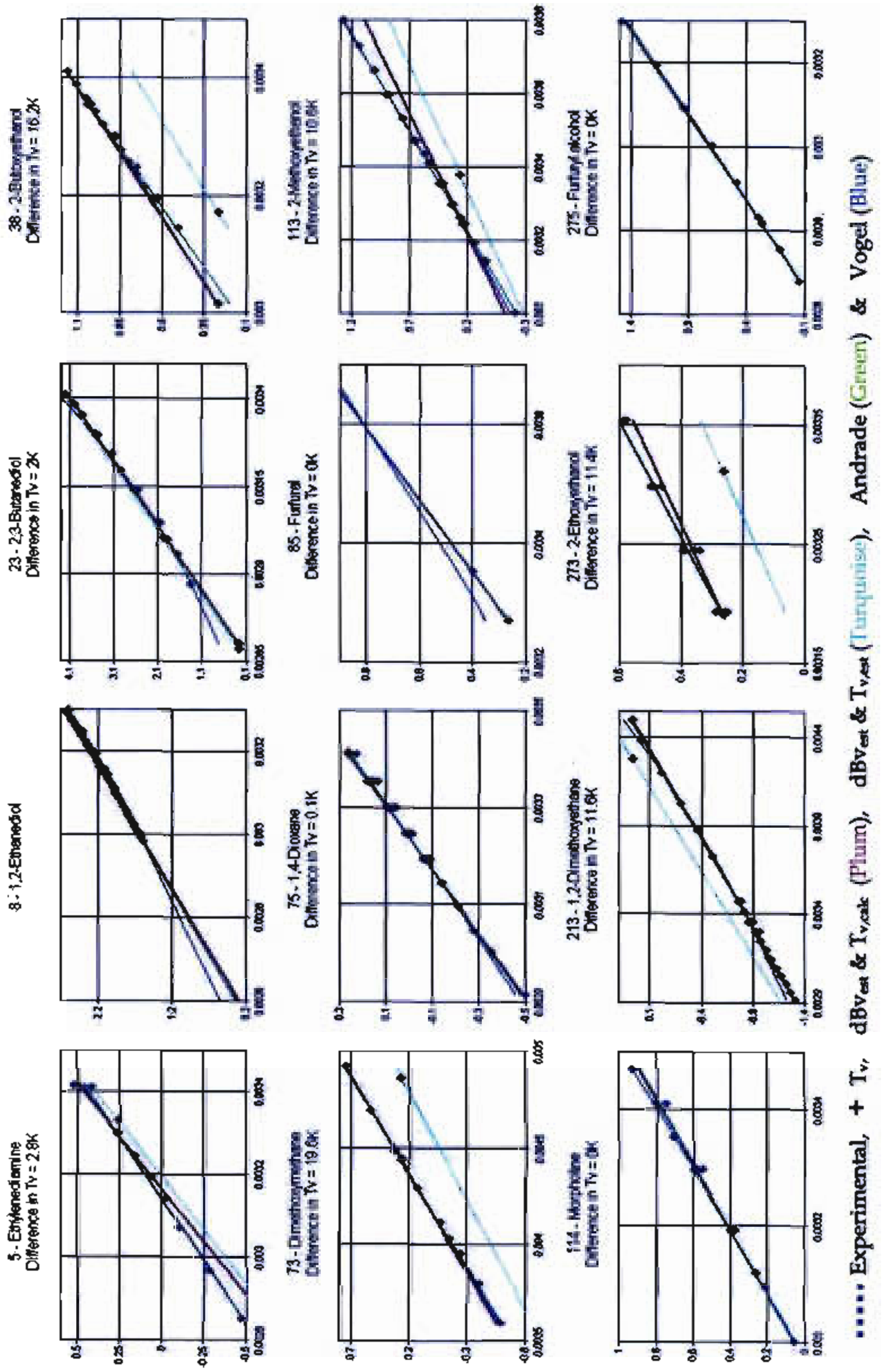


Figure 9-32: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for multi-functional compounds.

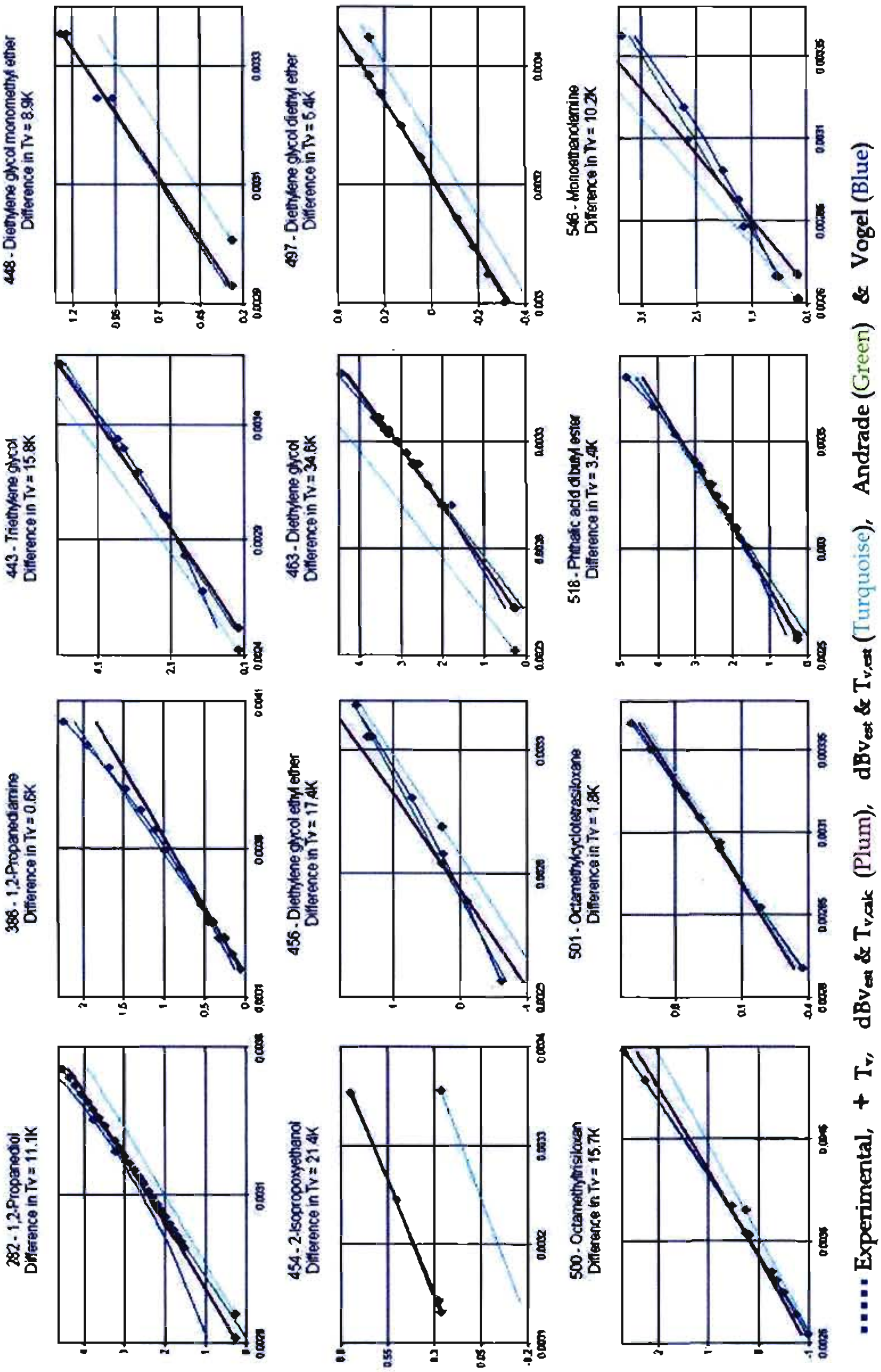


Figure 9-33: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for multi-functional compounds.

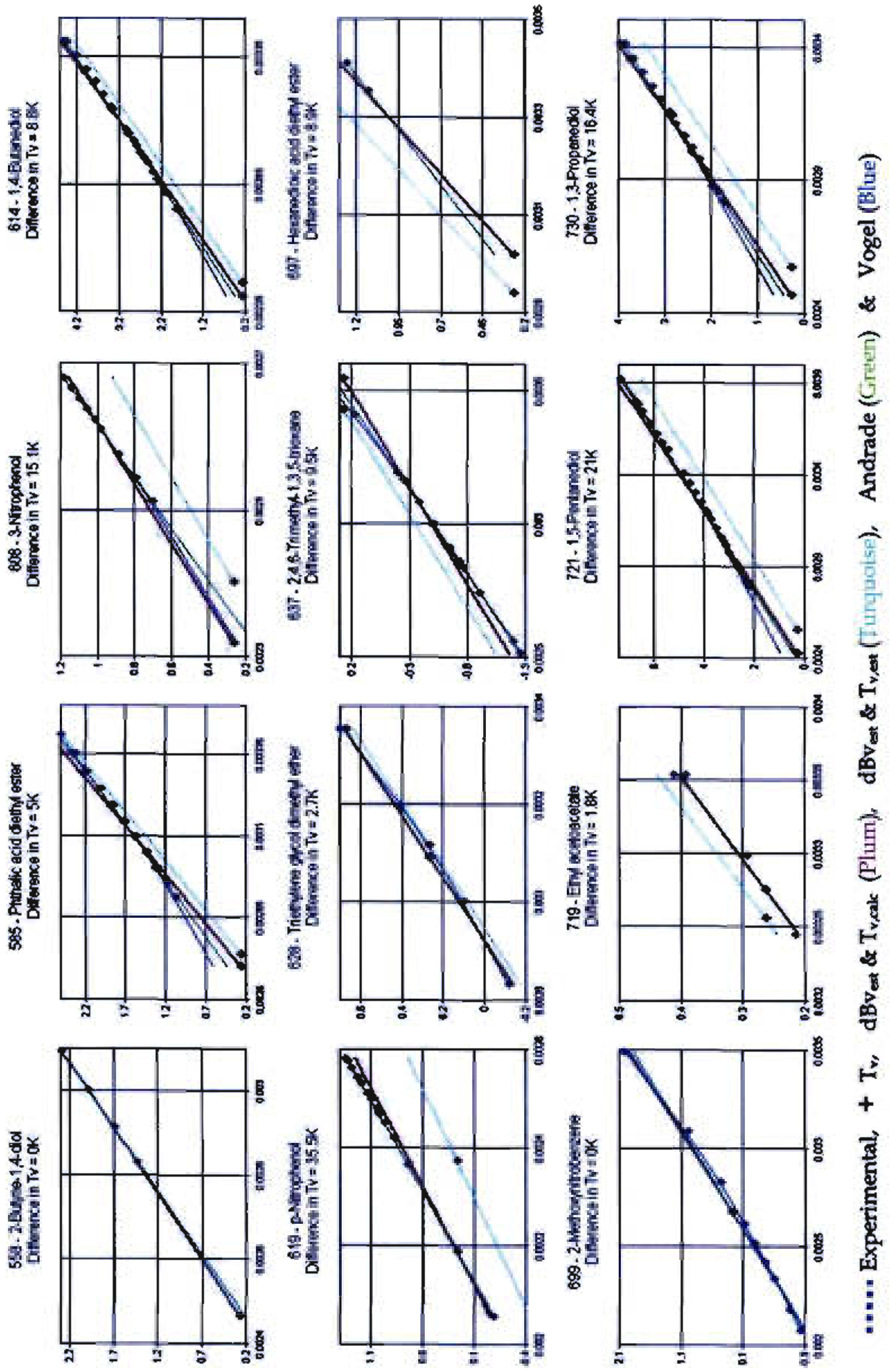


Figure 9-34: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for multi-functional compounds.

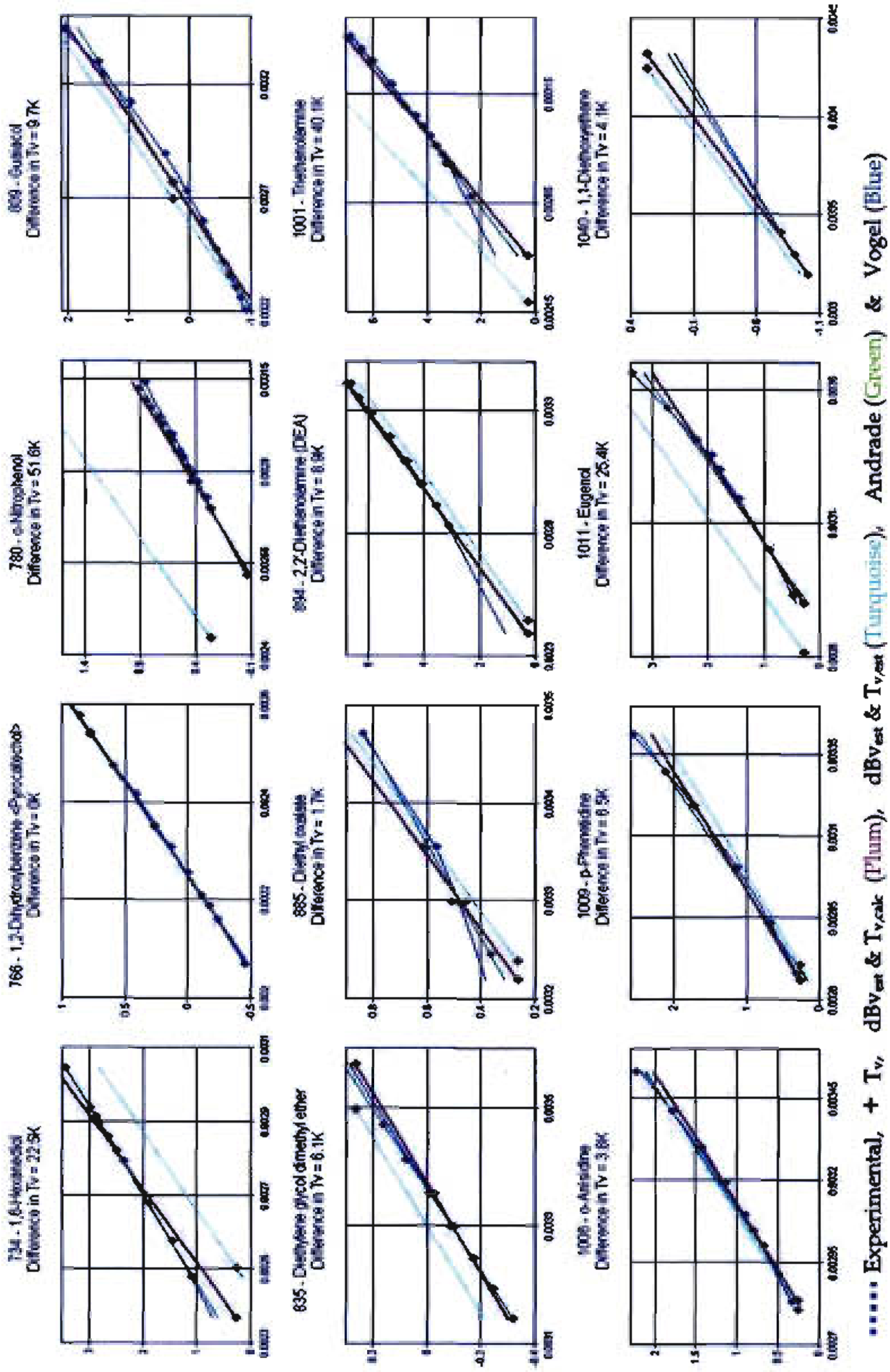


Figure 9-35: Multiple plot (Ln (μ) vs. 1/T [K^{-1}]) of experimental and estimated liquid viscosities for multi-functional compounds.

9.5 Overall Discussion

9.5.1 Overall Results

For the group contribution estimation of *dBv*, the proposed method reported an average absolute deviation of 0.2 or 3.3% for 829 components. This estimation error is acceptable as there are a number of cases where the data are of poor quality. There were also no relatively high deviations (> 26%).

The results for the estimation of liquid viscosities for all data points from this work and correlative models are presented in Table 9-19. Overall, the proposed method yields results that are in comparable accuracy to the correlative models.

Table 9-19: Liquid viscosity average absolute deviations of this work and correlative models for all compounds.

		Average Absolute Deviation (Number of data points as Superscript)			
	NC	**ELP**	**LP**	**MP**	**AV**
This work (%)	829	5.6^{1363}	3.5^{7896}	2.5^{4431}	3.4^{13690}
Andrade (%)	829	2.6^{1363}	1.6^{7896}	1.8^{4431}	1.8^{13690}
Vogel (%)	723	3.0^{1304}	2.1^{7606}	4.3^{4244}	2.9^{13154}

The proposed method may yield a slightly higher deviation as compared to the correlative models, but some errors are attributed to the inconsistent and unreliable experimental data. These errors are usually for components where the data were taken from older references. For many components, data from only one reference were available.

9.5.2 Test of the Predictive Capability

There were less data points available for liquid viscosity as compared to the liquid vapour pressure. Thus, all data points were used in the regression and no test set was prepared.

During the development of the liquid viscosity method, no significant qualitative differences to the modelling of the liquid vapour pressure and critical property data were observed. It is therefore improbable that the method for liquid viscosity estimation would perform significantly different when applied to a test set.

Extrapolation from small molecules to high molecular weight components is especially difficult for strongly associating compounds. In this case, not only the size of the molecule changes but also the effect of the associating group which eliminates the property of small species in the series. At the same time, the behaviour of large molecules approaches that observed for higher molecular weight alkanes.

Examples are shown in Figures 9-36 and 9-37 for 1-alcohols and mono-functional carboxylic acids, respectively. It is obvious that the estimation method is able to reproduce this simultaneous change in molecular size and association strength.

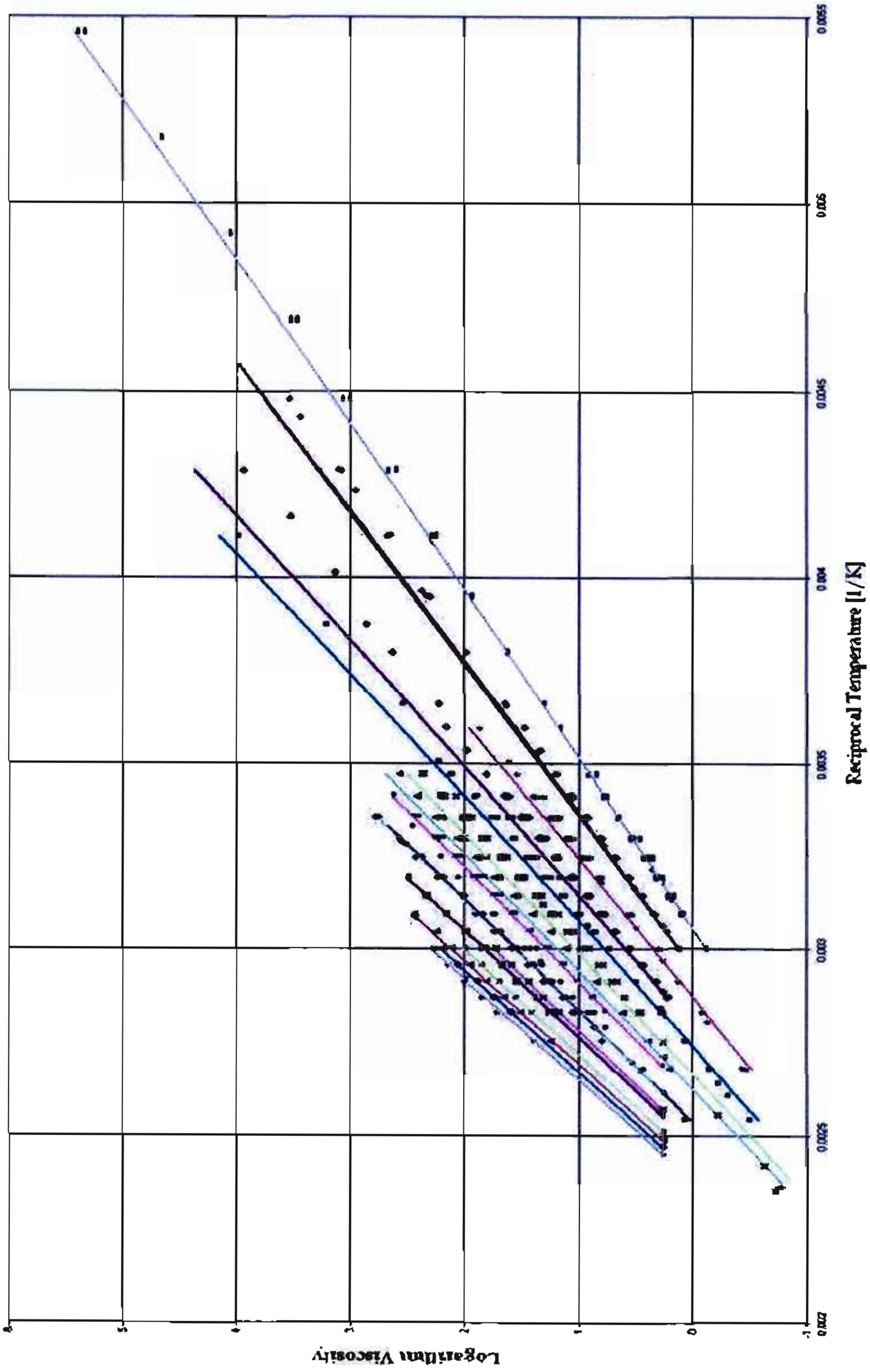


Figure 9-36: Series plot of experimental and estimated liquid viscosities for 1-alcohols from this work.

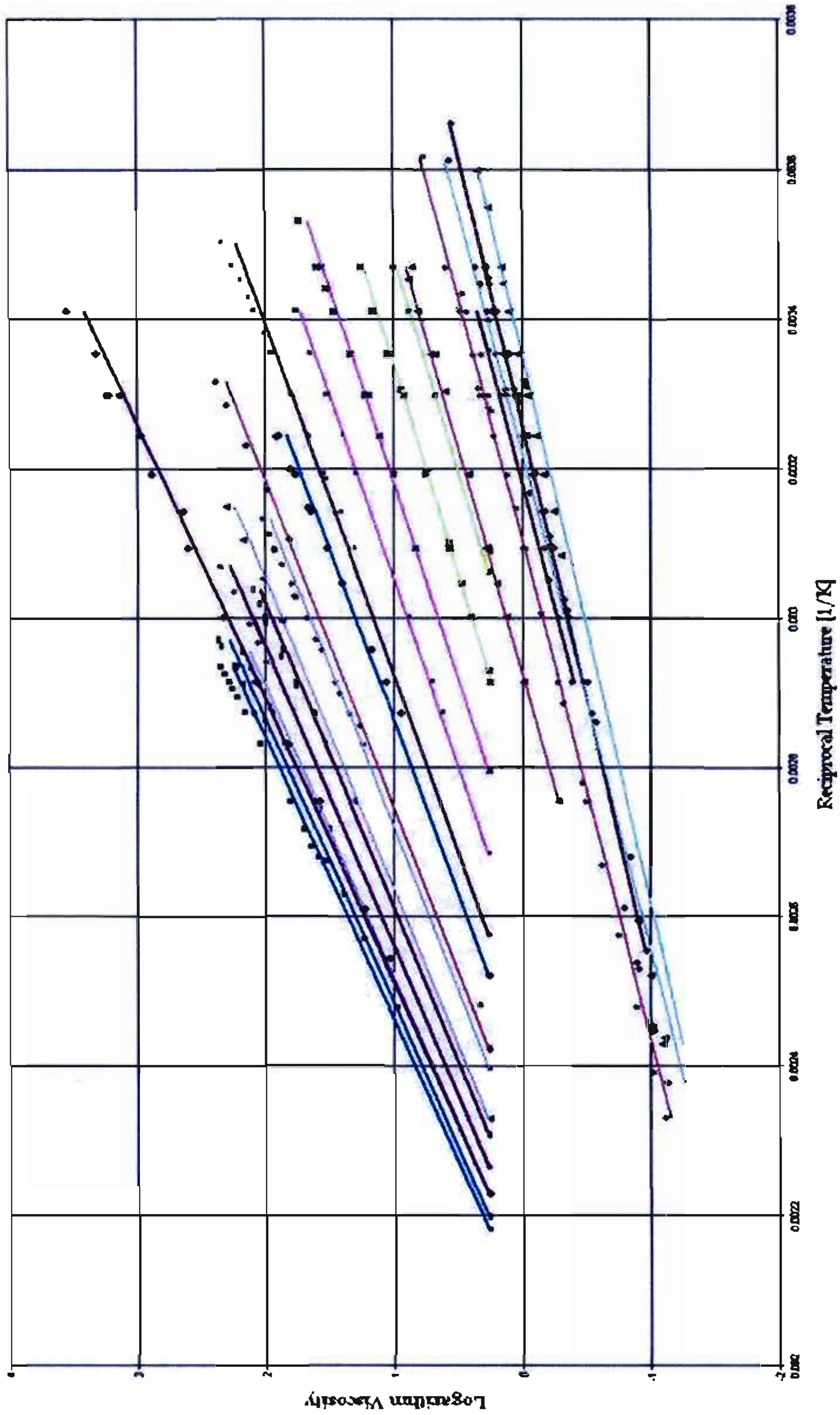


Figure 9-37: Series plot of experimental and estimated liquid viscosities for mono-functional carboxylic acids from this work.

In contrary to the other methods developed in this work, the model employed for the viscosity reference temperature contains two competing terms which may lead to erroneous behaviour as a function of molecular weight. For this reason, as mentioned earlier, the competing terms were regressed separately. To confirm the validity of the resulting equation, a plot of the estimated viscosity reference temperature for n-alkanes as a function of the number of carbon atoms is presented in Figure 9-38. For this estimation, components missing experimental normal boiling points were estimated by the previous method, Nannoolal (2004) & Nannoolal *et al.* (2004). The viscosity reference temperatures do not show any physically unrealistic behaviour with respect to molecular size. The viscosity reference temperature also asymptotically approaches a fixed temperature with increasing molecular weight.

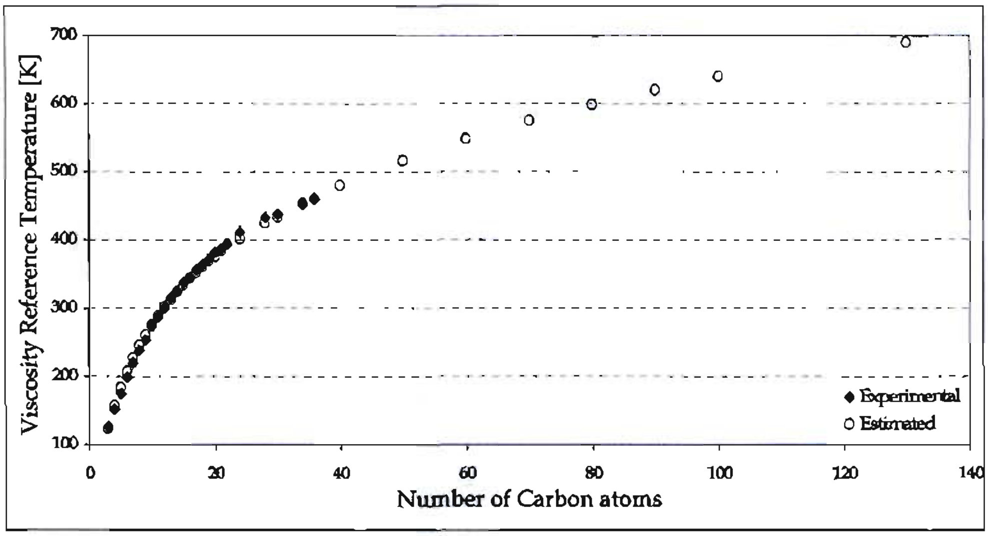


Figure 9-38: Plot of adjusted ('experimental') and estimated viscosity reference temperatures for n-alkanes.

9.5.3 Reference Temperature Omission

Using a single experimental liquid viscosity allows one to calculate the viscosity reference temperature from Equation 9-5. For the regression set of components employed in this work, the back calculation of the viscosity reference temperature produced an average absolute deviation of 3.1 K for extremely low vapour pressures (*ELP*), 1.6 K for low vapour pressures (*LP*), 3.0 K for moderate pressures (*MP*) and

1.8 K for all points. Some errors must be attributed to unreliable data, but overall, a single liquid viscosity point will be sufficient for the proposed estimation method.

If there are no viscosity data available, two options can be used to estimate the fixed point. The first is an empirical method to estimate the liquid viscosity at the normal boiling point, Smith *et al.* (2003). This method proposes empirical rules to estimate the viscosity of organic compounds containing carbon, hydrogen, oxygen, nitrogen, chlorine and bromine at the normal boiling point. Smith *et al.* (2003) reported that the available temperature dependant viscosity correlations were improved for 250 compounds from a set of more than 800 compounds obtained from DIPPR using these rules.

The above method is usually only reliable for mono-functional compounds and extreme caution is necessary in case of multi-functional compounds. An alternate method is to employ the group contribution method proposed in this chapter to estimate the temperature at a viscosity of 1.3 cP. For this method, an average absolute deviation of 7.1 K (2.5%) for 813 components was obtained. This result is satisfactory as errors must be also attributed to the interpolation and optimisation of this point as well as experimental errors.

If the estimated viscosity reference temperature is used instead of the adjusted value to estimate the liquid viscosity, an average absolute deviation of 15.3 % is obtained for 813 components or 12139 data points. For the Van Velzen method, an average absolute deviation of 92.8 % is obtained for 670 components or 11115 data points. This method shows extremely large deviations for compounds that were probably not in the training set. The proposed method was in nearly all cases more accurate than the Van Velzen method. For other group contribution methods, much higher errors and in some cases disastrous estimations were found. For example, the Sastri and Rao method reports an error of greater than 800 % for tertiary and multi-functional alcohols and even greater errors for fluorine compounds. Thus, the proposed method which employs only the molecular structure for the estimation proves to be far more accurate than other group contribution methods, and at the same time has an extended range of applicability.

9.5.4 Probability of Prediction Failure

Cases of slightly higher errors in the slope prediction (*dBv*) were only observed in case of smaller compounds in the amine, nitro and alcohol series. The data available for these components were mostly not from reputable sources and errors could easily arise from the limited quality of the measurements. Apart from these cases, the method showed no serious prediction failures.

The probability of predicting the viscosity reference temperature within a given error is plotted in Figure 9-39. 10% of the estimations show a deviation greater than approximately 16 K. As discussed throughout this work, the larger errors were nearly solely for smaller compounds or compounds that are the first members in their respective homologous series. First members generally do not follow the trend of the series. Data are usually available for these components and even if there is only a single point, the back calculation of the viscosity reference temperature using an estimated slope is a safer option.

Estimations in case of multi-functional compounds that are largely influenced by mesomeric and inductive effects also resulted in large errors.

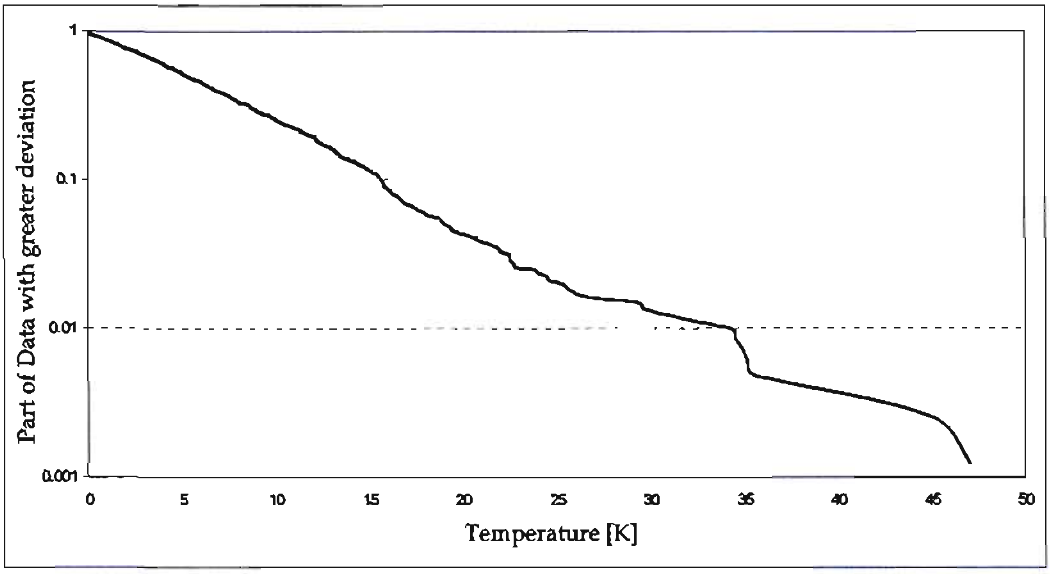


Figure 9-39: Fraction of the data with deviations for viscosity reference temperature larger than a given temperature.

9.5.5 Final Discussion

As in the case of the vapour pressure estimation method, the viscosity method carries knowledge of the chemical nature of components. Correlative models depend on the data for a single component and reproduce not only the behaviour of the liquid but also the systematic errors of the measurements. Consequently, a higher error but at the same time higher reliability of the proposed method as compared to the correlative models should be expected. This was discussed in detail in the final discussion of the vapour pressure method (Section 8.6.5). Most of the items discussed there also apply to the method described in this chapter.

For the other methods in this work, verifying the group contribution values involves comparing the numerical value to that of other chemically similar groups. This applies to the contribution values of both *dBv* and the viscosity reference temperature. As a result of this analysis, most group contribution values were found to be acceptable. The only exception is the group interaction Ketone-Ketone (ID - 194) which has a relatively high value and is based on data for only a single compound. The source reporting these data, George *et al.* (1998), is a recent publication that also contains vapour pressure data. These were verified during the development of the *dB* estimation method and accepted as reliable.

Overall, no specific problems of the method were observed. The core parameters for few frequent groups like CH, CH_2, etc, can be considered final and missing or questionable contributions can be regressed as new data become available.

Chapter Ten

Conclusions

In the first part of this work, a group contribution method was developed for the prediction of critical properties. The method performed significantly better than the methods used for comparison. In addition, it gives physically realistic extrapolations to larger molecules and has by far the largest range of applicability.

The method is based on the group contribution method previously developed for the normal boiling point estimation (Nannoolal (2004) & Nannoolal *et al.* (2004)) with a few minor modifications. This has the advantage that the required differentiation is derived from and validated using a much larger set of experimental data and one data point of good quality was sufficient to calculate a group contribution increment.

The performance of the proposed method is compared to a large number of literature methods and results were shown for an extensive set of substance classes that provide information about the expected accuracy. This work reported an average absolute deviation of 4.3 K (0.74%), 100 kPa (2.96%) and 6.4 $cm^3.mol^{-1}$ (1.79%) for a set of 588 critical temperatures, 486 critical pressures and 348 critical volumes, respectively. For the estimation of the critical temperature, knowledge of the normal boiling point is required. If the normal boiling point is also estimated and used in the training set instead of an experimental value, the results are still significantly better than other methods that do not require knowledge of the auxiliary property. The critical pressure and volume can be estimated from chemical structure alone.

The method showed the lowest probability of prediction failure for all critical properties while producing a physically realistic extrapolation. A test of the predictive capability by employing data that was not used in the training or regression set was also shown. Also in this case, the results were favourable.

In the second part of this work, a group contribution method was developed for the temperature dependant saturated liquid vapour pressure curve. This work presented a new technique for the estimation of a temperature dependant property by developing a two-parameter equation where separate parameters model the absolute value and slope while at the same time the equation must be able to approximate the non-linearity of the curve.

The fixed point or absolute value chosen was the normal boiling point for which a large amount of experimental data is available. This work then presented a group contribution estimation of the slope which showed nearly no probability of prediction failure (high deviation). Employing experimental normal boiling points in the method, an absolute relative deviation of 6.2% in pressure for 1663 components or 68835 data points was obtained. This result is in comparable accuracy to correlative models such as the Antoine and DIPPR equations. Estimations are possible up to the inflection point at a reduced normal boiling temperature of approximately 1.2.

If there are no experimental normal boiling points available, then there are two options to obtain this property. The first and more reliable is to back calculate the auxiliary property if there is information of the boiling point at other pressures. Results shown for this calculation are quite similar to cases where experimental normal boiling points are used. The second possibility is to estimate the property using the previous method.

In the final part of this work, a group contribution method was developed for another temperature dependant property which is the saturated liquid viscosity. This approach employed a similar technique as used with the liquid vapour pressures, i.e. a two-parameter equation models the absolute value, slope and the non-linearity of the curve.

Unfortunately, there was no experimental knowledge of a convenient reference point at a standard viscosity to model the absolute value (viscosity reference temperature). Thus an algorithm was developed to calculate this temperature which was chosen at a viscosity of 1.3 cP. This work then presented a group contribution estimation of the slope and using calculated or adjusted reference temperatures, an absolute relative deviation of 3.4% in viscosity for 829 components or 12861 data points was obtained. This result is in comparable accuracy to correlative models such as the Andrade and

Vogel equations. The estimation method has an upper temperature limit which is similar to the limit in case of liquid vapour pressures.

If there are no data for the viscosity at 1.3 cP, then, as in case of the vapour pressure estimation method, the temperature can be back calculated from data at other viscosity values.

A group contribution method was then developed for the viscosity reference temperature. This method reported an average absolute deviation of 7.1 K (2.5%) for 813 components.

In case both the slope and absolute value were estimated for the liquid viscosity curve, an average absolute deviation of 15.3 % in viscosity for 813 components or 12139 data points was obtained. This molecular structure estimation method was shown to be far more accurate than other applicable group contribution methods. Its also has an extended range of applicability and lower probability of prediction failure.

Chapter Eleven

Recommendations

This work has presented an extension of the group contribution estimation method for normal boiling points of organic compounds developed in Nannoolal (2004) & Nannoolal *et al.* (2004) to:

1) Critical temperatures, pressures and volumes which are scalar (not temperature dependant) properties.
2) Temperature dependant saturated liquid vapour pressure which has a convenient reference point at atmospheric pressure.
3) Temperature dependant saturated liquid viscosity with no convenient reference point for a standard viscosity.

The first method is an extension of the previous method whereby the group definitions and predictive capabilities were analysed and slightly improved. Furthermore, due to the limited number of experimental data points for critical properties, retaining the extrapolative capabilities of the method was of great importance.

The second method extends the approach to a temperature dependant property, the liquid vapour pressure which has a convenient reference point. This reference point is the normal boiling point for which a large amount of experimental data is available. This work has developed a new methodology. A two-parameter equation was developed where separate parameters model the absolute value (normal boiling point) and slope and at the same time was able to approximate the non-linearity of the *ln(P)* vs. *1/T* behaviour.

The third method extends the approach to a further temperature dependant property, the saturated liquid viscosity. This approach employed a similar technology as in case of the vapour-liquid equilibrium curve. A two-parameter equation was developed to model the absolute value, slope and the non-linearity of the curve. Unfortunately there was no convenient reference point at a standard viscosity available to model the absolute value. Consequently a new methodology was developed to obtain this value.

All three models proved to be highly successful and the latter two methods required new developmental procedures that would allow the work to be extended to further properties.

The following sections recommend approaches for the estimation of further properties and give comments on the required knowledge, algorithms and development strategies. Most of these procedures have been tried out for a limited number of examples within this work.

11.1 Estimation of the Melting Point

Property estimation in this work has only dealt with methods for vapour-liquid and liquid properties. It is recommended to extend the group contribution concept to solid-liquid and solid-vapour equilibrium properties (melting temperature, heat of fusion and entropy of fusion).

The melting point of a solid is the temperature at which the solid and liquid are in equilibrium at a given pressure (usually atmospheric pressure). The melting point and heat of fusion are determined quite easily experimentally, for example by Differential Scanning Calorimetry (DSC), but at the same time are very difficult to predict. Nevertheless it is important to have reliable methods for estimating this property to avoid the necessity to have a pure sample of the component available.

An excellent description of the melting phenomenon and review of prediction methods for this property is presented in Tesconi & Yalkowsky (2000). This section will not present a detailed description or review of the melting point but merely recommend a possible strategy for the development of an estimation method.

11.1.1 Model Development

The relationship between the melting point and the enthalpy and entropy of phase change is given in Equation 11-1 (see also Equation 5-1). This relationship is similar to that for the normal boiling point but with the enthalpy and entropy of melting replacing that of vaporisation.

$$T_m = \left(\frac{\Delta H^m}{\Delta S^m} \right)_{P=1atm} \tag{11-1}$$

ΔH^m and ΔS^m each show a different dependence on molecular structure and Tesconi & Yalkowsky (2000) therefore suggested that, in order to predict the melting point, both properties should be treated separately.

As mentioned in Section 5.2.1, the enthalpy of any state is governed by the attractive and repulsive forces between the molecules. In the case of the solid-liquid phase change, the enthalpy in both phases is significantly lower than that in the gas phase. While the total interaction between the molecules can be assumed to be estimated with some reliability from a group contribution method, the difference between the interaction in the liquid and solid phase is much more difficult to estimate.

The entropy can be defined in terms of the number of mechanical states a molecule can achieve. These can be categorised into four contributions:

1. expansional – the entropy resulting from translational motion,
2. positional – the entropy gained on going from an ordered crystal lattice to the disordered state of association in the liquid,
3. rotational – the entropy gained from rotational freedom and
4. internal – the entropy from the greater number of conformations possible for a flexible molecule in the liquid phase.

A detailed discussion can be found in Yalkowsky (1979) and will not be repeated here. To summarise though, the major difference between the entropy of vaporisation and melting is that the latter depends on the geometric shape of the molecule. Thus a geometric contribution will be required in conjunction with a group contribution concept to estimate this property.

11.1.2 Melting Point Recommendations

The strategy for the development of a group contribution estimation method for the melting point should follow a similar strategy as employed in this work. For illustration purposes, the results of a regression of n-alkanes using the group contribution method proposed in this work is presented in Figure 11-1. The group contributions were modelled using Equation 11-2 which is similar to the equation used to estimate the normal boiling point.

$$T_m = \frac{\sum_i^m N_i C(T_m)_i}{n^a + b} + c \tag{11-2}$$

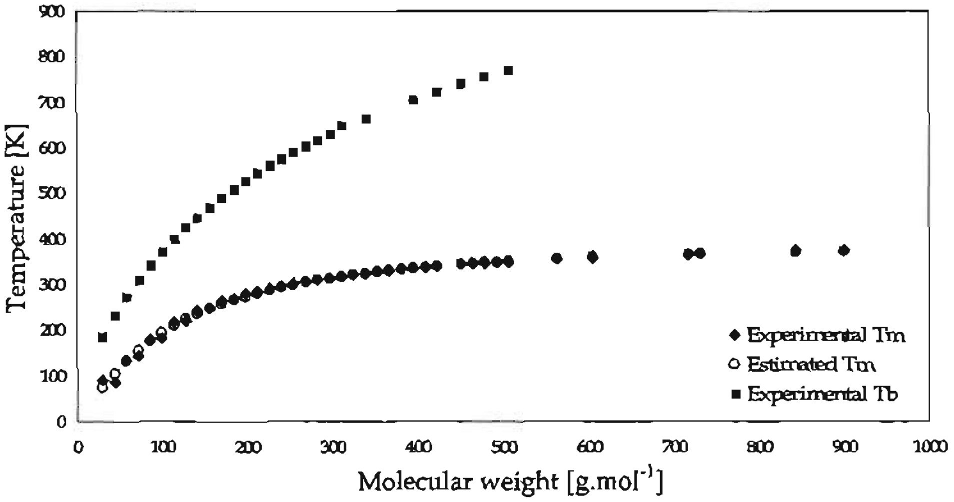


Figure 11-1: Plot of estimated T_m, experimental T_m and T_b as a function of molecular weight for n-alkanes.

The estimation results show that the melting points of higher molecular weight n-alkanes interacting by weak London forces can be accurately correlated by a group contribution approach. This subsequently shows that group additivity is maintained. In case of small n-alkanes the difference between even and odd number of carbon atoms was not reproduced by the correlation as no contribution was included to account for molecular symmetry.

It can be seen from Figure 11-1 that the slope for smaller molecules is different than for higher molecular weight compounds. It has been mentioned throughout this work that smaller molecules generally do not follow the trend in the series and this was also observed in the case of experimental normal boiling points. More significantly, in the case of melting points, the slope is changing stronger from small to large molecular weight compounds than in case of normal boiling points. This is because smaller molecules are roughly spherical and have a high rotational symmetry number (σ) which significantly influences the entropy of melting (introduced in Section 9.4.1).

The results for 1-alcohols are presented in Figure 11-2. The behaviour observed in case of n-alkanes can also be found here.

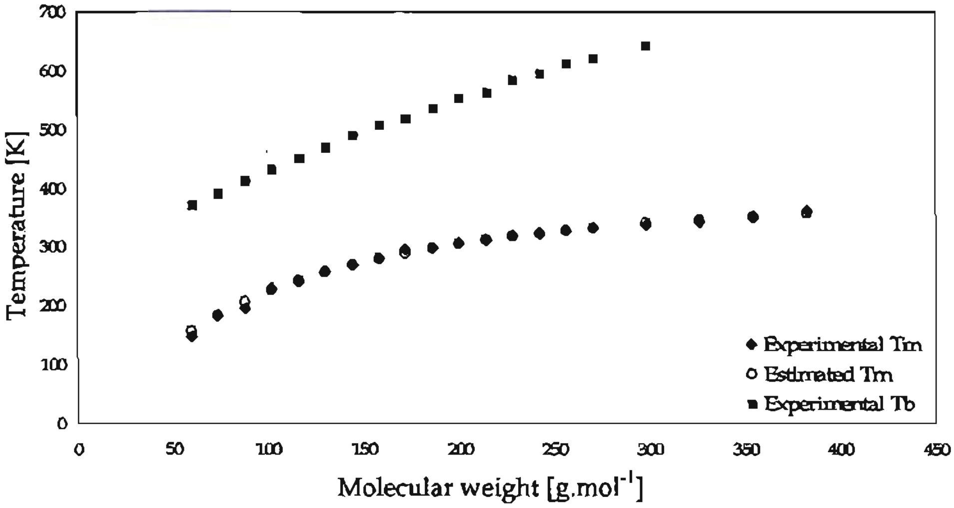


Figure 11-2: Plot of estimated T_m, experimental T_m and T_b as a function of molecular weight for 1-alcohols.

The purpose of the presentation of the regression results for n-alkanes and 1-alcohols is to show that the proposed group contribution concept can model the experimental results of simple homologous series. Unfortunately, if the regression is based on all compounds and not only individual series, a reliable representation of the experimental results would not be possible. This is due, for example, to the high rotational symmetry number associated with spherical molecules.

The correlation of the rotational symmetry number with the entropy of fusion can be, for example, found in Dannenfelser *et al.* (1993), who related this number to the rotational entropy. Molecules in a solid are restricted to a single conformation in the crystal lattice. If they have mostly the same orientation in the liquid, then they have a higher probability (proportional to the rotational symmetry number) of being promoted into the crystal lattice (smaller entropy change). Thus molecules that are more symmetrical (can conform more easily) will usually have lower entropy of fusion and a higher melting point.

Apart from the smaller spherical molecules that have a high symmetry number, there are some other examples. The melting point of cyclohexane ($\sigma = 12$) is 149.1 K higher than that of its isomer methylcyclopentane ($\sigma = 1$). The melting point of benzene ($\sigma = 12$) is 100.5 K higher than that of toluene ($\sigma = 2$), even though the latter compound has a higher molecular weight. Toluene also has the same melting point as ethyl benzene ($\sigma = 1$) even though the latter compound has a higher molecular weight. Thus it can be concluded that additivity is not maintained and symmetry effects have to be taken into account.

There is also a number of other contributions that need to be taken into account by a melting point prediction method and which are adequately described in Tesconi & Yalkowsky (2000). The difference though between these factors and the rotational symmetry is that the latter number is difficult to compute. One example is the molecular flexibility which was also recognised by Dannenfelser *et al.* (1993) who related this number to the internal entropy. This number can be calculated by adding the number of sp^3, sp^2 atoms and rings in the compound.

For the extension of the proposed group contribution concept to the melting point, this work recommends that an algorithm to calculate the rotational symmetry number should be developed. Existing calculation methods have been tested and found to be inadequate for this purpose.

For instance, even though *Gaussian* (discussed later) reports these numbers, it was found that these results were for the specific conformer only. Alternatively, Muller *et al.* (1991) proposed a topological approach to calculate the rotational symmetry number by means of a factorised representation of molecules. Walters & Yalkowsky (1996) suggested that even though the method works well in many cases, it breaks down in determining the focus or centre of symmetry for ring compounds connected with chains. Thus, they proposed the use of graph potentials (Golender *et al.* (1981)) to obtain the centre of symmetry of all molecules. An analysis of both methods revealed errors in predicting the symmetry of compounds that have multiple rings with at least one non-planar ring. To conclude, a detailed analysis and serious improvement of the methods to obtain the rotational symmetry numbers will be required to ascertain their reliability before implementation.

11.2 QSPR - Estimation of the Normal Boiling Point Using Group Contribution and the Dipole Moment

Recently, approaches employing multiple linear regression or neural networks with molecular descriptors or quantitative structure property relationships (QSPR) have been used for the prediction of boiling points and other properties. These approaches employ descriptors that often correspond to electronic and geometrical properties of the molecule. They also have the advantage that they can be calculated for any molecule of interest. Because the three-dimensional structure is used, these methods also offer the possibility of modelling properties that depend on a variety of structural effects such as molecular conformations. On the other hand, they also require selection of one or several representative conformers.

A brief review of several QSPR methods for the estimation of the normal boiling point and critical properties was presented by Poling *et al.* (2000). The main difficulty in reviewing these methods is that the estimations require access to certain software programs to obtain the molecular structure and properties. These methods may also require users to have knowledge about the software and its calculation options to ensure that the calculated molecular properties are consistent with the ones used for the model parameter regression.

Currently, available QSPR methods that estimate the normal boiling point or critical properties and are not restricted to individual classes of compounds include methods proposed by Jurs and co-workers (Egolf *et al.* (1994), Wessel & Jurs (1995) and Turner *et al.* (1998)) and Katritzky *et al.* (1998). These methods employ only a few hundred components in their training sets and their extrapolative capabilities have not been proven. Even for these small sets of data, they report deviations that are higher than those presented in this and the previous works.

Even though QSPR methods represent an interesting alternative for property estimation, the conventional approach using group contribution methods seems to be more reliable and allow a more rational development. This type of method has been employed throughout this work with great success. Group contribution methods are easy to use and implemented in many commercial software packages.

However, there are some problems that have been discussed earlier in case of methods for the critical properties and viscosity reference temperatures that could be at least partly solved by taking into account information on the electronic configuration of the molecule. This can be achieved by simultaneous regression of group contribution parameters and one or more suitable molecular properties. This hybrid approach will be denoted as GC-QSPR further on and will be applied to the estimation of the normal boiling point.

The normal boiling point (the boiling point at atmospheric pressure) was chosen due to the experience gathered with this property during the previous work, its great practical importance and the large amount of available data.

As some molecular properties, such as the dipole moment, depend to a certain extent on the position of the structural groups relative to each other, their effect on the estimation result cannot be described by simple group contribution. It should therefore, after a brief introduction to computational chemistry, be evaluated, whether dipole moments calculated by semi-empirical or quantum-chemical methods can be used to improve the predictive capability of a group contribution method.

11.2.1 Introduction to Computational Chemistry

Computational chemistry of single molecules is to a great part aimed at calculating the structure of molecules and their reactivity. This can be achieved by different approaches of different complexity and computational effort. The two most important are molecular mechanics and electron structure theory. Both compute the energy of a particular molecular structure and the vibrational frequencies resulting from the interatomic motion within the molecule and feature geometric optimisation by locating the conformation with the lowest energy.

Molecular mechanic calculations employ the laws of classical physics to estimate the structure and properties of a molecule. There are many different types of molecular mechanic methods; each one is characterised by its particular parameterized force field. A force field has different components that compute the potential energy variation with the location of its atoms, a series of atom types that define the characteristics of an element and parameter sets that were fitted to experimental data.

Molecular mechanics performs computations based on the interactions of the nuclei. Electronic effects are implicitly included in force fields through parameterisation. The advantage of a molecular mechanic computation is that it is computationally inexpensive and can be used for very large systems containing many atoms. However, there are several limitations of which the most important are:

- Each force field is only applicable to a class of molecules to which it has been parameterised.
- Neglection of electrons implies that molecular mechanics cannot treat systems where electronic effects predominate.

Electronic structure methods (quantum-chemical methods) employ laws of quantum mechanics for their basis of computation. Quantum mechanics states that energy and other related properties of a molecule can be obtained by solving the Schrödinger equation (Equation 11-3).

$$H\Psi = E\Psi \qquad (11\text{-}3)$$

Exact solutions to the Schrödinger equation are not computationally realistic. Consequently, electronic structure methods are characterised by various mathematical approximations to the solution. There are three major types of these methods; semi-empirical, *ab initio* and Density Functional Theory (DFT) methods.

Semi-empirical methods employ parameters regressed to experimental data to simplify the computation. They solve for an approximate form of the Schrödinger equation that depends on having appropriate parameters available. Such methods are for example MNDO, MINDO/3, AM1, and PM3. These methods are characterised by the different parameter sets employed.

Ab initio computations are based solely on the laws of quantum mechanics and on the values of a small number of physical constants such as the speed of light. Unlike molecular mechanic and semi-empirical methods, *ab initio* methods require no parameters regressed to experimental data in their computations.

Semi-empirical and *ab initio* methods are implemented in programs such as *Gaussian* and MOPAC (for the former method). These methods differ in the trade-off between computational time and accuracy of the simulation results. Semi-empirical simulations are computationally inexpensive and provide reasonable quantitative predictions for systems where good parameter sets exists. However, they are limited to these parameter sets and subsequently to specific classes of compounds. As a consequence, they are not as valuable to QSPR relationships which estimate properties for a broad range of compounds.

In contrast, *ab initio* methods provide high quality quantitative predictions for a broad range of compounds. Modern programs such as *Gaussian* that employ these methods can handle any type of atom and size of a component, although the latter is dependant on the CPU performance. Unfortunately, this method is computationally very expensive. For instance, it could take about a week to simulate thirty random components using *Gaussian*.

Recently, a third class of electronic structure methods has come into wide use, Density Functional Theory (DFT). These methods are similar in some ways to *ab initio* methods in determining the molecular electronic structure. They are also similar to semi-empirical methods since many of the most common functionals use parameters derived from empirical data, or from more complex calculations. So it is best to treat them as a class of their own. In DFT, the total energy is expressed in terms of the total electron density rather than the wave functions. In this type of calculation, there is an approximate Hamiltonian and an approximate expression for the total electron density. DFT methods prove to be similar in accuracy to some of the more expensive *ab initio* methods at essentially a smaller computational cost. The drawback though, is that, unlike *ab initio* methods, there is no systematic way to improve the methods by improving the form of the function.

All methods discussed here usually calculate structure and energies of isolated molecules (ideal gas phase). In order to obtain more realistic results for molecules in the dense liquid phase, the calculation of Coulomb interactions and electrostatic energies can be performed using a typical liquid dielectric constant instead of that of the vacuum. Even more realistic calculations employ the concepts of a "reaction field" (RF) or a "self consistent reaction field" (SCRF), where the charge distribution in the molecule polarizes the (continuous) solvent.

To avoid the expensive re-optimisation of the structure and energy calculation in different solvents, the solvent can be viewed as an ideal conductor. In this case, the solvent continuum is field-free and the reaction field reduces to surface charges on the wall of the molecular cavity which are compensated by surface shielding charges of the molecule.

Based on this approach, Klamt (1995) and Klamt & Eckert (2000) developed the COSMO-RS method, which describes the interaction between molecules via the electrostatic interaction between the shielding charges on the molecular surfaces and a hydrogen-bonding interaction.

The method is independent of experimental data and generally applicable to a broad range of compounds. One important application of the COSMO-RS method is to compute activity coefficients in liquid mixtures.

COSMO-RS has been extended to pure component property estimation (Klamt & Eckert (2000) and Sandler *et al.* (2004)). It usually leads to much less reliable results than the methods developed in this and previous works but has the advantage that it can be applied to practically any component.

Surface interactions computed by COSMO-RS may also prove useful in QSPR or GC-QSPR-methods.

11.2.2 GC-QSPR - Preliminary Assessment

In order to develop a GC-QSPR-method, specific descriptors calculated via computational chemistry have to be available for all or most components in the training set.

Unfortunately, the calculation of these descriptors is computationally very expensive when performed on the ab-initio or DFT level and the results depend on the conformer chosen. (On a single PC running only, for example, the *Gaussian* program, it can take about a week to calculate one conformer each of thirty random molecules. One solution would be to run the simulations on a supercomputer or cluster of computers but this would require further investment not available in this work).

Instead of the time-consuming *ab initio* method, another option is to use semi-empirical methods using for example the program MOPAC (a freeware version was used in this case which was obtained from Shchepin & Litviniov (2000) who use a slightly modified DOS version of MOPAC7 (Stewart (1993b))). This program is a general-purpose semi-empirical molecular orbital package for the study of chemical structures and reactions. The semi-empirical Hamiltonians PM3 (Stewart (1990)), AM1 (Dewar *et al.* (1985)), MNDO (Dewar & Thiel (1977)) and MINDO/3 (Bingham *et al.* (1975)) are used in the electronic part of the calculation to obtain molecular orbitals, the heat of formation and its derivative with respect to molecular geometry.

Three-dimensional structures for almost 15000 compounds were available from the DDB. These files, which contain the cartesian co-ordinates of a molecule, were converted to MDL (with extension .mol) files whereby the first line of the latter file contains the parameters required for the simulation. VBA was then employed to communicate with the MOPAC7 executable program while supplying the .mol files as input. Once a simulation for a component was completed, several descriptors were extracted from the output file and stored in a database. The Hamiltonians chosen for the simulation were in the order presented above, so that, in cases where the simulation failed, the next Hamiltonian in that order was taken. The time required for the simulation of all components on a single computer was approximately two weeks.

The current MOPAC7 executable program produced some problems in the simulation:

- there was a limit on the total number of atoms (except hydrogen) of sixty,
- a limit on time for the simulation to complete and
- the polarizability was not shown in the results even though the settings contained the term POLAR for this property output.

As the source code of MOPAC93 (Stewart (1993a)) was available, these limitations could have been in principle overcome. At this point, it was decided that no further time should be invested as the results already available were sufficient for this preliminary evaluation.

Since the polarizabilities were not available, the dipole moment was used in the GC-QSPR approach. A severe disadvantage of the procedure used lies in the fact, that only one more or less arbitrary conformer of each molecule was calculated and that the calculation was performed for an equilibrium structure in the vapour phase. On the other hand, calculation of a representative ensemble of conformers was beyond the resources of this work and would also prove too difficult for the later application of the method.

From an analysis of the dipole moments from the calculation results and values stored in the DDB, it is ascertained that this property is independent of molecular weight (Figure 11-3 - only calculated dipole moments are shown). For polar compounds (such as hydrogen bonding components), the dipole moment varies between 0 and 7 debye. Since the effect of the intermolecular forces for these components decrease with increasing molecular weight, the dipole moment was divided by the total number of atoms (except hydrogen) in the molecule. This phenomenon is shown in Figure 11-4 where the hydrogen bonding 1-alcohol normal boiling temperatures approaches the non-polar n-alkane temperatures with increasing molecular weight. For non-polar components, the dipole moment is close to 0 and the division is of no consequence but nevertheless is still employed.

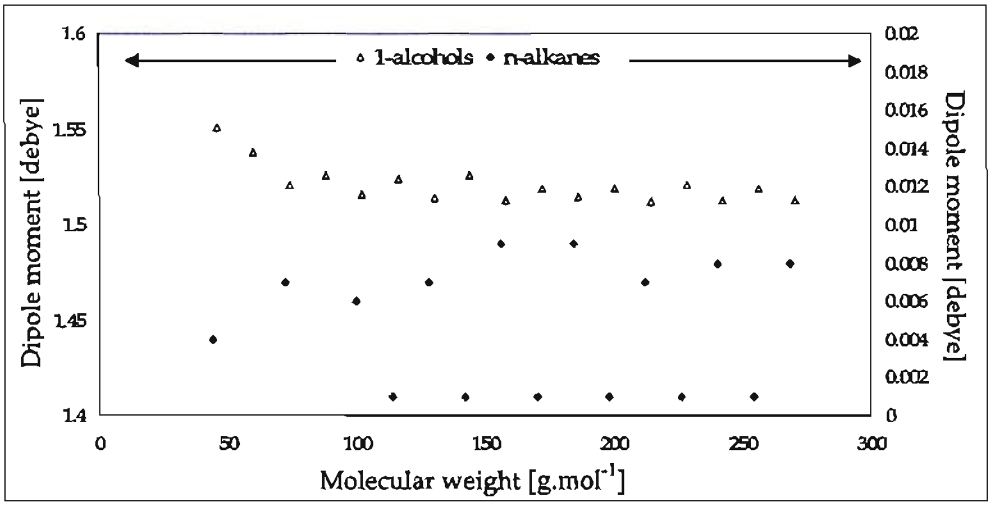


Figure 11-3: Plot of dipole moments for n-alkanes and 1-alcohols as a function of molecular weight.

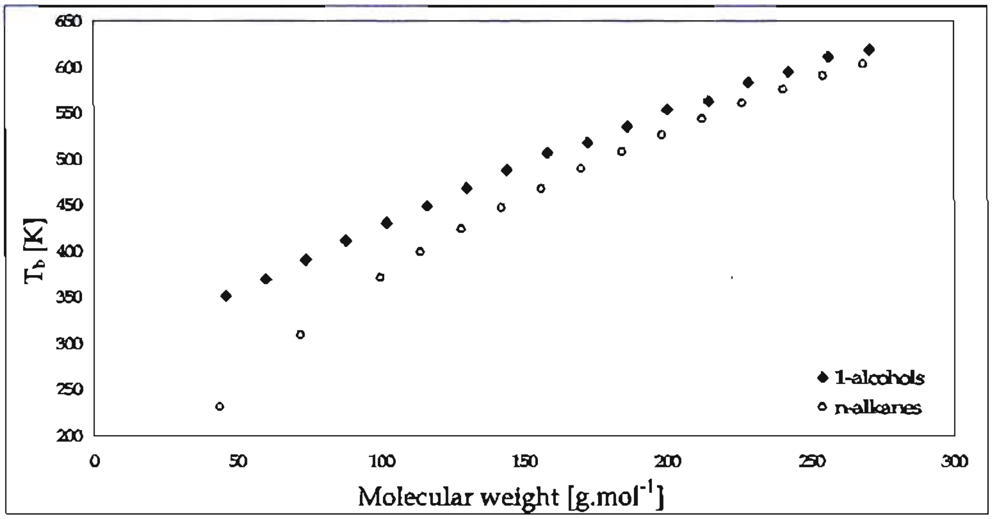


Figure 11-4: Plot of normal boiling temperature for n-alkanes and 1-alcohols as a function of molecular weight.

To include the effect of the dipole moment (μ') into a GC-QSPR approach, three linear models which differ in the application to different pre-defined classes of compounds are recommended (Equation 11-4):

1) a single contribution for all compounds ($\mu'_x = \mu'$, $\mu'_y = \mu'_z = 0$),
2) two contributions for where the components are non-polar ($\mu'_x = \mu'$, $\mu'_y = \mu'_z = 0$) or associating ($\mu'_y = \mu'$, $\mu'_x = \mu'_z = 0$) and
3) three contributions for where the component is non-polar ($\mu'_x = \mu'$, $\mu'_y = \mu'_z = 0$), has a dipole-dipole (or dipole-induced dipole) interaction ($\mu'_y = \mu'$, $\mu'_x = \mu'_z = 0$) or a hydrogen bond ($\mu'_z = \mu'$, $\mu'_x = \mu'_y = 0$).

$$T_b = \frac{\sum_i^m N_i C(T_b)_i + \dfrac{\mu'_x C(\mu'_x) + \mu'_y C(\mu'_y) + \mu'_z C(\mu'_z)}{n}}{n^a + b} + c \qquad (11\text{-}4)$$

Where C (μ'_x, μ'_y, μ'_z) is the group or category contribution.

The category a molecule belongs to could be automatically derived from the structure with the help of the filter meta-language described previously.

The reason for assuming different effects of the dipole moment on the total molecular interaction, and hence on the normal boiling point, lies in the fact that this required a certain ordering on the molecules in the liquid phase. This ordering influence competes with other ordering interactions is case of, for example, hydrogen bonding components.

11.2.3 QSPR - Conclusive Assessment

The results for the estimation of the normal boiling point of all components using the different approaches are summarised in Table 11-1. The comparison also includes a regression where the dipole moments were not used. The regressions for all approaches are based on a common set of components for which the dipole moment could be calculated by MOPAC7. The group contribution method employs the previous group definitions (Nannoolal (2004) & Nannoolal *et al.* (2004)) and not the modified version presented in this work. In addition, no contribution tables or examples will be presented in this work as this is just a preliminary approach.

Table 11-1: Normal boiling temperature average absolute deviations (K) for the different approaches in modelling the dipole moment.

	Number of Components	**AAD (K)[*] No dipole contribution[†]**	**AAD (K) Approach (1)**	**AAD (K) Approach (2)**	**AAD (K) Approach (3)**
All compounds	2482	6.19	6.03	6.02	6.03
Interaction type					
Non-polar	236	4.17	3.83	3.85	3.81
Dipole-dipole[‡]	1701	6.19	6.03	6.01	6.03
Hydrogen bond	545	7.07	6.97	7.02	6.99

All three approaches depict similar results in all cases and the improvement with respect to the regression without using the dipole moment was minor. This could be attributed to

- the low quality calculated dipole moments obtained from MOPAC7 (both because of the semi-empirical methods and the use of only a single conformer). For instance, from a set of 373 components for which dipole moments are stored in the DDB, an average relative error of 26.3% was obtained. Based on this result, it can be assumed that with higher quality quantitative molecular properties, the method might be more successful.
- the fact that only in a limited number of cases the dipole moment is not correlated to the structural groups and at the same time has a significant effect on the normal boiling point.

As assumed above, the largest improvement is obtained for non-polar compounds where no competing ordering forces exist.

---

[*] Denotes average absolute deviation

[†] Estimations based on a regression of components that are common to the other approaches ($\mu_x = \mu_y = \mu_z = 0$)

[‡] Includes dipole-induced dipole interactions

It is recommended for further developments to employ also the polarizabilities as a descriptor for the regression of the GC-QSPR method. A further option would be to use also charge misfit energies from COSMO-RS in the regression.

11.3 Additional Recommendations

The success in the estimation of temperature dependant properties in this work can also be extended to other properties. For example, an estimation method for liquid thermal conductivities and surface tensions would follow the same methodology as in case of liquid viscosities. A two parameter model should be developed that models the absolute value, slope and non-linearity of the curve. Since there is no fixed reference temperature for a fixed thermal conductivity or surface tension value, the algorithm to obtain this fixed value which was developed for liquid viscosities, should be employed.

The range of applicability of the methods is limited by the number of functional groups used in this work. Thus it is recommended to extend the range of applicability by first reviewing the normal boiling point estimation method. In this case all experimental data were already used in the group definitions and it is unlikely that there is significantly new information available. This is especially true for complex multi-functional compounds since they readily decompose before the normal boiling temperature is reached. Fortunately, there is a large amount of information available for these compounds at lower temperatures (or pressures). Since also an algorithm has been developed to calculate reference temperatures from temperature ranges that do not include the reference point, it is recommended in this work that the normal boiling point is calculated using this technology from low vapour pressure data. It is also recommended that the future data verification procedure for normal boiling points include the vapour pressure method presented in this work as there were a number of cases where errors in the former property were evident (Chapter 8).

The dataset generated from this extrapolation to the normal boiling point will include a large amount of data for multi-functional compounds. These compounds will also include contributions for interaction parameters that are currently backed up by only a few components. Thus it is recommended that a careful analysis of the behaviour of these compounds is carried out in order to verify and possibly improve the current concept of interaction parameters.

The estimation method for the vapour-liquid equilibrium curve could also be extended to the vapour-solid equilibrium curve (Figure 11-5). This would require knowledge of the melting point (absolute value), enthalpy of fusion (slope) and maybe the difference in heat capacity between the liquid and solid phase (curvature). In some cases, also the knowledge of transition temperatures and enthalpies might be required.

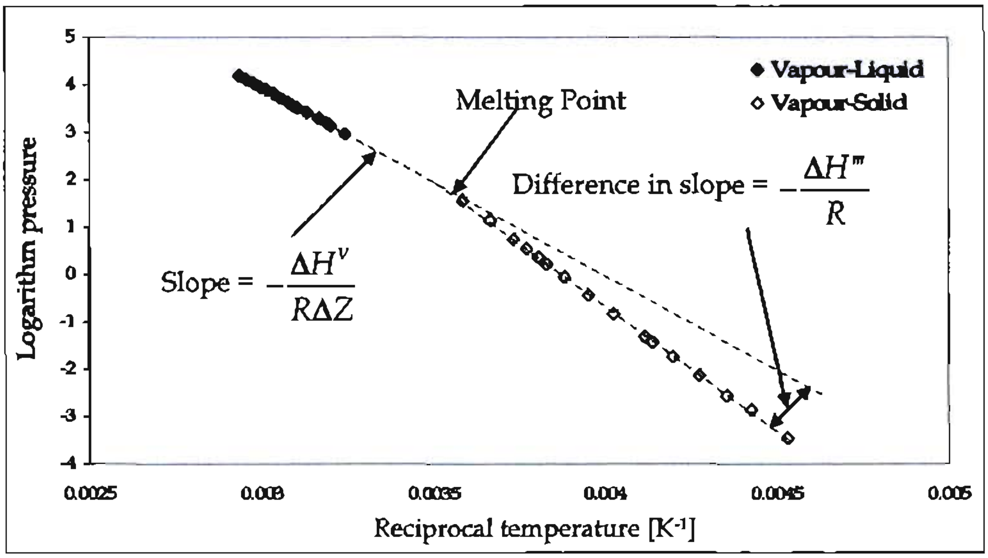


Figure 11-5: Plot of solid and liquid vapour pressures for benzene.

During the development of the different estimation methods within this work, a large number of property estimations were performed for the new methods and available literature methods and compared to experimental results stored in the DDB. A quality assessment was presented for these methods based on a filter system that allows the identification of the different subclasses a component belongs to. It is recommended that a further development of the filter system is undertaken, that will allow an identification of the chemical "families" a component belongs to. This should result in the ability to select the "most similar" components from a data bank with available experimental data. Based on the assumption that group contribution methods show similar errors for similar components, the experimental data and estimation results for the unknown and similar components would then allow a compensation of the error from the estimation. This would then improve the reliability and quality of the results.

References

Abas-zade A. K., The Laws of Heat Conduction of Liquids and Vapors. *Zh. Eksp. Teor. Fiz.*, 23, 60-64. (1952).

Abildskov J. *Development of a New group Contribution Method.* Danish Technical University. (1994).

Abrams D. S., Massaldi H. A., Prausnitz J. M., Vapor Pressures of Liquids as a function of Temperature. Two-Parameter Equation Based on Kinetic Theory of Fluids. *Ind. Eng. Chem. Fund.*, 13(3), 259-262. (1974).

Ahlers J., Gmehling J., Development of an universal group contribution equation of state. I. Prediction of liquid densities for pure compounds with a volume translated Peng-Robinson equation of state. *Fluid Phase Equilib.*, 191, 177-188. (2001).

Ahlers J., Gmehling J., Development of a Universal Group Contribution Equation of State. 2. Prediction of Vapor-Liquid Equilibria for Asymmetric Systems. *Ind. Eng. Chem. Res*, 41, 3489-3498. (2002a).

Ahlers J., Gmehling J., Development of a Universal Group Contribution Equation of State. III. Prediction of Vapor-Liquid Equilibria, Excess Enthalpies, and Activity Coefficients at Infinite Dilution with the VTPR Model. *Ind. Eng. Chem. Res*, 41, 5890-5899. (2002b).

Ambrose D., Vapor Pressure Equations. *National Physical Laboratory NPL Rep. Chem*, 19. (1972).

Ambrose D., The correlation and estimation of vapor pressure. Pt. I: A comparison of three vapor-pressure equations., *J. Chem. Thermodynamics*, 10, 765-769. (1977).

Ambrose D., Correlation and Estimation of Vapor-Liquid Critical Properties. I. Critical Temperatures of Organic Compounds. *National Physical Laboratory NPL Rep. Chem*, 92. (1978a).

Ambrose D. *The correlation and estimation of vapor pressures.* Paper presented at the NPL. (1978b).

Ambrose D., Correlation and Estimation of Vapor-Liquid Critical Properties. II. Critical Pressures and Volumes of Organic Compounds. *National Physical Laboratory NPL Rep. Chem*, 98. (1979).

Ambrose D., Vapor-Pressure Equations. *National Physical Laboratory NPL Rep. Chem*, 114. (1980).

Ambrose D., The correlation and estimation of vapor pressrures. Pt III: Observations on Wagner's method of fitting equations to vapor pressures., *J. Chem. Thermodynamics*, 18, 45. (1986).

Ambrose D., Counsell J. F., Hicks C. P., The correlation and estimation of vapor pressures. Pt. II: A new procedure for estimation and extrapolation., *J. Chem. Thermodynamics*, 10, 771. (1978).

Ambrose D., Ghiassee J., Vapour pressures and critical temperatures and critical pressures of some alkanoic acids: C1 to C10., *J. Chem. Thermodynamics*, 19, 505-519. (1987).

Ambrose D., Patel N. C., The correlation and estimation of vapour pressures IV. Extrapolation of vapour pressures and estimation of critical pressures by the principle of corresponding states using two reference fluids with non-spherical molecules *J. Chem. Thermodynamics*, 16, 459. (1984).

Ambrose D., Tsonopoulos C., Vapor-Liquid Critical Properties of Elements and Compounds. 2. Normal Alkanes. *J. Chem. Eng. Data*, 40, 531-546. (1995).

Ambrose D., Young C. L., Vapor-Liquid Critical Properties of Elements and Compounds. 1. An Introductory Survey. *J. Chem. Eng. Data*, 40, 345-357. (1995).

Andrade E. N. d. C. Theory of Viscosity of Liquids - Part I. *London Edinb. Dub. Phil. Mag. J. Sci.*, 17, 698-732. (1934a).

Andrade E. N. d. C. Theory of Viscosity of Liquids - Part II. *London Edinb. Dub. Phil. Mag. J. Sci.*, 17, 497-511. (1934b).

Andrews T., On the continuity of the gaseous and liquid states of matter (Cited by Ambrose & Young (1995)). *Proc. Roy. Soc. (London)* 18, 42-45. (1869).

Antoine C., Vapor Pressure: A New Relation between Vapor Pressure and Temperature. *Compt. rend.*, 107, 836. (1888a).

Antoine C., Vapor Pressure: A New Relation between Vapor Pressure and Temperature (Thermodynamique, Tensions des Vapeurs: Novelle Relation entre les Tensions et les Temperatures). *Compt. rend.*, 107, 681-684. (1888b).

Atkins P. W. *Physical Chemistry*,(5 ed.). Oxford: Oxford University Press. (1994).

Barrow G. M. *Physical Chemistry*,(4 ed.). Singapore: McGraw-Hill. (1985).

Batschinski A. J., Investigation of Internal Friction in Fluids. Z. *Physik. Chem.*, 84, 643. (1913).

Beilstein. *Crossfire Beilstein Database, Beilstein Chemiedaten und Software GmbH and MDL Information Systems; http://www.beilstein.com)*. Germany. (2002).

Benson S. W., Cruickshank F. R., Golden D. M., Haugen G. R., O'Neal H. E., Rodgers A. S., Shaw R., Walsh R., Additivity Rules for the Estimation of Thermochemical Properties. *Chem. Rev.*, 69, 279-324. (1969).

Berthoud A., Brum R., Recherches sur les proprietes physiques de quelques composes organiques. *J. Chem. Phys.*, 21, 143-160. (1924).

Bingham E. C., Stookey S. D., Relation Between Fluidity, Temperature and Chemical Constitution of Pure Liquids. *J. Am. Chem. Soc.*, 61, 1625-1630. (1939).

Bingham R. C., Dewar M. J. S., Lo D. H., Ground states of molecules (XXV to XXIX). *J. Am. Chem. Soc.*, 97(6), 1285-1318. (1975).

Brebach W. J., Thodos G., Viscosity: Reduced State Correlation for Diatomic Gases. *Ind. Eng. Chem.*, 50, 1095-1100. (1958).

Brush S. G., Theories of Liquid Viscosity. *Rept. No. UCRL-6400*, 106. (1961).

Calingeart G., Davis D. S., *Ind. Eng. Chem.*, 17, 1287-1289. (1925).

Chen C., Watanasiri S., Mathias P., De Leeuw V. V. *Industry Perspective on the Economic Value of Applied Thermodynamics and the Unmet Needs of AspentTech Clients*. In T. Letcher (Ed.), Chemical Thermodynamics for Industry (pp. 166-179): Royal Society of Chemistry. (2004).

Chwolson O. D. *Traile de physique* (Vol. 3, pp. 766-778). Paris. (1910).

Constantinou L. *Estimation of Properties of Acyclic Organic Compounds through Conjugation*. University of Maryland, College Park. (1993).

Constantinou L., Gani R., New Group Contribution Method for Estimating Properties of Pure Compounds. *AIChE J.*, 40(10), 1697-1710. (1994).

Constantinou L., Prickett S. E., Mavrovouniotis M. L., Estimation of Thermodynamical and Physical Properties of Acyclic Hydrocarbons Using the ABC Approach and Conjugation Operators. *Ind. Eng. Chem. Res*, 32(8), 1734. (1993).

Constantinou L., Prickett S. E., Mavrovouniotis M. L., Estimation of Properties of Acyclic Organic Compounds using Conjugation Operators. *Ind. Eng. Chem. Res,* 39, 395. (1994).

Cordes W., Rarey J., A New Method for the Estimation of the Normal Boiling Point of Non-Electrolyte Organic Compounds. *Fluid Phase Equilib.*, 201, 409-433. (2001).

Cordes W., Rarey J., Delique F., Gmehling J. *Software Development in Chemistry 7, Proceedings of Computer in the Chemie 7.* Paper presented at the D. Ziessow (Ed.), Springer-Verlag, Berlin. (1993).

Cornelissen J., Waterman H. I., The Viscosity Temperature Relationship of Liquids. *Chem. Eng. Sci*, 4, 238-246. (1955).

Cox, Pressure-Temperature Chart for Hydrocarbon Vapors. *Ind. Eng. Chem.*, 15(6), 592-593. (1923).

Cramer R. D., BC(DEF) Parameters. 1. The Intrinsic Dimensionality of Intermolecular Interactions in the Liquid State. 2. An Emperical Structure-Based Scheme for the Prediction of Some Physical Properties. *J. Am. Chem. Soc.*, 102, 1837 - 1849. (1980).

Dalton J. Experimental Essays On the Constitution of mixed Gases; on the Force of Steam or Vapour from Water and other Liquids in different temperatures, both in a Torricellian Vacuum and in Air; on Evaporation; and on the Expansion of Gases by Heat. *Mem. Proc. Manchester Lit. & Phil. Soc.*, 5, 535-602. (1801).

Dannenfelser R. M., Surendran N., Yalkowsky S. H., Molecular Symmetry and Related Properties. *SAR and QSAR in Environmental Research*, 1, 273-292. (1993).

Daubert T. E., State-of-the-art-Property predictions. *Hydrocarb. Process,* 107-112. (1980).

Daubert T. E., Vapor-Liquid Critical Properties of Elements and Compounds. 5. Branched Alkanes and Cycloalkanes. *J. Chem. Eng. Data,* 41, 365-372. (1996).

DDB. *Dortmund Data Bank (www.ddbst.de).* Oldenburg, Germany: DDBST GmbH. (2006).

de Guzman J., Relation between fluidity and heat of fusion. *Anales Soc. Espan. Fiz. y Quim.*, 11, 353-362. (1913).

Derr E. L., Deal C. H. J., Analytical Solution of Groups. *Inst. Chem. Eng. Symp. Ser.(London),* 3, 40. (1969).

Dewar M. J. S., Thiel W., Ground States of Molecules. 38: The MNDO Method. Approximations and Parameters. *J. Am. Chem. Soc.*, 99, 4899. (1977).

Dewar M. J. S., Zoebisch E. G., Healy E. F., Stewart J. P. P., A New General Purpose Quantum Mechanical Molecular Model. *J. Am. Chem. Soc.*, 107, 3902-3909. (1985).

Dillier D. E., Hanley H. J. M., Roder H. M., The Density and Temperature Dependance of the Viscosity and Thermal Conductivity of Dense Simple Fluids. *Cryogenics,* 286-294. (1970).

DIPPR. *Design Institute for Physical Property Data.* New york: AIChE Design Institute for Physical Properties. (1992).

Drucker A., Cited by Skubla (1985). *Z. Physik. Chem.*, 92, 287. (1918).

Dyke D. E. L., Rowlinson J. S., Thacker R., The Physical Properties of Some Fluorine Compounds and their Solutions. *Trans. Faraday. Soc.*, 55(903-910). (1959).

Dykyj J., Svoboda J., Wilhoit R. C., Frenkel M., Hall K. R. *Vapor Pressure and Antoine Constants for Hydrocarbon, and Sulfur, Selenium, Tellurium, and Halogen Containing Organic Compounds.*, Vapor Pressure of Chemicals - Subvolume A. Landolt-Bornstein: Springer. (1999).

Dykyj J., Svoboda J., Wilhoit R. C., Frenkel M., Hall K. R. *Vapor Pressure and Antoine Constants for Oxygen Containing Organic Compounds.*, Vapor Pressure of Chemicals - Subvolume B. Landolt-Bornstein: Springer. (2000).

Dykyj J., Svoboda J., Wilhoit R. C., Frenkel M., Hall K. R. *Vapor Pressure and Antoine Constants for Nitrogen Containing Organic Compounds*, Vapor Pressure of Chemicals - Subvolume C. Landolt-Bornstein: Springer. (2001).

Eakin B. E., Ellington R. T., Predicting the Viscosity of Pure Light Hydrocarbons. *J. Petr. Technology*, 15(2), 210-214. (1965).

Egolf L. M., Wessel M. D., Jurs P. C., Prediction of Boiling Points and Critical Temperatures of Industrially Important Compounds from Molecular Structure. *J. Chem. Inf. Comput. Sci.*, 34, 947-956. (1994).

Eversteijn F. C., Stevels J. M., Waterman H. I., The Viscosity of Liquids as a Function of Temperature. *Chem. Eng. Sci*, 11, 267-273. (1960).

Fedors R. F., A relationship between chemical structure and the critical properties. *Chem. Eng. Comm.*, 16, 149-151. (1982).

Feng G., Liu H., Hu Y., Vapor-liquid equilibria of Freon 22 and hexafluoropropylene binary system under moderate pressures. *J. East China Inst. Chem. Techn.*, 12, 225-232. (1986).

Feynman R. P. *"Surely You're Joking, Mr. Feynman!" (Adventures of a Curious Character)*: W. W. Norton Company inc. (1989).

Fredenslund A., Gmehling J., Rasmussen P., Vapor Liquid Equilibria using UNIFAC. *Elsevier Scientific, Amsterdam.* (1977).

Friend J. N., Hargreaves W. D., Viscosity at the boiling point. The rheochor., *London Edinb. Dub. Philos. Mag. J. Sci.*, 34, 643-650. (1943).

Friend J. N., Hargreaves W. D., Viscosities at the Boiling Point of Some Primary Amines, Cyclohexane and Some of its Derivates. *London Edinb. Dub. Philos. Mag. J. Sci.*, 35, 57-64. (1944).

George M. A., Young K. M., Robertson-III E. A., Beck S. E., Vapor pressure and viscosity of 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione. *J. Chem. Eng. Data*, 43, 60-64. (1998).

Girifalco L. A., Temperature Dependence of Viscosity and Its Relation to Vapor Pressure for Associated Liquids. *J. Chem. Phys.*, 23, 2446-2447. (1955).

Gmehling J. (2006). Personal Communication.

Golender V. E., Drboglav V. V., Rosenblit A. B., Graph Potentials Method and Its Application for Chemical Information Processing. *J. Chem. Inf. Comput. Sci.*, 21, 196-204. (1981).

Groenier W. S., Thodos G., Viscosity and Thermal Conductivity of Ammonia in the Gaseous and Liquid States. *J. Chem. Eng. Data*, 6, 240-244. (1961).

Gubbins K. E. *Thermal Transport Coefficients for Simple Dense Fluids, in Statistical Mechanics - Volume 1.* In S. K. (Ed.), Specialist Periodical Reports, The Chemical Society (pp. 194-253). (1973).

Gude M., Teja A. S., Vapor-Liquid Critical Properties of Elements and Compounds. 4. Aliphatic Alkanols. *J. Chem. Eng. Data*, 40, 1025-1036. (1995).

Guldberg C. M., Uber die Gesetze der Molekularvolumina und der Siedepunkte. *Z. Physik. Chem.*, 5, 374. (1890).

Gutmann F., Simmons L. M., The Temperature Dependence of the Viscosity of Liquids. *J. Appl. Phys.*, 23(9), 977-978. (1952).

Haggenmacher J. E., The Heat of Vaporization as a Function of Pressure and Temperature. *J. Am. Chem. Soc.*, 68, 1633-1634. (1946).

Hansen C. E., Hughes R. L., Thermal properties of methyl borate. *U.S. Dep. Commer. Off. Tech. Serv. PB Rep.*, 1-45. (1959).

Hojendahl K., A simple apparatus for determining the orthobaric curve, critical density and temperature. Data for ethylene chloride and bor tribromide., *Chem. Zentralbl.*, 2, 2569-2569. (1942).

Hovorka F., Lankelma H. P., Axelrod A. E., Thermodynamic properties of the hexyl alcohols. III. 2-Methylpentanol-3 and 3-Methylpentanol-3., *J. Am. Chem. Soc.*, 62, 187-189. (1940).

Hsu H. C., Sheu Y. w., Tu C. H., Viscosity estimation at low temperatures ($T_r < 0.75$) for organic liquids from group contributions. *Chem. Eng. J.*, 88, 27-35. (2002).

Innes K. K., Temperature Dependence of Viscosity of Liquids. *J. Phys. Chem*, 60, 817-818. (1956).

Janik J., Janik J. A., Determination of the density of liquids and their saturated vapours as a function of temperature at pressures higher than one atmosphere. Part II. Measurements with methyl mercaptan., *Acta Phys. Pol.*, 20, 691-699. (1961).

Jensen T., Fredenslund A., Rasmussen P., Pure-component vapor pressures using UNIFAC group contribution. *Ind. Eng. Chem. Fund.*, 20, 239-246. (1981).

Joback K. G., Reid R. C., Estimation of pure-component properties from group-contributions. *Chem. Eng. Comm.*, 57, 233-243. (1987).

Joback S. M. *Thesis (Cited by Joback (1987))*. Massachusetts Institute of Technology, Cambridge. (1984).

Kahlbaum G. W. A., Studien über Dampfkraftmessungen. Erste Abteilung., Z. *Physik. Chem.*, 13, 14-55. (1894).

Kapadi U. R., Hundiwale D. G., Patil N. B., Lande M. K., Effect of temperature on excess molar volumes and viscosities of binary mixtures of ethylenediamine and water. *Fluid Phase Equilib.*, 205, 267-274. (2003).

Katritzky A. R., Lobanov V. S., Karelson M., Normal Boiling Points for Organic Compounds: Correlation and Prediction by a Quantitative Structure-Property Relationship. *J. Chem. Inf. Comput. Sci.*, 38, 28-41. (1998).

Kestin J., Wang J. E., On the Correlation of Experimental Viscosity Data. *Physica*, 24, 604-608. (1968).

Kirchhoff G., Cited by Thompson (1946). *Ann. Physik*, 104, 612. (1858).

Klamt A., Conductor-Like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena. *J. Phys. Chem*, 99, 2224. (1995).

Klamt A., Eckert F., COSMO-RS: A Novel and Efficient Method for the a priori Prediction of Thermophysical Data of Liquids. *Fluid Phase Equilib.*, 172, 43. (2000).

Klamt A., Jonas V., Burger T., Lohrenz J. C. W., COSMO and COSMO-RS. *J. Phys. Chem*, 102, 5074. (1998).

Klincewicz K. M., Reid R. C., Estimation of Critical Properties with Group Contribution Methods. *AIChE J.*, 137-142. (1984).

Kobe K. A., Lynn R. E., The Critical Properties of Elements and Compounds. *Chem. Rev.*, 52, 117-236. (1953).

Kreglewski A., Cited in Somayajulu (1989). *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, 9, 163. (1961).

Kreglewski A., Zwollinski B. J., A NEW RELATION FOR PHYSICAL PROPERTIES OF n-ALKANES AND n-ALKYL COMPOUNDS (Cited in Somayajulu (1989)). *J. Phys. Chem*, 65(6), 1050-1052. (1961).

Kreglewski A., Zwollinski B. J., Cited in Somayajulu (1989). *J. Rocz. Chem.*, 35, 1041-1059. (1966).

Kreibich U. T., Schaefer K., Hoepfner A., Niedermolekulare binäre organische Nichtelektrolytsysteme polarer und unpolarer Flüssigkeiten. *Ber. Bunsen-Ges. Phys. Chem*, 74(10), 1020-1024. (1970).

Kudchadker A. P., Ambrose D., Tsonopoulos C., Vapor-Liquid Critical Properties of Elements and Compounds. 7. Oxygen Compounds Other Than Alkanols and Cycloalkanols. *J. Chem. Eng. Data*, 46, 457-479. (2001).

Kulikov D., Verevkin S. P., Heintz A., Determination of vapor pressures and vaporization enthalpies of the aliphatic branched C5 and C6 alcohols. *J. Chem. Eng. Data*, 46(6), 1593-1600. (2001).

Kurata M., Isida S. I., Theory of Normal Paraffin Liquids. *J. Chem. Phys.*, 23, 1126-1131. (1955).

Lee B. I., Kesler M. G., A generalized thermodynamic correlation based on three-parameter corresponding states. *AIChE J.*, 21(3), 510-527. (1975).

Lewis W. K., Squires L. The Structure of Liquids and the Mechanism of Viscosity. *Refin.Nat.Gasol.Manuf*, 13, 448-454. (1934).

Li C., Feng Y., Wu Z., Vapor Pressure of Hexafluoropropylene. *J. Chem. Eng. Chin. Univ. (Chinese)*, 10(1), 64-66. (1996).

Lucas K., Stephan K., Equations of State for the Transport Properties of Pure Liquid Materials. *Chem. Ing. Tech.*, 45(5), 265-271. (1973).

Lucas M., Lucas K., Viscosity of Liquids: An Equation with Parameters Correlating with Structural Groups. *AIChE J.*, 32(1), 139-141. (1986).

Lydersen A. L., Estimation of Critical Properties of Organic Compounds. *Univ. Coll. Exp. Stn. Rept.*, 3. (1955).

Lyman A. L., Reehl W. F., Rosenblatt D. H. *Handbook of Chemical Property Estimation Methods.* Washington DC: American Chemical Society. (1990).

Majer V., Svoboda V., Pick J. *Heats of Vaporization of Fluids.* Amsterdam: Elsevier. (1989).

Marrero-Morejon J., Gani R., Group-contribution based estimation of pure components properties. *Fluid Phase Equilib.*, 183184, 183-208. (2001).

Marrero-Morejon J., Pardillo-Fontdevilla E., Estimation of pure compound properties using group-interaction contributions. *AIChE J.*, 45(3), 615-621. (1999).

Marschalko B., Barna J., Cited by Poling et. al. (2000). *Acta Tech. Acad. Sci. Hung.*, 19, 85. (1957).

Massey B. S. *Mechanics of Fluids:* Von Nostrand Reinhold. (1983).

Mazo R. M. *Statistical Mechanical Theories of Transport Properties, in The International Encyclopedia of Physical Chemistry and Chemical Physics,* Topic 9, Transport Phenomena: Pergamon Press. (1967).

Mcgarry J., Correlation and prediction of the vapor pressures of pure liquids over large pressure ranges. *Ind. Eng. Chem. Process Des. Dev.,* 22(2), 313-322. (1983).

Medani M. S., Hasan M. A., Viscosity of Organic Liquids at Elevated Temperatures and the Corresponding Vapour Pressures. *Can. J. Chem. Eng,* 55, 203-209. (1977).

Mehrotra A. K., Generalized one-parameter viscosity equation for light and medium liquid hydrocarbons. *Ind. Eng. Chem. Res,* 30(420), 1367. (1991).

Mehrotra A. K., Monnery W. D., Scrcek W. Y., A review of practical calculation methods for the viscosity of liquid hydrocarbons and their mixtures. *Fluid Phase Equilib.,* 117, 344. (1996).

Miller A. A., Free Volume and the Viscosity of Liquid Water. *J. Chem. Phys.,* 38(7), 1568-1571. (1963a).

Miller A. A., Free Volume and Viscosity of Liquids: Effects of Temperature. *J. Phys. Chem,* 67, 1031-1035. (1963b).

Mitra S. S., Chakravarty D. N., Relation between vapor pressure and viscosity of liquids (Cited by Skubla (1985)). *J. Chem. Phys.,* 22, 775. (1954).

Monnery W. D., Scrcek W. Y., Mehrotra A. K., Viscosity: A Critical review of practical Predictive and Correlative Methods. *Can. J. Chem. Eng,* 73, 3-40. (1995).

Muller C., Scacchi G., Come G. M., A Topological Method for Determining the External Symmetry Number of Molecules. *Computers Chem*, 15(1), 17-27. (1991).

Mussell A. G., Thole F. B., Dunstan A. E., The Viscosity of compounds containing tervalent nitrogen. Part I. The amines., *J. Chem. Soc. London*, 101, 1008-1016. (1912).

Nannoolal Y. *Development of a Group Contribution Method for the Prediction of Normal Boiling Points of Non-electrolyte Organic Compounds.* University of KwaZulu-Natal, Durban. (2004).

Nannoolal Y., Rarey J., Ramjugernath D., Cordes W., Estimation of Pure Component Properties, Part 1: Estimation of the Normal Boiling Point of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions. *Fluid Phase Equilib.*, 226(45-63). (2004).

Nelder J. A., Mead R., A simplex method for function minimization. *Computer J.*, 308-313. (1965).

Nesterov I. A., Nesterova T. N., Pimerzin A. A., Die Thermodynamik der Sorption und Verdampfung von den Alkylbenzolen. III. Kritische Dämpfe. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 43(1), 22-30. (2000).

Nesterova T. N., Nesterov I. A., Pimerzin A. A., Die Thermodynamik der Sorption und Verdampfung von Alkylbenzolen. II. Kritische Temperaturen. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 43(1), 14-22. (2000).

Onken U., Fischer K., Rarey J. *Estimation of Physical Properties*,(6 ed.): Ullmann's Encyclopedia of Industrial Chemistry. (1998).

Orrick C., Erbar J. H. (1974). Cited by Poling et. al. (2000): Personal communication.

Pardillo E. F., Gonzalez-Rubio R., A Group-Interaction Contribution Approach. A New Strategy for the Estimation of Physical-Chemical Properties of Branched Isomers. *Chem. Eng. Comm*, 163, 245. (1997).

Piacente V., Fontana D., Scardala P., Enthalpies of Vaporization of a Homologous Series of n-Alkanes Determined from Vapor Pressure Measurements. *J. Chem. Eng. Data*, 39(2), 231-237. (1994).

Plank R., Riedel L., A new criterion for the course of the vapor pressure curve at the critical point. *Ing. Arch.*, 16, 255. (1948).

Platt J. R., Influence of Neighbor Bonds on Additive Bond Properties in Paraffins. *J. Chem. Phys.*, 15(6), 419-420. (1947).

Platt J. R., Prediction of Isomeric Differences in Paraffin Properties. *J. Phys. Chem*, 56(3), 328-336. (1952).

Poling B. E., Prausnitz J. M., O'Connell J. P. *The Properties of Gases and Liquids*,(5 ed.). New York: McGraw Hill. (2000).

Porter A., Notes on the Viscosity of Liquids (Cited by Skubla (1985)). *Phil. Mag.*, 23, 458. (1912).

Press W. H., Teukolsky S. A., Vetterling W. T., Flannery B. P. *Numerical Recipes in Fortran 77: The Art of Scientific Computing*,(2 ed. Vol. 1). Cambridge: Cambridge University Press. (1986).

Rankine W. J. M., Cited by Thompson (1946). *Edinburgh New Phil. J.*, 94, 235. (1849).

Reid R. C., Prausnitz J. M., Poling B. E. *The Properties of Gases and Liquids*,(4 ed.). New York: McGraw Hill. (1987).

Reid R. C., Sherwood t. K. *The Properties of Gases and Liquids*. New York: McGraw Hill. (1958).

Rice S. A., Boon J. P., Davis H. T. *Comments on the Experimental and Theoretical Study of Transport Phenomena in Simple Liquids, in Simple Dense Fluids* In h. L. Frisch & Z. W. Salzburg (Eds.) (pp. 251-402): Academic Press. (1968).

Rice S. A., Gray P. *The Statistical Mechanics of Simple Liquids*: Interscience. (1965).

Riedel L., Estimation of unknown critical pressures of organic compounds. Z. *Elektrochem.*, 53, 222-228. (1949).

Riedel L., Extension of the theorem of corresponding states. III. Critical coefficient, density of saturated vapor, and latent heat of vaporization., *Chem. Ing. Tech.*, 26, 679-683. (1954).

Roger J. D., Brickwedde F. G., Excess Transport Properties of Light Molecules. *AIChE J.*, 11(2), 304-310. (1965).

Sandler S. I., Lin S., Chang J., Wang S., Goddard W. A., Prediction of Vapor Pressures and Enthalpies of Vaporization Using a COSMO Solvation Model. *J. Phys. Chem*, 108, 7429-7439. (2004).

Sastri S. R. S., Ramana Rao M. V., Estimating liquid viscosities (Cited by Sastri & Rao (1992)). *Chem. Age of India*, 21(7), 409. (1970).

Sastri S. R. S., Rao K. K., A new group contribution method for predicting viscosity of organic liquids. *Chem. Eng. J.*, 50, 9-25. (1992).

Schmidt A., Exponential function applicable to the representation of many physico-chemical phenomena. *J. Chem. Phys.*, 15, 97-153. (1917).

Schmidt G. G., Cited by Ambrose & Young (1995). *Gilbert's Ann.*, 76, 343-345. (1823).

Shchepin R., Litviniov D. *Winmopac* (Version 7.21). (2000).

Shimotake H., Thodos G., Viscosity: Reduced State Correlation for the Inert Gas. *AIChE J.*, 4, 257-262. (1958).

Skubla P., Prediction of Viscosity of Organic Liquids. *Collect. Czech. Chem. Comm.*, 50, 1907-1916. (1985).

Smith G. J., Wilding W. V., Oscarson J. L., Rowley R. L. *Correlation of Liquid Viscosity at the Normal Boiling Point.* Paper presented at the Fifteenth Symposium of Thermophysical Properties, Boulder, Colorado, USA. (2003).

Somayajulu G. R., Estimation procedures for critical constants. *J. Chem. Eng. Data*, 34(1), 106-120. (1989).

Steele W. A. *Time-Correlations Functions, in Transport Phenomena in Fluids* In H. J. M. Hanley (Ed.) (pp. 209-312): Dekker. (1969).

Steele W. V., Chirico R. D., Cowell A. B., Knipmeyer S. E., Nguyen A., Thermod. properties and id.-gas enthalpies of form.for 2-aminoisobutyric acid, acetic acid, (Z)-5-ethylidene-2-norbornene, mesityl oxide, 4-methylpent-1-ene, 2,2'-bis(phenylthio)pronane, glycidyl phenyl ether. *J. Chem. Eng. Data*, 42, 1053-1066. (1997a).

Steele W. V., Chirico R. D., Knipmeyer S. E., Nguyen A., The thermodynamic properties of thianthrene and phenoxanthiin. *J. Chem. Thermodynamics*, 25, 965-992. (1993).

Steele W. V., Chirico R. D., Knipmeyer S. E., Nguyen A., Vapor pressure, heat capacity, and density along the saturation line, measurements for dimethyl isophthalate, dimethyl carbonate, 1,3,5-triethylbenzene, pentafluorophenol, 4-tert-butylcatechol,... *J. Chem. Eng. Data,* 42, 1008-1020. (1997b).

Stein S. E., Brown R. L., Estimation of Normal Boiling Points from Group Contribution. *J. Chem. Inf. Comput. Sci.,* 34, 581-587. (1994).

Stephan K., Lucas K. *Viscosity of Dense Fluids.* New York: Plenum Publishing Corp. (1969).

Stewart J. P. P., Mopac: A semiempirical molecular orbital program. *J. Comput.-Aided Mol. Des.,* 4, 1. (1990).

Stewart J. P. P. *MOPAC93.* Tokyo: Fujitsu Ltd. (1993a).

Stewart J. P. P. *MOPAC 7.0: Quantum Chemistry Program Exchange* (Version 7). Bloomington: Indiana University. (1993b).

Teja A. S., Lee D. J., Rosenthal D., Anselme M., Correlation of the Critical Properties of Alkanes and Alkanols. *Fluid Phase Equilib.,* 56, 153-169. (1990).

Telang M. S., Correlation of Viscosities of Liquids with Temperatures. *J. Phys. Chem,* 49, 579-582. (1945).

Tesconi M., Yalkowsky S. H. *Melting point.* In R. S. Boethling & D. Mackay (Eds.), Handbook of Property Estimation Methods for Chemicals: Environmental and Healt Sciences (pp. 3-27). Boca Raton: CRC Press LLC. (2000).

Thek R. E., Stiel L. I., A new reduced vapor pressure equation. *AIChE J.,* 12(3), 599-602. (1966).

Thodos G., Vapor Pressures of Normal Saturated Hydrocarbons. *Ind. Eng. Chem.,* 42(8), 1514-1526. (1950).

Thole F. B., Mussel A. G., Dunstan A. E., Viscosity maxima and their interpretation., *J. Chem. Soc. London*, 103, 1108-1119. (1913).

Thompson G. W., The Antoine Equation for Vapor Pressure Data. *Chem. Rev.*, 38(7), 1. (1946).

Thompson G. W. *Techniques of Organic Chemistry, A. Weissberger*,(Vol. 1). New york: Interscience. (1959).

Thorpe E., Rodger J. W., On the Relations Between the Viscosity (Internal Fiction) of Liquids and their Chemical Nature. *Philos. Trans. Roy. Soc. London*, 185, 397-710. (1894).

Touloukian Y. S., Saxena S. C., Hestermans P. *Viscosity, Volume 11 - in Thermophysical Properties of Matter - The TPRC Data Series.* New York: Plenum Publishing Corp. (1975).

Tour De La C., Cited by Ambrose & Young (1995). *Ann. Chim. Physik.*, 21(2), 127-132. (1822).

Tour De La C., Cited by Ambrose & Young (1995). *Ann. Chim. Physik.*, 22(2), 410-415. (1823).

Tsonopoulos C., Ambrose D., Vapor-Liquid Critical Properties of Elements and Compounds. 3. Aromatic Hydrocarbons. *J. Chem. Eng. Data*, 40, 547-558. (1995).

Tsonopoulos C., Ambrose D., Vapor-Liquid Critical Properties of Elements and Compounds. 6. Unsaturated Aliphatic Hydrocarbons. *J. Chem. Eng. Data,* 41, 645-656. (1996).

Tsonopoulos C., Ambrose D., Vapor-Liquid Critical Properties of Elements and Compounds. 8. Organic Sulfur, Silicon, and Tin Compounds (C + H + S, Si, and Sn). *J. Chem. Eng. Data*, 46, 480-485. (2001).

Tu C. H., Group-contribution method for the estimation of vapor pressures. *Fluid Phase Equilib.*, 99, 105-120. (1994).

Tu C. H., Group-Contribution Estimation of Critical Temperature With Only Chemical Structure. *Chem. Eng. Sci.*, 50(22), 3515-3520. (1995).

Turner B. E., Costello C. L., Jurs P. C., Prediction of Critical Temperatures and Pressures of Industrially Important Organic Compounds from Molecular Structure. *J. Chem. Inf. Comput. Sci.*, 38, 639-645. (1998).

Van Velzen D., Cardozo R. L., LangenKamp H., A liquid viscosity-temperature-chemical constitution relation for organic compounds. *Ind. Eng. Chem. Fund.*, 11(1), 20-25. (1972).

Van Wyk W. R., Van Der Veen J. H., Brinkman H. C., Seeder W. A., The influence of the temperature and the specific volume on the viscosity of liquids. III. *Physica A*, 7, 45-56. (1940).

Vetere A., Methods for predicting and Correlating the Vapor Pressures of pure Compounds. *AIChE J.*, 43, 191-203. (1988).

Vetere A., The Riedel equation. *Ind. Eng. Chem. Res*, 30(11), 2487-2492. (1991).

Viswanath D. S., Natarajan G. *Book on the Viscosity of Liquids*: Hemisphere Publishing. (1989).

Vogel H., Das Temperaturabhaengigkeitsgesetz der Viskositaet von Fluessigkeiten. *Phys. Z.*, 22, 645-646. (1921).

VonNiedernhausern D. M., Wilson G. M., Giles N. F., Critical Point and Vapor Pressure Measurements for 17 Compounds by a Low Residence Time Flow Method. *J. Chem. Eng. Data,* 51, 1990-1995. (2006a).

VonNiedernhausern D. M., Wilson G. M., Giles N. F., Critical Point and Vapor Pressure Measurements for Four Compounds by a Low Residence Time Flow Method. *J. Chem. Eng. Data,* 51, 1986-1989. (2006b).

VonNiedernhausern D. M., Wilson G. M., Giles N. F., Critical Point and Vapor Pressure Measurements for Seven Compounds by a Low Residence Time Flow Method. *J. Chem. Eng. Data,* 51, 1982-1985. (2006c).

VonNiedernhausern D. M., Wilson L. C., Giles N. F., Wilson G. M., Critical-Point Measurements for Nine Compounds by a Flow Method. *J. Chem. Eng. Data,* 45(2), 154-156. (2000).

Voutsas E., Lampadariou M., Magoulas K., Tassios D., Prediction of vapor pressures of pure compounds from knowledge of the normal boiling point temperature. *Fluid Phase Equilib.*, 198, 81-93. (2002).

Vowles C. *Cited by Reid et. al. (1987).* Massachusetts Institute of Technology, Massachusetts. (1951).

Wagner W., New vapour pressure measurements for argon and nitrogen and a new method for establishing rational vapour pressure equations. *Cyrogenics,* 13(8), 470. (1973).

Wagner W. *A New Correlation Method for Thermodynamic Data Applied to the Vapor Pressure Curve on Argon, Nitrogen and Water.* London: IUPAC Thermodynamic Tables Project Centre. (1977).

Waller M., On the Influence of Molecular Structure on the Variation of Viscosity between the Melting- and Boiling Points. *London Edinb. Dub. Philos. Mag. J. Sci.,* 18, 579-594. (1934).

Walters W. P., Yalkowsky S. H., ESCHER - A Computer Program for the Determination of External Rotational Symmetry Numbers from Molecular Topology. *J. Chem. Inf. Comput. Sci.,* 36, 1015-1017. (1996).

Wang L., Ahlers J., Gmehling J., Development of a Universal Group Contribution Equation of State. 4. Prediction of Vapor-Liquid Equilibria of Polymer Solutions with the Volume Translated Group Contribution Equation of State. *Ind. Eng. Chem. Res,* 42, 6205-6211. (2003).

Wen X., Quiang Y., A New Group Contribution Method for Estimating Critical Properties of Organic Compounds. *Ind. Eng. Chem. Res.,* 40, 6245-6250. (2001).

Wessel M. D., Jurs P. C., Prediction of Normal Boiling Points for a Diverse Set of Industrially Important Organic Compounds from Molecular Structure. *J. Chem. Inf. Comput. Sci.,* 35, 841-850. (1995).

Whipple G. H., Vapor-Liquid Equilibria of Some Fluorinated Hydrocarbon Systems. *Ind. Eng. Chem.,* 44(7), 1664-1667. (1952).

Wiberg E., Suetterlin W., Zur Kenntnis einiger Verbindungen vom Typus BCl3-n(OR)n ; über alkoxyl-substituierte Borchloride. *Z. Anorg. Allg. Chem.,* 202. (1931).

Wilson M., Jasperson L. V. *Cited by Poling et. al. (2000).* Paper presented at the AIChE Meeting, New Orleans, LA. (1996).

Yair O. B., Fredenslund A., Extension of the UNIFAC group contribution method for the prediction of pure-component vapor rpessures. *Ind. Eng. Chem. Process Des. Dev.,* 22, 433-436. (1983).

Yalkowsky S. H., Estimation of Entropies of Fusion of Organic Compounds. *Ind. Eng. Chem. Fund.*, 18(2), 108-111. (1979).

Yan X., Dong Q., Hong X., Reliability Analysis of Group-Contribution Methods in Predicting Critical Temperatures of Organic Compounds *J. Chem. Eng. Data,* 48(2), 374-380. (2003).

Zhuravlev E. Z., Sivkova V. N., Shabalina L. A., Ivanov M. G., Ortobar-Dichte von einigen organischen Isocyanaten. *Oniitekhim*, Code 427-91, 1-8. (1991).

Appendix A

Literature Group Contribution Tables

Table A-1: Group Contributions for Lydersen (1955) & Riedel (1949)

	Riedel	Lydersen		
Group Name	$C(T_c)$	$C(T_c)$	$C(P_c)$	$C(V_c)$
$-CH_3$, $-CH_2-$	0.016	0.020	0.227	55.0
$>CH$	0.013	0.012	0.210	51.0
$-C<$	0.003	-	0.210	41.0
$=CH_2$, $=CH$	0.015	0.018	0.198	45.0
$=C<$, $=C=$	0.003	-	0.198	36.0
$\equiv C-H$, $\equiv C-$	-	0.005	0.153	36.0
Ring Atom	-0.005	-	-	-
$-CH_2-$ (r*)	-	0.013	0.184	44.5
$>CH-$ (r)	-	0.012	0.192	46.0
$>C<$ (r)	-	-0.007	0.154	31.0
$=CH-$, $=C<$, $=C=$ (all r)	-	0.011	0.154	37.0
-F	0.015	0.018	0.224	18.0
-Cl	0.013	0.017	0.320	49.0
-Br	0.010	0.010	0.500	70.0
-I	-	0.012	0.830	95.0
-OH	0.070	0.082	0.060	18.0
-OH (a†)	0.029	0.031	-0.020	3.0
-O-	0.020	0.021	0.160	20.0
-O- (r)	-	0.014	0.120	8.0
$>C=O$	0.046	0.040	0.290	60.0
$>C=O$ (r)	-	0.033	0.200	50.0
$HC=O-$	0.046	0.048	0.330	73.0

---

[*] Ring increment

[†] Aromatic increment

-COOH	0.070	0.085	0.400	80.0
-COO-	0.039	0.047	0.470	80.0
-NH_2	0.027	0.031	0.095	28.0
>NH	0.027	0.031	0.135	37.0
>NH (r)	-	0.024	0.090	27.0
>N	0.012	0.014	0.170	42.0
>N- (r)	-	0.007	0.130	32.0
-CN	0.053	0.060	0.360	80.0
-NO_2	-	0.055	0.420	78.0
-SH, -S-	0.012	0.015	0.270	55.0
-S- (r)	-	0.008	0.240	45.0
=S	-	0.003	0.240	47.0
>Si<	-	0.030	0.540	-
-B<	-	0.030	-	-

Table A-2: Group Contributions for Ambrose (1978a), (1979).

Group Name	$C(T_c)$	$C(P_c)$	$C(V_c)$
Carbon atoms in alkyl groups	0.138	0.226	55.1
Corrections:			
>CH- (each)	-0.043	-0.006	-8.0
>C< (each)	-0.120	-0.030	-17.0
Double bonds	-0.050	-0.065	-20.0
Triple bonds	-0.200	-0.170	-40.0
Delta Platt number	-0.023	-0.026	-
Aliphatic functional groups			
-O-	0.138	0.160	20.0
>CO	0.220	0.282	60.0
-CHO	0.220	0.220	55.0
-COOH	0.578	0.450	80.0
-CO-O-OC-	1.156	0.900	160.0
-CO-O-	0.330	0.470	80.0
-NO_2	0.370	0.420	78.0

-NH_2	0.208	0.095	30.0
-NH-	0.208	0.135	30.0
>N-	0.088	0.170	30.0
-CN	0.423	0.360	80.0
-S-	0.105	0.270	55.0
-SH	0.090	0.270	55.0
-SiH_3	0.200	0.460	119.0
-O-Si(CH_3)$_2$	0.496	-	-
-F	0.055	0.223	14.0
-Cl	0.055	0.318	45.0
-Br	0.055	0.500	67.0
-I	0.055	-	90.0
Halogen correction in aliphatic compounds:			
F is present	0.125	-	-
F is absent, but Cl, Br and I present	0.055	-	-
Aliphatic alcohols[*]	[†]	[‡]	15.0
Ring compound increments (listed only when different from aliphatic values):			
-CH_2-	0.090	0.182	44.5
>CH- (in fused rings)	0.030	0.182	44.5
Double bonds	-0.030	-	-15.0
-O-	0.090	0.117	10.0
-NH-	0.090	0.049	-
-S-	0.090	-	30.0
Aromatic compounds:			
Benzene	0.448	0.924	[§]
Pyridine	0.448	0.850	222.0
C_4H_4 (fused as in naphthalene)	0.220	0.515	180.4
-F	0.080	0.183	14.0

---

[*] Includes naphthenic alcohols and glycols but not aromatic alcohols such as xylenol

[†] First determine the hydrocarbon homomorph, i.e. substitute -CH_3 for each -OH and calculate the Σ for this compound. Subtract 0.138 from Σ for each -OH substituted. Next add $0.87 - 0.11n + 0.003n^2$ where $n = [T_b(\text{alcohol/K}) - 314]/19.2$. Exceptions include methanol ($\Sigma = 0$), ethanol ($\Sigma = 0.939$) and any alcohol whose value of n exceeds 10.

[‡] Determine hydrocarbon homomorph as in [†] above. Calculate Σ and subtract 0.226 for each -OH substituted. Add $0.100 - 0.013n$, where n is computed as in [2] above.

[§] When determining the critical volumes of aromatic substances, use alkyl group values

-Cl	0.080	0.318	45.0
-Br	0.080	0.600	67.0
-I	0.080	0.850	90.0
-OH	0.198	-0.025	15.0
Corrections for non-halogenated substitutions:			
First	0.010	-	-
Each Subsequent	0.030	0.020	-
Ortho pairs containing -OH	-0.080	-0.050	-
Ortho pairs with no -OH	-0.040	-0.050	-
Highly fluorinated aliphatic compounds:			
-CF$_3$, -CF$_2$, >CF-	0.200	0.550	-
-CF$_2$, >CF- (ring)	0.140	0.420	-
>CF- (fused ring)	0.030	-	-
-H (mono-substitution)	-0.050	-0350	-
Double bond (nonring)	-0.150	-0.500	-
Double bond (ring)	-0.030	-	-

Table A-3: Group Contributions for Daubert (1980)

Group Name	C(T$_c$)	C(P$_c$)
C-(H) (C)	14.932	65.441
C-(H)$_2$(C)$_2$	19.931	47.049
C-(H)(C)$_3$	18.607	28.004
C-(C)$_4$	14.718	5.911
C-(H)$_2$(C=)(C)	19.953	52.233
C-(H)(C=)(C)$_2$	19.585	30.689
C-(H)$_2$(C≡)(C)	3.030	-
C-(H)$_2$(C)(Cb[*])	17.481	57.975
C-(H)(Cb)(C)$_2$	8.450	41.175
C-(Cb)(C)$_3$	5.340	25.056
C-(H)$_2$(Cb)$_2$	25.078	20.585
C=(H)$_2$	11.407	56.334

---

[*] Denotes benzene atom

Group Name	C(T_c)	C(P_c)
C=(H)(C)	18.554	40.880
C=(C)$_2$	24.880	28.953
C=(H)(C=)	18.691	45.036
C=(H)(Cb)	13.872	42.041
C≡(H)	17.707	44.949
C≡(C)	13.022	31.557
Cb-(H)	12.962	40.938
Cb-(C)	24.394	25.831
Cb-(Cb)	17.699	2.685
Cbf*-(Cbf)	17.816	29.085
=C=(Cb)	15.235	-
O-(H)(C)	93.051	21.786
O-(H)(Cb)	25.083	24.338
O-(H)(CO)	73.708	89.349
O-(C)$_2$	75.719	37.882
O-(C)(C=)	41.291	47.714
O-(C)(Cb)	65.809	45.772
O-(C)(CO)	49.214	75.202
O-(Cb)$_2$	10.829	-
CO-(H)(C)	75.710	-
CO-(H)(Cb)	28.161	-
CO-(H)(O)	31.403	26.821
CO-(C)$_2$	94.169	227.265
CO-(C)(O)	54.520	87.178
CO-(C=)(O)	28.401	-
CO-(O)(CO)	122.236	145.665
C-(H)$_3$(O)	-11.130	62.355
C-(H)$_2$(O)(C)	-11.167	34.763
C-(H)$_2$(O)(C=)	-5.793	-
C-(H)$_2$(O)$_2$	-9.546	14.619

---

* Denotes fused benzene atom

Group Name	C(T_c)	C(P_c)
C-(H)(O)(C)$_2$	-24.308	22.561
C-(O)(C)$_3$	-15.344	-5.491
C-(H)$_3$(CO)	-7.109	-15.215
C-(H)$_2$(CO)(C)	-2.599	-41.098
C-(H)(CO)(C)$_2$	-3.811	-55.201
C=(H)(CO)	28.401	-
C=(O)	26.049	-
Cb-(CO)	29.161	28.478
C-(N)(H)$_3$	-25.896	-13.771
C-(N)(C)(H)$_2$	-25.169	-36.867
C-(N)(C)$_2$(H)	-38.614	-85.365
C-(N)(C)$_3$	-34.505	-78.104
N-(C)(H)$_2$	77.950	132.406
N-(C)$_2$(H)	119.626	184.213
N-(C)$_3$	146.657	253.096
N-(Cb)(H)$_2$	4.218	-3.789
N-(Cb)(C)(H)	49.046	-6.375
N-(Cb)(C)$_2$	74.614	96.290
N-(Cb)$_2$(H)	17.491	28.995
N-(Cb)(Cbf)(H)	14.103	-
Cb-(N)	58.398	62.930
Cbf-(Cbf)(Cb)(N)	17.816	-
C-(CN)(C)(H)$_2$	90.123	175.804
Cb-(CN)	72.611	128.600
C-(F)$_3$(C)	32.864	107.651
C-(F)$_2$(H)(C)	39.071	91.749
C-(F)(H)$_2$(C)	35.071	80.752
C-(F)$_2$(C)$_2$	19.921	47.138
C-(F)(H)(C)$_2$	58.873	-
C-(F)(C)$_3$	10.285	-6.424
C-(F)$_2$(Cl)(C)	41.065	121.473

Group Name	$C(T_c)$	$C(P_c)$
C-(F)(Cl)$_2$(C)	49.879	151.520
C-(F)(Cl)(Br)(C)	54.866	176.218
C-(F)$_2$(Br)(C)	45.430	144.916
C-(Cl)$_3$(C)	71.401	203.701
C-(Cl)$_2$(H)(C)	63.973	159.531
C-(Cl)(H)$_2$(C)	38.690	112.477
C-(Cl)(H)(C)$_2$	45.902	-
C-(Br)(H)$_2$(C)	67.899	70.898
C-(I)(H)$_2$(C)	55.312	-
C-(C=)(F)$_3$	32.864	107.651
C-(C=)(C)(F)$_2$	35.403	-
C-(C=)(Cl)(H)$_2$	38.690	112.477
C-(Cb)(F)$_3$	19.841	84.524
C=(F)$_2$	24.703	73.299
C=(Cl)$_2$	46.143	72.221
C=(Br)$_2$	68.988	206.927
C=(F)(C)	24.421	-
C=(F)(H)	15.265	38.622
C=(Cl)(H)	34.464	105.790
C=(F)(Cl)	-	106.706
Cb-(F)	20.695	48.369
Cb-(Cl)	34.599	64.412
Cb-(Br)	38.164	126.345
Cb-(I)	47.690	141.419
C-(S)(H)$_3$	14.932	65.441
C-(S)(C)(H)$_2$	22.486	44.159
C-(S)(C=)(H)$_2$	9.309	-
C=(H)(S)	8.555	75.202
S-(C)(H)	25.371	85.573
S-(C)$_2$	25.965	72.818
S-(C)(C=)	9.309	-

S-(C=)$_2$	11.733	-7.868
S-(S)(C)	7.350	-

Table A-4: Group Contributions for Klincewicz & Reid (1984)

Group Name	C(T$_c$)	C(P$_c$)	C(V$_c$)
-CH$_3$	-2.433	0.026	16.2
-CH$_2$	0.353	-0.015	16.1
-CH$_2$- (r*)	4.253	-0.046	8.2
>CH	6.266	-0.083	12.1
>C- (r)	-0.335	-0.027	7.4
>C<	16.416	-0.136	9.0
>C< (r)	12.435	-0.111	-6.6
=CH$_2$	-0.991	-0.015	13.9
=CH	3.786	-0.050	9.8
=CH- (r)	3.373	-0.066	5.1
=C=, >C=	7.169	-0.067	2.7
>C= (r)	5.623	-0.089	0.2
≡CH	-4.561	-0.056	7.5
≡C	7.341	-0.112	3.0
-OH	-28.930	-0.190	-24.0
-O	5.389	-0.143	-26.1
-O- (r)	7.127	-0.116	-36.6
-CHO, >CO	4.332	-0.196	-6.7
-COOH	-25.085	-0.251	-37.0
-CO-O	8.890	-0.277	-28.2
-NH$_2$	-4.153	-0.127	-0.1
>NH	2.005	-0.180	53.7
>NH (r)	2.773	-0.172	-8.0
>N	12.253	-0.163	-0.7
=N- (r)	8.239	-0.104	-18.4
-CN	-10.381	-0.064	12.0

---

* Ring increment

-SH	28.529	-0.303	-27.7
-S	23.905	-0.311	-27.3
-S- (r)	31.537	-0.208	-61.9
-F	5.191	-0.067	-34.1
-Cl	18.353	-0.244	-47.4
-Br	53.456	-0.692	-148.1
-I	94.186	-1.051	-270.6
-XCX[*]	-1.770	0.032	0.8
-NO$_2$	11.709	-0.325	-39.2

Table A-5: Group Contributions for Joback & Reid (1987)

Group Name	C(T_c)	C(P_c)	C(V_c)	C_a	C_b
Non-ring increments					
-CH$_3$	0.0141	-0.0012	65	548.29	-1.719
-CH$_2$-	0.0189	-	56	94.16	-0.199
>CH-	0.0164	0.002	41	-322.15	1.187
>C<	0.0067	0.0043	27	-573.56	2.307
=CH$_2$	0.0113	-0.0028	56	495.01	-1.539
=CH-	0.0129	-0.0006	46	82.28	-0.242
=C<	0.0117	0.0011	38	-	-
=C=	0.0026	0.0028	36	-	-
≡CH	0.0027	-0.0008	46	-	-
≡C-	0.002	0.0016	37	-	-
Ring increments					
-CH$_2$-	0.01	0.0025	48	-394.29	1.251
>CH-	0.0122	0.0004	38	-	-

---

[*] X = Halogen. The number of pairwise interactions of halogen atoms attached to the same carbon, e.g. -CHF$_2$ contains 1 XCX while -CCL$_3$ contains three XCX Cramer (1980).

>C<	0.0042	0.0061	27	259.65	-0.702
=CH-	0.0082	0.0011	41	-245.74	0.912
=C<	0.0143	0.0008	32	-	-
Halogen increments					
-F	0.0111	-0.0057	27	625.45	-1.814
-Cl	0.0105	-0.0049	58	738.91	-2.038
-Br	0.0133	0.0057	71	809.55	-2.224
-I	0.0068	-0.0034	97	2173.72	-5.057
Oxygen increments					
-OH	0.0741	0.0112	28	3018.17	-7.314
-OH (a [*])	0.024	0.0184	-25	122.09	-0.386
-O- (c [†])	0.0168	0.0015	18	440.24	-0.953
-O- (r [‡])	0.0098	0.0048	13	340.35	-0.350
>C=O (c)	0.038	0.0031	62	-	-
>C=O (r)	0.0284	0.0028	55	740.92	-1.713
O=CH-	0.0379	0.003	82	1317.23	-2.578
-COOH	0.0791	0.0077	89	483.88	-0.966
-COO-	0.0481	0.0005	82	675.24	-1.340
=O (except as above)	0.0143	0.0101	36	-	-
Nitrogen increments					
$-NH_2$	0.0243	0.0109	38	-	-
>NH (c)	0.0295	0.0077	35	-	-
>NH (r)	0.013	0.0114	29	-	-
>N- (c)	0.0169	0.0074	9	-	-
-N= (c)	0.0255	-0.0099	0	-	-
-N= (r)	0.0085	0.0076	34	-	-

---

[*] Denotes aromatic group
[†] Denotes chain group
[‡] Denotes ring group

=NH	-	-	-	-	-
-CN	0.0496	-0.0101	91	-	-
$-NO_2$	0.0437	0.0064	91	-	-
Sulphur increments					
-SH	0.0031	0.0084	63	-	-
-S- (c)	0.0119	0.0049	54	-	-
-S- (r)	0.0019	0.0051	38	-	-

Table A-6: Group Contributions for Somayajulu (1989)

Group Name	$C(T_c)$	$C(P_c)$	$C(V_c)$
$-CH_3$	1.000	1.000	1.000
$>CH_2$	1.000	1.000	1.000
>CH	0.849	1.079	0.970
>C<	0.494	1.104	0.987
C-C-C-C (gauche)	-0.197	-0.133	-0.086
$-CH_2-$ (r)	0.640	0.805	0.809
>CH- (r)	0.640	0.805	0.809
>C< (r)	0.420	0.805	0.809
>CH- fused (r)	0.250	0.625	0.809
$=CH_2$	0.900	0.900	0.820
=CH	0.800	0.800	0.780
=C<	0.800	0.800	0.780
=C=	0.400	0.600	0.400
Trans alkene	-0.200	-0.150	0.000
=CH- (r)	0.542	0.681	0.672
=C< (r)	0.542	0.681	0.653
=C< fused (r)	0.250	0.460	0.653
≡CH	1.180	0.690	0.635
≡C	0.680	0.540	0.635

---

[*] Denotes ring group

Group Name	$C(T_c)$	$C(P_c)$	$C(V_c)$
Phenyl substitution[*]	-1.000	-1.000	0.000
Isopropyl	2.849	3.079	2.970
Isobutyl	3.849	4.079	3.970
sec-butyl	3.652	3.946	3.884
Tert-butyl	3.494	4.104	3.987
Isopentyl	4.652	4.946	4.884
Neopentyl	4.494	5.104	4.987
Cyclobutyl	2.560	3.220	3.236
Cyclopentyl	3.200	4.025	4.045
Cyclohexyl	3.840	4.830	4.854
Phenyl	3.252	4.086	4.032
Naphthyl	4.836	6.368	6.682
Vinyl	1.700	1.700	1.600
Allyl	2.600	2.600	2.560
-OH (water)	0.870	-0.236	0.290
-OH (methanol)	4.000	0.284	0.290
-OH (ethanol)	4.670	0.360	0.290
-OH (propanol)	4.080	0.280	0.290
-OH (butanol)	3.490	0.200	0.290
-OH (pentanol)	2.900	0.120	0.290
-OH (hexanol)	2.310	0.040	0.290
-OH (heptanol)	1.720	-0.040	0.290
-OH (octanol)	1.130	-0.120	0.290
-OH (phenols)	1.530	-0.100	-0.014
-OH and X (ortho)[†]	-0.340	-0.100	0.000
X and Y (ortho)[‡]	-0.100	-0.100	0.000
X and Y (meta)[§]	0.200	0.100	0.000
C-C-C-OH (gauche)	-0.500	0.000	0.000

---

[*] Applies to benzene ring

[†] X stands for any group attached to an aromatic ring in the ortho position to a -OH group

[‡] X and Y stand for any groups other than -OH in the ortho positions. Also, both groups cannot be halogens.

[§] X and Y stand for any groups in the meta position

Group Name	$C(T_c)$	$C(P_c)$	$C(V_c)$
-O- (nr)*	0.870	0.710	0.363
-O- (r)	0.800	0.710	0.363
>CO (nr)	2.300	1.250	1.070
C-C-C=O	-0.500	0.000	0.000
>CO (r)	3.300	1.540	1.100
CHO	2.800	1.250	1.070
-C-C-CHO	-0.500	0.000	0.000
-CHO (a)[1]	1.250	1.100	1.070
-COOH	4.000	2.000	1.360
C-C-COOH	0.400	0.000	0.000
-COO- (formates)	2.100	2.080	1.433
-COO- (others)	2.400	2.080	1.433
-COO- (a)	2.200	2.080	1.433
-CO-O-CO	8.200	3.035	2.503
=O	1.000	0.660	0.290
$-NH_2$	1.700	0.420	0.580
-NH- (nr)	1.500	0.420	0.580
-NH- (r)	1.000	0.260	0.580
>N- (nr)	0.600	0.800	0.580
$-NH_2$ (a)	1.500	0.280	0.580
>NH (a)	1.500	0.280	0.580
>N- (a)	1.500	0.500	0.580
>N- (r)	0.050	0.260	0.580
=N- (general)	0.542	0.355	0.580
N(V)	-0.400	0.040	0.580
-CN (normal)	3.000	1.580	1.450
-CN (a)	1.800	1.330	1.450
$-NO_2$	2.700	2.000	1.420
$-CONH_2$	4.000	1.670	1.650

---

* Denotes nonring group

[1] Denotes aromatic group

Group Name	$C(T_c)$	$C(P_c)$	$C(V_c)$
$-ONH_2$	2.600	1.130	0.943
≡N	1.250	1.260	0.900
HN (nb*)	2.000	-0.135	0.000
-SH	0.650	1.200	1.000
-S- (nr)	0.760	1.200	1.000
-S- (r)	0.460	1.130	0.570
=S	0.260	1.200	1.000
S(IV)	0.400	1.200	1.000
S(VI)	0.800	0.800	1.000
-F (c†)	0.688	1.072	0.230
-Cl (c)	0.570	1.409	0.820
-Br (c)	0.570	2.800	1.150
-I (c)	0.570	4.068	1.620
-F (a)	0.572	0.827	0.230
-Cl (a)	0.642	1.400	0.820
-Br (a)	0.642	2.800	1.150
-I (aromatic)	0.642	4.068	1.620
HF (nb)	0.230	-0.130	0.000
HCl (nb)	0.093	-0.040	0.000
HBr (nb)	0.040	0.000	0.000
HI (nb)	0.040	0.000	0.000
FCl (nb)	0.070	0.000	0.000
FBr (nb)	-0.030	0.000	0.000
FI (nb)	-0.030	0.000	0.000
ClBr (nb)	-0.030	0.000	0.000
ClI (nb)	-0.050	0.000	0.000
BrI (nb)	-0.050	0.000	0.000
FC (nb)	-0.230	-0.180	0.000
FC (nonbonded in ring and alkenes)	0.120	-0.140	-0.030

---

* Denotes nonbonded group

† Denotes aliphatic group

Group Name	C(T$_c$)	C(P$_c$)	C(V$_c$)
-CF$_3$ (normal)	3.064	4.216	1.690
-CF$_3$[*]	2.604	3.856	1.690
>CHF$_2$ (normal)	2.836	2.884	1.460
>CHF$_2^{w}$	2.836	2.524	1.460
>CH$_2$F (normal)	2.148	1.812	1.230
>CF$_2$ (normal)	2.376	3.144	1.460
>CF$_2^{w}$	1.456	2.424	1.460
>CF- (normal)	1.688	2.072	1.230
>CF^{w}	0.998	1.532	1.230
>CF$_2^{w}$ (r)	1.546	2.389	1.199
>CHF^{w} (r)	1.328	1.467	0.969
>CF^{w} (r)	-0.400	1.417	0.969
=CF$_2$ (normal)	2.276	3.044	1.269
=CF$_2^{w}$	2.036	2.764	1.199
=CHF^{w}	1.698	1.702	1.015
=CF[†]	1.138	1.522	1.015
=CCl$_2^{w}$	1.800	3.438	2.390
=CHCl^{w}	1.443	2.129	1.605
=CFCl^{w}	1.988	3.101	1.800
=CF^{w} (r)	1.095	1.508	0.902
-CF$_2$Cl (normal)	3.086	4.553	2.280
-CF$_2$Cl^{w}	2.626	4.193	2.280
-CFCl$_2$ (normal)	2.968	4.890	2.870
-CFCl$_2^{w}$	2.508	4.530	2.870
-CF$_2$Br (normal)	2.886	5.944	2.610
-CF$_2$Br^{w}	2.426	5.584	2.610
-CRClBr^{w}	2.378	5.921	2.610
-CCl$_3$ (normal)	2.710	5.227	3.460
-CCl$_3^{w}$	2.250	4.867	3.460

---

[*] Applies to perhalogenated compounds

[†] Applies to perfluoroalkenes

Group Name	$C(T_c)$	$C(P_c)$	$C(V_c)$
$-CHCl_2$	2.326	3.738	2.640
$-CH_2Cl$	1.756	2.329	1.820
$-CH_2Br$	1.650	3.800	2.150
$-CHBr_2$	2.220	6.600	3.300
$-CH_2I$	1.650	5.068	2.620
Se(II)	0.400	2.700	1.500
Te(II)	0.800	3.600	1.600
Si(IV)	1.500	2.400	2.100
$-O-Si(CH_3)_2$	3.600	5.110	4.463
$-O-Si(C_2H_5)_2$	2.800	7.110	6.463
>Si< (r)	0.800	2.400	2.100
C-C-Si-O	-0.900	0.000	0.000
Ge(IV)	2.000	3.200	2.000
Sn(IV)	2.000	4.500	2.400
Ti(IV)	1.200	1.800	2.100
Zr(IV)	14.000	1.800	2.200
Hf(IV)	20.000	3.600	2.200
V(III)	1.700	1.800	2.200
Nb(V)	2.000	1.800	2.200
Ta(V)	2.000	3.500	2.400
Mo(VI)	0.500	2.000	2.900
W(VI)	0.500	3.900	2.000
Hg(II)	0.250	3.600	0.800
B(III)	1.500	2.000	1.200
Al(III)	6.000	4.000	1.500
Ga(III)	5.000	4.000	1.500
P(III)	1.000	1.700	1.600
P(V)	0.750	1.700	1.600
As(III)	1.000	1.500	1.400
W(VI)	0.500	3.900	2.000
Hg(II)	0.250	3.600	0.800

Group Name	$C(T_c)$	$C(P_c)$	$C(V_c)$
B(III)	1.500	2.000	1.200
Al(III)	6.000	4.000	1.500
Ga(III)	5.000	4.000	1.500
P(III)	1.000	1.700	1.600
P(V)	0.750	1.700	1.600
As(III)	1.000	1.500	1.400
Sb(III)	0.750	1.500	1.800
Bi(III)	0.500	1.500	1.500
U(VI)	0.500	4.200	2.400
Re(VI)	0.500	4.200	2.500
Os(VIII)	0.500	4.200	2.500
-D	0.100	0.050	0.000
Xe(VI)	0.900	2.000	1.500
-H (partially ionic)	3.000	0.125	0.220

Table A-7: First order Group Contributions for Constantinou & Gani (1994)

Group Name	$C(T_c)$	$C(P_c)$	$C(V_c)$
CH_3	1.6781	0.019904	0.0750
CH_2	3.4920	0.010558	0.0558
CH	4.0330	0.001315	0.0315
C	4.8823	-0.010404	-0.0003
CH_2=CH	5.0146	0.025014	0.1165
CH=CH	7.3691	0.017865	0.0954
CH_2=C	6.5081	0.022319	0.0918
CH=C	8.9582	0.012590	0.0733
C=C	11.3764	0.002044	0.0762
CH_2=C=CH	9.9318	0.031270	0.1483
A[*] CH	3.7337	0.007542	0.0422
AC	14.6409	0.002136	0.0399
$ACCH_3$	8.2130	0.019360	0.1036

---

[*] Denotes aromatic group

Group Name	$C(T_c)$	$C(P_c)$	$C(V_c)$
$ACCH_2$	10.3239	0.012200	0.1010
ACCH	10.4664	0.002769	0.0712
OH	9.7292	0.005148	0.0390
ACOH	25.9145	-0.007444	0.0316
CH_3CO	13.2896	0.025073	0.1340
CH_2CO	14.6273	0.017841	0.1120
CHO	10.1986	0.014091	0.0864
CH_3COO	12.5965	0.029020	0.1589
CH_2COO	13.8116	0.021836	0.1365
HCOO	11.6057	0.013797	0.1057
CH_3O	6.4737	0.020440	0.0875
CH_2O	6.0723	0.015135	0.0729
CH-O	5.0663	0.009857	0.0587
FCH_2O	9.5059	0.009011	0.0686
CH_3NH	12.1726	0.012558	0.1313
$CHNH_2$	10.2075	0.010694	0.0753
CH_3NH	9.8544	0.012589	0.1215
CH_2NH	10.4677	0.010390	0.0996
CHNH	7.2121	-0.000462	0.0917
CH_3N	7.6924	0.015874	0.1260
CH_2N	5.5172	0.004917	0.0671
$ACNH_2$	28.7570	0.001120	0.0636
C_5H_4N	29.1528	0.029565	0.2483
C_5H_3N	27.9464	0.025653	0.1703
CH_2CN	20.3781	0.036133	0.1583
COOH	23.7593	0.011507	0.1019
CH_2Cl	11.0752	0.019789	0.1156
CHCl	10.8632	0.011360	0.1035
CCl	11.3959	0.003086	0.0792
$CHCl_2$	16.3945	0.026808	0.1695
CCl_2	-	-	-

Group Name	$C(T_c)$	$C(P_c)$	$C(V_c)$
CCl_3	18.5875	0.034935	0.2103
ACCL	14.1565f	0.013135	0.1016
CH_2NO_2	24.7369	0.020974	0.1653
$CHNO_2$	23.2050	0.01224	0.1423
$ACNO_2$	34.5870	0.015050	0.1426
CH_2SH	13.8058	0.013572	0.1025
I	17.3947	0.002753	0.1081
Br	10.5371	-0.001771	0.0828
CH≡C	7.5433	0.014827	0.0933
C≡C	11.4501	0.004115	0.0763
Cl-(C=C)	5.4334	0.016004	0.0569
ACF	2.8977	0.013027	0.0567
$HCON(CH_2)_2$	-	-	-
CF_3	2.4778	0.044232	0.1148
CF_2	1.7399	0.012884	0.0952
CF	3.5192	0.004673	-
COO	12.1084	0.011294	0.0859
CCl_2F	9.8408	0.035446	0.1821
HCClF	-	-	-
$CClF_2$	4.8923	0.039004	0.1475
F (except as above) [*]	1.5974	0.014434	0.0378
$CONH_2$	65.1053	0.004266	0.1443
$CONHCH_3$	-	-	-
$CONHCH_2$	-	-	-
$CON(CH_3)_2$	36.1403	0.040149	0.2503
$CONCH_3CH_2$	-	-	-
$CON(CH_2)_2$	-	-	-
$C_2H_5O_2$	17.9668	0.025435	0.1675
$C_2H_4O_2$	-	-	-
CH_3S	14.3969	0.016048	0.1302

---

[*] The method is not applied to highly partial fluorinated compounds

Group Name	$C(T_c)$	$C(P_c)$	$C(V_c)$
CH_2S	17.7916	0.011105	0.1165
CHS	-	-	-
C_4H_3S	-	-	-
C_4H_2S	-	-	-

Table A-8: Second order Group Contributions for Constantinou & Gani (1994)

Group Name	$D(T_c)$	$D(P_c)$	$D(V_c)$
$(CH_3)_2CH$	-0.5334	0.000488	0.00400
$(CH_3)_3C$	-0.5143	0.001410	0.00572
$CH(CH_3)CH(CH_3)$	1.0699	-0.001849	-0.00398
$CH(CH_3)C(CH_3)_2$	1.9886	-0.005198	-0.01081
$C(CH_3)_2C(CH_3)$	5.8254	-0.013230	-0.02300
3 membered ring	-2.3305	0.003714	-0.00014
4 membered ring	-1.2978	0.001171	-0.00851
5 membered ring	-0.6785	0.000424	-0.00866
6 membered ring	0.8479	0.002257	0.01636
7 membered ring	3.6714	-0.009799	-0.02700
$CH_n=CH_m-CH_p=CH_k$, k,n,m,p e (0,2)	0.4402	0.004186	-0.00781
$CH_3-CH_m=CH_n$, m,n e (0,2)	0.0167	-0.000183	-0.00098
$CH_2CH_m=CH_n$, m,n e (0,2)	-0.5231	0.003538	0.00281
$CH-CH_m=CH_n$ or $C-CH_m=CH_n$, m,n e (0,2)	-0.3850	0.005675	0.00826
Alicyclic side chain $C_{cyclic}C_m$, m >1	2.1160	-0.002546	-0.01755
CH_3CH_3	2.0427	0.005175	0.00227
CHCHO or CCHO	-1.5826	0.003659	-0.00664
CH_3COCH_2	0.2996	0.001474	-0.00510
CH_3COCH or CH_3COC	0.5018	-0.002303	-0.00122
$C_{cyclic}(=O)$	2.9571	0.003818	-0.01966
ACCHO	1.1696	-0.002481	0.00664
CHCOOH or CCOOH	-1.7493	0.004920	0.00559
ACCOOH	6.1279	0.000344	-0.00415
CH_3COOCH or CH_3COOC	-1.3406	0.000659	-0.00293

$COCH_2COO$ or COCHCOO or COCCOO	2.5413	0.001067	-0.00591
CO-O-CO	0.0000	0.000000	0.00000
ACCOO	-2.7617	-0.004877	-0.00144
CHOH	-3.4235	-0.000541	0.02605
COH	-2.8035	-0.004393	-0.00777
$CH_m(OH)CH_n(OH)$, m,n e (0,2)	-3.5442	0.000178	0.01511
$CH_{mcyclic}$-OH, m e (0,1)	5.4941	0.005052	0.00397
$CH_m(OH)CH_n(NH_p)$, m, n, p e (0,3)	0.3233	0.006917	-0.02297
$CH_m(NH_2)CH_n(NH_2)$, m,n e (0,2)	5.4864	0.001408	0.00433
$CH_{mcyclic}$-NH_p-$CH_{ncyclic}$, m,n,p e (0,2)	2.0699	0.002148	0.00580
CH_m-O-CH_n=CH_p, m,n,p e (0,2)	2.1345	-0.005947	-0.01380
AC-O-CH_m, m e (0,3)	1.0159	-0.000878	0.00297
$CH_{mcyclic}$-S-$CH_{ncyclic}$, m,n e (0,2)	-5.3307	-0.002249	-0.00045
CH_m=CH_n-F, m,n e (0,2)	4.4847	0.000000	0.00000
CH_m=CH_n-Br, m,n e (0,2)	-0.4996	0.000319	-0.00596
CH_m=CH_n-I, m,n e (0,2)	-1.9334	-0.004305	0.00507
ACBr	0.0000	0.000000	0.00000
ACI	-2.2974	0.009027	-0.00832
$CH_m(NH_2)$-COOH m e (0,2)	2.8907	0.008247	-0.00341

Table A-9: Group Contributions for Tu (1995)

Group	$C(T_c)$	Group	$C(T_c)$
$-CH_3$	0.9300	$-CH_2$	0.9172
>CH	0.7937	>C<	0.7924
$=CH_2$	0.7428	=CH	0.9726
=C<	1.0545	=C=	1.5043
≡CH	0.9777	≡C	1.4785
$-CH_2$- (r)	1.1227	>CH- (r)	1.0331
>C< (r)	0.5867	=CH- (r)	1.1515
=C< (r)	1.9844	-OH	3.2436

---

[*] Denotes a group in a ring

-OH (a[*])	4.1764	CHO	3.4039
-O	1.0768	-CO	3.3980
-COOH	7.1082	-COO	3.5275
$-NH_2$	2.4882	-NH	1.6467
>N	1.0145	=N- (r)	2.0825
-CN	5.1393	$-NO_2$	6.4594
-NH- (r)	4.0274	-F	$0.9960/N_f^{0.991}$
-F (perfluoro)	$0.2000/N_{fv}^{0.99}$	-F (a)	$-1.2431/N_f^{0.20}$
-Cl	$2.6088/N_f^{0.25}$	-Cl (a)	$2.1263/N_f^{0.15}$
-Br	$3.5414/N_f^{0.10}$	-I	$5.0922/N_f^{0.10}$
-S-	3.3967	-S- (r)	4.4355
-SH	3.5155	-O- (r)	1.9106

Table A-10: Group (Bond) Contributions for Marrero-Morejon & Pardillo-Fontdevilla (1999).

Group	$C(T_c)$	$C(P_c)$	$C(V_c)$
Interactions with CH_3- (via single bond)			
CH_3-	-0.0213	-0.0618	123.2
CH_2-	-0.0227	-0.043	88.6
CH-	-0.0223	-0.0376	78.4
>C<	-0.0189	-0.0354	69.8
=CH-	0.8526	0.0654	81.5
=C<	0.1792	0.0851	57.7
>C< (r [‡])	0.3818	-0.232	65.8
>CH- (r)	-0.0214	-0.0396	58.3
>C- (r)	0.1117	-0.0597	49
=C< (r)	0.0987	-0.0746	71.7
-F	-0.037	-0.0345	88.1
-Cl	-0.9141	-0.0231	113.8
-Br	-0.9166	-0.0239	-

---

[*] Denotes a group attached to a ring

[†] N_f is the number of halogen groups

[‡] Denotes ring group

-I	-0.9146	-0.0241	-
-OH (a [*])	-0.0876	-0.018	92.9
-O-	-0.0205	-0.0321	66
>CO	-0.0362	-0.0363	88.9
-CHO	-0.0606	-0.0466	128.9
-COOH	-0.089	-0.0499	145.9
-COO (o [†])	0.0267	0.1462	93.3
-COO (c [‡])	-0.0974	-0.229	108.2
NH$_2$-	-0.0397	-0.0288	-
>NH	-0.0313	-0.0317	-
>N-	-0.0199	-0.0348	76.3
-CN	-0.0766	-0.0507	147.9
-NO$_2$	-0.0591	-0.0385	148.1
-SH	-0.9192	-0.0244	119.7
-S-	-0.0181	-0.0305	87.9
Interactions with non-ring -CH$_2$- (via single bond)			
-CH$_2$-	-0.0206	-0.0272	56.6
>CH-	-0.0134	-0.0219	40.2
>C<	-0.0098	-0.0162	32
=CH-	0.8636	0.0818	50.7
=C<	0.1874	0.101	24
≡C-	0.416	-0.2199	33.9
>CH- (r)	-0.0149	-0.0265	31.9
>C< (r)	0.1193	-0.0423	-
=C< (r)	0.1012	-0.0626	52.1
-F	-0.0255	-0.0161	49.3
-Cl	-0.0162	-0.015	80.8
-Br	-0.0205	-0.014	101.3
-I	-0.021	-0.0214	-
-OH (a)	-0.0786	-0.0119	45.2

---

[*] Denotes chain group
[†] Interaction with oxygen atom
[‡] Interaction with carbon atom

-O-	-0.0205	-0.0184	34.5
>CO	-0.0256	-0.0204	62.3
-CHO	-0.0267	-0.021	106.1
-COOH	-0.0932	-0.0253	114
-COO (o)	0.0276	0.1561	69.9
-COO (c)	-0.0993	-0.215	79.1
NH_2-	-0.0301	-0.0214	63.3
>NH	-0.0248	-0.0203	49.4
>N-	-0.0161	-0.017	32.7
-CN	-0.0654	-0.0329	113.5
-NO_2	-0.0137	-0.0163	93.3
-SH	-0.0192	-0.0173	57.9
Interactions with non-ring >CH- (via single bond)			
>CH-	-0.0039	-0.0137	18.3
>C<	0.0025	-0.0085	8.6
=CH-	0.8547	0.0816	48.9
=C<	0.1969	0.108	4.3
>CH- (r)	0.0025	-0.0168	-
=C- (r)	0.1187	-0.0556	-
-F	-0.02	-0.0147	37.7
-Cl	-0.0142	-0.0131	68.6
-OH (a)	-0.0757	-0.0093	45.6
-O-	-0.0162	-0.0155	23.7
>CO	-0.0194	-0.0112	39.3
-CHO	-0.0406	-0.028	92.2
-COOH	-0.1054	-0.0358	110.2
-COO (o)	-0.0918	-0.2098	72.3
-NH_2	-0.0286	-0.0212	39.2
>NH-	-0.0158	-0.0162	-
Interactions with non-ring >C< (via single bond)			
>C<	0.0084	0.0002	22.7
=CH-	0.8767	0.0953	23.4

=C<	0.2061	0.1109	8.8
>CH- (r)	0.0049	-0.0111	-
=C- (r)	0.1249	-0.051	-
-F	-0.0176	-0.0161	30
-Cl	-0.0133	-0.0129	63.7
-Br	-0.0084	-0.0121	85.7
-OH (a)	-0.078	-0.0094	40.6
-O-	-0.0156	-0.0103	40.8
>CO	-0.0114	-0.0085	62.1
-COOH	-0.1008	-0.0455	89
Interactions with non-ring =CH$_2$ (via double bond)			
=CH$_2$	-0.9129	-0.0476	105.3
=CH-	-0.8933	-0.1378	77.4
=C<	-0.4158	-0.2709	99.2
=C=	-0.0123	-0.0239	68.4
Interactions with non-ring =CH- (via double bond)			
=CH-	-1.766	-0.2291	47.8
=C<	-1.2909	-0.3613	73.6
=C=	-0.8945	-0.1202	43.6
=CH-	1.7377	0.1944	42.1
=C<	1.0731	0.2146	16.6
≡C-	1.2865	-0.1087	26.3
=C< (r)	0.9929	0.0533	-
-F	0.8623	0.0929	41.4
-Cl	0.8613	0.0919	68.7
-O-	0.8565	0.0947	36.4
-CHO	0.8246	0.0801	-
-COOH	0.7862	0.0806	107.4
-COO (o)	0.8818	0.2743	55.2
-COO (c)	0.778	-0.1007	64.1
-CN	0.8122	0.0771	107.4

Interactions with non-ring =C< (via double bond)			
=C<	-0.8155	-0.492	93.7
=C=	-0.4009	-0.2502	58.1
Interactions with non-ring =C< (via simple bond)			
=C<	0.3043	0.0705	-
-F	0.1868	0.1064	14.6
-Cl	0.1886	0.1102	43.3
Interactions with non-ring =C= (via triple bond)			
=O	-0.0159	-0.001	51.4
Interactions with non-ring ≡CH (via triple bond)			
≡CH	-0.0288	-0.0226	87.6
≡C-	-0.4222	0.186	73.1
Interactions with non-ring ≡C- (via triple bond)			
≡C-	-0.7958	0.3933	64.3
Interactions with ring -CH$_2$- (via single bond)			
-CH$_2$- (r)	-0.0098	-0.0221	47.2
>CH- (r)	-0.0093	-0.0181	47.5
>C< (r)	-0.1386	0.0081	49.9
=CH- (r)	0.0976	-0.1034	42.5
=C< (r)	0.1089	-0.0527	-
-O- (r)	-0.0092	-0.0119	29.2
>CO (r)	-0.0148	-0.0177	50.7
>NH (r)	-0.0139	-0.0127	38.8
-S- (r)	-0.0071	-	-
Interactions with ring >CH- (via single bond)			
>CH- (r)	-0.0055	-0.0088	33.9
>C< (r)	-0.1341	0.0162	-
-O- (r)	-0.0218	-0.0091	19.2
>CH- (r)	-0.0059	0.0071	-
-OH (p)	-0.0737	-0.022	-

Interactions with ring >C< (via single bond)			
>C< (r)	0.0329	-0.0071	36.2
=C< (r)	-0.0038	-0.0072	-
>C< (r)	0.0662	-0.0509	-
=C< (r)	0.1615	0.1542	53.9
-F	-0.0314	-0.0119	18.4
Interactions with ring =CH- (via double bond)			
>CH- (r)	-0.2246	0.1542	36.5
=C< (r)	-0.3586	0.149	34.4
=N- (r)	0.3913	0.1356	8.3
Interactions with ring =CH- (via single bond)			
>CH- (r)	0.2089	-0.1822	39.3
=C< (r)	0.219	-0.1324	29.8
-O- (r)	0.1	-0.09	40.3
>NH (r)	0.0947	-	-
=N- (r)	-0.4067	-0.1491	65.9
-S- (r)	0.1027	-0.0916	40.8
Interactions with ring =C< (via double bond)			
=C< (r)	-0.4848	0.1432	37.8
=N- (r)	0.2541	-	-
Interactions with ring =C< (via single bond)			
=C< (r)	0.2318	-0.0809	20.6
-O- (r)	0.2424	-0.0792	51.7
=N- (r)	0.1104	-0.0374	-0.3
=C< (r)	-0.3972	-0.0971	35.6
-F	0.1069	-0.0504	23.7
-Cl	0.1028	-0.0512	60.3
-Br	0.106	-0.0548	83.2
-I	0.1075	-0.0514	110.2
-OH (p [*])	0.0931	-0.0388	8.5
-O-	0.0997	-0.0523	-

---

[*] Denotes aromatic group

>CO	0.1112	-0.0528	46.3
-CHO	0.0919	-0.0597	-
-COOH	0.0313	-0.0684	100.2
-COO (c)	0.0241	-0.2573	55.2
NH_2-	0.083	-0.0579	33.2
>NH	0.0978	-0.0471	-
>N-	0.0938	-0.0462	-
-CN	0.0768	-0.0625	-
Interaction with -Cl (via single bond)			
CO	-0.0191	-0.0125	84
Interactions with -O- (via single bond)			
CO	0.1987	0.3209	-
=N- (r)	-	-	-
Interactions with non-ring >CO (via single bond)			
CO	-0.5957	-	-
Interactions with -H (forming formaldehyde. Formic acid, ...)			
-CHO	-0.0422	-0.0123	-
-COOH	-0.0690	-	-
-COO-	-0.0781	-0.1878	51. 2
Interactions with -NH_2 (via single bond)			
>NH	-0.0301	-	-
Interactions with non-ring -S- (via single bond)			
-S-	-0.0124	-	-

Table A-11: Group-Adjacent Atom Pair Contributions for Wen & Quiang (2001)

Adjacent Atom	$C(T_c)$	$C(P_c)$	$C(V_c)$	$C'(T_c)$
-CH_3 group paired with				
-H	-2.885	9.361	125.58	-8.8072
>C<	2.424	4.035	86.72	-1.1863
=C<	0.048	2.682	70.64	2.0695

≡C-	22.766	7.267	105.31	0.8880
>C< (r)	-3.404	9.548	45.38	0.4312
=C< (r)	2.495	3.297	91.08	-2.9673
-O-	2.275	1.286	62.82	-5.6886
-S-	2.602	2.797	113.65	-1.8098
>N-	-1.601	5.280	49.86	-0.5794
=N-	-	-	-	-0.0174
-NO$_2$	35.848	2.517	200.24	4.5913
>CH$_2$ group paired with				
>C<	2.124	1.454	28.22	2.2116
=C<	-0.708	0.314	14.98	5.2478
≡C-	22.576	5.065	44.98	0.5832
>C< (r)	-3.085	9.483	0.07	3.3562
=C< (r)	1.578	2.239	46.54	-0.2371
-O-	-0.030	0.038	13.89	-0.0296
-S-	2.256	1.497	57.95	2.8167
>N-	-2.322	3.545	-20.09	2.9084
-F	2.549	1.851	81.10	1.0111
-Cl	13.769	1.707	103.74	-0.8130
-Br	20.882	1.517	127.10	-1.3763
-I	25.177	3.345	-	-0.0022
>CH- group paired with				
>C<	1.934	0.460	5.53	2.7600
=C<	-3.377	0.358	2.54	7.5553
≡C-	-	-	-	-
>C< (r)	0.000	6.274	-	-
=C< (r)	-1.765	1.087	16.98	0.3694
-O-	-3.163	0.187	1.47	0.9548
>N-	-5.588	3.501	-46.51	3.9991
-F	0.830	2.770	55.26	1.6760
-Cl	11.483	1.318	84.21	0.5273

---

* Denotes ring or aromatic atom

>C< group paired with				
>C<	2.183	-0.282	-4.52	2.7770
=C<	-7.415	0.141	-16.38	5.3585
≡C-	0.007	6.690	-	-0.0076
>C< (r)	-0.651	-0.032	-	0.8857
=C< (r)	0.178	-0.013	-0.08	-0.0093
-O-	-4.384	0.214	-3.45	0.7629
-F	-0.502	2.885	44.84	0.7647
-Cl	6.664	2.880	75.12	1.6201
-Br	9.639	2.604	98.04	0.4661
=CH$_2$ group paired with				
=C-	2.262	3.648	78.05	1.7766
=C=	-1.648	4.393	80.34	4.6760
=C< (r)	-	-	-	-
=CH- group paired with				
>C<	5.838	2.686	38.30	-1.4353
=C<	2.218	0.731	23.00	1.5808
≡C-	10.659	5.158	136.00	-5.4993
=C=	-2.228	3.462	28.40	13.0182
C< (r)	0.017	-	-	-0.1973
=C< (r)	3.541	-0.290	-	-5.5762
-O-	-0.748	-1.534	21.77	-2.5308
-F	-1.248	3.842	68.06	-1.7201
-Cl	9.056	2.532	98.13	-0.9027
=C< group paired with				
>C<	4.564	1.624	20.29	0.4717
=C<	2.737	0.305	5.01	0.9585
≡C-	-	-	-	-0.0014
=C=	1.136	2.352	3.48	6.5524
=C< (r)	-0.008	-	-	0.0038
=O	13.166	-0.864	62.65	-4.2721

>N-	-0.009	-0.854	-99.32	0.0060
-F	-2.298	3.177	48.52	1.3320
-Cl	9.242	2.036	77.32	0.6099
≡CH group paired with				
≡C-	1.143	1.668	69.56	-1.1118
≡C- group paired with				
>C<	-11.918	0.000	0.01	-6.0111
=C<	0.007	-0.001	-95.79	-0.0038
≡C-	-0.953	-3.595	18.23	4.4394
>C< (r)	-	-	-	-
=C< (r)	-	-	-	-
=C= group paired with				
=C<	5.993	-1.661	14.19	-6.3639
=O	3.162	-0.802	77.52	-0.8632
=N-	-	5.880	-	-
>CH$_2$ (r) group paired with				
>C< (r)	2.707	1.006	27.84	0.5719
=C< (r)	3.180	2.175	46.55	1.2736
-O- (r)	6.070	0.535	38.22	-0.1301
-S- (r)	13.625	-	-	-0.9306
>N- (r)	7.842	-0.152	50.59	0.1783
>CH- (r) group paired with				
>C<	5.897	-4.382	-0.02	2.0133
=C<	0.004	-	-	0.0204
≡C-	-781.237	-	-	-
>C< (r)	2.367	0.464	34.33	0.0094
=C< (r)	-	-	-	-
-O-	-7.274	4.682	-	0.7476
-O- (r)	3.798	1.848	36.94	2.4465

>C< (r) group paired with				
>C<	5.571	-5.905	0.04	4.1358
>C< (r)	2.446	0.883	36.83	-1.5784
-F	-1.223	1.355	4.71	4.0418
=CH- (r) group paired with				
>C< (r)	0.754	-0.296	-	-1.1378
=C< (r)	2.852	0.680	23.60	0.3159
-O- (r)	2.013	0.853	51.71	-0.1566
-S- (r)	7.937	0.275	52.22	-1.1410
>N- (r)	14.661	-0.001	-	0.4046
=N- (r)	10.141	0.189	45.09	-0.0075
=C< (r) group paired with				
>C<	-0.603	1.671	-2.49	5.6200
=C<	2.172	2.011	112.28	7.6978
≡C-	-	4.716	-	-
>C< (r)	0.009	-0.004	-	-0.0180
=C< (r)	4.660	-0.064	9.87	1.2080
-O-	-2.465	-0.225	-49.16	-4.5849
-O- (r)	3.701	-1.345	5.85	0.8675
>N-	1.700	5.744	-64.77	7.0762
=N- (r)	6.344	-0.319	5.54	2.7730
-F	-5.547	3.029	40.93	0.7764
-Cl	5.600	3.476	78.55	1.3463
-Br	12.840	4.375	95.28	0.2835
-I	28.472	3.073	122.28	0.0770
-CHO group paired with				
-H	10.144	1.662	-	0.6733
>C<	18.220	2.422	113.89	-1.1847
=C<	15.436	1.621	-	5.4387
=C< (r)	20.655	0.037	-	-4.3184

>CO group paired with				
>C<	11.326	1.516	46.35	1.0536
=C< (r)	13.047	-0.543	-81.99	-3.2089
-COOH group paired with				
-H	34.349	-2.792	-	6.8866
>C<	35.591	1.524	127.31	12.5998
=C<	34.476	-0.406	112.99	14.3778
=C< (r)	35.009	0.855	-	10.1056
-COO- group paired with				
-H	7.041	-0.026	74.01	2.6863
>C<	9.909	2.966	60.54	5.4168
=C<	9.193	1.840	89.13	11.1070
=C< (r)	1.933	2.188	-68.36	8.7813
-C_2O_3 group paired with				
=C<	16.126	1.785	-	15.4803
=C< (r)	23.640	-0.332	-28.91	-0.4178
(>CO)C group paired with				
>C< (r)	9.697	-0.622	17.46	2.5145
-CN group paired with				
-H	15.542	5.780	165.84	9.8751
>C<	3.835	0.078	94.53	9.4595
=C<	11.598	0.001	-0.01	15.4000
≡C-	4.679	1.800	-	1.3670
=C< (r)	22.777	-	-	7.2107

Table A-12: Group Contributions for Wen & Quiang (2001)

Group	$D(T_c)$	$D(P_c)$	$D(V_c)$	$D'(T_c)$
-OH	18.847	-1.320	58.88	12.1779
-O-	8.357	4.158	46.41	11.7647
-O- (r)	0.003	0.005	0.01	0.0013
-OH (a*)	11.032	-1.452	101.11	6.3813

---

* Denotes ring atom

-SH	14.462	-2.250	59.67	-4.7655
-S-	16.658	-0.001	-	2.7693
-S- (r)	1.251	-	-	-0.5727
-NH$_2$	15.982	-3.152	110.06	1.4762
>NH	17.609	-4.585	138.33	4.2350
>N-	16.935	-7.394	131.47	7.5331
=N-	16.840	-	-	5.1503
>NH (r)	0.001	-	-	0.0019
=N- (r)	0.004	-0.002	-0.01	0.0590

Table A-13: Group Contributions for Tu (1994)

Group	**A_i**	**B_i**	**C_i**	**D_i**
Alkanes				
CH$_4$	18.3662	-14.4079	6.3518	-2.3592
CH$_3$	11.7714	-12.5737	2.2841	-0.2608
CH$_2$	3.2193	-9.0445	1.3134	-0.066
CH	-4.4782	-5.1317	1.9526	-0.2331
C	-37.4783	34.4263	-17.2189	2.3381
Alkenes				
=CH$_2$	11.2767	-11.1067	1.5073	-0.0519
=CH	5.6569	-12.5108	3.8423	-0.5502
=C	-7.6051	-2.6066	-0.6709	0.0722
=C$_2$	13.3695	-25.865	13.2055	-2.6484
Alkynes				
≡CH	-2.3899	5.9453	-13.5683	2.8676
≡C	31.9325	-50.1135	28.6956	-4.9136
Aromatics				
CH (a[†])	12.919	-20.0023	6.9269	-0.8458
C (a)	-10.7912	4.9887	-5.3565	0.8294

---

[*] Denotes aromatic atom

[†] Denotes aromatic group

Alcohols				
CH_3OH	32.2058	-60.8324	6.7966	-0.6097
CH_2OH	11.5277	-39.9951	-7.2416	1.9198
CHOH	50.8829	-99.9544	29.3664	-3.0041
COH	91.0039	-159.648	67.889	-8.4641
Aldehydes				
HCHO	-21.2585	27.9625	-54.8211	12.9193
CHO	16.9447	-33.558	2.0406	0.2633
Acids				
HCOOH	41.6876	-72.9309	17.07	-2.3461
COOH	-22.3639	6.7934	-27.2066	3.6193
Ketones				
CO	11.4451	-33.7548	4.7095	-0.2817
CO (r)	15.7318	-35.7242	0.6442	1.3149
Esters				
HCOO	30.6109	-52.9005	13.9862	-1.6838
COO	26.7818	-55.0233	16.2873	-1.8386
Ethers				
-O-	6.295	-15.6498	3.5276	-0.4449
Amines				
NH_2	14.5523	-28.1233	-0.0641	0.5749
NH	8.3018	-24.0019	1.1789	0.5033
Nitriles				
HCN	82.3928	-121.561	49.9955	-7.0105
CN	23.3144	-50.7044	6.9185	-0.511
Thiols				
CH_3SH	26.7086	-40.4972	4.3364	-0.2641
CH_2SH	50.9212	-81.154	28.7811	-3.4574
CHSH	26.1946	-52.7165	15.4828	-1.5672
CSH	19.7497	-48.3419	18.1297	-2.1625

' Denotes ring group

Chlorides				
CH_3Cl	40.0173	-54.4986	18.7193	-3.0053
CH_2Cl	27.5618	-45.0267	12.3851	-1.4923
CHCl	24.7329	-46.5664	19.2748	-2.9568
CCl	25.5987	-54.2423	29.0348	-4.9523
Cycloparaffins				
3-Membered ring				
CH_2 (r)	16.3562	-21.8909	9.0876	-1.4623
CH (r)	1.1698	-9.4777	13.2312	-3.246
4-Membered ring				
CH_2 (r)	16.6125	-23.6312	11.9783	-2.2372
=CH (r)	20.1476	-28.2782	18.8008	-4.1441
5-Membered ring				
CH (r)	5.4635	-9.2804	0.7044	-0.0038
CH (r)	25.3819	-43.959	21.4162	-2.6314
C (r)	7.5975	-23.0268	18.2736	-2.9451
=CH (r)	11.102	-16.4049	5.8475	-0.8299
6-Membered ring				
CH_2 (r)	7.2243	-11.9475	2.6978	-0.3025
CH (r)	-5.6954	-0.7688	-1.3039	0.2787
Cr (r)	-36.5572	36.0631	-19.6856	2.9408
=CH (r)	4.3838	-8.661	-0.4299	0.2775
7-Membered ring				
CH_2 (r)	7.636	-13.0975	3.1908	-0.3519
8-Membered ring				
CH_2 (r)	11.8302	-19.5165	6.3215	-0.7243
10-Membered ring				
CH_2 (r)	4.9192	-9.8869	1.587	-0.1242
12-Membered ring				
CH_2 (r)	3.9563	-8.6204	1.1261	-0.0721

Table A-14: Structural correction constants (ξ_1) for Tu (1994)

Compound	s_0	s_1	s_2	s_3
Alkylbenzenes				
1-substituent	-0.0005	0.005	0.0204	-
2-substituent	-0.0336	0.0185	0.011	-0.0218
3-substituent	-0.106	0.0354	-	0.0276
Others	-0.1467	0.0534	-	-0.0521

Table A-15: Structural correction values for nonring q_1 for Tu (1994)

Compound	α_{ln}	β_{ln}	γ_{ln}	δ_{ln}
Alkanes ($N_{cm} \geq 21$)	-1.5775	4.4318	-0.6435	-0.0323
Double and triple branched alkanes				
With position 3	-0.4179	0.4465	-0.0812	0.0093
other positions	0.4061	-0.4338	0.0788	-0.009
1,3-Dialkanes	1.5443	-3.4154	1.049	-0.1502
Alkylcyclohexanes				
Cis-1,2	-0.9974	-0.0384	-0.0652	0.0139
Cis-1,3	-0.1253	-0.0169	-0.0287	0.0061
Trans-1,4	0.1595	0.0215	0.0365	-0.0078
1,4-Dienes	-0.8066	-1.5936	0.0791	-0.0511

Table A-16: Structural correction values for ring q_1 for Tu (1994)

Compound	α_{lr}	β_{lr}	γ_{lr}	δ_{lr}
Alkylbenzenes	10.7912	-4.9887	5.3565	-0.8293
Napthalene	9.077	-15.8513	-2.8016	1.2162
Substituted naphthalene				
α position	8.8047	-15.3758	-2.7176	1.1798
(α, α ') positions[*]	7.897	-13.7907	-2.4374	1.0581
(α, β) positions	8.4598	-14.7734	-2.6111	1.1335
(β, β ') positions	8.9681	-15.6611	-2.768	1.2016

---

[*] α positions of different benzene rings on napthalene

Table A-17: Correction values for ξ_2 and q_2 for Tu (1994)

Compounds	f_0	f_1	f_2	f_3	f_4
Primary alcohols	0.6135	-0.3526	0.0225	-0.0005	-
Secondary alcohols	-	-	-	-	-
-2-ol	2.098	-1.022	0.1234	-0.0051	-
-3-ol	0.6605	-0.3627	0.0177	-	-
-4-ol	0.6497	-0.3627	0.0177	-	-
Tertiary acohols	-	0.2191	-0.0546	-	-
Aldehydes	1.0035	-0.6175	0.0634	-0.0021	-
Acids	-0.3746	0.1991	-0.021	0.0005	-
Ketones	1.4707	-0.6618	0.0597	-0.0018	-
Cyclo-ones	-7.1818	2.8475	-0.309	0.0114	-
Formates	1.621	-1.1558	0.197	-0.0122	-
Esters	0.1967	0.2456	-0.1453	0.015	-0.0004
Ethers	-0.0388	0.2216	-0.1152	0.0089	-
Primary thiols	0.1169	-0.0962	0.0217	-0.0013	-
Secondary thiols	0.174	-0.13	0.024	-	-
Tertiary thiols	-2.756	1.123	-0.1085	-	-
Primary amines ($N_{cm} \geq 2$)	-0.1603	-0.196	0.0134	-	-
Secondary amines ($N_{cm} \geq 3$)	-	-0.2269	0.0086	-	-
1-Chloroalkanes ($N_{cm} \geq 2$)	-	-0.2269	0.0086	-	-
q_2	α_2	β_2	γ_2	δ_2	
	3.2193	-9.0445	1.3134	-0.066	

Table A-18: Group contributions for Orrick & Erbar (1974)

Group	A_i	B_i
Carbon atoms[*]	- (6.95 + 0.21N)	275 + 99N
-CR_3	-0.15	35
CR_4	-1.20	400
Double bond	0.24	-90
Five-membered ring	0.10	32

---

[*] N = number of carbon atoms not including those in other groups shown in table above.

Six-membered ring	-0.45	250
Aromatic ring	0.00	20
Ortho substitution	-0.12	100
Meta substitution	0.05	-34
Para substitution	-0.01	-5
Chlorine	-0.61	220
Bromine	-1.25	365
Iodine	-1.75	400
-OH	-3.00	1600
-COO-	-1.00	420
-O-	-0.38	140
>C=O	-0.50	350
-COOH	-0.90	770

Table A-19: Group contributions for Van Velzen *et al.* (1972)

Group	ΔN	ΔB
n-Alkanes	...	...
Alkene	-0.152 - 0.042N	-44.94 + 5.410NE
Acid $3 \leq N \leq 10$	6.795 + 0.365N	-249.12 + 22.449NE
$N > 10$	10.71	-249.12 + 22.449NE
Ester	4.337 - 0.230N	-149.13 + 18.695NE
Primary alcohol	10.606 0.276N	-589.44 + 70.519NE
Secondary alcohol	11.200 –0.605N	497.58
Tertiary alcohol	11.200 -0.605N	928.83
Diol	Alcohol correction + configurational factor	557.77
Ketone	3.265 - 0.122N	-117.21 + 15.781NE
Ether	0.298 + 0.209N	-9.39 + 2.848NE
Primary amine	3.581 + 0.325N	25.39 + 8.744NE
Secondary amine	1.390 + 0.461N	25.39 + 8. 744NE
Tertiary amine	3.27	25.39 + 8.744NE
Fluoride	1.43	5.75
Chloride	3.21	-17.03

Bromide	4.39	-101.97 + 5.954NE
Iodide	5.76	-85.32
Aromatic and 1-Nitro	7.812 - 0.236N	-213.14 + 18.330NE
2-Nitro	5.84	-213.14 + 18.330NE
3-Nitro	5.56	-338.01 + 25.086NE
4-, 5-Nitro	5.36	-338.01 + 25.086NE

Table A-20: Configurational factors for Van Velzen *et al.* (1972)

Correction	ΔN	ΔB
Correction for Aromatic Nucleus		
Alkyl-, halogen-, nitrobenzenes, secondary and tertiary amines $8 \leq N \leq 15$	0.60	-140.04 + 13.869NE
$N > 15$	3.055 - 0.161N	-140.04 + 13.869NE
Acids	4.81	-188.40 + 9.558NE
Esters	-1.174 + 0.376N	-140.04 + 13.869NE
Alcohols: OH attached to nucleus: take for all phenolic compounds NE = 16.17 [*]	-	213.68
Alcohols: OH is side chain	-0.16	213.68
Ketones	2.70	-760.65 + 50.478NE
Ethers: take for all aromatic ethers NE = 11.50 [†]	-	-140.04 + 13.869NE
Primary amines: NH_2 attached to nucleus: take for all anilinic compounds NE = 15.04 [‡]	-	-
Primary amines: NH_2 in side chain	-0.16	-
Various		
Polyphenyls	-5.340 + 0.815N	-188.40 + 9.558NE
Ortho configuration: OH group present	0.51	-571.94
without OH	-	54.84
Meta configuration	0.11	27.25
Para configuration	-0.04	-17.57

---

[*] Other substituents, such as Cl, CH_3, NO_2, are neglected for the determination of *NE*. For the calculation of *B*, they have to be taken into account.

[†] See I

[‡] See I

Cyclopentane	$7 \leq N \leq 15$	0.205 + 0.069N	-45.96 + 2.224NE
	$N > 15$	3.971 – 0.172N	-339.67 + 23.135NE
Cyclohexane	$8 \leq N \leq 16$	1.48	-272.85 + 25.041NE
	$N > 16$	6.517 – 0.311N	-272.85 + 25.041NE
Iso Configuration			
Alkanes		1.389 - 0.238N	16.61
Double iso in alkanes (extra correction)		0.93	-
Alkenes		1.389 - 0.238N	8.93
Alcohols		0.24	94.23
Esters, alkylbenzenes, halogenides, ketones		-0.24	8.93
Acids		-0.24	-
Ethers, amines		-0.50	8.93
Various			
$C(Cl)_X$ configuration		1.91 - 1.495X	-26.38
-CCl-CCl-		0.96	-
$-C(Br)_X-$		0.50	81.34 - 86.850X
-CBr-CBr-		1.60	-57.73
CF_3- (in alcohols)		-3.93	341.68
(other compounds)		-3.93	25.55
Diols		-2.50 + N	See alcohols

Table A-21: Group contributions and functions for Skubla (1985)

Group	ΔA	Group	ΔB
n-Alkyl			
N_c[*] =1	0.1202	N_c =1	-0.1532
N_c =2 to 20	0.18873 + 0.01049N_c	N_c =2 to 16	0.12341 + 0.0016N_c
		N_c =17 to 18	-0.1045
		N_c =19 to 20	0.1007
1-Alkenyl			
N_c =2 to 4	0.01532 + 0.07325N_c	N_c =2	0.1534

---

[*] Denotes the total number of carbon atoms, only for n-alkyls and 1-alkenyls it denotes the total number of carbon atoms in the corresponding chain

N_c =5 to 7	-0.13897 + 0.02639N_c	N_c =3	-0.1640
N_c =8 to 9	0.3181	N_c =4 to 11	0.13755 + 0.00471N_c
N_c =10 to 20	0.2508 + 0.00723N_c	N_c =12 to 20	-0.0970
Cyclohexyl			
-C_6H_{11}	0.1378	-C_6H_{11}	0.1305
Cyclopentyl			
-C_5H_9	0.1052	-C_5H_9	0.0995
Phenyl			
-C_6H_5	0.0432	-C_6H_5	-0.0970
Hydrogen:			
In n-alkanes and 1-olefins			
N_c =1 to 4	0.3060 + 0.3150 + logN_c + 0.2908log^2N_c	N_c =1	-0.0986
N_c =5 to 20	(0.7709N_c + 4.7391) / (4.9159N_c + 5.5997)	N_c =2 to 10	-0.04911 – 0.00677N_c
		N_c =11 to 20	0.16006 + 0.00374
In cyclohexane	0.2421	In cyclohexane	-0.2529
In cyclopentane	0.0623	In Cyclopentane	-0.1619
In benzene	0.0800	In Benzene	0.2135
In formic acid and In formamide	0.2415	In formic acid and In formamide	-0.2674
-OH in primary alcohols			
N_c =1 to 3	0.2531N_c + 0.0564	N_c =1 to 4	0.0524N_c + 0.0728
N_c =4 to 8	0.0480N_c + 0.8257	N_c =5 to 8	0.0340N_c + 0.4771
-COOH in acids			
N_c =1 to 2	0.2672	N_c =1 to 2	-0.1259
N_c =3 to 12	0.1008 + 0.01831N_c	N_c =3 to 18	-0.1066
N_c =14 to 18	0.6872 + 0.02158N_c		
Esters[*]		Esters	
Formate N_c =2 to 5	-0.0533	Formate N_c =2 to 5	-0.2323
Acetate N_c =3 to 6	-0.1142	Acetate N_c =3 to 6	-0.2323

---

[*] For esters, values of the contribution ΔA and ΔB are equal directly to the parameters A and B

Propionate N_c =4 to 7	-0.1481	Propionate N_c =4 to 7	-0.2323
Butyrate and isobutyrate		Butyrate and Isobutyrate	
N_c =5 to 8	-0.1356	N_c =5 to 8	-0.2323
-NH₂ in primary amines		-NH₂ in primary amines	
N_c =1	0.0761	N_c =1	-0.1246
N_c =3 to 8	$0.3766 + 0.0209N_c$	N_c =3 to 8	0.1782
=NH in secondary amines		=NH in secondary amines	
N_c=2 to 14	$0.2632 + 0.00517N_c - 0.000178N_c^2$	N_c=2 to 14	$0.0560 + 0.00194N_c - \log N_c + 0.0437\log^2 N_c$
Amides of carboxylic acids -CONH₂		Amides of carboxylic acids -CONH₂	
N_c=1 to 4	$(0.6059N_c - 0.6950) / (1.1225N_c - 0.8688)$	N_c=1 to 4	$(1.0986N_c - 1.0160) / (3.666N_c + 0.5953)$
Nitriles of carboxylic acids -CN		Nitriles of carboxylic acids –CN	
N_c=2 to 6	$(0.6163N_c - 1.804) / (3.402N_c - 1.734)$	N_c=2 to 6	$(1.6426N_c - 2.788) / (14.452N_c + 11.791)$
n-alkyl ethers -O-		n-alkyl ethers -O-	
N_c=4	0.1478	N_c=4 to 10	0.0030
N_c=5 to 10	0.2798		
n-alkanethiols –S-		n-alkanethiols –S-	
N_c=3 to 8	$0.4404 - 0.7104N_c - \log N_c + 0.2662\log^2 N_c$	N_c=3 to 8	$0.0959 + 0.0023N_c$
1-bromoalkanes –Br		**1-bromoalkanes –Br**	
N_c=2 to 3	0.1988	N_c=2 to 10	-0.1051
N_c=4 to 10	0.1693		
Aromates:			
NH₂	0.1514		-0.2870
-OH	0.3219		-0.3093
NO₂	-0.0921		-0.1333
-F	0.0185		-0.2432
-Cl	-0.1194		0.1227

-Br	-0.0718	0.1100
-I	-0.0346	-0.1123
Postion:		
Ortho	0.614	-0.0642
Meta	0.1008	-0.0461
Para	0.1228	-0.0526

Table A-22: Contribution of hydrocarbon groups for Sastri & Rao (1992)

Functional group		$\Delta\mu_b$	ΔN	Remarks
		Non-ring		
$-CH_3$		0.105	0.000	For n-alkanes C> 8, ΔN = 0.05
$>CH_2$		0.000	0.000	
>CH		-0.110	0.050	(i) If both groups are present ΔN = 0.05 only (ii) ΔN values applicable only in case of aliphatic hydrocarbons and halogenated derivatives of aliphatic compounds, in other case ΔN = 0.
>C<		-0.180	0.100	
$=CH_2$		0.085	0.000	For n-alkenes C>8, ΔN = 0.05
=CH-		-0.005	0.000	
=C<		-0.100	0.000	
HC≡C-		0.190	0.000	For n-alkynes C>8, ΔN = 0.05
		Ring		
$>CH_2$		0.060	0.000	
>CH-		-0.085	0.000	
>C<		-0.180	0.000	
=CH-	Alicyclic	0.040	0.000	
=CH-	Others	0.050	0.000	
=CH<	Alicyclic	-0.100	0.000	
=C<	Others	-0.120	0.000	
=C<	Fused	-0.040	0.000	

Table A-23: Contribution of hydrocarbon ring structures (chain length) for Sastri & Rao (1992)

Functional group	$\Delta\mu_{bcor}$	ΔN	Remarks
All monocyclic and saturated polycyclic hydrocarbon rings (unsubstituted)		0.100	
Methyl substituted compounds of the above		0.050	
Monocyclic monoalkyl hydrocarbons (alicyclic)			
$1 < Cbr^{*} \leq 5$		0.025	
$Cbr > 5$		0.050	
Monocyclic multisubstituted alkyl alicyclic hydrocarbons		0.025	
Monoalkyl benzenes			
$Cbr > 1$		0.025	
Bicyclic hydrocarbons partly or fully unsaturated		0.050	
Unsaturated tricyclic hydrocarbons		0.100	
Position correction for multiple substitution in aromatics by hydrocarbon/nitro groups or combinations of these			
Ortho		0.050	
meta and para		0.000	
1, 3, 5		0.100	
1, 2, 4		0.050	
1, 2, 6		0.125	Contribution of other functional groups to be neglected
$\Delta\mu_{bcor}$ for multiple substitution in aromatics by hydrocarbon groups	0.070		

---

[*] Denotes branched ring

Table A-24: Contribution of halogen groups for Sastri & Rao (1992)

	$\Delta\mu_b$ halogen attached to						ΔN_b in		
Functional group	-CH_3 or >$CH2_a$	>CH-	>C<[a]	=CH-	=C<	Others	Aliphatics	Alicyclics	Aromatics
-F[c]	0.185	0.155	0.115	-	-	0.185	0.000	0.075	0.025
-Cl[a]	0.185	0.170	0.170	0.180	0.150	0.170	0.000	0.075	0.025
-Br	0.240	0.210	0.210	0.240	0.210	0.210	0.000	0.075	0.025
-I	0.260	0.260	-	-	-	0.260	0.000	0.075	0.025

[a] Special configurations/function group structure combination	ΔN_{cor}	Remarks
(1) X-$(CH_2)_n$ - X, where X is halogen	0.050	
(2) Cl-C-Cl ring	0.050	For each group
[b] Presence of non-hydrocarbon group in cyclic compounds functional group/ structure combinations		
(1) Halogen attached to ring carbon in compounds containing		
(A) - NH_2	−0.100	
(B) other functional groups	−0.050	
(2) Halogen attached to non-hydrocarbon functional group	−0.050	

[c] Fluorine groups in perfluorocompounds

Group	$\Delta\mu_b$	Remarks
Non-ring		
-CF_3	0.210	ΔN_b = 0.150 for all peflouro n-compounds
>CF_2	0.000	
>CF-	-0.080	ΔN_b = 0.200 for all isocompounds
Ring		
-CF_2-	0.120	ΔN_b = 0.200 for all cyclic compounds
>CF-	-0.170	

Table A-25: Contribution of oxygen groups Sastri & Rao (1992)

Functional group		$\Delta\mu_b$	ΔN	Remarks
-O-	Non-ring, attached to ring carbon	0.020	0.050	In compounds containing $-NH_2$ group attached to ring carbon special values $\Delta\mu_b = 0.150$, ΔN = 0.200 for the combination
-O-	Ring	0.140	0.050	In compound containing >CO group special value ΔN = 0.125 for the combination
-O-	Others	0.000	0.050	(i) In aliphatic compounds containing -OH special value ΔN = 0.100 for the combination (ii) In cyclic compounds containing >CO group (with or without other functional groups) special value ΔN = 0.125 for the combination
>CO	Non-ring, attached to ring carbon	0.030	0.050	(i) In cyclic compounds containing -O- group (with or without other functional groups) special value ΔN = 0.125 for the combination (ii) In cyclic compounds containing >NH group $\Delta\mu_{bcor} = 0.100$
>CO	Ring	0.055	0.100	(i) In cyclic compounds containing >NH group $\Delta\mu_{bcor} = 0.100$ (ii) In compounds containing –O- group special value ΔN = 0.125 for the combination
>CO	Others	0.030	0.025	(i) For aliphatic compounds containing >NH2 groups Δμbcor = 0.100 (ii) For cyclic compounds containing >NH groups $\Delta\mu_{bcor} = 0.100$ (iii) In aliphatic compounds containing –OH special value ΔN = 0.125 for the combination
CO-O-CO	Anhydride	0.060	0.050	
-CHO		0.140	0.050	In compounds containing –OH- (phenolic) special value ΔN = 0.125 for the combination
-COO-		0.040	0.050	(i) ΔN value for each –COO- group (ii) For -H in formates $\Delta\mu_{bcor} = 0.165$

-COOH	In aliphatics			
	saturated	0.220	0.100	For C = 3 or 4 $\Delta N = 0.050$
	unsaturated	0.250	0.100	
	In aromatics	0.195	0.172	

Table A-26: Contribution of hydroxyl groups for Sastri & Rao (1992)

Functional group	$\Delta\mu_b$	ΔN	Remarks
-OH in aliphatic saturated primary -n	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$ for $C \leq 10$	0.3 for $2 < C < 12$ 0.15 for others	(i) In compounds containing -O- group special values $\Delta N = 0.100$ for the combination
	0.200 for $C > 10$		(ii) In compounds containing >NH groups special value $\Delta N = 0.300$ for the combination
Branched	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$	0.375	
Secondary saturated chain	$0.67 - 0.092C + 0.004C^2 - 10^{-0.58C}$	0.425 for $C \leq 5$ 0.300 for $C > 5$	
Secondary branched	$0.67 - 0.092C + 0.004C^2 - 10^{-0.58C}$	0.425 for $C \leq 10$ 0.300 for $C > 10$	
Tertiary	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$	0.650	In compounds containing >CO / -O- groups special value $\Delta N = 0.125$ for the combination
Unsaturated	0.300	0.200	
In cyclic alcohols	0.270	0.150	
Phenolics	0.210	0.275	In compounds containing $-NO_2$ / -CHO groups special values $\Delta N = 0.125$ for the combination

Table A-27: Contribution of nitrogen groups for Sastri & Rao (1992)

Functional group		$\Delta\mu_b$*	ΔN	Remarks
-NH_2	In aliphatic n-amines	0.170	0.100	(i) $\Delta\mu b = 0.220$ in $NH_2 - (CH_2)_n - NH_2$ (ii) In compounds containing >CO $\Delta\mu_{bcor} = 0.100$
-NH_2	In aliphatic isoamines attached to >CH	0.200	0.100	
-NH_2	In monocyclic compounds, attached to side chain	0.170	0.100	
-NH_2	In monocyclic compounds, attached to ring carbon	0.150	0.200	See Table 2 note c for $\Delta\mu_{bcor}$ for compounds containing halogens
-NH_2	In other aromatics	0.150	0.100	
>NH	In aliphatic	0.020	0.075	In compounds containing -OH special value $\Delta N = 0.300$ for the combination
>NH	In aromatic compounds, attached to side chain	0.020	0.075	
>NH	In aromatic compounds, attached to ring carbon	0.020	0.010	In cyclic compounds containing >CO $\Delta\mu_{bcor} = 0.100$
>NH	Ring	0.200	0.050	In cyclic compounds containing >CO $\Delta\mu_{bcor} = 0.100$
>N-	In aliphatics	-0.115	0.050	
>N-	In aromatic compounds, attached to side chain	-0.115	0.050	
>N-	In aromatic compounds, attached to ring carbon	- 0.060	0.050	
>N-	Ring	0.100.	0.050	
-$N0_2$	In aliphatics	0.180	0.050	For multiple presence $\Delta N = 0.100$
	In aromatics	0.160	0.050	(i) For multiple presence $\Delta N = 0.100$ (ii) See Table 1 for position correction (iii) In compounds containing -OH (phenolic) special value $\Delta N = 0.125$ for the combination
-CN		0.110	0.050	$\Delta\mu_b = 0.135$ in $CN - (CH_2)_n - CN$

---

* $\Delta\mu_b = 0.080$ for -H compounds containing hydrocarbon functional groups (e.g. formanalide)

Table A-28: Contribution of sulphur groups for Sastri & Rao (1992)

Functional group	**Δμb**	**ΔN**
-S- Non-ring	0.045	0.000
-S- ring	0.150	0.050
-SH	0.150	0.025

Appendix B

Structural Group and Correction Definitions

Table B-1: Group definitions (ID- identification number, PR - priority)

Abbreviations: (e) - very electronegative neighbors (N, O, F, Cl)
(ne) - not very electronegative neighbors (not N, O, F, Cl)
(na) - non-aromatic atom or neighbor
(a) - aromatic atom or neighbor
(c) - atom or neighbor is part of a chain
(r) - atom or neighbor is part of a ring
(z) - groups considered to be non-additive

Group	Description	Name	ID PR	occurs e.g. in
Periodic Group[*] 17				
Fluorine				
F-	F- connected to nonaromatic C or Si	F-(C,Si)	19 87	2-Fluoropropane, trimethylfluorosilane
	F- connected to C or Si with at least one F or Cl neighbor and one other atom	F-((C,Si)-([F,Cl]))-a	22 84	1-Chloro-1,2,2,2-tetrafluoroethane[R124], difluoromethylsilane
	F- connected to C or Si already substituted with at least one F and two other atoms	F-((C,Si)-([F]))-b	21 81	1,1,1-Trifluoroethane, 2,2,3,3-tetrafluoropropionic acid
	F- connected to C or Si already substituted with at least one Cl and two other atoms	F-((C,Si)-(Cl))-b	102 82	Trichlorofluoromethane[R11], 1,1-dichloro-1-fluoroethane [R141B]

---

[*] Periodic group number of the most significant element in the structural group. Periodic group numbers are used as defined in the IUPAC version of the periodic table of elements.

	F- connected to C or Si already substituted with two F or Cl	F-((C,Si)-([F,Cl]$_2$))	23 83	1,1,1-Trifluorotoluene, 2,2,2-trifluoroethanol, trifluoroacetic acid
	F- connected to an aromatic C	F-(C(a))	24 86	Fluorobenzene, 4-fluoroaniline
	F- on a C=C (vinylfluoride)	F-C=C<	20 85	Vinyl fluoride, trifluoroethene, perfluoropropylene
Chlorine				
Cl-	Cl- connected to C or Si not already substituted with F or Cl	Cl- (C,Si)	25 71	Butyl chloride, 2-chloroethanol, chloroacetic acid
	Cl- connected to C or Si already substituted with one F or Cl	Cl-((C,Si)-([F,Cl]))	26 70	Dichloromethane, dichloroacetic acid, dichlorosilane
	Cl- connected to C or Si already substituted with at least two F or Cl	Cl-((C,Si)-([F,Cl]$_2$))	27 68	Ethyl trichloroacetate, trichloroacetonitrile
	Cl- connected to an aromatic C	Cl-(C(a))	28 72	Chlorobenzene
	Cl- on a C=C (vinylchloride)	Cl-C=C<	29 69	Vinyl chloride
COCl-	COCl- connected to C (acid chloride)	COCl-	77 18	Acetyl chloride, phenylacetic acid chloride
Bromine				
Br-	Br- connected to a non-aromatic C or Si	Br-(C,Si(na))	30 65	Ethyl bromide, bromoacetone
	Br- connected to an aromatic C	Br-(C(a))	31 66	Bromobenzene
Iodine				
I-	I- connected to C or Si	I-(C,Si)	32 63	Ethyl iodide, 2-iodotoluene

Periodic Group 16				
Oxygen				
-OH	-OH for aliphatic chains with less than five C (cannot be connected to aromatic groups)	-OH (< C_5) (z)	36 92	Ethanol, propanediol
	-OH connected to C or Si substituted with one C or Si in an at least five C or Si containing chain (primary alkanols)	-OH (> C_4) (z)	35 88	1-Nonanol, tetrahydrofurfuryl alcohol, ethylene cyanohydrin
	-OH connected to a C or Si substituted with two C or Si in at least three C or Si containing chain (secondary alkanols)	HO-((C,Si)$_2$H-(C,Si)-(C,Si)-) (z)	34 90	2-Butanol, cycloheptanol
	-OH connected to C which has four non-hydrogen neighbors (tertiary alkanols)	-OH tert	33 91	Tert-butanol, diacetone alcohol
	-OH connected to an aromatic C (phenols)	HO-(Ca) (z)	37 89	Phenol, methyl salicylate
-O-	-O- connected to two neighbors which are each either C or Si (ethers)	(C,Si)-O-(C,Si) (z)	38 94	Diethyl ether, 1,4-dioxane
	-O- in an aromatic ring with aromatic C as neighbors	(C(a))-O(a)-(C(a)) (z)	65 93	Furan, furfural
-CHO	CHO- connected to non-aromatic C (aldehydes)	CHO-(Cna) (z)	52 53	Acetaldehyde, pentanedial
	CHO- connected to aromatic C (aldehydes)	CHO-(Ca) (z)	90 52	Furfural, benzaldehyde

>C=O	-CO- connected to two non-aromatic C (ketones)	O=C<(Cna)$_2$ (z)	51 4	Acetone, methyl cyclopropyl ketone
	-CO- connected to two C with at least one aromatic C (ketones)	(O=C<(C)$_2$)a (z)	92 54	Acetophenone, benzophenone
	-CO connected to N	>N-(C=O)	109 39	Methyl thioacetate
	-CO connected to two N (urea)	>N-(C=O)-N<	100 3	Urea-1,1,3,3-tetramethyl
	1,2-diketone (Do not fragment)	O=C-C=O	118 1	2,3-Butandione
O=C(-O-)$_2$	Non-cyclic carbonate diester	O=C(-O-)$_2$	79 14	Dimethyl carbonate
COOH -	-COOH connected to C (carboxylic acid)	COOH-(C) (z)	44 23	Acetic acid
-COO -	HCOO- connected to C (formic acid ester)	HCOO-(C) (z)	46 26	Ethyl formate, phenyl formate
	-COO- connected to two C (ester) in a chain	(C)-COO-(C) (z)	45 24	Ethyl acetate, vinyl acetate
	-COO- in a ring, C is connected to C (lactone)	-C(r)OO- (z)	47 25	ε-Caprolactone, crotonolactone
-OCOO-	-CO connected to two O (carbonates)	-OCOO-	103 33	Propylene carbonate, 1,3 dioxolan-2-one
-OCON<	-CO connected to O and N (carbamate)	-OCON<	99 2	Trimethylsilyl methylcarbamate
>(OC$_2$)<	>(OC$_2$)< (epoxide)	>(OC$_2$)< (z)	39 50	Propylene oxide
-CO-O-CO-	Anhydride connected to two C	-C=O-O-C=O-	76 11	Acetic anhydride, butyric anhydride

	Cyclic anhydride connected to two C connected by a double bond or aromatic bond	(-C=O-O-C=O-)r	96 10	Maleic anhydride, phthalic anhydride
-O-O-	Peroxide	-O-O-	94 31	Di-tert-butylperoxide
Sulphur				
-S-S-	-S-S- (disulfide) connected to two C	(C)-S-S-(C)	55 51	Dimethyldisulfide, 1,2-dicyclopentyl-1,2-disulfide
-SH	-SH connected to C (thiols, mercaptanes)	SH-(C) (z)	53 73	1-Propanethiol
-S-	-S- connected to two C (thioether)	(C)-S-(C) (z)	54 74	Methyl ethyl sulfide
	-S- in an aromatic ring (aromatic thioether)	-S(a)- (z)	56 75	Thiazole, thiophene
$-SO_2-$	Non-cyclic sulfone connected to two C (sulfone)	(C)-SO_2-(C)	82 17	Sulfolane, divinylsulfone
$>SO_4$	Sulfates	$>SO_4$	104 34	Dimethyl sulfate
$-SO_2N<$	$-S(=O)_2$ connected to N (sulfonamide)	$-SO_2N<$	105 35	N,N-diethylmethanesulfonamide
>S=O	Sulfoxide	>S=O	107 37	1,4-Thioxane-S-oxide, tetramethylene sulfoxide
SCN-	SCN- (isothiocyanate) connected to C	SCN-(C)	81 19	Allyl isothiocyanate
Selenium				
>Se<	>Se< connected to at least one C or Si	>Se<	116 46	Dimethyl selenide

Periodic Group 15				
Nitrogen				
NH_2-	NH_2- connected to either C or Si (primary amine)	NH_2-(C,Si) (z)	40 96	Hexylamine, ethylenediamine
	NH_2- connected to an aromatic C (aromatic primary amine)	NH_2-(Ca) (z)	41 95	Aniline, benzidine
-NH-	-NH- connected to two C or Si neighbors (secondary amine)	(C,Si)-NH-(C,Si) (z)	42 100	Diethylamine, diallyl amine
	-NH- connected to two C or Si neighbors in a ring (cyclic secondary amine)	(C,Si)r-NH-(Ca,Si)r (z)	97 99	Morpholine, pyrrolidine
>N<	>N- connected to three C or Si neighbors (tertiary amine)	$(C,Si)_2$>N-(C,Si)	43 101	N,N-dimethylaniline, nicotine
	>N> connected to four C or Si (quartenary amine)	$(C,Si)_2$>N<$(C,Si)_2$	101 32	N,N,N,N-tetramethylmethylenediamine
=N-	Double bonded amine connected to at least a C or Si	(C,Si)=N-	91 102	Acetonin
-N-	Aromatic -N- in a five membered ring, free electron pair	=N(a)- (r5) (z)	66 98	Piperidine, thiazole
=N-	Aromatic =N- in a six membered ring	=N(a)- (r6) (z)	67 97	Pyridine, nicotine
C≡N-	-C≡N (cyano-group) connected to C (cyanide)	(C)-C≡N (z)	57 55	Acetonitrile, 2,2'-dicyano diethyl sulfide
	-C≡N (cyano-group) connected to N (cyanamide)	(N)-C≡N	111 41	Dimethylcyanamide

	-C≡N (cyano-group) connected to S (thiocyanate)	(S)-C≡N	108 38	Methyl thiocyanate
CNCNC-r	Imadizole (aromatic 5-ring)	..=CNC=NC=..	106 36	1-Methyl-1-imadizole
-CONH<	-CONH$_2$ (amide)	-CONH$_2$	50 27	Acetamide
	-CONH- (monosubstituted amide)	-CONH-	49 48	N-methylformamide, 6-caprolactam
	-CON< (disubstituted amide)	-CON<	48 49	N,N-dimethylformamide (DMF)
OCN-	OCN- connected to C or Si (isocyanate)	OCN- (z)	80 28	Butylisocyanate, hexamethylene diisocyanate
ONC-	ONC- (oxime)	ONC-	75 29	Methyl ethyl ketoxime
-ON=	-ON= connected to C or Si (isoazole)	-ON=(C,Si)	115 45	Isoxazole, 5-phenyl isoxazole
NO$_2$-	Nitrites (esters of nitrous acid)	O=N-O-(C)	74 22	Ethyl nitrite, nitrous acid methyl ester
	NO$_2$- connected to aliphatic C	NO$_2$-(C)	68 20	1-Nitropropane
	NO$_2$- connected to aromatic C	NO$_2$-(C(a)) (z)	69 21	Nitrobenzene
NO$_3$-	Nitrate (esters of nitric acid)	NO$_3$-	72 13	N-butylnitrate, 1,2-propanediol dinitrate
Phosphorous				
>P(O-)$_3$	Phosphate triester	PO(O-)$_3$	73 9	Triethyl phosphate, tris-(2,4-dimethylphenyl) phosphate

>P<	Phosphorus connected to at least one C or S (phosphine, phosphane)	>P-(C,Si)	113 43	Triphenylphosphine, trietylphosphane
Arsine				
$AsCl_2$-	$AsCl_2$ connected to C	$AsCl_2$-	84 16	Ethylarsenic dichloride
Periodic Group 14				
Carbon				
-CH_3	CH_3- not connected to either N, O, F or Cl	CH_3-(ne)	1 105	Decane
	CH_3- connected to either N, O, F or Cl	CH_3-(e)	2 103	Dimethoxymethane, methyl butyl ether
	CH_3- connected to an aromatic atom (not necessarily C)	CH_3-(a)	3 104	Toluene, p-methyl-styrene
-CH2-	-CH_2- in a chain	-C(c)H_2-	4 112	Butane
	-CH_2- in a ring	-C(r)H_2-	9 113	Cyclopentane
>CH-	>CH- in a chain	>C(c)H-	5 119	2-Methylpentane
	>CH- in a ring	>C(r)H-	10 118	Methylcyclohexane
>C<	>C< in a chain	>C(c)<	6 121	Neopentane
	>C< in a chain connected to at least one aromatic carbon	>C(c)<(a)	8 109	Ethylbenzene, diphenylmethane
	>C< in a chain connected to at least one F, Cl, N or O	>C(c)<(e)	7 108	Ethanol
	>C< in a ring	>C(r)<	11 120	Beta-pinene

	>C< in a ring connected to at least one aromatic carbon	>C(r)<(Ca)	14 107	Indene, 2-methyl tetralin
	>C< in a ring connected to, at least one N or O which are not part of the ring, or one Cl or F	>C(r)<(e,c)	12 110	Cyclopentanol, menthol
	>C< in a ring connected to at least one N or O which are part of the ring	>C(r)<(e,r)	13 111	Morpholine, nicotine
=C(a)<	Aromatic =CH-	=C(a)H-	15 106	Benzene
	Aromatic =C< not connected to either O,N,Cl or F	=C(a)<(ne)	16 117	Ethylbenzene, benzaldehyde
	Aromatic =C< with three aromatic neighbors and three aromatic bonds	(a)=C(a)<$_2$(a)	18 115	Naphthalene, quinoline
	Aromatic =C< connected to either O,N,Cl or F	=C(a)<(e)	17 114	Aniline, phenol
	Aromatic =C< with three aromatic neighbors and two aromatic bonds (aliphatic bridge bond between aromatic rings)	C(a)=C(a)<C$_2$(a) (bridge)	214 116	Biphenyl, m-terphenyl
>C=C<	H$_2$C=C< (1-ene)	H$_2$C(c)=C<	61 57	1-Hexene
	>C=C< (both C have at least one non-H neighbor)	>C(c)=C(c)<	58 62	2-Heptene, mesityl oxide
	Non-cyclic >C=C< connected to at least one aromatic C	>C(c)=C(c)<(C(a))	59 59	Isosafrole, cinnamic alcohol

	Cyclic >C=C<	>C(r)=C(r)<	62 60	Cyclopentadiene
	Non-cyclic >C=C< substituted with at least one F, Cl, N or O	-(e)C(c)=C(c)<	60 58	Trans-1,2-dichloroethylene, perfluoroisoprene
-C≡C-	HC≡C- (1-ine)	HC≡C-	64 56	1-Heptyne
	-C≡C- with two non-H neighbors	-C≡C-	63 61	2-Octyne
>C=C=C<	Two cumulated double bonds	>C=C=C<	87 5	1,2-Butadiene, dimethyl allene
>C=C-C=C<	Two conjugated double bonds in a ring	>C=C-C=C<	88 6	Cyclopentadiene, abietic acid
>C=C-C=C<	Two conjugated double bonds in a chain	>C=C-C=C<	89 7	Isoprene, 1,3-hexadiene
-C≡C-C≡C-	Two conjugated triple bonds	-C≡C-C≡C-	95 8	2,4-Hexadiyne
Silicon				
>Si<	>Si<	>Si<	70 80	Butylsilane
	>Si< attached to no carbon or hydrogen	>Si<(C,H)$_0$	216 76	Tetrachlorosilane, tetramethoxysilane
	>Si< attached to one carbon or hydrogen	>Si<(C,H)$_1$	215 77	Trichlorosilane, methyltrichlorosilane
	>Si< attached to two carbon or hydrogen	>Si<(C,H)$_2$	93 78	Dichlorodimethylsilane, dichlorodiethylsilane
	>Si< attached to three carbon or hydrogen	>Si<(C,H)$_3$	71 79	Hexamethyl disiloxane
Germanium				
>Ge<	>Ge< connected to four carbons	(C)$_2$>Ge<(C)$_2$	86 67	Tetramethylgermane
GeCl$_3$-	GeCl$_3$- connected to carbons	GeCl$_3$-	85 12	Fluorodimethylsilyl (trichlorogermanyl)methane

Tin				
>Sn<	>Sn< connected to four carbons	$(C)_2>Sn<(C)_2$	83 64	Tetramethylstannane
Periodic Group 13				
Boron				
$B(O-)_3$	Non-cyclic boric acid ester	$B(O-)_3$	78 15	Triethyl borate
Aluminum				
>Al<	>Al< connected to at least one C or Si	>Al<	117 47	Triethylaluminum

Table B-2: Second order groups and corrections

Name Contribution [K]	**Description**	**ID**	**Example (s)**
C=C-C=O	-C=O connected to sp^2 carbon	134	Benzaldehyde furfural
$(C=O)-C([F,Cl]_{2,3})$	Carbonyl connected to carbon with two or more halogens	119	Dichloroacetyl chloride
$(C=O)-(C([F,Cl]_{2,3}))_2$	Carbonyl connected to two carbon with two or more halogens each	120	Perfluoro-2-propanone
$C-[F,Cl]_3$	Carbon with three halogens	121	1,1,1-Triflourotoluene
$(C)_2-C-[F,Cl]_2$	Secondary carbon with two halogens	122	2,2-Dichloropropane
No Hydrogen	Component has no hydrogen	123	Perfluoro compounds
One Hydrogen	Component has one hydrogen	124	Nonafluorobutane
3/4 Ring	A three or four-membered non-aromatic ring	125	Cyclobutene
5 Ring	A five-membered non-aromatic ring	126	Cyclopentane

Ortho Pair(s)	Ortho position - counted only once and only if there are no meta or para pairs	127	o-Xylene
Meta Pair(s)	Meta position - counted only once and only if there are no para or ortho pairs	128	m-Xylene
Para Pair(s)	Para position - counted only once and only if there are no meta or ortho pairs	129	p-Xylene
$((C=)(C)C-CC_3)$	Carbon-carbon bond with four single bonded and one double bonded carbon neighbor	130	Tert-butylbenzene
C_2C-CC_2	Carbon-carbon bond with four carbon neighbors, two on each side	131	Bicyclohexyl
C_3C-CC_2	Carbon-carbon bond with five carbon neighbors	132	Ethyl bornyl ether
C_3C-CC_3	Carbon-carbon bond with six carbon neighbors	133	2,2,3,3-Tetrametylbutane
Si < (F, Cl, Br, I)	A silicon attached to a halogen atom	217	Trichloroethylsilane

Appendix C

Group Contributions for the Proposed Methods

Table C-1: Critical temperature group contributions, number of components used for regressing these values and deviations for these components.

Group ID	Group Contribution, T_{ci} ($\times 10^3$)	Number of Components	Mean Absolute Error (K)	Mean Absolute Error (%)	Standard Deviation (K)
1	41.8682	357	4.5	0.8	6.6
2	33.1371	51	3.9	0.7	5.8
3	-1.0710	42	3.7	0.5	5.1
4	40.0977	245	4.4	0.7	6.0
5	30.2069	66	4.2	0.7	6.0
6	-3.8778	21	2.5	0.4	3.5
7	52.8003	231	5.1	0.9	7.3
8	9.4422	18	2.2	0.3	3.1
9	21.2898	35	3.7	0.6	5.8
10	26.3513	11	3.5	0.5	4.5
11	-17.0459	3	4.7	0.7	5.6
12	51.7974	10	5.5	1.2	6.2
13	18.9549	11	4.3	0.8	8.1
14	-29.1568	3	4.6	0.6	5.9
15	16.1154	115	3.8	0.5	5.7
16	68.2045	76	3.5	0.5	5.0
17	68.1923	50	3.6	0.5	5.0
18	29.8039	12	5.9	0.7	9.7
19	15.6068	11	3.1	0.7	3.5
20	11.0757	5	3.3	0.9	4.0
21	18.1302	56	3.7	0.8	5.1
22	19.1772	12	4.4	1.0	6.2
23	20.8519	3	2.7	0.7	2.9
24	-24.0220	17	2.2	0.4	3.1

25	-1.3329	14	5.8	1.0	7.1
26	2.6113	7	2.8	0.6	3.5
27	15.5010	22	3.2	0.7	3.9
28	-16.1905	7	4.2	0.7	4.7
29	60.1907	3	4.7	1.1	4.9
30	5.2621	7	1.4	0.3	1.9
31	-21.5199	2	1.3	0.2	1.3
32	-8.6881	4	3.9	0.7	4.0
33	84.8567	4	8.1	1.5	10.5
34	79.3047	27	7.9	1.3	11.1
35	49.5968	28	7.4	1.1	9.0
36	130.1320	16	6.6	1.0	10.7
37	14.0159	15	4.0	0.6	4.7
38	12.5082	82	6.0	1.1	9.0
39	41.3490	3	1.4	0.3	1.7
40	18.3404	10	3.0	0.6	4.0
41	-50.6419	1			
42	17.1780	7	3.8	0.8	5.6
43	-0.5820	3	5.1	1.0	6.0
44	199.9042	13	4.7	0.7	6.1
45	75.7089	45	3.3	0.5	4.2
46	58.0782	6	2.3	0.4	2.7
47	109.1930	1			
48	102.1024	2	2.0	0.3	2.0
51	56.1572	25	2.7	0.4	3.7
52	44.2000	9	2.3	0.4	2.7
53	-7.1070	7	4.2	0.7	5.6
54	0.5887	10	5.5	0.9	9.6
56	-7.7181	4	1.2	0.2	1.5
57	117.1330	10	8.3	1.3	10.6
58	45.1531	4	2.4	0.5	2.9
60	67.9821	5	4.0	1.0	4.4
61	45.4406	26	5.0	0.9	7.0
62	56.4059	6	5.7	0.9	5.9
63	-19.9737	1			
64	36.0883	2	0.2	0.0	0.2
65	10.4146	4	1.3	0.2	1.7

66	18.9903	2	0.0	0.0	0.0
67	10.9495	13	4.6	0.6	7.1
68	82.6239	1			
70	25.4209	2	2.6	0.5	2.8
71	72.5587	9	8.6	1.4	12.8
76	164.3355	1			
78	157.3401*	1			
79	97.2830	1			
80	153.7225	6	8.8	1.2	10.4
82	90.9726	1			
83	62.3642	1			
87	53.6350	1			
88	24.7302	1			
90	38.4681	1			
92	63.6504	1			
93	34.2058	11	9.9	1.5	14.4
97	27.3441	3	1.6	0.3	1.9
98	34.5325	1			
102	1.3231	4	1.0	0.2	1.3
103	764.9595*	1			
110	23.4707	2	3.9	0.6	3.9
115	36.0361	1			
118	(do not estimate)				
214	48.1680	6	6.5	0.8	8.4
215	0.2842	5	3.9	0.7	4.0
216	-0.6536	3	12.6	2.2	12.8

---

* Questionable group contribution values (See Table 7-35)

Table C-2: Critical temperature second-order contributions, number of components used for regressing these values and deviations for these components.

Group ID	Group Contribution, T_{ci} ($\times 10^3$)	Number of Components	Mean Absolute Error (K)	Mean Absolute Error (%)	Standard Deviation (K)
119	32.1829	2	0.0	0.0	0.0
120	11.4437	2	0.9	0.2	0.9
121	-1.3023	56	3.1	0.7	4.1
122	-34.3037	21	6.0	1.3	7.3
123	-1.3798	44	3.7	0.8	5.0
124	-2.7180	17	3.0	0.7	3.6
125	11.3251	9	4.6	1.0	5.6
126	-4.7516	18	3.5	0.7	6.5
127	1.2823	29	4.1	0.6	5.3
128	6.7099	13	2.5	0.4	3.1
130	-33.8201	2	0.0	0.0	0.0
131	-18.4815	12	2.9	0.5	3.4
132	-23.6024	7	2.8	0.5	3.9
133	-24.5802	3	1.4	0.2	1.5
134	-35.6113	4	2.0	0.3	3.1
217	62.0286	7	5.9	1.1	7.0

Table C-3: Critical temperature group interaction contributions, interacting groups, number of components used for regressing these values and deviations for these components.

Group ID	Interacting Groups	Group Contribution, T_{ci} ($\times 10^3$)	Number of Components	Mean Absolute Error (K)	Mean Absolute Error (%)	Standard Deviation (K)
135	OH - OH	-434.8568	5	13.1	1.7	17.7
136	OH - NH2	120.9166	2	0.0	0.0	0.0
137	OH - NH	-30.4354	1	0.0	0.0	0.0
140	OH - EtherO	-146.7881	10	3.3	0.5	4.2
148	OH(a) - OH(a)	144.4697	1	0.0	0.0	0.0

157	NH2 - NH2	-60.9217	1	0.0	0.0	0.0
159	NH2 - EtherO	-738.0515	1	0.0	0.0	0.0
165	NH - NH	-49.7641	1	0.0	0.0	0.0
176	OCN – OCN	-1866.0970*	3	12.8	1.7	13.9
178	EtherO – EtherO	162.6878	31	9.4	1.6	12.8
179	EtherO – Epox	707.4116*	1	0.0	0.0	0.0
180	EtherO – Ester	128.2740	6	1.5	0.2	1.8
183	EtherO – Teth	-654.1363*	1	0.0	0.0	0.0
185	EtherO - CN	741.8565	3	13.8	1.8	16.0
189	Ester - Ester	366.2663	2	1.6	0.2	1.7
194	Ketone - Ketone	1605.5640	1	0.0	0.0	0.0
205	Teth - Teth	-861.1528*	1	0.0	0.0	0.0
208	AtS - AN5	131.7924	1	0.0	0.0	0.0
210	AO - AN5	24.0243	1	0.0	0.0	0.0
212	AN6 - AN6	-32.3208	1	0.0	0.0	0.0
218	COOH – NH2	(do not estimate)	-			

Table C-4: Critical pressure group contributions, number of components used for regressing these values and deviations for these components.

Group ID	Group Contribution, P_{ci} (x10^4)	Number of Components	Mean Absolute Error (kPa)	Mean Absolute Error (%)	Standard Deviation (kPa)
1	8.1620	287	91.5	2.8	138.2
2	5.5262	40	130.1	3.0	208.1
3	4.1660	26	89.8	2.4	115.0
4	5.2623	180	83.4	2.7	123.7
5	2.3009	48	93.0	2.8	134.8
6	-2.9925	20	86.0	3.1	119.1
7	3.4310	187	111.4	3.4	157.3
8	2.3665	20	78.4	2.8	88.8

9	3.4027	28	76.7	1.8	127.2
10	3.6162	6	28.3	0.9	36.9
11	-5.1299	1			
12	4.1421	11	141.6	5.3	151.9
13	0.8765	10	109.0	2.5	175.1
14	-0.1320	3	15.2	0.4	20.4
15	2.1064	87	84.5	2.4	122.8
16	4.1826	59	76.8	2.3	105.6
17	3.5500	27	83.5	2.0	134.5
18	1.0997	9	55.8	1.5	70.4
19	0.7328	17	122.9	4.8	144.8
20	4.3757	5	218.1	5.1	248.8
21	3.4933	72	111.2	4.4	145.3
22	2.6558	15	101.4	3.8	132.1
23	1.6547	3	153.3	3.0	176.1
24	0.5236	12	61.8	1.7	72.7
25	-2.2611	5	195.7	3.8	234.9
26	-1.4992	7	160.4	3.8	189.2
27	0.4883	25	74.1	1.8	118.6
28	-0.9280	3	24.7	0.7	25.5
29	11.8687	3	195.5	5.1	213.0
30	-4.3170	6	235.9	5.3	268.0
31	-2.2409	2	140.9	3.7	145.2
32	-4.7841	2	115.6	2.7	116.0
33	-7.4244	3	130.1	3.5	154.3
34	-4.4735	17	78.3	2.0	108.4
35	-1.8153	28	63.3	2.3	113.8
36	-6.8991	14	169.6	2.9	222.6
37	-12.1664	6	168.2	3.3	219.2
38	2.0592	72	111.1	3.7	153.1
39	0.1759	2	0.0	0.0	0.0
40	-4.4164	10	222.2	4.5	338.4
41	-9.0065	1			
42	-0.4086	7	146.5	5.6	202.0
43	2.3625	5	88.1	2.4	148.3
44	3.9873	13	148.3	3.9	243.5
45	4.3592	27	97.5	3.6	130.2

46	1.0266	3	235.8	4.6	277.4
47	0.4329	1			
48	0.5172	1			
51	0.1190	17	60.2	1.7	89.8
52	-2.3615	7	102.9	2.9	121.3
53	-9.4154	2	411.0	6.4	415.5
54	-8.2595	5	89.8	2.3	128.2
56	-4.9259	4	57.7	1.3	70.8
57	5.1666	6	157.0	4.3	172.7
58	7.1581	4	53.8	1.4	60.6
60	-6.2791	5	198.0	5.2	238.2
61	9.6413	21	112.0	3.3	137.7
62	3.4731	3	75.3	1.6	82.4
63	-2.2718	1			
64	2.4489	2	157.2	3.1	158.3
65	-0.5403	4	48.3	1.1	65.1
66	8.3052	2	0.0	0.0	0.0
67	-4.7101	4	89.6	1.7	117.5
68	-5.0929	1			
70	5.7270	2	147.4	5.7	168.7
71	2.7602	9	59.9	4.0	95.7
76	4.0458	1			
78	12.6786*	1			
79	0.2822	1			
82	-23.9221	1			
83	0.7043	1			
87	12.6128	1			
88	-10.2451	1			
90	-4.0133	1			
92	-5.0403	1			
93	3.2023	10	51.6	3.3	68.2
97	-4.3834	2	0.0	0.0	0.0
98	-13.6078	1			
102	3.3971	5	28.8	0.7	38.3
103	58.9190*	1			
110	0.1812	2	37.2	1.1	37.3
115	-5.1116	1			

118	(do not estimate)	-	-	-	-
214	1.5574	6	172.8	6.0	213.2
215	3.8751	4	62.0	2.2	82.2
216	4.4882	5	39.1	1.2	48.4

Table C-5: Critical pressure second-order contributions, number of components used for regressing these values and deviations for these components.

Group ID	Group Contribution, P_{cI} ($x10^4$)	Number of Components	Mean Absolute Error (kPa)	Mean Absolute Error (%)	Standard Deviation (kPa)
119	7.3149	4	162.3	7.5	204.2
120	4.1439	2	25.5	0.9	25.5
121	0.4387	70	115.0	4.1	154.8
122	-4.2678	28	138.4	6.6	174.2
123	4.8944	51	102.2	4.0	132.5
124	2.8103	21	149.8	4.4	184.0
125	-0.3035	6	79.3	2.5	115.1
126	0.0930	18	89.5	2.8	145.4
127	0.7061	15	121.4	3.8	152.3
128	-0.7246	8	112.8	3.4	123.8
130	-8.8457	3	73.1	2.6	100.2
131	-2.2542	11	66.5	3.1	85.4
132	-3.2460	5	55.6	2.0	58.5
133	-5.3113	3	58.3	2.1	63.8
134	1.0934	7	58.9	2.7	76.4
217	8.6126	10	58.2	1.7	76.6

Table C-6: Critical pressure group interaction contributions, interacting groups, number of components used for regressing these values and deviations for these components.

Group ID	Interacting Groups	Group Contribution, P_{ci} (x10^4)	Number of Components	Mean Absolute Error (kPa)	Mean Absolute Error (%)	Standard Deviation (kPa)
135	OH - OH	-5.6023	5	268.4	4.0	303.5
136	OH - NH2	69.8200	2	0.0	0.0	0.0
137	OH - NH	6.1331	1			
140	OH - EtherO	7.3373	10	83.3	2.3	126.9
148	OH(a) - OH(a)	57.8350*	1			
157	NH2 - NH2	-0.6754	1			
159	NH2 - EtherO	-125.5983	1			
165	NH - NH	22.1871	1			
178	EtherO - EtherO	2.6751	21	69.7	3.0	96.2
179	EtherO - Epox	88.8752*	1			
180	EtherO - Ester	-1.0295	5	91.1	3.3	108.7
183	EtherO - Teth	25.8246	1			
189	Ester - Ester	0.5195	2	30.5	1.0	30.5
194	Ketone - Ketone	-78.2743	1			
205	Teth - Teth	43.9001*	1			
208	AtS - AN5	-19.7033	1			
210	AO - AN5	-35.1998	1	0.0	0.0	0.0
212	AN6 - AN6	12.5371	1	0.0	0.0	0.0
218	COOH – NH2	(do not estimate)	-			

Table C-7: Critical volume group contributions, number of components used for regressing these values and deviations for these components.

Group ID	Group Contribution, V_{ci}	Number of Components	Mean Absolute Error (cm³/mol)	Mean Absolute Error (%)	Standard Deviation (cm³/mol)
1	28.7855	196	6.2	1.5	9.1
2	28.8811	24	6.3	2.4	9.6
3	26.7237	13	5.2	1.5	7.2
4	32.0493	136	6.2	1.4	9.1
5	32.1108	29	8.7	2.1	11.7
6	28.0534	12	9.7	2.4	12.2
7	33.7577	122	6.5	1.9	9.9
8	28.8792	7	1.5	0.3	2.5
9	24.8517	23	7.5	2.0	11.1
10	30.9323	8	12.9	2.9	16.5
11	5.9550	3	15.0	3.1	17.3
12	29.5901	7	8.7	2.2	11.0
13	20.2325	7	5.0	1.9	6.9
14	10.5669	3	6.6	1.4	8.4
15	19.4020	58	4.8	1.4	7.6
16	25.0434	31	3.2	0.8	5.5
17	5.6704	21	7.8	2.2	10.9
18	16.4118	8	3.8	0.9	5.6
19	-5.0331	11	6.2	1.9	7.9
20	1.5646	5	4.8	2.8	5.5
21	3.3646	46	6.9	2.2	10.4
22	1.0897	9	10.8	4.8	16.2
23	1.1084	3	2.6	1.6	2.6
24	19.3190	10	7.9	2.2	9.4
25	22.0457	4	14.1	4.3	15.7
26	23.9279	5	5.0	1.5	6.1
27	26.2582	20	4.4	1.6	5.9
28	36.7624	7	11.8	3.2	13.8
29	34.4110	3	4.1	1.7	4.8
30	36.0223	11	5.5	2.0	6.7

31	30.7004	1			
32	48.2989	1			
33	10.6790	1			
34	5.6645	20	5.0	1.1	6.2
35	2.0869	10	4.8	0.9	6.3
36	3.7778	7	2.7	1.2	3.3
37	25.6584	2	0.0	0.0	0.0
38	11.6284	41	11.6	3.2	15.3
39	46.7680	2	0.0	0.0	0.0
40	13.2571	4	9.1	3.3	10.0
41	73.7444	1			
42	20.5722	3	3.9	0.8	4.9
43	6.0178	2	4.3	1.0	4.9
44	40.3909	5	9.8	3.2	13.5
45	42.6733	12	5.1	1.3	8.8
46	36.1286	3	2.2	1.0	2.4
48	64.3506	1			
51	30.9229	26	4.1	0.8	6.0
52	25.5034	4	1.2	0.6	1.3
53	34.7699	3	11.5	4.9	13.8
54	38.0185	5	2.3	0.7	3.3
56	20.3127	4	5.1	1.7	6.8
57	43.7983	1			
60	51.0710	5	4.4	2.0	5.2
61	48.1957	15	6.9	2.2	10.4
62	34.1240	6	15.1	3.8	18.1
63	40.9263	1			
64	29.8612	2	2.2	1.2	2.2
65	4.7476	4	6.8	2.9	9.1
66	-25.3680	2	0.0	0.0	0.0
67	23.6094	5	7.1	2.4	9.6
68	34.8472	1			
70	75.7193	1			
71	69.5645	6	17.0	1.5	21.1
79	52.8789	1			
80	27.1026	9	17.5	3.8	21.1
82	68.0701	1			

88	64.4616	1			
90	20.0440	1			
92	28.7127	1			
93	55.3822	6	14.9	1.4	18.6
97	29.3068	2	0.0	0.0	0.0
102	1.3597	4	1.7	0.6	2.3
115	16.2688	1			
118	(do not estimate)	-			
214	16.3122	6	5.3	0.9	6.3
215	37.0423	4	14.6	2.7	19.0
216	55.7432	6	10.4	2.7	11.3

Table C-8: Critical volume second-order contributions, number of components used for regressing these values and deviations for these components.

Group ID	Group Contribution, V_{ci}	Number of Components	Mean Absolute Error (cm³/mol)	Mean Absolute Error (%)	Standard Deviation (cm³.mol⁻¹)
119	-3.8033	2	0.0	0.0	0.0
120	27.5326	1			
121	1.5807	50	6.3	2.2	9.8
122	-2.6235	16	9.1	2.1	11.1
123	-5.3091	42	6.9	1.9	9.1
124	-6.1909	18	7.3	3.2	11.9
125	3.2219	6	8.9	2.2	12.8
126	-6.3900	11	4.8	1.5	7.2
127	-3.5964	11	4.4	1.2	6.7
128	1.5196	5	3.3	0.7	4.6
130	-4.6483	2	0.0	0.0	0.0
131	-5.0563	10	9.5	2.1	12.6
132	-6.3267	5	12.9	2.8	15.7
133	4.9392	1			
134	2.8889	4	0.0	0.0	0.0
217	19.4348	9	8.9	2.5	9.9

Table C-9: Critical volume group interaction contributions, interacting groups, number of components used for regressing these values and deviations for these components.

Group ID	Interacting Groups	Group Contribution, V_{ci}	Number of Components	Mean Absolute Error (cm³/mol)	Mean Absolute Error (%)	Standard Deviation (cm³/mol)
137	OH - NH	-8.0423	1			
140	OH - EtherO	19.7707	4	3.0	0.9	3.5
148	OH(a) - OH(a)	97.5425	1			
165	NH - NH	-57.1233	1			
176	OCN - OCN	44.1062	4	21.8	3.9	25.7
178	EtherO - EtherO	-23.6366	12	15.7	3.0	19.2
179	EtherO - Epox	-329.5074*	1			
180	EtherO - Ester	-55.5112	2	20.9	4.7	21.0
183	EtherO - Teth	-37.2468	1			
189	Ester - Ester	-74.8680	1			
194	Ketone - Ketone	-413.3976	1			
205	Teth - Teth	-403.1196*	1			
208	AtS - AN5	164.2930	1			
210	AO - AN5	217.9243	1			
212	AN6 - AN6	-26.4556	1			
218	COOH – NH2	(do not estimate)	-			

Table C-10: Vapour-liquid equilibrium curve slope (*dB*) group contributions, number of components used for regressing these values and deviations for these components.

Group ID	Group Contribution, dB_i (x10³)	Number of Components	Mean Absolute Error (cm³/mol)	Mean Absolute Error (%)	Standard Deviation (cm³/mol)
1	13.3063	1031	0.1	9.6	0.1
2	91.8000	121	0.1	280.9	0.2
3	50.1939	109	0.1	27.0	0.1
4	54.6564	653	0.1	5.9	0.1

5	45.7437	143	0.1	60.5	0.1
6	-31.7531	52	0.1	54.2	0.1
7	37.8485	549	0.1	2.3	0.2
8	96.1386	84	0.1	27.4	0.1
9	22.2573	207	0.1	38.7	0.1
10	32.8162	98	0.1	58.7	0.1
11	4.8500	22	0.1	24.4	0.1
12	23.6411	44	0.1	17.6	0.2
13	49.8237	51	0.1	40.9	0.1
14	-3.6950	15	0.1	19.9	0.1
15	32.7177	368	0.1	85.5	0.1
16	69.8796	276	0.1	100.5	0.1
17	41.5534	142	0.1	25.0	0.1
18	43.7191	46	0.1	25.3	0.1
19	79.5429	33	0.1	27.6	0.1
20	51.2880	6	0.1	111.4	0.2
21	42.0887	120	0.1	192.6	0.1
22	56.9998	20	0.1	40.4	0.2
23	142.1060	3	0.1	56.7	0.1
24	45.9652	21	0.1	53.3	0.1
25	93.6679	61	0.1	11.2	0.1
26	67.8082	30	0.1	10.0	0.1
27	55.9304	43	0.1	32.8	0.1
28	46.0435	47	0.1	26.3	0.1
29	84.9162	20	0.1	10.8	0.1
30	104.9291	33	0.1	126.9	0.1
31	-40.1837	10	0.1	57.0	0.2
32	134.3501	12	0.1	15.0	0.1
33	719.3666	27	0.1	15.1	0.1
34	758.4218	42	0.2	19.9	0.2
35	700.7226	57	0.2	18.7	0.2
36	756.0824	29	0.2	22.3	0.2
37	441.8437	30	0.1	17.1	0.1
38	108.4964	169	0.1	197.9	0.1
39	286.9731	12	0.1	37.2	0.1
40	251.9212	36	0.1	28.0	0.2
41	361.7760	18	0.1	16.7	0.1

42	193.7667	20	0.1	28.3	0.2
43	-102.7252	29	0.1	120.0	0.2
44	1074.1000	35	0.2	17.3	0.2
45	355.7381	130	0.1	25.3	0.2
46	350.5184	12	0.1	32.7	0.1
47	292.8046	2	0.0	22.9	0.0
48	269.2471	9	0.1	75.7	0.2
49	736.9540	4	0.1	18.9	0.1
50	1216.0700	1	0.0	0.0	0.0
51	255.8480	55	0.1	35.0	0.2
52	252.9059	22	0.1	115.7	0.1
53	123.2143	41	0.1	114.3	0.1
54	127.3380	30	0.1	94.0	0.1
55	222.2789	4	0.1	36.0	0.1
56	20.1604	13	0.1	85.0	0.1
57	226.1873	33	0.1	29.5	0.1
58	86.4601	87	0.1	41.3	0.1
59	224.2238	4	0.0	4.7	0.0
60	134.9382	18	0.1	6.0	0.2
61	34.2541	121	0.1	27.5	0.1
62	97.4210	55	0.1	31.0	0.1
63	206.6665	22	0.1	18.7	0.1
64	128.0247	16	0.1	46.6	0.1
65	48.8839	8	0.0	23.5	0.1
66	375.0486	11	0.2	36.5	0.2
67	126.3340	30	0.1	59.5	0.1
68	375.8217	3	0.0	5.9	0.0
69	238.2066	13	0.1	17.2	0.1
70	2.8992	25	0.1	30.6	0.1
71	9.3624	28	0.1	8.5	0.1
72	603.5347	4	0.2	60.7	0.2
73	662.0582	3	0.2	20.1	0.2
74	510.9666	2	0.1	24.1	0.1
75	1317.4360	6	0.0	2.9	0.0
76	681.3525	4	0.1	18.7	0.1
77	564.1116	7	0.3	141.9	0.4
78	391.3697	6	0.1	21.0	0.1

79	318.2350	2	0.0	2.1	0.0
80	435.8446	16	0.2	25.8	0.2
81	218.6012	3	0.0	33.4	0.0
82	381.5945	2	0.0	3.1	0.0
83	80.2735	3	0.0	1.2	0.0
84	231.3919	6	0.0	32.1	0.0
85	186.9204	3	0.0	6.7	0.0
86	48.5026	1	0.0	0.0	0.0
87	168.3007	4	0.0	35.0	0.0
88	108.5277	5	0.1	6.9	0.1
89	213.7165	11	0.1	64.4	0.1
90	183.1130	4	0.0	15.6	0.0
91	1178.1950*	1	0.0	0.0	0.0
92	158.3258	9	0.1	36.5	0.1
93	-47.3420	27	0.1	34.9	0.1
94	186.7950	1	0.0	0.0	0.0
95	392.2006	1	0.0	0.0	0.0
96	595.1778	2	0.0	8.4	0.0
97	268.7081	11	0.1	47.5	0.1
98	183.3467	3	0.1	20.1	0.1
99	612.9546	2	0.2	37.2	0.2
100	258.9924	1	0.0	0.0	0.0
101	-316.4392	3	0.2	72.7	0.2
102	64.0566	8	0.0	25.0	0.1
103	660.2247	2	0.2	40.0	0.2
104	554.7941	2	0.1	14.1	0.1
105	420.7591	3	0.1	30.7	0.1
107	-237.2124	1	0.0	0.0	0.0
110	37.0590	4	0.1	99.5	0.1
111	319.4879	1	0.0	0.0	0.0
113	118.8412	3	0.1	148.7	0.1
115	305.1341	1	0.0	0.0	0.0
116	191.5058	1	0.0	0.0	0.0
117	423.5251	1	0.0	0.0	0.0
118	(do not estimate)				
118	0.0000				

---

* Questionable group contribution values

214	86.9450	11	0.1	22.6	0.1
215	-66.5670	11	0.1	78.0	0.1
216	-81.1543	8	0.1	31.6	0.2

Table C-11: Vapour-liquid equilibrium curve slope (*dB*) second-order contributions, number of components used for regressing these values and deviations for these components.

Group ID	Group Contribution, dB_i ($\times 10^3$)	Number of Components	Mean Absolute Error (cm³/mol)	Mean Absolute Error (%)	Standard Deviation ($cm^3.mol^{-1}$)
119	34.3545	14	0.2	56.4	0.2
120	2.5030	2	0.0	31.7	0.0
121	-83.3326	115	0.1	208.6	0.1
122	-64.4854	53	0.1	46.3	0.2
123	-125.9208	85	0.1	3.4	0.1
124	-47.2962	29	0.1	32.9	0.1
125	33.9765	37	0.1	0.8	0.1
126	-7.0982	106	0.1	1.7	0.1
127	-45.0531	89	0.1	30.3	0.1
128	-3.2036	56	0.1	27.9	0.2
130	-20.6706	9	0.1	10.2	0.1
131	-36.3170	47	0.1	0.0	0.1
132	-1.1994	20	0.1	4.2	0.1
133	123.7433	4	0.1	2.4	0.1
134	-15.9694	59	0.1	32.3	0.2
217	36.7574	31	0.1	12.0	0.1

Table C-12: Vapour-liquid equilibrium curve slope (*dB*) group interaction contributions, interacting groups, number of components used for regressing these values and deviations for these components.

Group ID	Interacting Groups	Group Contri-bution, dB_i ($x10^3$)	Number of Com-ponents	Mean Absolute Error (cm³/mol)	Mean Absolute Error (%)	Standard Deviation (cm³/mol)
135	OH - OH	-561.5153	20	0.2	15.0	0.3
136	OH - NH2	1067.6660	3	0.2	13.5	0.2
137	OH - NH	42.4825	3	0.2	29.2	0.3
140	OH - EtherO	-799.5332	23	0.1	17.3	0.2
141	OH - Epox	-618.2760	1	0.0	0.0	0.0
142	OH - Ester	-1797.6930	2	0.2	32.3	0.2
143	OH - Ketone	-1181.5990	4	0.1	20.8	0.1
145	OH - CN	1431.2430	1	0.0	0.0	0.0
146	OH - AO	1132.0400	1	0.0	0.0	0.0
148	OH(a) - OH(a)	-97.6205	2	0.1	11.8	0.1
151	OH(a) - EtherO	-751.6676	3	0.0	2.2	0.0
152	OH(a) - Ester	548.4352	1	0.0	0.0	0.0
157	NH2 - NH2	1085.8320	7	0.2	25.1	0.3
158	NH2 - NH	-206.7811	2	0.2	28.5	0.2
159	NH2 - EtherO	-198.2791	1	0.0	0.0	0.0
160	NH2 - Ester	-1676.4770	1	0.0	0.0	0.0
162	NH2 - Nitro	1659.0340	2	0.1	13.3	0.1
165	NH - NH	-307.1018	2	0.0	1.9	0.0
166	NH - EtherO	65.4421	1	0.0	0.0	0.0
170	SH - SH	240.3037	10	0.1	21.7	0.1
172	COOH - COOH	-2601.7090	2	0.0	1.8	0.0
175	COOH - Ketone	-787.8563	1	0.0	0.0	0.0
176	OCN - OCN	-3929.1300	3	0.2	36.6	0.2
178	EtherO - EtherO	144.6074	61	0.1	18.0	0.2
179	EtherO - Epox	1118.9580	1	0.0	0.0	0.0
180	EtherO - Ester	-225.7802	7	0.1	21.2	0.1
181	EtherO - Ketone	1981.2980	1	0.0	0.0	0.0
182	EtherO - Alde	362.7540	1	0.0	0.0	0.0
183	EtherO - Teth	-1425.0170	1	0.0	0.0	0.0

185	EtherO - CN	743.3353	2	0.0	8.9	0.0
187	Epox - Epox	-3748.8180	1	0.0	0.0	0.0
189	Ester - Ester	920.3138	24	0.2	24.3	0.3
190	Ester - Ketone	1594.1640	2	0.3	42.6	0.3
192	Ester - CN	108.1305	2	0.4	140.8	0.4
193	Ester - AO	1590.3210	1	0.0	0.0	0.0
194	Ketone - Ketone	-1270.0830	3	0.2	18.9	0.2
201	Alde - Alde	946.7309	1	0.0	0.0	0.0
204	Alde - AO	705.3049	1	0.0	0.0	0.0
205	Teth - Teth	838.3372	1	0.0	0.0	0.0
206	Nitro - Nitro	-1501.3550	2	0.0	8.4	0.0
208	AtS - AN5	675.0414	2	0.2	58.0	0.2
209	CN - AN6	994.4996	1	0.0	0.0	0.0
210	AO - AN5	135.5896	1	0.0	0.0	0.0
212	AN6 - AN6	-29.6785	3	0.2	296.4	0.2
218	COOH – NH2	(do not estimate)	-			

Table C-13: Saturated liquid viscosity curve slope (*dBv*) group contributions, number of components used for regressing these values and deviations for these components.

Group ID	Group Contribution, dBv_i ($x10^3$)	Number of Components	Mean Absolute Error (cm^3/mol)	Mean Absolute Error (%)	Standard Deviation (cm^3/mol)
1	13.9133	520	0.2	3.2	0.3
2	11.7002	70	0.2	3.2	0.3
3	-11.0660	46	0.2	3.3	0.3
4	2.1727	344	0.2	3.0	0.3
5	4.5878	90	0.2	3.0	0.4
6	37.0296	22	0.3	5.1	0.5
7	21.3473	331	0.2	3.4	0.4
8	5.9452	28	0.4	7.6	0.5
9	10.8799	73	0.2	3.5	0.4
10	-7.2202	37	0.2	3.8	0.4
11	142.1976	3	0.5	7.6	0.6
12	61.0811	12	0.4	4.8	0.7

13	28.7351	19	0.1	2.5	0.2
14	-12.3456	3	0.2	5.0	0.2
15	-2.7840	184	0.2	4.3	0.4
16	45.9403	114	0.2	4.4	0.4
17	80.5124	89	0.2	4.3	0.4
18	37.4124	13	0.2	3.9	0.3
19	5.1640	8	0.1	3.6	0.2
21	2.8323	38	0.2	3.3	0.2
22	0.7129	15	0.1	3.3	0.2
23	-36.3189	2	0.0	0.6	0.0
24	-61.9434	6	0.0	0.5	0.0
25	4.7579	32	0.2	3.3	0.3
26	5.8228	18	0.1	3.0	0.2
27	4.6555	30	0.1	2.1	0.1
28	-67.3989	23	0.3	5.4	0.5
29	-9.6209	5	0.0	0.6	0.0
30	0.5164	29	0.1	3.7	0.2
31	-18.1984	6	0.1	3.8	0.2
32	-17.3110	15	0.2	3.9	0.3
33	336.8834	10	0.7	7.6	1.0
34	365.8067	38	0.4	4.5	0.6
35	249.0118	40	0.4	5.2	0.6
36	218.8000	23	0.3	4.4	0.4
37	160.8315	16	0.3	4.9	0.4
38	-35.3055	99	0.2	3.8	0.3
39	85.3693	3	0.0	0.2	0.0
40	58.9131	20	0.2	2.9	0.3
41	44.0698	16	0.4	6.8	0.6
42	13.6479	10	0.2	2.8	0.2
43	-58.7354	10	0.3	4.5	0.4
44	54.7891	26	0.2	3.8	0.3
45	17.6757	69	0.2	2.9	0.3
46	0.4267	9	0.1	1.2	0.1
47	47.6109	1	0.0	0.0	0.0
48	12.6717	6	0.1	2.7	0.2
49	129.8293	3	0.5	8.7	0.6
50	202.2864	3	0.1	1.4	0.1

51	24.2524	24	0.1	2.7	0.2
52	18.4961	7	0.0	0.3	0.0
53	30.5022	12	0.1	2.5	0.2
54	-0.0276	13	0.0	0.8	0.0
55	-13.4614	2	0.0	0.1	0.0
56	18.5507	3	0.0	0.5	0.0
57	23.1459	19	0.1	2.2	0.2
58	9.5809	8	0.1	2.0	0.2
59	152.2693	2	0.2	2.4	0.2
60	18.5983	4	0.0	0.6	0.0
61	21.4560	29	0.1	1.4	0.2
62	19.7836	5	0.2	3.6	0.2
63	-165.0071	1	0.0	0.0	0.0
64	13.3585	3	0.4	8.1	0.5
65	42.7958	3	0.0	0.0	0.0
66	151.9493	2	0.2	3.1	0.2
67	52.5900	18	0.2	3.9	0.3
68	-34.3948	6	0.1	1.7	0.1
69	-6.5626	11	0.3	6.5	0.5
70	-25.5950	2	0.0	0.2	0.0
71	-28.3943	10	0.2	4.5	0.2
72	-30.6156	2	0.0	0.0	0.0
73	45.9972	4	0.1	1.6	0.1
74	-7.3298	5	0.0	0.2	0.0
75	369.8367	1	0.0	0.0	0.0
76	16.3525	4	0.1	2.6	0.2
77	-2.6553	6	0.0	1.0	0.1
78	-61.2368	6	0.1	1.1	0.1
79	-7.5067	2	0.0	0.9	0.0
80	4.1408	8	0.1	1.9	0.1
81	-46.5613	2	0.0	1.1	0.0
82	122.6902	3	0.0	0.7	0.0
86	-70.9713	1	0.0	0.0	0.0
88	29.0985	1	0.0	0.0	0.0
89	125.0861	2	0.0	0.2	0.0
90	-14.2823	3	0.0	0.0	0.0
92	-8.5352	4	0.2	4.0	0.2

93	9.9037	13	0.2	4.8	0.3
96	102.0816	2	0.1	2.7	0.1
97	74.0520	3	0.0	0.4	0.0
98	43.6079	5	0.2	3.7	0.3
100	54.4769	1	0.0	0.0	0.0
102	5.7765	3	0.0	0.5	0.0
103	95.6531	1	0.0	0.0	0.0
104	56.9133	2	0.3	5.9	0.3
105	64.7133	3	0.1	1.0	0.1
107	22.9969	1	0.0	0.0	0.0
108	23.2473	2	0.1	1.4	0.1
110	-45.7263	4	0.2	4.1	0.2
118	(do not estimate)	-			
214	37.5669	5	0.1	2.6	0.2
215	64.6600	3	0.0	0.6	0.0
216	68.4952	4	0.0	0.9	0.0

Table C-14: Saturated liquid viscosity curve slope (*dBv*) second-order contributions, number of components used for regressing these values and deviations for these components.

Group ID	Group Contribution, dBv_i (x10^3)	Number of Components	Mean Absolute Error (cm^3/mol)	Mean Absolute Error (%)	Standard Deviation (cm^3.mol^{-1})
119	0.3041	7	0.1	2.7	0.2
121	-6.1420	48	0.1	3.4	0.2
122	-26.4635	11	0.2	3.6	0.2
123	-14.9636	30	0.1	3.4	0.2
124	-25.9017	17	0.1	2.9	0.1
125	-57.3789	7	0.0	0.9	0.0
126	-21.2204	32	0.1	2.3	0.2
127	-20.1917	53	0.2	3.9	0.4
128	-34.5860	33	0.2	4.2	0.4
130	-110.7391	3	0.6	9.0	0.7
131	2.4859	18	0.3	4.1	0.5

132	-59.3670	4	0.0	1.0	0.0
134	13.1413	26	0.1	2.7	0.2
217	-76.1631	9	0.0	1.3	0.1

Table C-15: Saturated liquid viscosity curve slope (*dBv*) group interaction contributions, interacting groups, number of components used for regressing these values and deviations for these components.

Group ID	Interacting Groups	Group Contribution, dBv_i ($\times 10^3$)	Number of Components	Mean Absolute Error (cm³/mol)	Mean Absolute Error (%)	Standard Deviation (cm³/mol)
135	OH - OH	-112.4939	19	0.1	1.2	0.2
136	OH - NH2	1031.5920	3	0.2	1.7	0.2
137	OH - NH	853.2318	2	0.1	0.6	0.1
140	OH - EtherO	-423.9834	15	0.4	7.2	0.6
145	OH - CN	-683.0189	1	0.0	0.0	0.0
146	OH - AO	-557.5079	1	0.0	0.0	0.0
148	OH(a) - OH(a)	-1186.0500	1	0.0	0.0	0.0
151	OH(a) - EtherO	-333.5638	4	0.1	1.1	0.1
155	OH(a) - Nitro	-878.0615	3	0.3	5.3	0.3
157	NH2 - NH2	135.3183	3	0.6	9.0	0.7
159	NH2 - EtherO	219.9701	5	0.2	3.4	0.3
166	NH - EtherO	-134.4625	1	0.0	0.0	0.0
178	EtherO - EtherO	132.0275	40	0.2	3.9	0.3
180	EtherO - Ester	44.8702	1	0.0	0.0	0.0
181	EtherO - Ketone	-219.5265	2	0.1	1.9	0.1
182	EtherO - Alde	546.5846	1	0.0	0.0	0.0
184	EtherO - Nitro	-59.3635	1	0.0	0.0	0.0
189	Ester - Ester	964.0840	11	0.3	3.2	0.4
190	Ester - Ketone	126.0380	2	0.0	0.2	0.0
192	Ester - CN	539.2401	2	0.1	1.7	0.1
194	Ketone - Ketone*	3705.4400	1	0.0	0.0	0.0
204	Alde - AO	50.1063	1	0.0	0.0	0.0
206	Nitro - Nitro	896.3606	1	0.0	0.0	0.0

---

* Questionable group contribution values

209	CN - AN6	-196.6361	1	0.0	0.0	0.0
218	COOH – NH2	(do not estimate)	-			

Table C-16: Saturated liquid viscosity reference temperature (T_v) group contributions, number of components used for regressing these values and deviations for these components.

Group ID	Group Contribution, T_{vi}	Number of Components	Mean Absolute Error (cm³/mol)	Mean Absolute Error (%)	Standard Deviation (cm³/mol)
1	89.0803	509	6.7	2.3	8.8
2	216.0226	68	7.5	2.7	9.9
3	80.9698	46	4.8	1.6	6.2
4	60.3316	339	6.1	2.1	8.1
5	24.2637	88	7.0	2.5	9.2
6	244.4643	22	9.6	3.5	11.0
7	103.4109	327	6.9	2.3	9.5
8	-16.5212	28	7.3	2.1	9.6
9	174.1316	72	8.3	2.8	10.3
10	-37.7584	37	8.6	2.9	10.0
11	252.0190	3	8.8	3.0	10.2
12	251.9299	12	7.3	2.2	8.9
13	330.7100	18	5.4	1.7	7.8
14	294.3323	3	10.7	3.4	13.2
15	113.9028	184	7.2	2.2	10.8
16	-26.6195	114	6.4	2.0	9.6
17	133.5499	89	8.5	2.5	12.1
18	128.4739	13	3.6	1.0	4.1
19	208.3258	8	8.7	3.8	11.7
21	35.2688	38	6.0	2.7	7.5
22	207.3562	15	6.4	2.8	7.0
23	-15.8544	2	2.1	1.3	2.2
24	112.1172	6	11.3	4.6	12.2
25	329.0113	31	6.5	2.4	7.7
26	313.1106	18	7.9	3.0	9.7

27	194.6060	30	8.6	3.5	12.5
28	-8.6247	23	8.4	2.6	10.8
29	182.7067	5	4.0	1.7	4.3
30	456.3713	29	8.4	3.0	10.6
31	391.6060	6	6.7	2.2	7.0
32	499.2149	14	4.7	1.7	6.1
33	1199.4010	9	6.8	2.1	9.3
34	1198.1040	38	7.4	2.1	8.9
35	1078.0840	38	13.7	3.7	17.0
36	1284.7450	22	10.2	2.8	12.6
37	1134.1640	16	14.5	3.8	19.5
38	-34.9892	98	9.3	3.0	13.1
39	612.7222	3	5.3	2.4	5.6
40	458.7425	19	5.8	2.0	7.8
41	705.1250	16	6.2	1.8	8.2
42	159.5146	10	3.0	0.9	4.6
43	-284.4707	10	10.0	2.8	15.2
44	1446.0240	22	14.4	4.0	16.6
45	325.5736	69	5.5	1.8	7.5
46	454.1671	9	3.4	1.4	4.4
47	374.6477	1	0.0	0.0	0.0
48	289.9690	6	9.3	3.0	10.2
49	1150.8290	2	8.8	2.4	8.8
50	1619.1650	2	1.2	0.3	1.2
51	304.5982	24	6.5	2.4	7.4
52	394.7932	6	6.1	2.6	6.5
53	294.7319	12	7.2	2.9	8.9
54	206.6432	13	8.4	3.2	11.9
55	292.3613	2	2.6	1.0	2.6
56	302.2321	3	1.5	0.6	1.7
57	346.9998	18	5.1	1.9	6.4
58	-23.9801	8	7.1	2.3	9.1
59	238.3242	2	0.6	0.2	0.6
60	137.5408	4	4.6	2.1	4.7
61	74.4489	29	8.5	3.4	10.8
62	304.9257	5	12.3	4.8	13.7
63	-32.4179	1	0.0	0.0	0.0

64	57.8131	3	8.0	3.0	8.8
65	279.2114	3	0.0	0.0	0.0
66	662.0051	2	1.2	0.4	1.2
67	277.5038	18	3.3	1.0	5.1
68	369.4221	6	4.1	1.6	4.7
69	488.1136	11	15.3	4.1	21.1
70	-10.6146	2	9.8	3.9	10.3
71	-181.7627	9	20.5	6.6	22.7
72	351.0623	2	0.0	0.0	0.0
73	-15.2801	4	17.0	4.6	19.3
74	174.3672	5	1.5	0.7	1.9
75	1098.1570	1	0.0	0.0	0.0
76	549.1481	4	2.0	0.7	2.4
77	394.5776	6	2.6	1.0	3.3
78	10.3752	6	9.8	4.2	14.0
79	365.8081	2	5.6	2.2	5.6
80	164.8904	8	8.6	3.6	11.0
81	197.1806	2	0.9	0.4	0.9
82	1297.7560	3	6.6	1.6	7.1
86	35.4672	1	0.0	0.0	0.0
88	495.5141	1	0.0	0.0	0.0
89	551.9254	2	1.9	0.9	1.9
90	490.7224	3	0.0	0.0	0.0
92	669.0158	4	8.3	2.4	10.5
93	256.5078	13	16.4	5.0	19.4
96	1787.0390	2	12.2	3.2	12.2
97	220.0803	3	1.0	0.4	1.2
98	229.4135	5	4.0	1.2	4.8
100	131.2253	1	0.0	0.0	0.0
102	53.2507	3	2.1	0.9	2.3
103	288.4140	1	0.0	0.0	0.0
104	542.6641	2	4.8	1.5	4.8
105	714.0494	3	4.5	1.3	4.7
107	797.2271	1	0.0	0.0	0.0
108	253.5303	2	2.9	1.1	3.0
110	-237.2545	4	11.1	3.5	11.6
118	(do not estimate)	-			

214	192.1303	5	5.8	1.5	7.4
215	377.7146	3	30.0	12.5	31.9
216	806.8125	4	13.5	4.8	14.7

Table C-17: Saturated liquid viscosity reference temperature (T_v) second-order contributions, number of components used for regressing these values and deviations for these components.

Group ID	Group Contribution, T_{vi}	Number of Components	Mean Absolute Error (cm^3/mol)	Mean Absolute Error (%)	Standard Deviation (cm^3.mol^{-1})
119	-180.3686	7	8.6	2.7	11.0
121	241.8968	48	7.0	2.8	9.3
122	138.6555	11	4.6	1.8	5.6
123	-71.1647	30	8.0	3.1	10.2
124	-115.0418	17	8.7	3.5	11.1
125	-96.7544	7	6.4	2.6	7.3
126	-153.8442	31	7.5	2.6	9.4
127	-22.1041	53	8.4	2.5	12.1
128	24.7835	33	7.7	2.4	10.6
130	224.2439	3	9.1	2.3	10.9
131	24.2539	18	8.3	2.8	10.1
132	137.8708	4	9.6	3.6	11.0
134	-54.1782	26	8.3	2.6	11.1
217	-726.4291	8	19.5	8.1	22.4

Table C-18: Saturated liquid viscosity reference temperature (T_v) group interaction contributions, interacting groups, number of components used for regressing these values and deviations for these components.

Group ID	Interacting Groups	Group Contribution, T_{vi}	Number of Components	Mean Absolute Error (cm^3/mol)	Mean Absolute Error (%)	Standard Deviation (cm^3/mol)
135	OH - OH	-1313.5690	18	12.9	3.2	16.7
136	OH - NH2	-41.9608	3	13.0	3.4	13.3
137	OH - NH	-1868.6060	2	9.8	2.4	9.8
140	OH - EtherO	-643.4378	15	17.2	4.9	20.4
145	OH - CN	-345.7844	1	0.0	0.0	0.0
146	OH - AO	50.2582	1	0.0	0.0	0.0
148	OH(a) - OH(a)	-1146.1070	1	0.0	0.0	0.0
151	OH(a) - EtherO	-229.2406	4	16.3	4.3	17.3
155	OH(a) - Nitro	515.1511	3	34.1	8.6	37.2
157	NH2 - NH2	86.7249	3	2.9	0.8	3.5
159	NH2 - EtherO	-57.1437	5	6.9	1.8	7.5
166	NH - EtherO	54.2025	1	0.0	0.0	0.0
178	EtherO - EtherO	156.7495	40	11.0	3.4	15.1
180	EtherO - Ester	273.6616	1	0.0	0.0	0.0
181	EtherO - Ketone	-339.6071	2	1.9	0.5	1.9
182	EtherO - Alde	1050.3190	1	0.0	0.0	0.0
184	EtherO - Nitro	355.0508	1	0.0	0.0	0.0
189	Ester - Ester	167.7204	11	10.1	2.7	12.7
190	Ester - Ketone	244.0583	2	1.8	0.6	1.8
192	Ester - CN	334.4856	2	0.3	0.1	0.3
194	Ketone - Ketone	1985.8270*	1	0.0	0.0	0.0

---

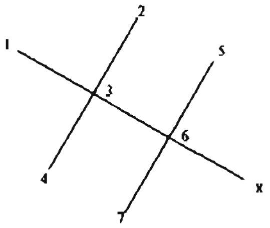
* Questionable group contribution values

204	Alde - AO	161.7447	1	0.0	0.0	0.0
206	Nitro - Nitro	1839.2630	1	0.0	0.0	0.0
209	CN - AN6	718.1262	1	0.0	0.0	0.0
218	COOH – NH2	(do not estimate)	-			

Appendix D

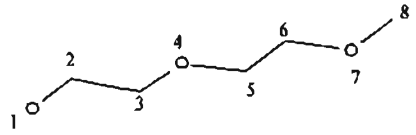
Property Calculation Examples

Table D-1: Estimation of the critical temperature (T_c) of 2,2,3,3-tetramethylbutane

Component: 2,2,3,3-Tetramethylbutane Number of atoms: 8				
Group	Atoms	frequency	contribution	Total
1	1,2,4,5,7,8	6	0.0418682	0.2512092
6	3,6	2	-0.0038778	-0.0077556
Steric Corrections				
Group	Bond	frequency	Contribution	Total
C3C-CC3 (133)	3-6	1	-0.0245802	-0.0245802
Total Sum				**0.2188734**

$$T_c = 379.6K\left(0.6990 + \frac{1}{0.9889 + 0.2188734^{0.8607}}\right) = 566.8K \qquad T_{c,exp} = 567.8\text{ K}$$

Table D-2: Estimation of the critical pressure (P_c) of diethylene glycol monomethyl ether

Component: Diethylene glycol monomethyl ether Number of atoms: 8 Molecular weight: 120.15				
Group	**atoms**	**frequency**	**contribution**	**Total**
2	8	1	0.00055262	0.00055262
7	2,3,5,6	4	0.00034310	0.00137240
35	1	1	-0.00018153	-0.00018153
38	4,7	2	0.00020592	0.00041184
Interactions				
Group	Atoms	frequency	Contribution	Total
OH-Ether (140)	1-4, 1-7	(2[*])/8	0.00073373	0.0001834325
Ether-Ether (178)	4-7	(1[*])/8	0.00026751	0.0000334388
Total Sum (rounded)				**0.00237220**

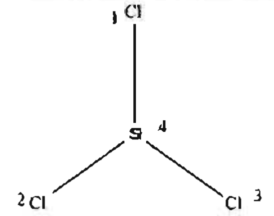
$$P_c = \frac{120.15^{-0.14041}}{(0.00939 + 0.00237220)^2} = 3689.9\,kPa$$

$P_{c,exp}$ = 3670.0 kPa

---

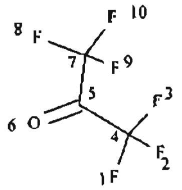
[*] From Equation 7-1:
m = 3 (one OH and two EtherO)
$GI = (C_{OH(1)-EtherO(4)} + C_{OH(1)-EtherO(7)} + C_{EtherO(4)-OH(1)} + C_{EtherO(7)-OH(1)} + C_{EtherO(4)-EtherO(7)} + C_{EtherO(7)-EtherO(4)}) / (n^*(m-1))$
$= (2C_{EtherO-EtherO} + 4C_{OH-EtherO}) / (n^*(m-1))$
$= (C_{EtherO-EtherO} + 2C_{OH-EtherO}) / n$

Table D-3: Estimation of the critical volume (V_c) of trichloro silane

<table>
<tr><td colspan="2">Component: Trichloro silane
Number of atoms: 4</td><td colspan="3"> </td></tr>
<tr><td>Group</td><td>atoms</td><td>frequency</td><td>contribution</td><td>Total</td></tr>
<tr><td>27</td><td>1,2,3</td><td>3</td><td>26.2582</td><td>78.7746</td></tr>
<tr><td>215</td><td>4</td><td>1</td><td>37.0423</td><td>37.0423</td></tr>
<tr><td colspan="5">Corrections</td></tr>
<tr><td>Group</td><td>atoms</td><td>frequency</td><td>contribution</td><td>Total</td></tr>
<tr><td>124</td><td>-</td><td>1</td><td>-6.1909</td><td>-6.1909</td></tr>
<tr><td>217</td><td>4</td><td>1</td><td>19.4348</td><td>19.4348</td></tr>
<tr><td colspan="4">Total Sum</td><td>129.0608</td></tr>
</table>

$V_c = \frac{129.0608}{4^{-0.2266}} + 86.1539 = 262.9 cm^3.mol^{-1}$ $V_{c,exp} = 268.0$ cm^3.mol^{-1}

Table D-4: Estimation of vapour-liquid equilibrium curve slope (*dB*) of perfluoro-2-propanone and liquid vapour pressure at 210.16K.

Component: Perflouro-2-propanone Number of atoms: 10				
Group	**atoms**	**frequency**	**contribution**	**Total**
7	4,7	2	0.0378485	0.0756970
21	1,2,3,8,9,10	6	0.0420887	0.2525322
51	5,6	1	0.255848	0.2558480
Corrections				
Group	atoms	frequency	contribution	Total
120	5	1	0.002503	0.0025030
121	4,7	2	-0.0833326	-0.1666652
123	-	1	-0.1259208	-0.1259208
Total Sum				**0.2939942**

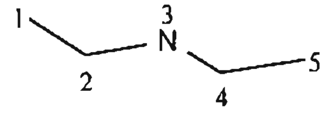
$dB = 0.2939942 - 0.176055 = 0.1179392$ $T_{b,exp} = 245.9$ K

$$P^S = \left[10^{(4.1012+0.1179392)\left(\frac{\frac{210.16}{245.9} 1}{\frac{210.16}{245.9} \frac{1}{8}}\right)} \right] * 101.325kPa = 14.63kPa$$

$P^s_{exp} = 14.05$ kPa

Table D-5: Estimation of saturated liquid viscosity curve slope (*dBv*) and reference temperature (T_v) of N,N-Diethylamine and liquid viscosity at 308.15K.

Component: N,N-Diethylamine
Number of atoms: 5
$T_{b,exp} = 329.0$ K



Group	atoms	Frequency	dBv_i	$T_{v,i}$
1	1,5	2	2 * 0.0139133	2 * 89.0803
7	2,4	2	2 * 0.0213473	2 * 103.4109
42	3	1	1 * 0.0136479	1 * 159.5146
Total Sum			**0.0841691**	**544.4970**

$$dBv = \frac{0.0841691}{10^{-2.5635} + 0.0685} + 3.777 = 4.7713112$$

$$T_{v,est} = 21.8444 * 329.0^{0.5} + \frac{544.4970^{0.9315}}{5^{0.6577} + 4.9259} - 231.1361 = 210.38K \qquad T_{v,calc} = 207.97K$$

$$\mu(dBv, T_{v,calc}) = \left[e^{(-4.7713112)\left(\frac{308.15-207.97}{308.15-\frac{207.97}{16}}\right)} \right] * 1.3mPa.s = 0.2574mPa.s$$

$$\mu(dBv, T_{v,est}) = \left[e^{(-4.7713112)\left(\frac{308.15-210.38}{308.15-\frac{210.38}{16}}\right)} \right] * 1.3mPa.s = 0.2674mPa.s$$

$\mu_{exp} = 0.2740$ mPa.s