Spring 1981

# Correlation and prediction of vapor-liquid equilibrium in electrolytic solutions

Anil Krishna Rastogi
*New Jersey Institute of Technology*

## Recommended Citation

Rastogi, Anil Krishna, "Correlation and prediction of vapor-liquid equilibrium in electrolytic solutions" (1981). *Dissertations*. 1261.
https://digitalcommons.njit.edu/dissertations/1261

INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.
2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame. If copyrighted materials were deleted you will find a target note listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in "sectioning" the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.

University
Microfilms
International

300 N. ZEEB RD., ANN ARBOR, MI 48106

8121970

RASTOGI, ANIL KRISHNA

# CORRELATION AND PREDICTION OF VAPOR-LIQUID EQUILIBRIUM IN ELECTROLYTIC SOLUTIONS

*New Jersey Institute of Technology* D.ENG.SC. 1981

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

# CORRELATION AND PREDICTION OF
# VAPOR-LIQUID EQUILIBRIUM IN
# ELECTROLYTIC SOLUTIONS

by

Anil Krishna Rastogi

Dissertation submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial fulfillment
of the requirements for the degree of
Doctor of Engineering Science
1981

# APPROVAL SHEET

Title of Thesis: Correlation and Prediction of Vapor-Liquid Equilibrium in Electrolytic Solutions

Name of Candidate: Anil Krishna Rastogi
Doctor of Engineering Science, 1981

Thesis and Abstract Approved:

Dimitrios Tassios
Professor
Department of Chemical
Engineering & Chemistry

Date

Date

Date

Date

Date

# VITA

Name: Anil Krishna Rastogi

Degree and date to be conferred: D. Eng. Sc., 1981

Secondary education: Government Intermediate College, Meerut City, India; June, 1965

| Collegiate institutions attended | Dates | Degree | Date of Degree |
|---|---|---|---|
| University of Roorkee, India | 7/69-5/73 | BE(ChE) | 1973 |
| New Jersey Institute of Technology, N.J. | 1/75-8/76 | MS(ChE) | 1977 |
| New Jersey Institute of Technology, N.J. | 9/76-5/81 | D.Eng.Sc. (ChE) | 1981 |

Major: Chemical Engineering

Publications: "Non-Equilibrium Parametric Pumps," H.T. Chen, A. Rastogi, C.Y. Kim, L. Rak, Separation Science, 11(4), 335, (1976)

"Prediction of Binary Vapor-Liquid Equilibrium from One Parameter Equations," A. Krumins, A. Rastogi, M. Rusak, and D. Tassios, Presented at 27th Canadian Chemical Engineering Conference, Alberta, Canada, (1977); Canadian Journal of Chem. Eng., Vol 58, p 663, Oct. (1980)

"Estimation of Thermodynamic Properties of Binary Aqueous Electrolytic Solutions in the Range 25-100°C," Anil Rastogi and D. Tassios, Ind. Eng. Chem. Process Design Develop., Vol 19, No 3, p 477, July (1980)

"Prediction and Correlation of VLE in Solutions Containing Two Non-electrolytes and One Electrolyte," Anil Rastogi and D. Tassios, to be submitted to AIChE Journal for Publication

Positions Held:

| | |
|---|---|
| 1978-1981 | Special Lecturer in Chemical Engineering, New Jersey Institute of Technology |
| May 1978 & May 1979 | Assistant Lecturer--on "Applied Distillation" offered by "The Center for Professional Advancement" |
| 1976-1978 | Teaching Assistant--New Jersey Institute of Technology, Chemical Engineering Laboratory |
| 1973-1974 | Chemical Engineer--Sahu Chemical and Fertilizers, Varanasi, India |

# ABSTRACT

Title of Thesis: Correlation and Prediction of Vapor-Liquid Equilibrium in Electrolytic Solutions

Anil Krishna Rastogi, Doctor of Engineering Science, 1981

Thesis directed by: Dimitrios Tassios, Professor of Chemical Engineering

Two expressions for the excess Gibbs free energy are presented which correlate and predict vapor-liquid equilibrium and the mean molal activity coefficient of an electrolyte in a ternary mixture containing water and either MeOH or EtOH. The proposed equations take into account coulombic forces between ions and the physical interaction forces between ion-solvent and solvent-solvent molecules in a solution.

Model #1 is a combination of an extended Debye and Hückel equation and the local composition of non-random two liquid (NRTL) model. A ternary mixture requires six adjustable binary parameters to predict activity coefficients. These six parameters are evaluated from three separate binary data reductions. Ternary data are predicted with an average error of $|\Delta Y|$ less than 0.03 up to $I = 2$. The parameters are considered temperature independent within a 30 to 40$^{o}$C temperature range for aqueous electrolyte mixtures and within a 15 to 20$^{o}$C temperature range for nonaqueous electrolyte mixtures. Both isothermal and isobaric ternary experimental data have been tested for ternary correlation. Iso-

thermal ternary data correlation for systems containing water-methanol solvents give results with an average error of $|\Delta Y|$ less than 0.01 up to $I = 6$. Whereas isobaric ternary data are correlated with an average error of $|\Delta Y|$ less than 0.02 up to $I = 4$. It is possible to extend this model to multi-component mixtures although this has not been investigated in this work.

Model #2 is a combination of the Bromley equation, the simplified NRTL equation and an additional ternary salting out expression. The behavior of each electrolyte-solvent binary is described by a one parameter form of the Bromley equation. The temperature dependency of the binary parameters has been established with a two constant equation. Prediction of aqueous electrolyte binary data ($\gamma_{\pm}$ and vapor pressure depression) is obtained with an average percent error less than 10.0 at intermediate temperatures. Correlation of ternary VLE and $\gamma_{\pm}$ data require four binary parameters and two additional ternary adjustable parameters. This model is limited to binary and ternary data correlation only. The maximum concentration range for the correlation of ternary systems containing water and methanol solvents is about $I = 3$. The correlation of vapor-liquid equilibrium data results in an average error of $|\Delta Y|$ less than 0.012, except for the $LiCl-H_2O-MeOH$ system at 60°C where the average error in $|\Delta Y|$ is 0.02.

# PREFACE

The thermodynamic study of electrolytic solutions can be categorized into three groups: one containing strong electrolytes in aqueous solvents; the second comprising volatile weak electrolytes in aqueous/nonaqueous solvents; and the third consisting of strong electrolytes in nonaqueous solvents or in mixed solvents.

The first type of system has been of interest in various chemical, metallurgical and geological problems. Debye and Hückel (1923) proposed the classic thermodynamic excess Gibbs free energy expression for strong electrolytes in a single solvent. Guggenheim (1935) extended the range of validity of the Debye-Hückel equation to 0.1 molal solutions. Recently, many workers have proposed semi-empirical correlations for concentrated electrolyte aqueous solutions viz, Bromley et al. (1972, 1973, 1974); Meissner et al. (1972); Pitzer et al. (1973, 1974, 1977, 1979); and Cruz and Renon (1978). Two important and different approaches among the above are by Bromley (1973) and Cruz and Renon. Bromley modified Guggenheim's equation to a one parameter form per binary whereas the Cruz and Renon expression is a combination of the Debye-Hückel equation, a salting out contribution given by the Born model, and the NRTL model.

The second type of systems recently became important due to the necessity of pollution control in the chemical and petroleum industries. The recovery of weak volatile electrolytes such as ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide and hydrogen cynanide from effluent streams requires the thermodynamic representation of vapor-liquid equilibrium. The most interesting work reported in this area is by Van Krevelen (1949); Van Krevelen, Hof zer and Hunt ens (1949); Edwards et al. (1975, 1978); Beutier and Renon (1978); Chen et al. (1979); and Mason and Kao (1979).

Theoretical and correlation for the third type of system, electrolytes in nonaqueous solvents and in mixed solvents is sparse. A knowledge of the VLE and electrolyte activities in such solutions could be useful in different chemical and electrochemical applications. The correlation work in the literature for this category are by Rousseau et al. (1972, 1975, 1978); Bakerman and Tassios (1975); Hala (1969); Chen et al. (1979) and Tomasula and Tassios (1980). The most systematic approach is given by Hala and Chen et al. They have considered different ion-ion, ion-solvent and solvent-solvent interactions in an electrolytic solution. Both have used two types of terms for the Gibbs free energy. One of these terms is the Debye-Hückel equation to represent ion-ion interactions. For the other interactions, Hala used the two suffix Margules equation, whereas Chen et al. used an expression based on the two liquid nonrandom theory. Unfortunately, none of the above approaches presents a predictive scheme for a ternary electrolytic solution; also they are complex in nature.

It would be appropriate to categorize the present state of the art for such systems as in a developmental stage. Therefore we have taken an approach to develop thermodynamic analytical expressions to represent VLE of the third type of electrolytic solutions. Our models also combine the two types of terms, which are derived by the modification of Bromley (1973) and Cruz and Renon (1978) binary equations. These are different than the equations of Hala and Chen et al. The proposed models require a minimum amount of information. Model I has the possibility of extension to multicomponent mixtures containing more than two solvents and single or multi electrolytes.

# DEDICATION

I dedicate this thesis to my parents whose encouragement and love made it possible.

# ACKNOWLEDGEMENT

I thank my advisor, Professor Dimitrios Tassios, for his suggestions, guidance and criticism throughout this research. His friendly attitude and subtle discussions during the preparation of this research are very much appreciated. Thanks are extended to Dr. R.P.T. Tomkins for his suggestions during the review of the manuscript, to Dr. C. Tsonopoulos, Dr. Deran Hanesian and Dr. R. Plastock for their comments.

The exchange of ideas and mutual discussions with John Ordoz, Gregory Czerwienski and the other members of Professor Tassios' research group (Thermo Club) were useful during this research.

Gratitude is expressed to Mrs. Diana Muldrow who typed the manuscript. Thanks are extended to the Department of Chemical Engineering and Chemistry, NJIT for financial support during my stay at the school and also to the Computer Center of NJIT for use of its facilities. Thanks are due to Mr. Frank Freund, Computer Services, for helping with computer programs.

Special thanks to Peggy Tomasula whose friendship and discussions about the research were valuable.

## TABLE OF CONTENTS

Chapter | Page

PREFACE. . . . . . . . . . . . . . . . . . . . . . . . ii

DEDICATION . . . . . . . . . . . . . . . . . . . . . . v

ACKNOWLEDGEMENT . . . . . . . . . . . . . . . . . . . . vi

LIST OF TABLES . . . . . . . . . . . . . . . . . . . . x

LIST OF FIGURES . . . . . . . . . . . . . . . . . . . . xiv

LIST OF COMPUTER PROGRAMS . . . . . . . . . . . . . . . xx

INTRODUCTION . . . . . . . . . . . . . . . . . . . . . 1

1 DEVELOPMENT OF FUNDAMENTAL RELATIONSHIPS FOR VAPOR-LIQUID EQUILIBRIUM IN ELECTROLYTIC SOLUTIONS . . . . . . . . . . . . . . . . . . . . 2

- 1.1 Criteria of Equilibria . . . . . . . . . . . 3
- 1.2 Mixture of Solvent (2) - Solvent (3) - Binary (2-3) . . . . . . . . . . . . . . . . 6
- 1.3 Mixture of an Electrolyte and a Solvent (Binary 1-2 or 1-3) . . . . . . . . . . . . 8
- 1.4 Mixture of an Electrolyte (1) - Solvent (2) - Solvent (3)(Ternary 1-2-3) . . . . . . 10
- 1.5 Criteria for the Excess Gibbs Free Energy . . . . . . . . . . . . . . . . . . . 11

2 CORRELATION AND PREDICTION OF VAPOR-LIQUID EQUILIBRIUM AND THE MEAN MOLAL ACTIVITY COEFFICIENT BY MODEL I IN ELECTROLYTIC SOLUTIONS . . . . . . . . . . . . . . . . . . . . 13

- 2.1 Excess Gibbs Free Energy Function . . . . . 14
- 2.2 Procedure: Data Reduction and Prediction . 18
  - A. Binary 2-3: Mixture of Solvent (2) - Solvent (3) . . . . . . . . . . . . . . . . 18
  - B. Binary 1-2 or 1-3: Mixture of an Electrolyte and a Solvent . . . . . . . 19

Chapter Page

C. Prediction of Ternary VLE ($y_2$, $y_3$, P and $\gamma_\pm$) . . . . . . . . . . . . . . . 20

D. Correlation of Ternary Data . . . . . . 22

E. Binary Data Prediction Using the Parameters Evaluated by Ternary Data Reduction . . . . . . . . . . . . . . . . 24

2.3 Results . . . . . . . . . . . . . . . . . . . 25

A. Binary Data Reduction . . . . . . . . . 25

B. Temperature Dependency of the Binary Parameters . . . . . . . . . . . . . . . 27

C. Maximum Molality Applicability . . . . 33

D. Ternary Data Prediction . . . . . . . . 33

E. Ternary Data Correlation . . . . . . . 37

F. Binary Data Prediction . . . . . . . . 40

2.4 Discussion . . . . . . . . . . . . . . . . 44

2.5 Conclusions . . . . . . . . . . . . . . . . 51

3 CORRELATION OF VAPOR-LIQUID EQUILIBRIUM AND MEAN MOLAL ACTIVITY COEFFICIENTS WITH MODEL II IN ELECTROLYTIC SOLUTIONS . . . . . . . . . . 52

3.1 Gibbs Free Energy Expression . . . . . . . 53

3.2 Procedure: Data Reduction . . . . . . . . 56

A. Solvent-Solvent Binary . . . . . . . . 56

B. Electrolyte-Solvent Binary . . . . . . 56

C. Electrolyte-Solvent-Solvent Ternary . . 57

3.3 Results . . . . . . . . . . . . . . . . . . . 62

A. Aqueous Electrolyte Binary . . . . . . 62

B. Nonaqueous Electrolyte Binary . . . . . 69

C. Isothermal Ternary Data Correlation . . 70

3.4 Discussion . . . . . . . . . . . . . . . . 72

Chapter Page

3.5 Conclusions . . . . . . . . . . . . . . . . . 77

4 A COMPARATIVE STUDY OF TWO MODELS IN CORRELATING AND PREDICTING BINARY/TERNARY $\gamma_\pm$ AND VLE DATA IN ELECTROLYTIC SOLUTIONS . . . . . 78

A. Binary Data Correlation . . . . . . . . . 79

B. Ternary Data Prediction and Correlation . 80

APPENDIX A EXPRESSIONS FOR THE ACTIVITY COEFFICIENT OF THE SOLVENT AND THE MEAN ACTIVITY COEFFICIENT OF AN ELECTROLYTE IN A BINARY MIXTURE FOR MODEL I . . . . . . . 82

APPENDIX B A STEPWISE PROCEDURE FOR THE DEVELOPMENT OF TERNARY ACTIVITY COEFFICIENT EXPRESSIONS FOR MODEL I . . . . . . . . . 86

APPENDIX C A STEPWISE PROCEDURE FOR THE DEVELOPMENT OF TERNARY ACTIVITY COEFFICIENT EXPRESSIONS FOR MODEL II . . . . . . . . 101

APPENDIX D DEBYE-HÜCKEL CONSTANTS, DIELECTRIC CONSTANTS AND DENSITIES OF PURE SOLVENTS AND MIXED SOLVENTS; VAPOR PRESSURE CONSTANTS OF PURE SOLVENTS . . . . . . . 115

APPENDIX E CALCULATION OF FUGACITY COEFFICIENTS AND POYNTING EFFECT . . . . . . . . . . . . . 130

APPENDIX F COMPUTER PROGRAMS . . . . . . . . . . . . . 134

APPENDIX G TABLES AND FIGURES FOR MODEL I . . . . . 203

APPENDIX H TABLES AND FIGURES FOR MODEL II . . . . . 243

NOMENCLATURE . . . . . . . . . . . . . . . . . . . . . 280

SELECTED BIBLIOGRAPHY . . . . . . . . . . . . . . . . . 285

# LIST OF TABLES

Table Page

2.1 Multiplicity of Roots in Model #1 for Aqueous Electrolytic Solutions with Preset Values of $\alpha_{A2} = 0.2$ and $\alpha_{B2} = 0.0$ . . . . . . . . . . . . . 29

2.2 Prediction of Binary VLE Data by Model #1 at One Temperature Using Binary Parameters (Second Pair of Roots) at Another Temperature with Preset Values of $\alpha_{A2} = 0.2$ and $\alpha_{B2} = 0.0$ . . . . . . . . . . . . . . . . . . . . 31

2.3 Performance of Model I in Correlating Binary VLE Data for Different Molality Ranges . . . . . 32

2.4 Prediction of $\gamma_\pm$ in Ternary Mixtures Using Binary Parameters from Tables G.4 (Binary 1-2); G.5 (Binary 1-3); and G.3 (Binary 2-3) . . . . . . . . . . . . . . . . . . . . . . . 34

2.5 Prediction of Vapor-Phase Composition and Total Pressure by Model #1 Using Binary Parameters from Tables G.4 (Binary 1-2); G.5 (Binary 1-3); and G.3 (Binary 2-3) . . . . . 35

2.6 Prediction of Binary VLE and $\gamma_\pm$ Data Using Parameters Obtained by Ternary Data Correlation, Tables G.11 and G.12 . . . . . . . . . 41

3.1 Data Sources . . . . . . . . . . . . . . . . . . . . 61

3.2 Effect of the Number of Data Points Used in Evaluating $B_{12}$ on the Accuracy of Calculated $\gamma_\pm$ Values ($T = 100°C$) . . . . . . . . . . . . . 65

3.3 Values of $B^*$ and $B_1^1$ in Equation (3-20) for the Systems in Figures H.5 and H.6 . . . . . . . . 67

D.1 Liquid Molar Volume Data at Three Temperatures . . 124

D.2 Liquid Density Data for the $H_2O$-MeOH System at 25°C . . . . . . . . . . . . . . . . . . . . . . 125

D.3 Liquid Density Data for the $H_2O$-EtOH System at 25°C . . . . . . . . . . . . . . . . . . . . . . 126

D.4 Constants for Calculating the Dielectric Constants of Water-EtOH Mixtures at Various Temperatures, Equation (D-10) . . . . . 127

Table Page

D.5 Constants for Calculating the Dielectric Constants of Water-MeOH Mixtures at Various Temperatures, Equation (D-10) . . . . . 128

D.6 Pure Component Vapor Pressure Constants (Equation D-12) . . . . . . . . . . . . . . . . . 129

E.1 Pure Component Properties . . . . . . . . . . . 133

E.2 Mixture Properties . . . . . . . . . . . . . . . 133

E.3 $\phi_i^o$, P.E., $\hat{\phi}_i^v$ and $F_i$ for Data Point #1 . . . . . . 133

E.4 $\phi_i^o$, P.E., $\hat{\phi}_i^v$ and $F_i$ for Data Point #2 . . . . . . 133

G.1 Binary Data Sources . . . . . . . . . . . . . . 204

G.2 Ternary Data Sources . . . . . . . . . . . . . . 206

G.3 Solvent-Solvent Binary Data Correlation . . . . . 207

G.4 Aqueous Electrolytic Binary Data Correlation with Two Objective Functions, Equations (2-9) and (2-10) . . . . . . . . . . . 208

G.5 Nonaqueous Electrolytic Binary Data Correlation with Two Objective Functions, Equations (2-9) and (2-10) . . . . . . . . . . . 209

G.6 Aqueous Electrolytic Binary Data Correlation with Temperature Independent Parameters Using Objective Function #2, Equation (2-10), and Presetting $\alpha_{A2} = 0.2$; $\alpha_{B2} = 0.0$ . . . . . . . . . . . . . . . . . . . . 210

G.7 Nonaqueous Electrolytic Binary Data Correlation with Temperature Independent Parameters Using Objective Function #2, Equation (2-10), and Presetting $\alpha_{A3} = 0.2$ $\alpha_{B3} = 0.0$ . . . . . . . . . . . . . . . . . . . . 211

G.8 Binary Data Correlation with Temperature Independent Parameters Using Objective Function #2, Equation (2-10) and Presetting $\alpha_{Ai} = 0.2$; $\alpha_{Bi} = -1.0$ . . . . . . . . . . . . . . 212

G.9 Binary Data Correlation with Temperature Independent Parameters Using Objective Function #2, Equation (2-10) and Presetting $\alpha_{Ai} = -1.0$; $\alpha_{Bi} = -1.0$ . . . . . . . . . . . . . . 213

Table Page

G.10 Prediction of Binary Data at One Temperature Using the Parameters at Another Temperature, Presetting $\alpha_{Ai} = 0.2$ and $\alpha_{Bi} = 0.0$ . . . . . 214

G.11 Isothermal Ternary $\gamma_{\pm}$ Data Correlation for the Four Parameters: $G_{\pm 2}$, $Z_{\pm 2}$, $G_{\pm 3}$ and $Z_{\pm 3}$, Presetting the Solvent-Solvent Binary Parameters Corresponding to $\alpha_{23} = -1.0$ . . 215

G.12 A Comparative Study of the Three Objective Functions [Equations (2-19), (2-20), (2-21)] in Correlating Ternary Isothermal Data with the Four Parameters [$G_{\pm 2}$, $Z_{\pm 2}$, $G_{\pm 3}$, $Z_{\pm 3}$] Presetting $\Delta g_{23}$ and $\Delta g_{32}$ from Table G.3 Corresponding to $\alpha_{23} = -1.0$ . . . . . . . . . . . . 216

G.13 Values of the Parameters Obtained with the Three Objective Functions for Isothermal Ternary VLE Data . . . . . . . . . . . . . . . . 217

G.14 A Comparative Study of the Three Objective Functions [Equations (2-19), (2-20), (2-21)] in Correlating Ternary Isobaric VLE Data with the Four Parameters [$\Delta g_{A2}$, $\Delta g_{B2}$, $\Delta g_{A3}$, $\Delta g_{B3}$] Presetting $\Delta g_{23}$ and $\Delta g_{32}$ Corresponding to $\alpha_{23} = -1.0$, Table G.3 and $\alpha_{A2} = 0.2$; $\alpha_{B2} = 0.0$; $\alpha_{A3} = 0.2$; $\alpha_{B3} = 0.0$ . . . . . . . . . . . 218

G.15 Values of the Parameters Obtained with the Three Objective Functions for Isobaric VLE Data . . . . . . . . . . . . . . . . . . . . . . 219

H.1 Typical m-DP Data from the Weast Compilation . . . 244

H.2 Values of $B_{12}$ and Quality of Correlation of the Weast Data . . . . . . . . . . . . . . . . 245

H.3 Quality of Results with the $B_{12}$ Value at 70°C Obtained by Interpolation of the $B_{12}$ (25°C) and $B_{12}$ (100°C) Values in Equation (3-20) . . . 249

H.4 Nonaqueous Electrolyte Binary Data Correlation with the Bromley Equation . . . . . . . . . . . 250

H.5 Aqueous Electrolytic Binary Data Correlation with the Bromley Equation . . . . . . . . . . . 251

H.6 Isothermal Ternary $\gamma_{\pm}$ Data Correlation with Model II . . . . . . . . . . . . . . . . . . . 252

Table Page

H.7 A Comparative Study of the Three Objective Functions [Equations (2-19), (2-20), (2-21)] in Correlating Ternary Isothermal VLE Data with Model II . . . . . . . . . . . . . . . . . 253

H.8 Values of the Parameters Obtained with Three Objective Functions for Model II . . . . . . . . 254

H.9 $B_{12}$ Values Obtained from Weast's Data and Equation (3-20) with the $B^*$ and $B_1^1$ Values from Table 3.3 . . . . . . . . . . . . . . . . . 255

H.10 $\gamma_\pm$ Values for $MgCl_2$ Using $B_{12}$ Values from Weast's Data and Equation (3-20) . . . . . . . . 256

# LIST OF FIGURES

Figure Page

1.1 Representation of the Vapor-Liquid Equilibrium in Electrolytic Solutions . . . . . . . . . . . 4

2.1 A Stepwise Scheme for Correlation and Prediction of the VLE and Mean Molal Activity Coefficients with Model I . . . . . . . . . . . 18

2.2 Comparison of Experimental Mean Molal Activity Coefficients and Vapor Pressure Depressions with those Predicted by Model I for the System NaCl-$H_2O$ at 25°C . . . . . . . . . . . . 27

2.3 Comparison of Experimental Vapor Pressure Depressions with those Predicted and Correlated by Model I for the System LiBr-MeOH at 15°C . . . . . . . . . . . . . . . . . . . . 28

2.4 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-$H_2O$-MeOH at 25°C . . . . . . . . . . . . . . . . . . . . 36

2.5 Comparison of Experimental VLE with that Predicted Using Model I for the System LiCl-$H_2O$-EtOH at 25°C . . . . . . . . . . . . . . . . 38

2.6 Comparison of Experimental VLE with that Predicted Using Model I for the System LiCl-$H_2O$-MeOH at 25°C . . . . . . . . . . . . . . . . 39

2.7 Prediction of $\gamma_\pm$ and DP Data for the System LiCl-$H_2O$ at 25°C Using the Parameters Obtained by Ternary Data Correlation with Model I . . . . . . . . . . . . . . . . . . . . 42

2.8 Contribution of Different Terms to $\ln\gamma_i$ for the System LiCl-$H_2O$-EtOH at 25°C in Model I . . 45

2.9 Thermodynamic Consistency Test for the System $H_2O$-MeOH at 25°C . . . . . . . . . . . . . . . . 47

3.1 A Stepwise Scheme for Correlation of the VLE and Mean Molal Activity Coefficients with Model II . . . . . . . . . . . . . . . . . . . . . 55

3.2 Activity and Osmotic Coefficients for the System Water-Sodium Chloride at 100°C . . . . . 64

Figure Page

3.3 Contribution of Different Terms to $\ln\gamma_i$ for the System LiCl-$H_2O$-EtOH at 25°C in Model II . . . . . . . . . . . . . . . . . . . . . . . 73

3.4 Contribution of the Salting Out Term to $\ln\gamma_i$ for the System LiCl-$H_2O$-EtOH at 25°C in Model II . . . . . . . . . . . . . . . . . . . . 75

D.1 Comparison of Experimental and Estimated Densities for the System $H_2O$-MeOH at 25°C . . . 118

D.2 Comparison of Experimental and Estimated Densities for the System $H_2O$-EtOH at 25°C . . . 119

D.3 Comparison of Experimental and Estimated Dielectric Constants of the Mixture $H_2O$-MeOH at 25°C . . . . . . . . . . . . . . . . . . . . 121

D.4 Comparison of Experimental and Estimated Dielectric Constants of the Mixture $H_2O$-EtOH at 25°C . . . . . . . . . . . . . . . . . . . . 122

G.1 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-$H_2O$-EtOH at 25°C and Constant $X_{EtOH}$ = 0.0417 . . . . . . 220

G.1A Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I up to m = 0.2 for the System HCl-$H_2O$-EtOH at 25°C and Constant $X_{EtOH}$ = 0.0417 . . . . . . . . . . . . . . . . . . . 221

G.2 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-$H_2O$-EtOH at 25°C and Constant $X_{EtOH}$ = 0.0891 . . . . . . 222

G.2A Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I up to m = 0.2 for the System HCl-$H_2O$-EtOH at 25°C and Constant $X_{EtOH}$ = 0.5 . . . . . . . . . . . . . . . . . . . . 223

G.3 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-$H_2O$-EtOH at 25°C and Constant $X_{EtOH}$ = 0.5 . . . . . . . . . 224

G.3A Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I up to m = 0.2 for the System HCl-$H_2O$-EtOH at 25°C and Constant $X_{EtOH}$ = 0.5 . . . . . . . . . . . . . . . . . . . . 225

Figure Page

G.4 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-$H_2O$-MeOH at 25°C and Constant $X'_{MeOH} = 0.0584$ . . . . 226

G.5 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-$H_2O$-MeOH at 25°C and Constant $X'_{MeOH} = 0.1233$ . . . . . . 227

G.6 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System LiCl-$H_2O$-MeOH at 25°C and Constant m = 0.02, 0.05, 0.1 . . . . 228

G.7 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System LiCl-$H_2O$-MeOH at 25°C and Constant m = 0.5, 1.0 . . . . . . . 229

G.8 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated for the System NaCl-$H_2O$-MeOH at 25°C and Constant m = 0.02, 0.05 . . . . . . . . . . . . . . . . . . 230

G.9 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated for the System NaCl-$H_2O$-MeOH at 25°C and Constant m = 0.2, 0.5 . . . . . . . . . . . . . . . . . . . 231

G.10 Comparison of Experimental Vapor Phase Compositions with those Predicted and Correlated by Model I for the System LiCl-$H_2O$-EtOH at 25°C and Constant m = 0.5 . . . . . . . . . . . . 232

G.11 Comparison of Experimental with Predicted and Correlated Vapor Phase Compositions Using Model I for the System LiCl-$H_2O$-EtOH at 25°C and Constant m = 1.0 . . . . . . . . . . . . . . 233

G.12 Comparison of Experimental with Predicted and Correlated Vapor Phase Compositions Using Model I for the System LiCl-$H_2O$-MeOH at 25°C and Constant m = 1.0 . . . . . . . . . . . . . . 234

G.13 Comparison of Experimental with Correlated Vapor Phase Compositions Using Model I for the System NaBr-$H_2O$-MeOH at 40°C . . . . . . . . . . 235

G.14 Comparison of Experimental with Correlated Vapor Phase Compositions Using Model I for the System NaBr-$H_2O$-MeOH at 25°C . . . . . . . . . . 236

Figure Page

G.15 Comparison of Experimental with Correlated Vapor Phase Compositions Using Model I for the System LiCl-$H_2O$-MeOH at 60°C . . . . . . . . 237

G.16 Comparison of Experimental with Correlated Vapor Phase Compositions Using Model I for the System LiCl-$H_2O$-MeOH at P = 1 atm . . . . . . . . 238

G.17 Comparison of Experimental with Correlated Vapor Phase Compositions Using Model I for the System NaBr-$H_2O$-MeOH at P = 1 atm . . . . . . . . 239

G.18 Comparison of Experimental with Correlated Vapor Phase Compositions Using Model I for the System KCl-$H_2O$-MeOH at P = 1 atm . . . . . . . . . 240

G.19 Comparison of Experimental with Correlated Vapor Phase Compositions Using Model I for the System NaF-$H_2O$-MeOH at P = 1 atm . . . . . . . . . 241

G.20 Contribution of the NRTL Term to $\ln\gamma_i$ for the System LiCl-$H_2O$-EtOH at 25°C in Model I . . . . 242

H.1 Test of the Bromley Equation for the System: NaCl-Water at 100°C . . . . . . . . . . . . . . . 257

H.2 Test of the Bromley Equation for the System: $CaCl_2$-$H_2O$ . . . . . . . . . . . . . . . . . . . . 258

H.3 Test of the Bromley Equation for the System: $MgSO_4$-$H_2O$ . . . . . . . . . . . . . . . . . . . . . 259

H.4 Activity Coefficients for the System: KBr-Water at 100°C . . . . . . . . . . . . . . . . . . 260

H.5 Test of Temperature Dependency of $B_{12}$, Equation (3-20) . . . . . . . . . . . . . . . . . 261

H.6 Test of Temperature Dependency of $B_{12}$, Equation (3-20) . . . . . . . . . . . . . . . . . 262

H.7 Test of the Bromley Equation for the System: LiBr-MeOH at 25°C . . . . . . . . . . . . . . . . 263

H.8 Test of the Bromley Equation for the System: LiCl-MeOH at 60°C . . . . . . . . . . . . . . . . 264

H.9 Test of the Bromley Equation for the System: $CaCl_2$-MeOH at 25°C . . . . . . . . . . . . . . . . 265

Figure Page

H.10 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-$H_2O$-EtOH at 25°C and Constant $X'_{EtOH}$ = 0.0417 . . . . . . . . . . . . . 266

H.11 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-$H_2O$-EtOH at 25°C and Constant $X'_{EtOH}$ = 0.0891 . . . . . . . . . . . . . 267

H.12 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-$H_2O$-EtOH at 25°C and Constant $X'_{EtOH}$ = 0.5 . . . . . . . . . . . . . . . 268

H.13 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-$H_2O$-MeOH at 25°C and Constant $X'_{MeOH}$ = 0.0584 . . . . . . . . . . . . . 269

H.14 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-$H_2O$-MeOH at 25°C and Constant $X'_{MeOH}$ = 0.1233 . . . . . . . . . . . . . 270

H.15 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-$H_2O$-MeOH at 25°C and Constant m = 0.02, 0.05, 0.5 . . . . . . . . . . . 271

H.16 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System NaCl-$H_2O$-MeOH at 25°C and Constant m = 0.02, 0.05 . . . . . . . . . . . . . 272

H.17 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System NaCl-$H_2O$-MeOH at 25°C and Constant m = 0.2, 0.5 . . . . . . . . . . . . . . 273

H.18 Comparison of Experimental and Correlated Vapor Phase Compositions Using Model II for the System LiCl-$H_2O$-EtOH at 25°C and Constant m = 0.5 . . . . . . . . . . . . . . . . . . . . . . 274

H.19 Comparison of Experimental and Correlated Vapor Phase Compositions Using Model II for the System LiCl-$H_2O$-EtOH at 25°C and Constant m = 1.0 . . . . . . . . . . . . . . . . . . . . . . 275

Figure Page

H.20 Comparison of Experimental with Correlated Vapor Phase Compositions Using Model II for the System LiCl-$H_2O$-MeOH at 25°C and Constant m = 1.0 . . . . . . . . . . . . . . . . . . . . . 276

H.21 Comparison of Experimental with Correlated Vapor Phase Compositions Using Model II for the System LiCl-$H_2O$-MeOH at 60°C . . . . . . . . . . . 277

H.22 Comparison of Experimental with Correlated Vapor Phase Compositions Using Model II for the System NaBr-$H_2O$-MeOH at 25°C . . . . . . . . . . . 278

H.23 Comparison of Experimental with Correlated Vapor Phase Compositions Using Model II for the System NaBr-$H_2O$-MeOH at 40°C . . . . . . . . . . . 279

# LIST OF COMPUTER PROGRAMS

Page

Description of the Programs . . . . . . . . . . . . . . . 135

Main Program . . . . . . . . . . . . . . . . . . . . . . 140

Subroutine INPDAT . . . . . . . . . . . . . . . . . . . 151

Subroutine FITIT . . . . . . . . . . . . . . . . . . . . 155

Subroutine POLIFI . . . . . . . . . . . . . . . . . . . 156

Function DETERM . . . . . . . . . . . . . . . . . . . . 158

Subroutine VAPPRE . . . . . . . . . . . . . . . . . . . 159

Subroutine TEMPD . . . . . . . . . . . . . . . . . . . . 160

Subroutine LSQ2 . . . . . . . . . . . . . . . . . . . . 161

Subroutine FN . . . . . . . . . . . . . . . . . . . . . 166

Subroutine FIBN . . . . . . . . . . . . . . . . . . . . 170

Subroutine FUNC . . . . . . . . . . . . . . . . . . . . 173

Subroutine NRTL1 . . . . . . . . . . . . . . . . . . . . 176

Subroutine BROML . . . . . . . . . . . . . . . . . . . . 177

Subroutine ADITON . . . . . . . . . . . . . . . . . . . 180

Subroutine FUNCB . . . . . . . . . . . . . . . . . . . . 182

Subroutine FUNCT . . . . . . . . . . . . . . . . . . . . 183

Subroutine NRTL2 . . . . . . . . . . . . . . . . . . . . 184

Subroutine DEBHUC . . . . . . . . . . . . . . . . . . . 186

Subroutine MINFUN . . . . . . . . . . . . . . . . . . . 189

Subroutine TITLE . . . . . . . . . . . . . . . . . . . . 190

Input Data Sequence . . . . . . . . . . . . . . . . . . 192

Sample Input . . . . . . . . . . . . . . . . . . . . . . 194

Sample Output . . . . . . . . . . . . . . . . . . . . . 197

# INTRODUCTION

Fundamental knowledge of the VLE behavior of electrolytic solutions and electrolytes in mixed solvents is limited at present. The characterization of equilibrium properties of such systems has become important in the process design and process simulation of different processes.

In this study, two semi-empirical models have been developed based on molecular and ionic interactions in the solutions. Both the models combine modified forms of the NRTL equation and some form of the extended Debye-Hückel equation for physical and coulombic forces in a solution, respectively.

In Chapter 1 thermodynamic relationships for the VLE of electrolytic solutions are presented. In Chapters 2 and 3 the two models are developed. Also, their performance in correlating and predicting binary and ternary data is investigated. In Chapter 4 a comparative study of the two models is discussed. The detailed development of the two models is given in Appendices A, B and C.

# CHAPTER 1

# DEVELOPMENT OF FUNDAMENTAL RELATIONSHIPS FOR VAPOR-LIQUID EQUILIBRIUM IN ELECTROLYTIC SOLUTIONS

## ASBSTRACT

In vapor liquid equilibrium calculations it might be necessary to find y-T data from known x-P data or to find y-P data from given x-T data or it may be required to interpolate or extrapolate the limited x-y-P-T data. Secondly, in chemical processes and electrochemical energy conversion, a knowledge of the activities of the solvents and the electrolyte may be useful to characterize the solution behavior. Therefore, in this chapter, some important thermodynamic relationships have been developed which are applied to a binary or a ternary electrolytic solution.

## 1.1 Criteria of Equilibria

Consider an electrolytic solution at equilibrium at a temperature 'T' and pressure 'P' as shown in (figure 1.1). In the liquid phase, the electrolyte will be in ionic equilibrium due to the dissociation of the electrolyte into ions. In a concentrated electrolytic solution, one expects the presence of ion-pairs and ions depending upon the degree of dissociation. However, in this work, the electrolyte is assumed to be completely dissociated into ions for the concentration range and solvents under consideration. Therefore the liquid-phase, specifically, will consist of solvent molecules and ions. The vapor phase will consist of solvent molecules and the electrolyte in molecular form (if the electrolyte is volatile), because, for the temperature range considered in this work, dissociation of the electrolyte in the vapor phase is negligible.

When two phases are in equilibrium, the chemical potential for component i in the two phases will be the same

$$\mu_i^L = \mu_i^V \qquad (1\text{-}1)$$

The chemical potential in a single phase can be related to the fugacity of component i in a mixture by--

$$d\bar{G}_i = d\mu_i = RT\, d\ln \hat{f}_i \qquad (1\text{-}2)$$

A combination of equations (1-1) and (1-2), results in--

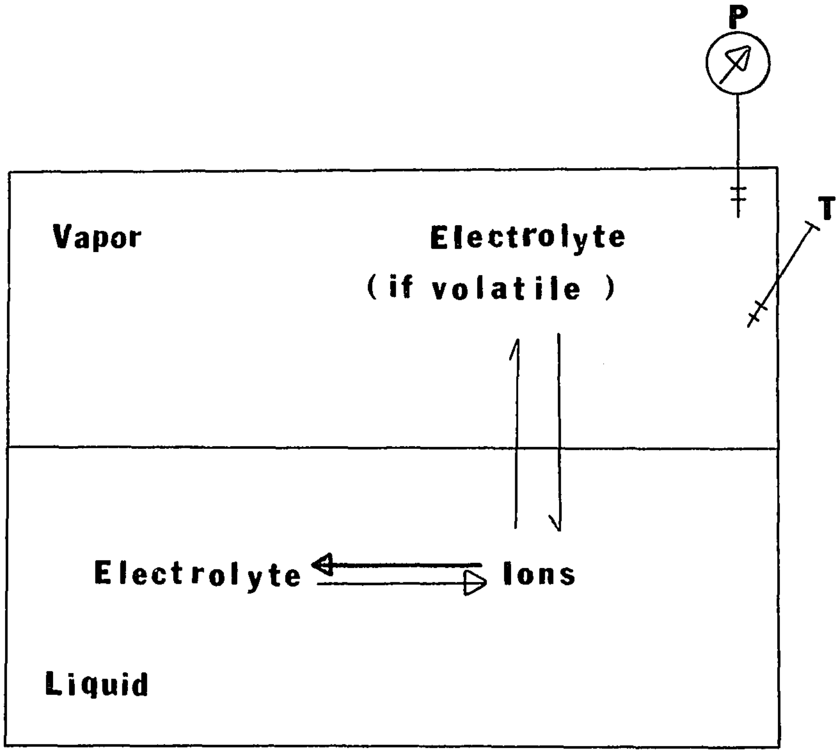


Figure 1.1 Representation of the Vapor-Liquid Equilibrium in Electrolytic Solutions

$$\hat{f}_i^L = \hat{f}_i^V \tag{1-3}$$

The fugacity of a component can be further expressed in terms of measurable quantities, viz., X,Y, P and T. A ternary mixture, in this study, is defined as a mixture of an electrolyte and two solvents and the ternary mixture, is considered a combination of three binary mixtures

(1) binary 1-2: electrolyte (1) - solvent (2)
(2) binary 1-3: electrolyte (1) - solvent (3)
(3) binary 2-3: solvent (2) - solvent (3)

An expression of the fugacity in terms of X-Y-P-T data, for an individual binary mixture and a ternary mixture, is considered in the following sections.

## 1.2 Mixture of Solvent (2) - Solvent (3) (Binary 2-3)

The liquid-phase fugacity for solvent 2 or 3 is given by

$$\hat{f}_i^L = X_i\gamma_i(P.E.)_i\phi_i^o\ P_i^o \qquad (1\text{-}4)$$

where,

$$(P.E.)_i = EXP[\int_0^{P_i^o} (\frac{v_i^{\circ L}}{RT})\,dP] \qquad (1\text{-}5)$$

$$\phi_i^o = EXP[-\ \frac{B_{ii}P_i^o}{RT}] \qquad (1\text{-}6)$$

The vapor phase fugacity is given by

$$\hat{f}_i^v = y_i\ P\ \hat{\phi}_i^v \qquad (1\text{-}7)$$

where,

$$\hat{\phi}_i^v = EXP[\frac{P}{RT}\ (B_{ii} + y_j^2\delta_{ij})] \qquad (1\text{-}8)$$

Combining equations (1-4) to (1-8) gives

$$X_i\gamma_iP_i^o = y_iP\ F_i \qquad (1\text{-}9)$$

and

$$F_i = \frac{\hat{\phi}_i^v}{\phi_i^o(P.E.)_i} \qquad (1\text{-}10)$$

At low pressures, and $T_{R_i} << 1.0$, $F_i \simeq 1.0$ (Appendix I)

This simplifies equation (1-9) to

$$X_i\gamma_iP_i^o = y_iP \qquad (1\text{-}11)$$

The total pressure is calculated by

$$P = X_2\gamma_2P_2^o + X_3\gamma_2P_3^o \qquad (1\text{-}12)$$

Equations (1-11) and (1-12) are used to correlate or predict the VLE in a solvent-solvent binary.

## 1.3 Mixture of an Electrolyte and a Solvent (Binary 1-2 or 1-3)

Case I volatile electrolyte

The liquid-phase fugacity for the electrolyte is given by

$$\hat{f}_1^L = m\gamma_\pm H_1 \tag{1-13}$$

where,

$$H_1 = f(T) \text{ at low pressures} \tag{1-14}$$

And the liquid-phase fugacity for the solvent is given by an equation similar to equation (1-11) in section (1-2)

$$f_i^L = X_i\gamma_i P_i^o \tag{1-15}$$

The vapor-phase fugacity for both the electrolyte and the solvent is

$$\hat{f}_\ell^v = y_\ell P, \text{ assuming } \hat{\phi}_\ell^v \simeq 1.0 \tag{1-16}$$

$$(\ell = \text{electrolyte or solvent})$$

Combining equations (1-13), (1-14) and (1-16)

$$m\gamma_\pm H_1 = y_1 P \tag{1-17}$$

$$X_i\gamma_i P^o = y_i P \tag{1-18}$$

Case II non-volatile electrolyte

The vapor phase will have only solvent molecules. Equation (1-18) will be the only equilibrium relationship for the solvent i

$$X_i\gamma_i P_i^o = P \tag{1-19}$$

Usually, binary electrolytic experimental data are expressed in terms of the osmotic coefficient $\phi$, which is defined as

$$\phi = - \frac{1000}{\nu m M_w} \ln \hat{a}_i \qquad (1\text{-}20)$$

for Case II, the activity and the activity coefficient of the solvent are interrelated by

$$\hat{a}_i = \frac{P}{P_i^o} = \gamma_i X_i \qquad (1\text{-}21)$$

## 1.4 Mixture of an Electrolyte (1) - Solvent (2) - Solvent (3) (Ternary 1-2-3)

Case I volatile electrolyte

The VLE relationship for the electrolyte and solvents (2) and (3) will be given by equations (1-17) and (1-18) respectively.

Case II non-volatile electrolyte

The vapor-phase will have only solvent (2) and (3) molecules. The VLE relationships will be the same as given in section (1.2), equations (1-11) and (1-12). In sections (1.2) to (1.4), the liquid mole-fraction of any component is defined, based on the complete dissociation of the electrolyte.

$$X_i = \frac{N_i}{\nu m + N_2 + N_3} \quad (i = 2 \text{ or } 3) \tag{1-22}$$

and

$$X_1 = \frac{m}{\nu m + N_2 + N_3} \tag{1-23}$$

Equations (1-1) to (1-23) developed in sections (1.1) to (1.4) are used for relating X-Y-P-T and mean molal activity coefficient data in a binary or a ternary mixture. However, in this work all the systems used are non-volatile, except for the HCl-$H_2O$ system where pressure is given as partial pressure of water.

### 1.5 Criteria for the Excess Gibbs Free Energy

In practical applications, where the liquid-phase composition and the temperature of the system are known, it is necessary to calculate the total pressure of the system and the vapor-phase composition or the mean molal activity coefficient of the electrolyte. In order to obtain this information the equations presented in sections (1.1) to (1.4) are applied, depending upon the type of system. For the above problem, the additional information needed are $P_i^o$, $H_1$ (if electrolyte is volatile) and liquid-phase activity coefficients ($\gamma_i$ and $\gamma_\pm$).

At a given temperature, the pure component vapor pressure can be estimated by equation (1-24) which expresses $P_i^o$ as a f(T)--

$$P_i^o = \mathrm{Exp}((C_1 + \frac{C_2}{C_3 + T} + C_4 T + C_5 T^2 + C_6 \ln T))760 \qquad (1\text{-}24)$$

At low pressures, the Henry's constant for the electrolyte (volatile) is expressed as a quadratic function of temperature--

$$H_1 = a_1^1 + b_1^1 T + c_1^1 T^2 \qquad (1\text{-}25)$$

For the activity coefficients, an expression is required in terms of the known variables i.e. liquid-phase composition and temperature of the system. In the liquid-phase the total excess Gibbs free energy can be developed as a function of known variables considering the different interaction forces in solution. The excess Gibbs free energy is then used to obtain expressions for the activity coefficients, as shown below--

$$\frac{G^E}{RT} = f(T,\ N_1,\ N_2\ \ldots) \qquad (1\text{-}26)$$

$$\ln\gamma_i = \frac{\partial G^E/RT}{\partial N_i}\Big]_{T,P,N_{\ell\neq i}} \qquad (1\text{-}27)$$

$$\ln\gamma_\pm^* = \frac{\partial G^E/RT}{\partial N_1}\Big]_{T,P,N_{\ell\neq 1}} \qquad (1\text{-}28)$$

$$\ln\gamma_\pm = \ln\gamma_\pm^* - \ln(0.001\nu m M_W + 1) \qquad (1\text{-}29)$$

where

$\gamma_\pm$ = mean molal activity coefficient

$\gamma_\pm^*$ = mean molar activity coefficient

In an electrolytic liquid solution, the total excess Gibbs free energy can be attributed to, mainly two type of molecular interactions. One interaction is due to the long-range electrostatic forces or ion-ion interactions. The other interaction takes into account the physical forces due to interactions of ion-solvent and solvent-solvent molecules. In Chapters 2 and 3, two different models have been considered for the excess Gibbs free energy. These models propose different forms of expressions to represent the non ideal behavior of a solution.

The equations developed in sections (1.1) to (1.5) are used first to fit experimental binary data with the activity coefficient expressions presented in Chapters 2 and 3. These are then extended to predict and/or correlate the ternary vapor-liquid equilibrium and mean molal activity coefficient data.

# CHAPTER 2

# CORRELATION AND PREDICTION OF VAPOR-LIQUID EQUILIBRIUM AND THE MEAN MOLAL ACTIVITY COEFFICIENT BY MODEL I IN ELECTROLYTIC SOLUTIONS

## ABSTRACT

Mean activity coefficient data and vapor pressure depression data of aqueous and nonaqueous electrolytic solutions are correlated successfully. The maximum molality applicable to model for aqueous-electrolytic and MeOH-electrolytic solutions can be approximated up to I = 6. The binary parameters are considered temperature independent within a 30 to 40$^{o}$C temperature range, presetting the ion-solvent nonrandom parameters $\alpha_{Ai}$ and $\alpha_{Bi}$ to 0.2 and 0.0 respectively. The prediction of ternary VLE and $\gamma_{\pm}$ is of acceptable quality with an average error of 0.028 in $\Delta Y$ and a 15% average error in $\gamma_{\pm}$ up to I = 2. Ternary data correlation of both isothermal and isobaric data are of good quality. In general, the prediction of binary data using the parameters obtained by ternary data regression is possible, with an average percent error in DP and $\gamma_{\pm}$ of 15%.

# Model I: Combination of the Extended Debye-Hückel Equation and the NRTL Equation

## 2.1 Excess Gibbs Free Energy Function

A complete theoretical account of the thermodynamic properties of electrolyte solutions must deal with both long range interionic and short range interactions between ions and solvent molecules. In a dilute electrolytic solution, the magnitude of the long range electrostatic forces is dominant. Based on this fact, Debye and Huckel developed a limiting law to predict the properties of a dilute solution by considering the electrical potential at a point in the solution in terms of the concentrations and charges of the ions and the properties of the solvent. Gronwall, Lamer and Sandved (1928) modified the Debye-Huckel equation by extending the potential functions with additional higher order terms. However, in a solution of an electrolyte in mixed solvents, the solvent-solvent interactions are of as much importance as those of ion-ion and ion-solvent interactions. Therefore, in Model I, an empirically extended form of the Debye-Huckel equation is combined with the non-random two liquid model (NRTL). The NRTL part of the equations not only accounts for solvent-solvent interactions, but describes unaccounted ion-solvent interactions also.

The equations for the excess Gibbs free energy, $G^E$, are as below

$$\frac{G^E}{RT}\bigg|_{\text{Total}} = \frac{G^E}{RT}\bigg|_{\text{Ext.D.H.}} + \frac{G^E}{RT}\bigg|_{\text{NRTL}} \tag{2-1}$$

$$\begin{aligned}\frac{G^E}{RT}\bigg|_{\text{Extended D.H.}} &= 2.303\nu \frac{M_w N_T}{1000} \frac{m}{I} |Z_+ Z_-| [-A_\gamma \frac{2}{\rho^3} \\ &\{(1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2}\} \\ &+ A_\gamma^2 \{\frac{2(aI - 2)}{3a^2} (1 + aI)^{1/2} + \frac{4}{3}\frac{1}{a^2}\}] \\ &+ N_T[(0.001\nu m M_w + 1)\ln(0.001\nu m M_w + 1) \\ &- 0.001\nu m M_w]\end{aligned} \tag{2-2}$$

where,

$\rho = 1.0$

$a = 1.5/|Z_+ Z_-|$

$A_\gamma$ = Debye-Hückel constant (see Appendix D)

$$\begin{aligned}\frac{G^E}{RT}\bigg]_{\text{NRTL}} &= \frac{1}{RT}[N_2 \frac{N_A Z_{\pm 2} + N_3 Z_{32}}{N_A G_{\pm 2} + N_3 G_{32} + N_2} \\ &+ N_3 \frac{N_A Z_{\pm 3} + N_2 Z_{23}}{N_A G_{\pm 3} + N_2 G_{23} + N_3} \\ &- N_A \frac{N_2 Z_{\pm 2}}{N_3 G_{32} + N_2} + \frac{N_3 Z_{\pm 3}}{N_2 G_{23} + N_3} \\ &+ N_A N_2 N_3 \frac{Z_{32} G_{\pm 2}}{(N_3 G_{32} + N_2)^2} + \frac{Z_{23} G_{\pm 3}}{(N_2 G_{23} + N_3)^2}]\end{aligned} \tag{2-3}$$

where,

$$Z_{ij} = \Delta g_{ij} G_{ij}$$

$$G_{ij} = \text{EXP}[-\alpha_{ij} \frac{\Delta g_{ij}}{RT}] \qquad (2\text{-}4)$$

$$\alpha_{ij} = \alpha_{ji}$$

$$\Delta g_{ij} \neq \Delta g_{ji}$$

$$Z_{\pm i} = Z_{Ai} + \frac{\nu_B}{\nu_A} Z_{Bi}$$

$$G_{\pm i} = G_{Ai} + \frac{\nu_B}{\nu_A} G_{Bi} \qquad (2\text{-}5)$$

$$Z_{Ai} = \Delta g_{Ai} G_{Ai} \text{ and } Z_{Bi} = \Delta g_{Bi} G_{Bi}$$

$$G_{Ai} = \text{EXP}[-\alpha_{Ai} \frac{\Delta g_{Ai}}{RT}]$$

$$G_{Bi} = \text{EXP}[-\alpha_{Bi} \frac{\Delta g_{Bi}}{RT}] \qquad (2\text{-}6)$$

A stepwise procedure for the development of these expressions is given in Appendix B, sections B.1 and B.2.

## 2.2 Procedure: Data Reduction and Prediction

In Model I, each of the three binaries have two adjustable parameters. In order to predict ternary behavior it is necessary to evaluate the binary parameters first. Also, the accuracy of the binary data correlation will justify the extension of Model I to ternary or multicomponent mixtures. A stepwise scheme for the data correlation and prediction is depicted in figure 2.1. A nonlinear subroutine LSQ2 is used in the binary or ternary data regression.

The detailed steps for binary and ternary correlation with different objective functions have been discussed separately, as below

### A. Binary 2-3: Mixture of Solvent (2) - Solvent (3)

The activity coefficient expressions for these type of systems are obtained by substituting m = 0.0 and $N_A$ = 0.0 in equations (2-2) and (2-3) and differentiating the resulting excess Gibbs free energy function. This results in the original NRTL equation of Renon and Prausnitz (1968)--

$$\ln\gamma_i \equiv \frac{x_j^2}{RT}\left[\frac{Z_{ji}G_{ji}}{(X_jG_{ji} + X_i)^2} + \frac{Z_{ij}}{(X_iG_{ij} + X_j)^2}\right] \qquad (2\text{-}7)$$

$G_{ij}$ and $Z_{ij}$ are given by equation (2-4).

The experimental X-y-P-T data for these binaries are correlated for the two temperature independent parameters--$\Delta g_{23}$ and $\Delta g_{32}$ by presetting $\alpha_{23}$ to -1.0 as recommended by Marina

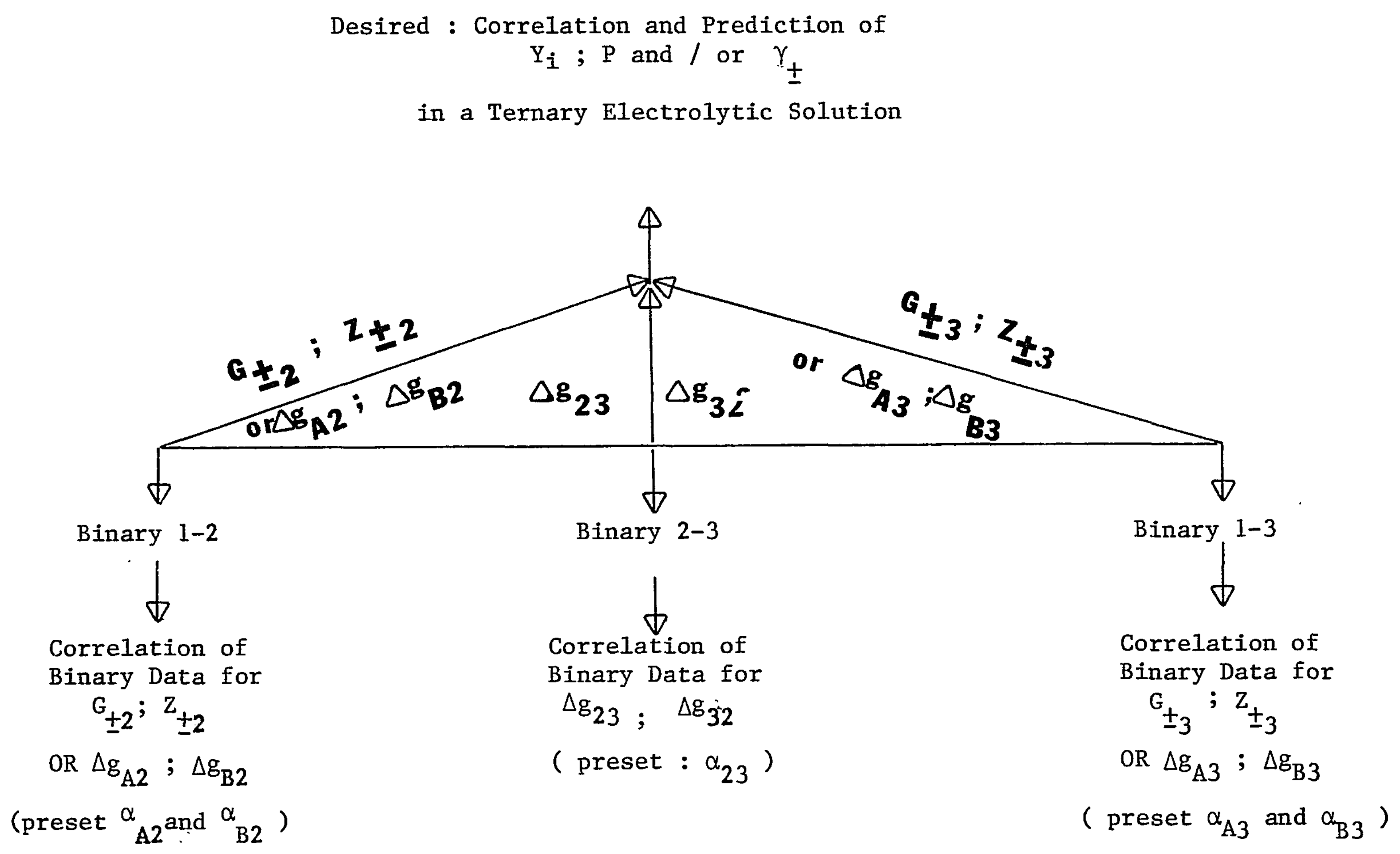


Figure 2.1 A Stepwise Scheme for Correlation and Prediction of the VLE and Mean Molal Activity Coefficients with Model I

and Tassios (1972) or to 0.2, 0.3, 0.47 as recommended by Renon and Prausnitz (1968). The objective function used in the regression for this type of binary system is

$$\text{o.f.} = \sum_{s=1}^{NP} \sum_{i=2}^{3} \left[\frac{\gamma_{s_{ca}} - \gamma_{s_E}}{\gamma_{s_E}}\right]_i^2 \qquad (2\text{-}8)$$

NP = # of points in a system

$\gamma_{s_E}$ is calculated using experimental X-y-P-T data with equations (1-11) and (1-12).

### B. Binary 1-2 or 1-3: Mixture of an Electrolyte and a Solvent

The activity coefficient expressions are given by equations (A-5), (A-10), (A-8), (A-12) and (A-9). Experimental binary data can be correlated either through regression for $G_{\pm i}$ and $Z_{\pm i}$ or $\Delta g_{Ai}$ and $\Delta g_{Bi}$ in equations (2-5) and (2-6). However, the temperature independent form ($\Delta g_{Ai}$ and $\Delta g_{Bi}$) would require values of $\alpha_{Ai}$ and $\alpha_{Bi}$. These two forms of the parameters make Model I applicable to both isothermal and isobaric data. Two objective functions are used to evaluate the binary parameters.

$$\text{o.f. \#1} = \sum_{s=1}^{NP} \left[\frac{\gamma_{s_{ca}} - \gamma_{s_E}}{\gamma_{s_E}}\right]_{i\,(=2\text{ or }3)}^2 + \sum_{s=1}^{NP} \left[\frac{\gamma_{\pm_{ca}} - \gamma_{\pm_E}}{\gamma_{\pm_E}}\right]^2 \qquad (2\text{-}9)$$

$$\text{o.f. \#2} = \sum_{s=1}^{NP} \left[\frac{DP_{ca} - DP_E}{DP_E}\right]_s^2 + \sum_{s=1}^{NP} \left[\frac{\gamma_{\pm_{ca}} - \gamma_{\pm_E}}{\gamma_{\pm_E}}\right]_s^2 \qquad (2\text{-}10)$$

where,

$$DP = P_i^o - P \qquad (2\text{-}11)$$

$\gamma_{i,EXP}$ and DP are calculated using equations (1-17) to (1-21). If experimental binary data are available only as vapor pressure vs molality, the second term in equations (2-9) and (2-10) is zero. In the case where the data are $\gamma_{\pm}$ vs molality only, the first term in equations (2-9) and (2-10) is zero.

### C. Prediction of Ternary VLE ($y_2$, $y_3$, P and $\gamma_{\pm}$)

The binary parameters obtained by individual binary data correlation with the best objective function [Equation (2-10)] are used to predict the activity coefficients $\gamma_2$, $\gamma_3$ and $\gamma_{\pm}$ in a ternary mixture with equations (2-12) to (2-18) and (1-29).

$$\ln\gamma_{\pm}^{*} = \ln\gamma_{\pm \mathrm{Ext.D.H.}}^{*} + \ln\gamma_{\pm \mathrm{NRTL}}^{*} \tag{2-12}$$

$$\ln\gamma_{\pm}^{*} = 2.303[-A_{\gamma}\frac{I^{1/2}}{1+\rho I^{1/2}} + A_{\gamma}^{2}\frac{I}{(1+aI)^{2}}]|Z_{+}Z_{-}| + \ln(0.001\nu m M_{w} + 1) \tag{2-13}$$

$$\ln\gamma_{\pm \mathrm{NRTL}}^{*} = \frac{\nu_A}{\nu}\frac{1}{RT}[\frac{X_2\{X_3G_{32}Z_{\pm 2} + X_2Z_{\pm 2} - X_3Z_{32}G_{\pm 2}\}}{(X_AG_{\pm 2} + X_3G_{32} + X_2)^2} + \frac{X_3\{X_2G_{23}Z_{\pm 3} + X_3Z_{\pm 3} - X_2Z_{23}G_{\pm 3}\}}{(X_AG_{\pm 3} + X_2G_{23} + X_3)^2} - \frac{X_2Z_{\pm 2}}{(X_3G_{32} + X_2)} - \frac{X_3Z_{\pm 3}}{(X_2G_{23} + X_3)} + \frac{X_2X_3Z_{32}G_{\pm 2}}{(X_3G_{32} + X_2)^2} + \frac{X_2X_3Z_{23}G_{\pm 3}}{(X_2G_{23} + X_3)^2}] \tag{2-14}$$

$$\ln\gamma_{i(2\text{ or }3)} = \ln\gamma_{i,\text{Ext.D.H.}} + \ln\gamma_{i,\text{NRTL}} \tag{2-15}$$

$$\ln\gamma_{i\text{Ext.D.H.}} = 2.303\ \frac{\nu m}{1000}[M_{wi}\ \frac{A_\gamma}{3}\ I^{1/2}\ \sigma_1(\rho I^{1/2})$$

$$-\ N_T\ M_w\ I^{1/2}\sigma_1^1(\rho I^{1/2})\ \frac{\partial A_\gamma}{\partial N_i} + M_{wi}\ A_\gamma^2\ \frac{I}{2}$$

$$\psi_1(aI) + N_T\ M_w\ A_\gamma\ \frac{\partial A_\gamma}{\partial N_i}\ I\ \psi_1^1(aI)]\,|Z_+Z_-|$$

$$+ \ln(0.001\nu mM_w + 1) - 0.001\nu mM_w \tag{2-16}$$

where,

$\sigma_1(\rho I^{1/2})$, $\psi_1(aI)$ are defined in equations (A-12) and (A-13)

$\sigma_1^1(\rho I^{1/2})$, $\psi_1^1(aI)$ are given by equations (B-35) and (B-36)

$$\ln\gamma_{i\text{NRTL}} = \frac{1}{RT}[\frac{X_AG_{\pm i}Z_{\pm i} + X_AX_jZ_{\pm i}G_{ji} + X_AX_jZ_{ji}G_{\pm i} + X_j^2Z_{ji}G_{ji}}{(X_AG_{\pm i} + X_jG_{ji} + X_i)^2}$$

$$+\ \frac{X_AX_jZ_{ij}G_{\pm j} - X_AX_jZ_{\pm j}G_{ij} + X_j^2Z_{ij}}{(X_AG_{\pm j} + X_iG_{ij} + X_j)^2}$$

$$+\ X_AX_j\ \frac{Z_{ji}G_{\pm i} - Z_{\pm i}G_{ji}}{(X_jG_{ji} + X_i)^2} + \frac{Z_{ij}G_{\pm j} + Z_{\pm j}G_{ij}}{(X_iG_{ij} + X_j)^2}$$

$$-\ 2X_AX_iX_j\ \frac{Z_{ji}G_{\pm i}}{(X_jG_{ji} + X_i)^3} + \frac{Z_{ij}G_{\pm j}G_{ij}}{(X_iG_{ij} + X_j)^3}\ ] \tag{2-17}$$

where,

$$X_A = \nu_AX_1 \tag{2-18}$$

$$i = 2 \text{ and } j = 3$$

or

$$i = 3 \text{ and } j = 2$$

In equations (2-13) and (2-16) the Debye Hückel constant and the slope of the Debye Hückel constant are calculated by a procedure given in Appendix D. Once the solvent activity coefficients are estimated, they are then used to predict $y_i$ and p with equations (1-11) and (1-12).

## D. Correlation of Ternary Data

The activity coefficient equations (2-12) to (2-18) with equations (1-29), (1-11) and (1-12) are used in ternary data correlation. Three objective functions are attempted

$$\text{o.f. \#1} = \sum_{s=1}^{NP} \sum_{j=2}^{NP} \left[\frac{\gamma_{j_{ca}} - \gamma_{j_E}}{\gamma_{j_E}}\right]_s^2 + \sum_{s=1}^{NP} \left[\frac{\gamma_{\pm_{ca}} - \gamma_{\pm_E}}{\gamma_{\pm_E}}\right]_s^2 \qquad (2\text{-}19)$$

$$\text{o.f. \#2} = \sum_{s=1}^{NP} \left[\frac{P_{ca} - P_E}{P_E}\right]_s^2 + \sum_{s=1}^{NP} \left[(Y_{3_{ca}} - Y_{3_E}) \times 10\right]_s^2$$

$$+ \sum_{s=1}^{NP} \left[\frac{\gamma_{\pm_{ca}} - \gamma_{\pm_E}}{\gamma_{\pm_E}}\right]_s^2 \qquad (2\text{-}20)$$

$$\text{o.f. \#3} = \sum_{s=1}^{NP} \sum_{j=2}^{NP} \left[\frac{\gamma_{j_{ca}} - \gamma_{j_E}}{\gamma_{j_E}}\right]_s^2 + \sum_{s=1}^{NP} \left[(Y_{3_{ca}} - Y_{3_E}) \times 10\right]_s^2$$

$$+ \sum_{s=1}^{NP} \left[\frac{\gamma_{\pm_{ca}} - \gamma_{\pm_E}}{\gamma_{\pm_E}}\right]_s^2 \qquad (2\text{-}21)$$

In equations (2-20) and (2-21), a weighing factor of ten is used for the deviation in the vapor-phase composition in order to make the magnitude of this term equal to that of the relative percent error in $\Delta P$ and $\gamma_{\pm}$. In the case where the ternary data are in the form of m-X-y-P-T only, the second term in equation (2-19) is zero and the third term in equations (2-20) and (2-21) is zero. If the data are m-X vs $\gamma_{\pm}$ only, the first term in equation (2-19), and the first and second terms in equations (2-20) and (2-21) are zero.

The activity coefficient expressions [(2-13) to (2-18)] have six adjustable parameters for a ternary mixture. However, in this work, data are regressed only for four parameters with preset values of $\Delta g_{23}$ and $\Delta g_{32}$ obtained by binary 2-3 data correlation, corresponding to $\alpha_{23} = -1.0$. If the experimental data are isothermal, the parameters evaluated are $G_{\pm 2}$, $Z_{\pm 2}$, $G_{\pm 3}$ and $Z_{\pm 3}$. For isobaric data, the temperature independent parameters $\Delta g_{A2}$, $\Delta g_{B2}$, $\Delta g_{A3}$ and $\Delta g_{B3}$ are evaluated.

A stepwise procedure was used for the rapid convergence of the regression program for the four parameters. In the case of isothermal data, first $G_{\pm 2}$ and $Z_{\pm 2}$ were set to the values obtained by binary aqueous electrolyte data correlation and the ternary data were regressed for $G_{\pm 3}$ and $Z_{\pm 3}$. The second time $G_{\pm 3}$ and $Z_{\pm 3}$ were fixed at the regressed values obtained in the first step and $G_{\pm 2}$ and $Z_{\pm 2}$ were evaluated by ternary data correlation. The third time, the values of $G_{\pm 2}$ and $Z_{\pm 3}$ obtained in the second trial were used and the step one was repeated to obtain new values of $G_{\pm 3}$ and $Z_{\pm 3}$. This procedure is performed for four or five trials. Finally, the four parameters are evaluated together by ternary data reduction using the values of $G_{\pm 2}$, $Z_{\pm 2}$, $G_{\pm 3}$ and $Z_{\pm 3}$ obtained from the last step as starting values in the regression.

### E. Binary Data Prediction Using the Parameters Evaluated by Ternary Data Reduction

The binary parameters [Section 2.2 D] obtained in ternary data correlation are used to predict the activity coefficients for binaries 1-2 and 1-3, with equations (A-5), (A-8), (A-10), (A-11) and (A-9). These are then used to calculate vapor pressure depressions.

## 2.3 Results

A list of binary and ternary systems used in this study is presented in Tables G.1 and G.2.

### A. Binary Data Reduction

The solvent-solvent binary data correlation was obtained with two values of $\alpha_{23}$. Both the values result in the same order of $\Delta Y_{AVG}$ and $\Delta P_{AVG}$, Table G.3. The quantities $\Delta Y_{AVG}$ and $\Delta P_{AVG}$ are defined below

$$\Delta Y_{AVG} = \frac{\sum_{s=1}^{NP} |\Delta Y|_s}{NP} \tag{2-22}$$

$$\Delta P_{AVG} = \frac{\sum_{s=1}^{NP} |\Delta P|_s}{NP} \tag{2-23}$$

where

$$\Delta Y = Y_{3_{ca}} - Y_{3_E} \tag{2-24}$$

$$\Delta P = P_{ca} - P_3 \tag{2-25}$$

The aqueous or nonaqueous electrolytic binary results are presented in Tables G.4 to G.7. The quantities used to define the accuracy of the correlation are as below

$$\text{Avg \% error in } \gamma_\pm = \frac{\sum_{s=1}^{NP} \left| \frac{\gamma_{\pm_{ca}} - \gamma_{\pm_E}}{\gamma_{\pm_E}} \right|_s \times 100}{NP} \tag{2-26}$$

$$\text{Avg \% error in DP} = \frac{\sum_{s=1}^{NP} \left| \frac{D_{P_{ca}} - D_{P_E}}{D_{P_E}} \right|_s \times 100}{NP} \tag{2-27}$$

The objective function #2, given in equation (2-10) gives a better fit of the data, Tables G.4 and G.5, specifically for the nonaqueous electrolytic binaries. In further studies, only objective function #2 is used in the binary data correlation, except for the HCl-$H_2O$ binary at $25^{o}C$. Since HCl is a volatile electrolyte, and the experimental data are in the form of partial pressure of water in the vapor phase, objective function #1 is used.

## B. Temperature Dependency of the Binary Parameters

Next, the temperature dependency of the binary parameters was determined. The parameters $\Delta g_{Ai}$ and $\Delta g_{Bi}$ (equation 2-6) were evaluated by presetting $\alpha_{Ai}$ and $\alpha_{Bi}$. The meaningful values of $\alpha_{Ai}$ and $\alpha_{Bi}$ will be those which can interrelate two forms of the parameters: $G_{\pm i}$; $Z_{\pm i}$ and $\Delta g_{Ai}$; $\Delta g_{Bi}$. It was observed that one of the two $\alpha$'s ($\alpha_{Ai}$ or $\alpha_{Bi}$) should be set to zero in order to represent one form of the parameters in terms of the other form. In this work, $\alpha_{Bi}$ is set to zero and the value of $\alpha_{Ai}$ was selected arbitrarily and is set equal to 0.2. The results of data reduction obtained for aqueous/nonaqueous electrolytic binaries in the temperature independent form are given in Tables G.6 and G.7. The accuracy of binary data correlation with $\Delta g_{Ai}$ and $\Delta g_{Bi}$ is of the same order as that obtained with $G_{\pm i}$ and $Z_{\pm i}$ (Tables G.4 and G.5). Typical results are given for the system NaCl-$H_2O$ at $25^{o}C$ in Figure 2.2 and the system LiBr-MeOH at $15^{o}C$, Figure 2.3. However, to test the validity of 0.2 and 0.0 for $\alpha_{Ai}$ and $\alpha_{Bi}$ respectively, different values of $\alpha_{Ai}$ and $\alpha_{Bi}$ were also tried, Tables G.8 and G.9. The

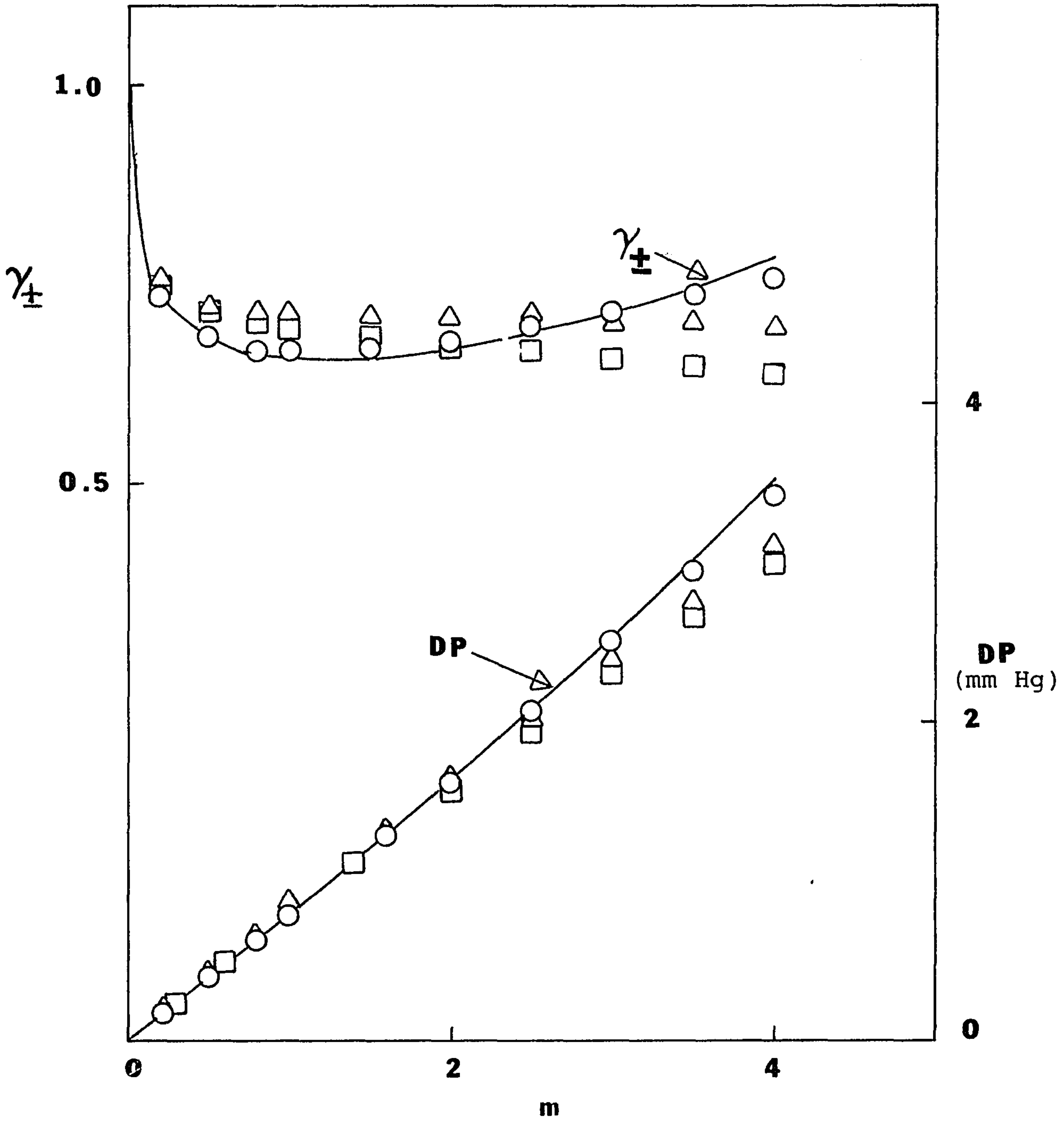


Figure 2.2 Comparison of Experimental Mean Molal Activity Coefficients and Vapor Pressure Depressions with those Predicted by Model I for the System NaCl-$H_2O$ at 25°C . ____ Experimental , Robinson & Stokes (1955) ; O Correlation Pair of Roots#1($\alpha_{A2}$=0.2 , $\alpha_{B2}$=0.0); Δ Correlation , Pair of Roots # 2 ( $\alpha_{A2}$=0.2, $\alpha_{B2}$=0.0) ; □ Predicted Using Parameters of 60°C (see Table 2.1 for the roots).

Figure 2.3 Comparison of Experimental Vapor Pressure Depressions with Predicted and Correlated by Model I for the System LiBr-MeOH at 15°C

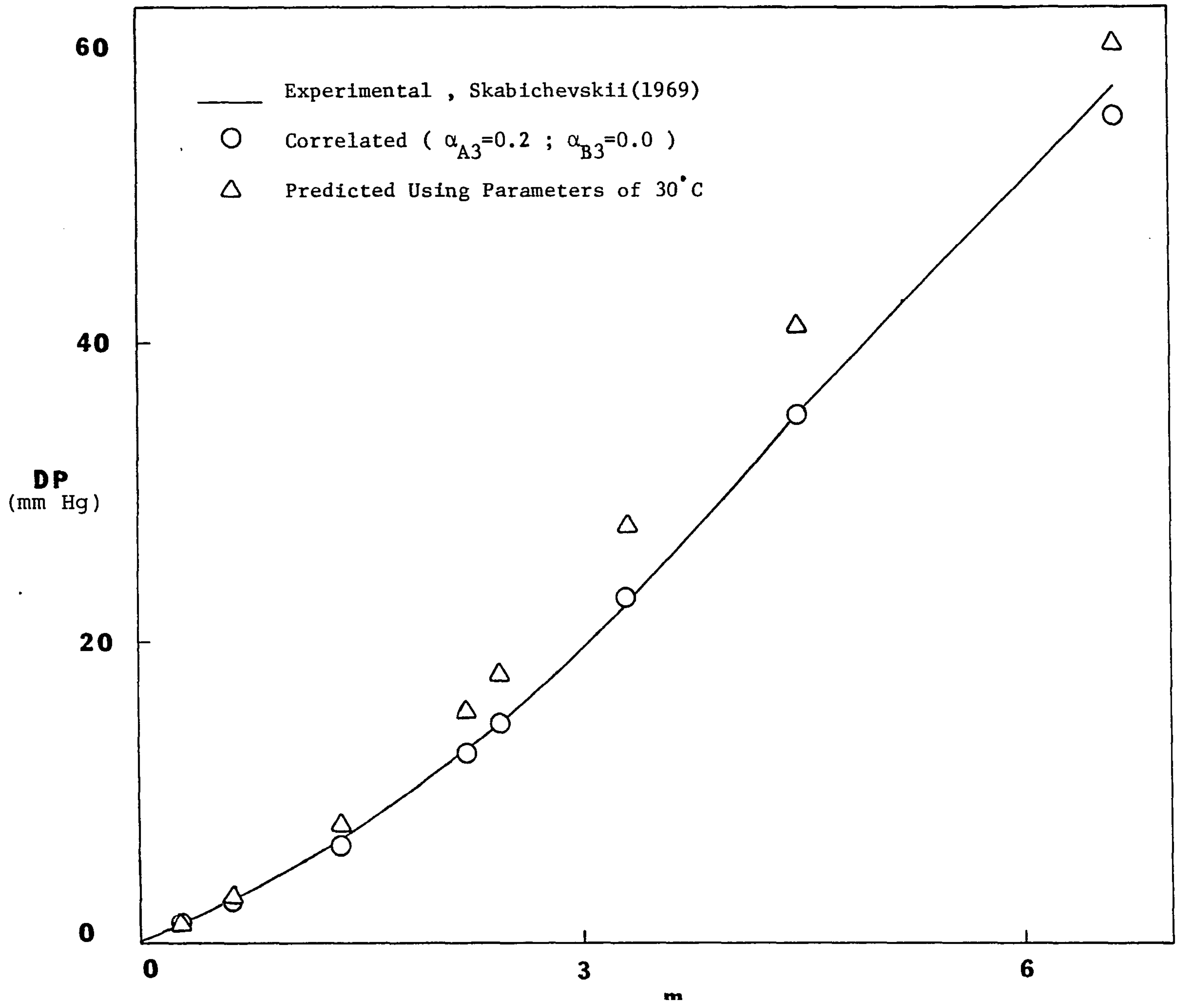


TABLE 2.1 Multiplicity of Roots in Model #1 for Aqueous Electrolytic Solutions with Preset Values of

$\alpha_{A2} = 0.2$ and $\alpha_{B2} = 0.0$

Maximum m = 4.0

| System | T (°C) | $\Delta g_{A2}$ | $\Delta g_{A3}$ | % Error in $\gamma_{\pm}$ Max | % Error in $\gamma_{\pm}$ Avg | % Error in DP Max | % Error in DP Avg |
|---|---|---|---|---|---|---|---|
| NaCl-$H_2O$ | 25 | -32.396 | 444.79 | 3.4 | 1.2 | 3.3 | 1.0 |
| NaCl-$H_2O$ | 60 | -34.009 | 399.74 | 2.6 | 1.4 | 2.2 | 0.9 |
| NaCl-$H_2O$ | 70 | -29.051 | 227.36 | 4.1 | 2.4 | 4.0 | 1.6 |
| NaCl-$H_2O$ | 80 | -34.000 | 349.27 | 2.2 | 1.2 | 2.0 | 0.9 |
| NaCl-$H_2O$ | 90 | -36.82 | 427.07 | 1.0 | 0.6 | 0.6 | 0.4 |
| NaCl-$H_2O$ | 100 | -30.668 | 228.68 | 3.9 | 2.2 | 5.0 | 2.2 |
| NaBr-$H_2O$ | 25 | -24.258 | 174.11 | 9.4 | 4.0 | 8.1 | 2.3 |
| NaCl-$H_2O$ | 25 | 156.75 | 18.271 | 11.0 | 6.0 | 11.7 | 3.7 |
| NaCl-$H_2O$ | 60 | 171.48 | 21.695 | 9.8 | 6.0 | 9.8 | 3.6 |
| NaCl-$H_2O$ | 70 | 187.42 | 24.751 | 10.1 | 6.1 | 10.3 | 3.8 |
| NaCl-$H_2O$ | 80 | 155.12 | 28.38 | 10.3 | 6.3 | 10.7 | 4.0 |
| NaCl-$H_2O$ | 90 | 199.24 | 32.278 | 11.0 | 6.5 | 11.0 | 4.2 |
| NaCl-$H_2O$ | 100 | 138.47 | 36.876 | 11.6 | 6.9 | 11.4 | 5.2 |
| NaBr-$H_2O$ | 25 | 163.29 | 12.545 | 12.8 | 6.0 | 11.6 | 3.3 |

results are of poor quality. This again reinforces the use of $\alpha_{Ai} = 0.2$ and $\alpha_{Bi} = 0.0$.

The parameters obtained with $\alpha_{Ai=0.2}$ and $\alpha_{Bi=0.0}$ were used to predict binary data from one temperature to another temperature (Table G.10). In general, for an aqueous electrolyte binary, the data are predicted with a 15 percent average error in $\gamma_{\pm}$ and a seven percent average error in DP within a 30-40°C temperature range. The prediction of binary data for the system NaCl-$H_2O$ at 25°C using the parameters obtained by the data correlation of the system NaCl-$H_2O$ at 60°C is depicted in Figure 2.2. The availability of nonaqueous electrolytic binary data is limited, therefore it is not possible to establish a temperature range for such binary systems. However, for the two systems LiBr-MeOH and LiCl-MeOH (Table G.10), the results show that the data prediction is less reliable than aqueous electrolytic binaries. The typical result for the system LiBr-MeOH at 15°C is shown in Figure 2.3.

Aqueous electrolytic binary data reduction also indicated a multiplicity of roots for binary parameters (Table 2.1). A binary has two pair of roots. It is interesting to note that the pair of roots with positive values of $\Delta g_{A2}$ should be used to predict data from one temperature to the other temperature, though these sets of parameters are less accurate in correlating binary data than the other pair of roots (Tables 2.1 and 2.2).

TABLE 2.2 Prediction of Binary VLE Data by Model #1 at One Temperature Using Binary Parameters (2nd Pair of Roots) at Another Temperature with Preset Values of $\alpha_{A2} = 0.2$ and $\alpha_{B2} = 0.0$

| System | # of Points | Max 'm' | T (°C) | Parameters Used of T (°C) | Parameters Used $\Delta g_{A2}$ | Parameters Used $\Delta g_{B2}$ | % Error in $\gamma_{\pm}$ Max | % Error in $\gamma_{\pm}$ Avg | % Error in DP Max | % Error in DP Avg |
|---|---|---|---|---|---|---|---|---|---|---|
| $NaCl-H_2O$ | 17 | 4.0 | 25 | 100 | 138.47 | 36.876 | 45.3 | 11.6 | 31.9 | 8.3 |
| $NaCl-H_2O$ | 11 | 4.0 | 60 | 100 | 138.47 | 36.876 | 35.9 | 11.6 | 24.2 | 8.2 |
| $NaCl-H_2O$ | 11 | 4.0 | 70 | 100 | 138.47 | 36.876 | 30.5 | 9.7 | 21.5 | 7.1 |
| $NaCl-H_2O$ | 11 | 4.0 | 80 | 100 | 138.47 | 36.876 | 24.4 | 7.8 | 18.3 | 6.1 |
| $NaCl-H_2O$ | 11 | 4.0 | 90 | 100 | 134.47 | 36.876 | 17.7 | 6.8 | 15.1 | 5.1 |
| $NaCl-H_2O$ | 11 | 4.0 | 60 | 25 | 156.75 | 18.271 | 13.2 | 7.6 | 6.6 | 3.2 |
| $NaCl-H_2O$ | 11 | 4.0 | 70 | 25 | 156.76 | 18.271 | 16.4 | 10.9 | 5.8 | 3.4 |
| $NaCl-H_2O$ | 11 | 4.0 | 80 | 25 | 156.75 | 18.271 | 21.2 | 14.9 | 7.0 | 4.0 |
| $NaCl-H_2O$ | 11 | 4.0 | 90 | 25 | 156.75 | 18.271 | 27.3 | 19.3 | 8.5 | 5.3 |
| $NaCl-H_2O$ | 11 | 4.0 | 100 | 25 | 156.275 | 18.271 | 35.4 | 24.6 | 10.7 | 8.0 |
| $NaCl-H_2O$ | 11 | 4.0 | 25 | 60 | 171.48 | 21.695 | 18.6 | 5.7 | 15.4 | 4.0 |
| $NaCl-H_2O$ | 11 | 4.0 | 70 | 60 | 171.48 | 21.695 | 12.7 | 7.4 | 7.5 | 3.5 |
| $NaCl-H_2O$ | 11 | 4.0 | 80 | 60 | 171.48 | 21.695 | 16.8 | 11.0 | 5.9 | 3.5 |
| $NaCl-H_2O$ | 11 | 4.0 | 90 | 60 | 171.48 | 21.695 | 22.3 | 15.3 | 7.3 | 4.1 |
| $NaCl-H_2O$ | 11 | 4.0 | 100 | 60 | 171.48 | 21.695 | 29.3 | 20.4 | 9.3 | 6.5 |

TABLE 2.3 Performance of Model I in Correlating Binary VLE Data for Different Molality Ranges

| System | Max 'm' | # of Points | T (°C) | $G_{\pm i}$ | $Z_{\pm i}$ | % Error in $\gamma_{\pm}$ |  | % Error in DP |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Max | Avg | Max | Avg |
| $CaCl_2$-$H_2O$ | 2.0 | 15 | 25 | 24.1 | 17.026 | 3.4 | 1.3 | 2.2 | 1.3 |
|  | 3.0 | 17 | 25 | 27.31 | 15.854 | 9.3 | 2.6 | 4.4 | 2.0 |
|  | 4.0 | 19 | 25 | 31.499 | 14.72 | 16.8 | 4.8 | 6.3 | 3.0 |
|  | 5.0 | 21 | 25 | 37.755 | 13.545 | 24.2 | 7.6 | 7.7 | 4.3 |
|  | 6.0 | 23 | 25 | 41.19 | 13.041 | 32.3 | 10.3 | 9.2 | 5.0 |
| LiCl-$H_2O$ | 4.0 | 6 | 60 | 0.0294 | -77.911 | - | - | 4.6 | 2.4 |
|  | 5.0 | 9 | 60 | 0.0316 | -245.0 | - | - | 7.2 | 4.2 |
|  | 6.0 | 11 | 60 | 0.0563 | -180.44 | - | - | 8.3 | 4.7 |
|  | 7.0 | 13 | 60 | 0.0213 | -585.13 | - | - | 9.4 | 5.1 |
|  | 8.0 | 14 | 60 | 0.029 | -465.38 | - | - | 10.0 | 5.4 |
|  | 9.0 | 16 | 60 | 0.054 | -286.8 | - | - | 10.8 | 5.7 |
| LiCl-MeOH | 4.0 | 8 | 60 | 5.877 | 84.288 | - | - | 12.2 | 5.8 |
|  | 5.0 | 10 | 60 | 5.3481 | 88.825 | - | - | 15.6 | 6.4 |
|  | 6.0 | 11 | 60 | 5.086 | 91.269 | - | - | 17.5 | 7.3 |
|  | 8.0 | 12 | 60 | 4.8525 | 93.557 | - | - | 21.7 | 8.6 |

No multiplicity of roots was observed for the nonaqueous electrolyte binaries.

## C. Maximum Molality Applicability

Before this model was extended to ternary systems, its maximum molality applicability was investigated. Three typical systems were used for this: $CaCl_2$-$H_2O$ at 25°C, LiCl-$H_2O$ at 60°C and LiCl-MeOH at 60°C (Table 2.3). The data correlation for binaries $CaCl_2$-$H_2O$ and LiCl-$H_2O$ indicate that for aqueous electrolytic mixtures the correlation yields a good fit up to $I = 9$, whereas for the system LiCl-MeOH, the data are fitted within an average fifteen percent error only up to $I = 6$. This molality limit will be different for different electrolytes, solvents and temperatures of the system. Based on the above study in water and MeOH solvents, the maximum concentration range of an electrolyte is considered $I = 6$.

## D. Ternary Data Prediction

The binary parameters obtained by the individual binary data reduction were used to predict isothermal $\gamma_\pm$, vapor phase compositions and the total pressures in ternary solutions. For the solvent-solvent binary, both sets of parameters were used corresponding to two different values of $\alpha_{23}$. The best results are tabulated in Tables 2.4 and 2.5.

Out of four ternary systems with m vs $\gamma_\pm$ data, only the two systems LiCl-$H_2O$-MeOH at 25°C and HCl-$H_2O$-MeOH at 25°C

TABLE 2.4 Prediction of $\gamma_\pm$ in Ternary Mixtures Using Binary Parameters from Tables G.4 (Binary 1-2); G.5 (Binary 1-3); and G.3 (Binary 2-3)

| System | # of Points | Max 'm' | T (°C) | $\alpha_{23}$ | $\Delta g_{23}$ | $\Delta g_{32}$ | $G_{\pm 2}$ | $Z_{\pm 2}$ | $G_{\pm 3}$ | $Z_{\pm 3}$ | % Error in $\gamma_\pm$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | Max | Avg |
| $HCl$-$H_2O$-MeOH | 48 | 2.0 | 25 | -1.0 | -150.9 | 336.47 | 0.1061 | -33.295 | 10.9 | 39.70 | 50.7 | 13.5 |
| $LiCl$-$H_2O$-MeOH | 45 | 1.0 | 25 | -1.0 | -150.9 | 336.47 | 0.0557 | -81.532 | 6.1745 | 56.382 | 52.0 | 15.3 |
| $HCl$-$H_2O$-MeOH | 48 | 2.0 | 25 | 0.3 | 806.1 | -321.4 | 0.1061 | -33.295 | 10.9 | 39.70 | 28.2 | 4.1 |
| $LiCl$-$H_2O$-MeOH | 45 | 1.0 | 25 | 0.3 | 806.1 | -321.4 | 0.1061 | -33.295 | 10.9 | 39.70 | 44.6 | 13.6 |
| *$LiCl$-$H_2O$-EtOH | 23 | 0.1 | 25 | -1.0 | 105.7 | 383.87 | 0.094 | -34.79 | 117.0 | 12.35 | 28.7 | 8.4 |

*Results are shown excluding two points because error for this two points is >60%.

TABLE 2.5 Prediction of Vapor-Phase Composition and Total Pressure by Model #1 Using Binary Parameters from Tables G.4 (Binary 1-2); G.5 (Binary 1-3); and G.3 (Binary 2-3)

| System | # of Points | Max 'm' | P or T (°C) | $\alpha_{23}$ | $\Delta g_{23}$ | $\Delta g_{32}$ | $\Delta g_{A2}$ or $G_{\pm 2}$ | $\Delta g_{B2}$ or $Z_{\pm 2}$ | $\Delta g_{A3}$ or $G_{\pm 3}$ | $\Delta g_{B3}$ or $Z_{\pm 3}$ | ΔY Max | ΔY Avg | ΔP (mmHg) Max | ΔP (mmHg) Avg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $LiCl-H_2O-EtOH$ | 20 | 1.0 | 25 | 0.3 | 894.5 | -62.0 | 0.0557 | -81.532 | 4.1 | 144.2 | 0.091 | 0.028 | 5.2 | 1.4 |
| $LiCl-H_2O-EtOH$ | 20 | 1.0 | 25 | -1.0 | 105.8 | 383.8 | 0.0557 | -81.532 | 4.1 | 144.2 | 0.078 | 0.028 | 5.9 | 1.4 |
| $LiCl-H_2O-MeOH$ | 5 | 1.0 | 25 | 0.3 | 806.1 | -321.4 | 0.0557 | -81.532 | 6.1745 | 56.832 | 0.053 | 0.032 | 3.6 | 1.9 |
| $LiCl-H_2O-MeOH$ | 5 | 1.0 | 25 | -1.0 | -150.9 | 336.47 | 0.0557 | -81.532 | 6.1745 | 56.382 | 0.054 | 0.033 | 3.5 | 1.9 |
| $NaBr-H_2O-MeOH$ | 6 | 1.9 | 25 | 0.3 | 806.1 | -321.4 | 36.949 | 1.261 | 6.876 | 54.598 | 0.068 | 0.025 | 9.0 | 4.7 |
| $NaBr-H_2O-MeOH$ | 6 | 1.9 | 25 | -1.0 | -150.9 | 336.47 | 36.949 | 1.261 | 6.876 | 54.598 | 0.034 | 0.019 | 8.8 | 4.9 |
| $LiCl-H_2O-MeOH$ | 10 | 2.0 | 60 | 0.3 | 431.65 | 43.59 | 0.0353 | -287.85 | 5.09 | 91.21 | 0.074 | 0.052 | 33.7 | 18.0 |
| $LiCl-H_2O-MeOH$ | 10 | 2.0 | 60 | -1.0 | 140.3 | 235.92 | 0.0353 | -287.85 | 5.09 | 91.21 | 0.069 | 0.048 | 31.7 | 14.2 |
| *$LiCl-H_2O-MeOH$ | 19 | 2.0 | 1 atm | -1.0 | 97.08 | 312.47 | 81.74 | -11.59 | 19.5 | 170.9 | 0.075 | 0.023 | 52.5 | 17.4 |
| **$NaBr-H_2O-MeOH$ | 19 | 2.0 | 1 atm | -1.0 | 97.08 | 312.50 | 163.3 | 12.55 | -21.56 | 177.3 | 0.081 | 0.027 | 42.9 | 16.5 |

*Binary parameters are used corresponding to the values evaluated at 60°C, Tables 6.6 and 6.7

**Binary parameters are used corresponding to the values evaluated at 25°C, Tables 2.1 and 6.7

NOTE: 1. a) Parameters $\Delta g_{A2}$, $\Delta g_{B2}$, $\Delta g_{A3}$ and $\Delta g_{B3}$ are used for isobaric data with $\alpha_{Ai} = 0.2$; $\alpha_{Bi} = 0.0$

b) Parameters $G_{\pm 2}$, $Z_{\pm 2}$, $G_{\pm 3}$ and $Z_{\pm 3}$ are used for isothermal data

2. In general, prediction is better with parameters corresponding to $\alpha_{23} = -1.0$, therefore isobaric data are predicted using $\alpha_{23} = -1.0$ only.

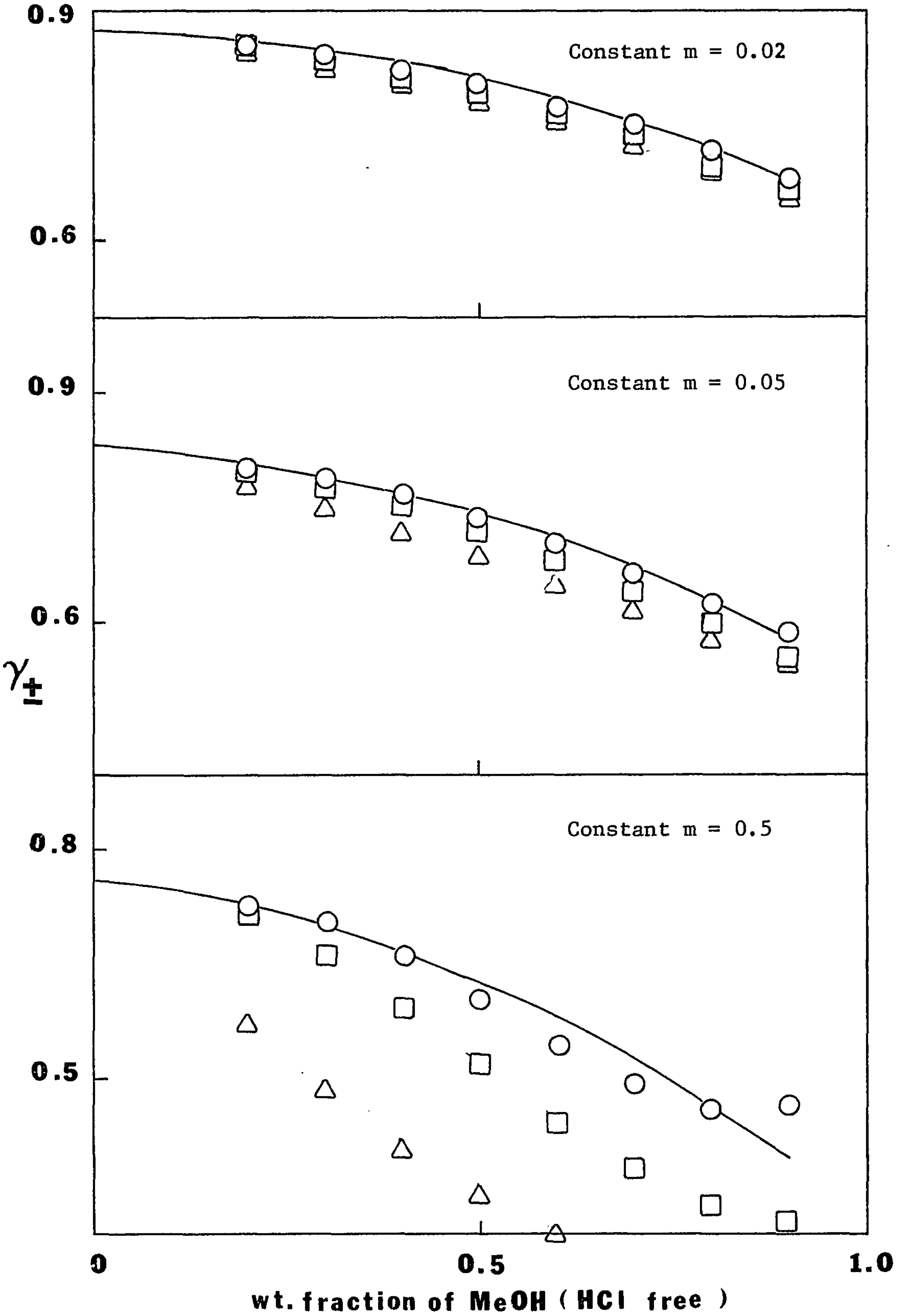


Figure 2.4 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-$H_2O$-MeOH at 25°C . ____ Experimental , Akerlof(1930); ○ Correlated ($\alpha_{23}$=-1.0 ); △ Predicted ( $\alpha_{23}$=-1.0 ); □ Predicted ($\alpha_{23}$=0.3 )

and HCl-$H_2O$-MeOH at 25°C gave acceptable results. The average errors for the HCl-$H_2O$-MeOH system at 25°C are 13.5 and 4.1 for two values of $\alpha_{23}$, -1.0 and 0.3, respectively [Figures 2.4, G.4 and G.5]. The maximum error with $\alpha_{23} = 0.3$ is 28%, which is of good quality. For the system LiCl-$H_2O$-MeOH at 25°C, again $\alpha_{23} = 0.3$ gives slightly better results with an average percent error of 14 and a maximum percent error a maximum of 45% (Figures G.6 and G.7). However, prediction of $\gamma_{\pm}$ for the system HCl-$H_2O$-EtOH at 25°C is possible only at low molalities and water concentration (HCl free) $\geq$ 95% [Figures G.1 to G.3]. The prediction of $\gamma_{\pm}$ data for the system NaCl-$H_2O$-MeOH at 25°C was not of acceptable quality.

Prediction of the vapor-phase composition and the total pressure was attempted for four systems, depending upon the availability of binary data (Table 2.5 and Figures G.1 to G.12). The average error in $\Delta Y$, in general, is about 0.028. Also, it is interesting to note that as the concentration of MeOH or EtOH increases, the prediction improves, Figures 2.4 and 2.5. However, prediction of the VLE for the system LiCl-$H_2O$-MeOH at 60°C is not of presentable quality.

### E. Ternary Data Correlation

All four isothermal ternary data for $\gamma_{\pm}$ were correlated alone, Table G.11 and Figures G.1 to G.9. In general, the ternary $\gamma_{\pm}$ data are correlated with an average percent error less than eight, except for the NaCl-$H_2O$-MeOH system at 25°C where the maximum percent error in $\gamma_{\pm}$ is 27.0. Typical results are

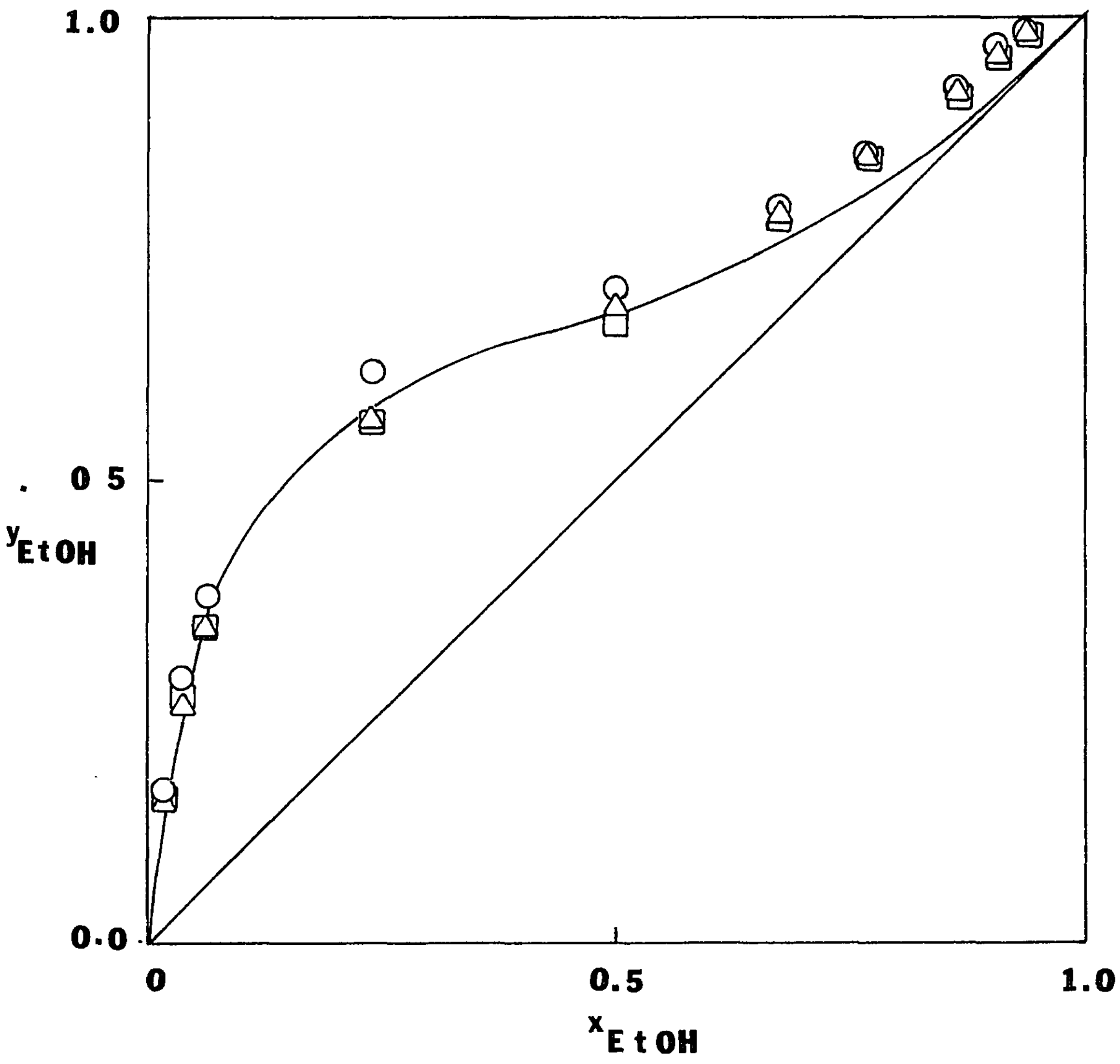


Figure 2.5 Comparison of Experimental VLE with that Predicted Using Model I for the System $LiCl$-$H_2O$-$EtOH$ at 25°C . _____ Experimental ( LiCl free ) Ciparis (1966); ○ Experimental with LiCl, Ciparis(1966) ; △ Predicted with LiCl ( $\alpha_{23}=0.3$ ) ; ☐ Predicted with LiCl ( $\alpha_{23}=-1.0$ )

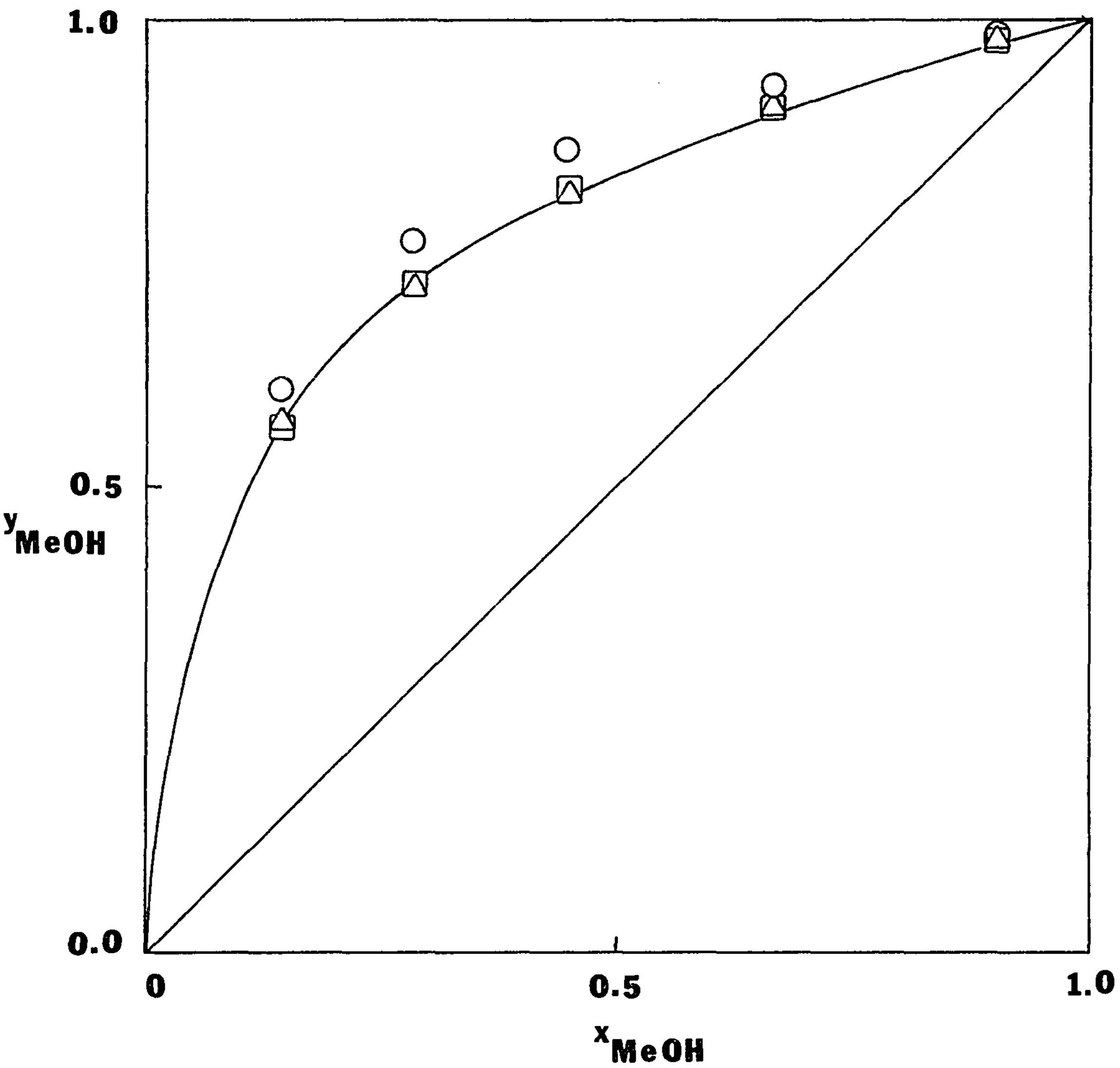


Figure 2.6 Comparison of Experimental VLE with that Predicted Using Model I for the System LiCl-$H_2O$-MeOH at 25°C . ____ Experimental (LiCl free), Ciparis(1966); ○ Experimental with LiCl, Ciparis(1966); △ Predicted ( $\alpha_{23}=0.3$ ) ; □ Predicted ( $\alpha_{23}=-1.0$ )

given for the HCl-$H_2O$-MeOH system at 25°C in Figure 2.4.

Five isothermal and four isobaric ternary VLE data are correlated with three objective functions. Objective function #2, equation 2.20, yields the best results for both $\Delta Y$ and $\Delta P$ (Tables G.13 and G.14 and Figures G.10 to G.19). In general, the average error in $\Delta Y$ is about 0.015. The correlation of ternary data for the NaBr-$H_2O$-MeOH system at 25°C and 40°C (Figures G.13 and G.14) is good, even for molalities greater than six, although it was not possible to predict the data for $m > 2$. For the LiCl-$H_2O$-MeOH system at 60°C the prediction of ternary data was not possible, yet the data are correlated successfully up to $I = 6$ with an average error in $\Delta Y$ of 0.015, Figure G.15. The data for the LiCl-$H_2O$-EtOH system at 25°C are fitted only up to $m = 1.0$, Figures G.11 and G.11. The data available at $m = 4.0$ for this system could not be fitted within acceptable quality, but this is expected since LiCl is incompletely dissociated in EtOH at this molality. The overall ternary data correlation is of good quality. The parameters obtained with three objective functions are listed in Tables G.13 and G.15.

## F. Binary Data Prediction

Finally, aqueous/nonaqueous electrolyte binary data are predicted using the parameters obtained by ternary data reduction, Table 2.6. In general, aqueous electrolyte binary data are predicted with an average percent error of 15 in $\gamma_\pm$

TABLE 2.6 Prediction of Binary VLE and $\gamma_\pm$ Data Using Parameters Obtained by Ternary Data Correlation, Tables G.11 and G.12

| System | # of Points | Max 'm' | T (°C) | $G_{\pm i}$ | $Z_{\pm i}$ | % Error in $\gamma_\pm$ |  | % Error in DP |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Max | Avg | Max | Avg |
| LiCl-$H_2O$ | 19 | 4.0 | 25 | 12.666 | 0.1983 | 27.6 | 5.8 | 15.9 | 3.7 |
| HCl-$H_2O$ | 15 | 2.0 | 25 | 19.677 | 1.7897 | 28.6 | 13.4 | - | - |
| LiCl-$H_2O$ | 11 | 6.0 | 60 | 15.463 | 5.126 | - | - | 28.8 | 22.1 |
| NaCl-$H_2O$ | 10 | 1.0 | 25 | 38.981 | 4.216 | 29.2 | 21.9 | 12.0 | 9.8 |
| HCl-EtOH | 8 | 0.1 | 25 | 9.4608 | 84.647 | 20.0 | 16.2 | - | - |
| NaCl-MeOH | 7 | 0.1 | 25 | 44.11 | 14.638 | 13.1 | 5.8 | - | - |
| LiCl-MeOH | 7 | 3.67 | 25 | 75.82 | -11.24 | - | - | 19.01 | 149.9 |
| NaBr-MeOH | 9 | 1.56 | 25 | 0.1382 | 601.16 | - | - | 114.9 | 104.5 |

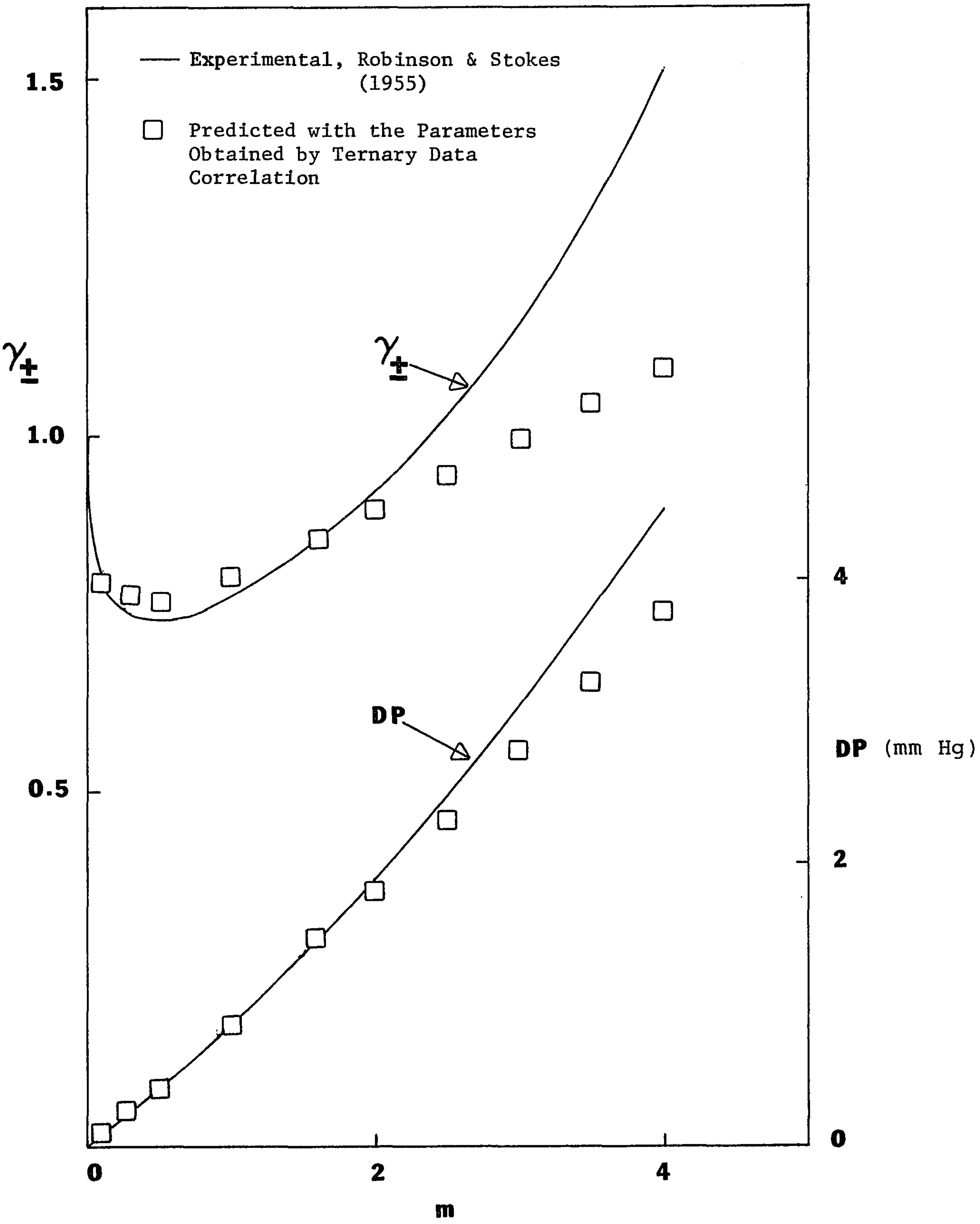


Figure 2.7 Prediction of $\gamma_{\pm}$ and DP Data for the System $LiCl-H_2O$ at 25°C Using the Parameters Obtained by Ternary Data Correlation with Model I

and DP. However, the prediction of DP for nonaqueous electrolyte is not possible. Typical results for the LiCl-$H_2O$ system at 25°C are compared with the experimental data in Figure 2.7.

## 2.4 Discussion

The main objective of this work is to be able to predict or correlate $\gamma_{\pm}$ and the salting out or salting in effect in ternary mixtures. The thermodynamic representation of ternary systems would serve as a guideline in the extension of this model to multicomponent mixtures. An additional term was required with the Debye-Hückel term to represent ternary mixture behavior. Therefore it would be important to analyze the contribution of different terms to understand the behavior of ternary mixtures physically.

In a ternary mixture the impact of the NRTL term, though shifted a little, follows the same trend as it does in a solvent-solvent binary, Figure G.20. However, the contribution of the Debye-Hückel term in a ternary mixture decreases as the dielectric constant of the solvent decreases, i.e.

$$\ln\gamma_{D.H.EtOH} < \ln\gamma_{D.H.MeOH} < \ln\gamma_{D.H.H_2O}$$

So, in a ternary mixture of LiCl-$H_2O$-EtOH, the Debye-Hückel term will always result in salting in for EtOH, Figure 2.8. This salting in effect is due to the Debye Hückel term and is not counterbalanced by the NRTL term. In reality, EtOH is salted-out, which is contrary to the effect of the Debye-Hückel term. Therefore it was necessary to include a higher order term ($\ln\gamma_{PHY}$) with the Debye-Hückel equation to cancel the salting-in effect, Figure 2.8. The extended term ($\ln\gamma_{PHY}$)

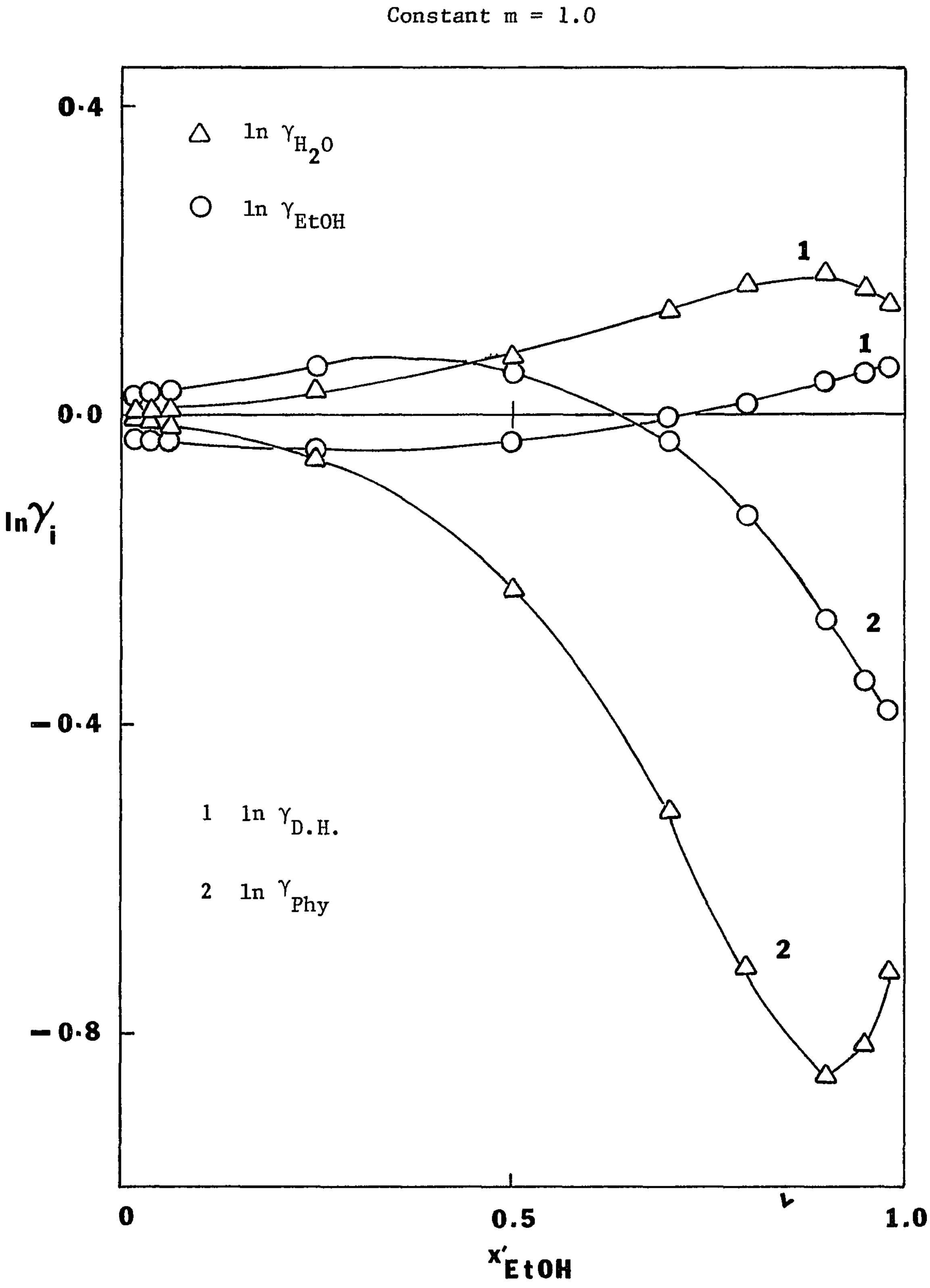


Figure 2.8 Contribution of Different Terms to $\ln\gamma_i$ for the System LiCl-$H_2O$-EtOH at 25°C in Model I

gives an opposite contribution to that of the Debye-Hückel term, i.e.

$$\ln\gamma_{PHY,EtOH} > \ln\gamma_{PHY,MeOH} > \ln\gamma_{PHY,H_2O}$$

Next, it is important to justify the assumption of complete dissociation of the electrolyte for the applicability of this model. In general, dissociation of an electrolyte in a liquid solution depends upon the characteristics of the electrolyte, properties of the solvent and temperature of the system. As the dielectric constant of the solvent decreases, the ionization of electrolyte decreases also. If dissociation data are not available, it would be appropriate to accept Waddington's (1969) approximation as a guideline. According to Waddington, an electrolyte can be considered completely dissociated up to a moderate concentration range in a solvent with dielectric constant $\geq$ 30. To determine the moderate range, the correlation of three typical binary data have been studied, Table 2.3. As mentioned in section 2.3, the maximum concentration range for water and MeOH solvents is accepted as I = 6.0. However, this is based on data at 25°C and 60°C, where the dielectric constant of MeOH is closed to 30. But, if the temperature of the system increases, the dielectric constant decreases and the molality range applicability should be expected to be less than I = 6.0. This is justified by the ternary VLE data correlation for the NaBr-$H_2O$-MeOH system at one atm (temperature range 65-100°C) and isothermal data

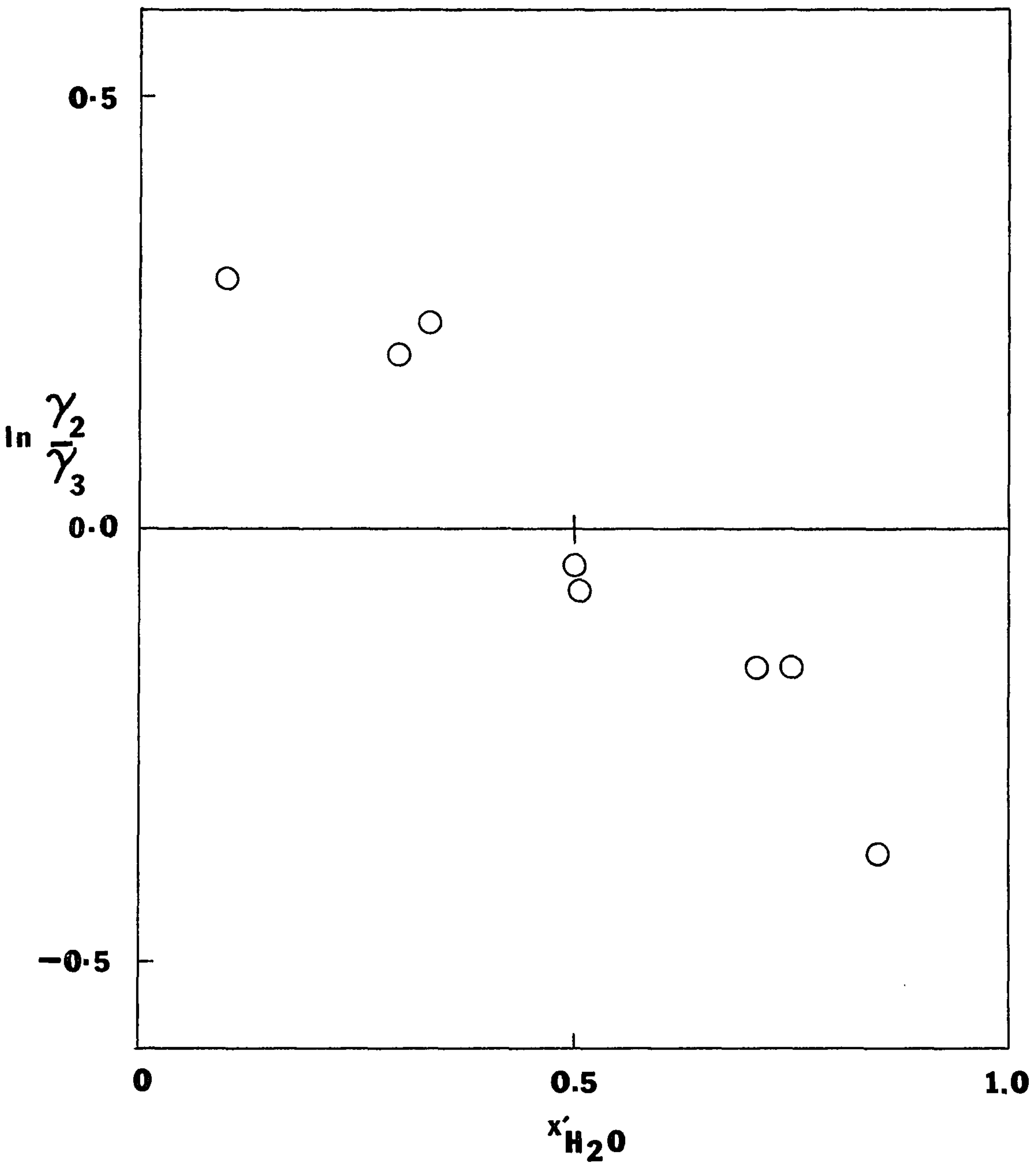


Figure 2.9 Thermodynamic Consistency Test for the System $H_2O$-MeOH at 25°C

at 25°C and 40°C. The average errors in $\Delta Y$ are 0.017 and 0.012 at 25°C and 40°C, respectively where the data are correlated up to I = 7.1 and I = 6.2 for the two temperatures respectively, Table G.12. However, for isobaric data at one atm, the average error goes up to 0.021, although data up to I = 4 only are used.

In general, ternary $\gamma_{\pm}$ and VLE data prediction, as shown in Tables 2.4 and 2.5, are of acceptable quality. These can be used as a guideline in preliminary design. Prediction of vapor phase composition and total pressure is better with $\alpha_{23} = -1.0$ than $\alpha_{23} = 0.3$. It is interesting to note that prediction of y and P data for two isobaric systems using the temperature independent parameters ($LiCl-H_2O-MeOH$ and $NaBr-H_2O-MeOH$ at P = 1 atm, Table 2.5) is obtained with an average error in $\Delta Y$ of 0.023 and 0.027, respectively. VLE data for four systems out of six systems presented in Table 2.5, are predicted with a $\Delta Y_{AVG}$ of less than 0.028. The average error in $\Delta Y$ for the other two systems $LiCl-H_2O-MeOH$ at 25°C and $LiCl-H_2O-MeOH$ at 60°C is larger than 0.028. However, it was found that the maximum concentration limits for reasonable prediction is I = 2. The large errors are observed at higher molality which are due to incomplete dissociation of an electrolyte in the solution.

As shown in Tables 2.4 and 2.5, large errors are obtained for some systems, e.g. especially for the prediction of $\gamma_{\pm}$ for the $HCl-H_2O-EtOH$ system at 25°C and the $NaCl-H_2O-MeOH$ system at 25°C and y and P data for the systems $LiCl-H_2O-MeOH$ at 60°C and $LiCl-H_2O-MeOH$ at 25°C. It is important as a first step to question the accuracy of binary or ternary data, because the performance of the model in the correlation or prediction of the data is equally dependent upon the quality of the data itself. A plot of ln $\gamma_2/\gamma_3$ vs $X_2$ (Figure 2.9) which enables the thermodynamic consistency of the data for the system $H_2O$-MeOH at 25°C shows a lot of scattering of the experimental data. This is the best set of data out of three sources which are definitely thermodynamically inconsistent. Hence, binary parameters evaluated for this binary will affect the prediction of $\gamma_\pm$ for the systems HCl-$H_2O$-MeOH at 25°C and NaCl-$H_2O$-MeOH at 25°C and y and P prediction for the systems LiCl-$H_2O$-MeOH at 25°C and NaBr-$H_2O$-MeOH at 25°C.

The solvent-solvent binary data can be tested for thermodynamic consistency, but there is no thermodynamic consistency test to check electrolyte-solvent binary or ternary data. In the literature, a great deal of aqueous electrolyte binary data are available and their quality and accuracy can be considered valid. However, the nonaqueous electrolyte binary or ternary data are not frequently available and those found in the literature can not be checked for accuracy. However, a comparison of isothermal and isobaric data prediction with the same binary parameters evaluated at 60°C indicate that isobaric data can be predicted with an average error in $\Delta Y$ of less than 0.028 whereas the error is large for isothermal ternary data prediction. This shows a possible inconsistency in the VLE data of the LiCl-$H_2O$-MeOH system at 60°C, though this can not be verified.

Another point to be examined in ternary prediction is the difference in the available molality range for binary and ternary systems. As in the case of the HCl-$H_2O$-EtOH system at 25°C, ternary data are available up to m = 2.5 for $x'_{EtOH} = 0.5$, whereas the corresponding HCl-EtOH binary data are available only up to 0.1 m. The data for m $\geq$ 0.1 for the HCl-EtOH binary can not be used with this model because of the incomplete dissociation of HCl. The binary parameters obtained in the regression of the HCl-EtOH data up to 0.1 m can not be expected to perform well for higher molalities in a ternary mixture, especially when the concentration of EtOH increases, (Figures G.1 to G.3). This is also observed with the system NaBr-$H_2O$-MeOH at 25°C. The prediction of this ternary is possible only up to m = 1.9, because the binary NaBr-MeOH data are available only up to m = 1.6, Table 2.5.

The performance of this model in correlating ternary data as tested with four isothermal systems for $\gamma_\pm$ (Table G.11) and nine systems for VLE (5 isothermal, Table G.12 and 4 isobaric, Table G.14) is of good quality. The data correlated for the NaBr-$H_2O$-MeOH system at 25°C are compared with the results of Chen et al. (1979)(Figure G.14). The results obtained by this model are definitely superior to their model.

Finally, the prediction of the binary data with the parameters obtained by ternary data correlation is generally of acceptable quality for aqueous electrolyte binaries, Table 2.6 and Figure 2.7. The average error in DP and $\gamma_\pm$ is about 15%.

But the prediction of DP data for nonaqueous electrolytes is not possible, as shown for the systems LiCl-MeOH at 25°C and NaBr-MeOH at 25°C (Table 2.6).

## 2.5 Conclusions

The main objective of this work, which was to represent the thermodynamic behavior of strong electrolytic solutions, is achieved. Aqueous/nonaqueous binary data (DP and $\gamma_\pm$ vs m) are correlated up to I = 6 with an average percent error of 7.0. The prediction of $\gamma_\pm$ for ternary systems up to I = 2 is possible with an average percent error of 15.0. The prediction of ternary VLE data as shown with six systems is possible with an average error in $\Delta Y$ of 0.028 up to I = 2, except for the LiCl-$H_2O$-MeOH at 60°C, where error in $\Delta Y$ is large even at I = 2. The prediction of VLE data above I = 2 results in large errors. This sets the limitation of the model for ternary prediction. The correlation of ternary $\gamma_\pm$ and VLE data for systems containing water and MeOH is of good quality up to I = 6. Ternary system containing water and ethanol was correlated only up to I = 1.

# CHAPTER 3

# CORRELATION OF VAPOR-LIQUID EQUILIBRIUM AND MEAN MOLAL ACTIVITY COEFFICIENTS WITH MODEL II IN ELECTROLYTIC SOLUTIONS

## ABSTRACT

Vapor pressure depression data (DP) of 53 aqueous electrolytes at 100°C were correlated with the one parameter ($B_{12}$) Bromley equation. These $B_{12}$ constants can be used to calculate mean molal activity coefficients up to I = 6. However, maximum molality applicability for MeOH-electrolyte solutions is only up to I = 3. In addition, these $B_{12}$ values, along with those at 25°C reported by Bromley, can lead to reliable estimates of DP and $\gamma_{\pm}$ in the temperature range 25-100°C.

The extended form of the Bromley equation with the additional NRTL equation and the salting-out term give excellent correlation of the isothermal ternary VLE and $\gamma_{\pm}$ data in electrolytic solutions. This model requires two ternary adjustable parameters, therefore prediction of ternary data with binary data only is not possible.

## Model II: Combination of the Bromley Equation, the Simplified NRTL Equation and the Salting Out Term

### 3.1 Gibbs Free Energy Expression

Bromley (1973) proposed a one parameter equation to correlate binary aqueous electrolytic mixtures. The same equation has been applied successfully to correlate nonaqueous binary data. This equation represents long-range electrostatic forces and ion-solvent interactions in a binary mixture. However, in a ternary mixture additional solvent-solvent molecular interactions must be considered. Therefore in Model II the Bromley equation has been extended to ternary mixtures and combined with a simplified form of the NRTL equation and an additional salting out term:

$$\frac{G^E}{RT}\Big]_{\text{Total}} = \frac{G^E}{RT}\Big]_{\text{Bromley}} + \frac{G^E}{RT}\Big]_{\text{NRTL-S}} + \frac{G^E}{RT}\Big]_{\text{Salting Out}} \qquad (3\text{-}1)$$

A stepwise procedure to obtain the total Gibbs free energy expression is presented in Appendix-C (Sections C.1, C.2 and C.3). The final forms of the equations are given below

$$\frac{G^E}{RT}\Big]_{\text{Bromley}} = 2.303\nu \frac{m}{I} \frac{N_T M_w}{1000}[-A_\gamma \frac{2}{\rho^3} \frac{1}{2}\{(1 + \rho I^{1/2})^2$$

$$- 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2}\}$$

$$+ \frac{(0.06 + 0.6\ B)}{a^2}\{\ln(1 + aI) + \frac{1}{(1 + aI)} - 1\}$$

$$+ \frac{B}{2} I^2] + N_T[(0.001\nu m M_w + 1)$$

$$\ln(0.001\nu m M_w + 1) - 0.001\nu m M_w] \qquad (3\text{-}2)$$

where,

$$B = B_{12}X_2' + B_{13}X_3' + B_{123} \frac{(X_2'X_3')^{1/2} e^{-\alpha X_3'}}{(1 + n_1^{1/2})^3} \qquad (3\text{-}3)$$

$B_{123}$ is ternary adjustable parameter

$$\frac{G^E}{RT}]_{NRTL-S} = \frac{N_T}{RT}[\{\frac{X_2X_3Z_{32}}{(X_A\frac{\nu}{\nu_A} + X_2 + X_3G_{32})} + \frac{X_2X_3Z_{23}}{(X_A\frac{\nu}{\nu_A} + X_3 + X_2G_{23})}\}$$

$$+ \frac{\nu}{\nu_A} X_AX_2X_3 \{\frac{Z_{32}}{(X_3G_{32} + X_2)^2} + \frac{Z_{23}}{(X_2G_{23} + X_3)^2}\}] \qquad (3\text{-}4)$$

where, $G_{ij}$ and $Z_{ij}$ are the binary solvent-solvent parameters, equation (2-4).

$$\frac{G^E}{RT}]_{\text{Salting Out}} = \frac{\delta_{123}}{e^{\alpha n_1^{1/2}}} \frac{\varepsilon^2}{KTD} \sum_k \frac{\nu_k Z_k^2}{b_k} \frac{n_1^2}{2} \delta' (N_2N_3)^{1/2} \qquad (3\text{-}5)$$

where,

$$\delta' = e^{\alpha X_2'}(X_2'B_{13} - X_3'B_{12}) \qquad (3\text{-}6)$$

$$\alpha = 2.0$$

$\delta_{123}$ is a ternary adjustable salting out parameter. A combination of equations (3-2) to (3-5) with equations (1-27) to (1-29) is used to derive activity coefficient expressions for solvents and the electrolyte. The detailed procedure is given in Appendix-C.

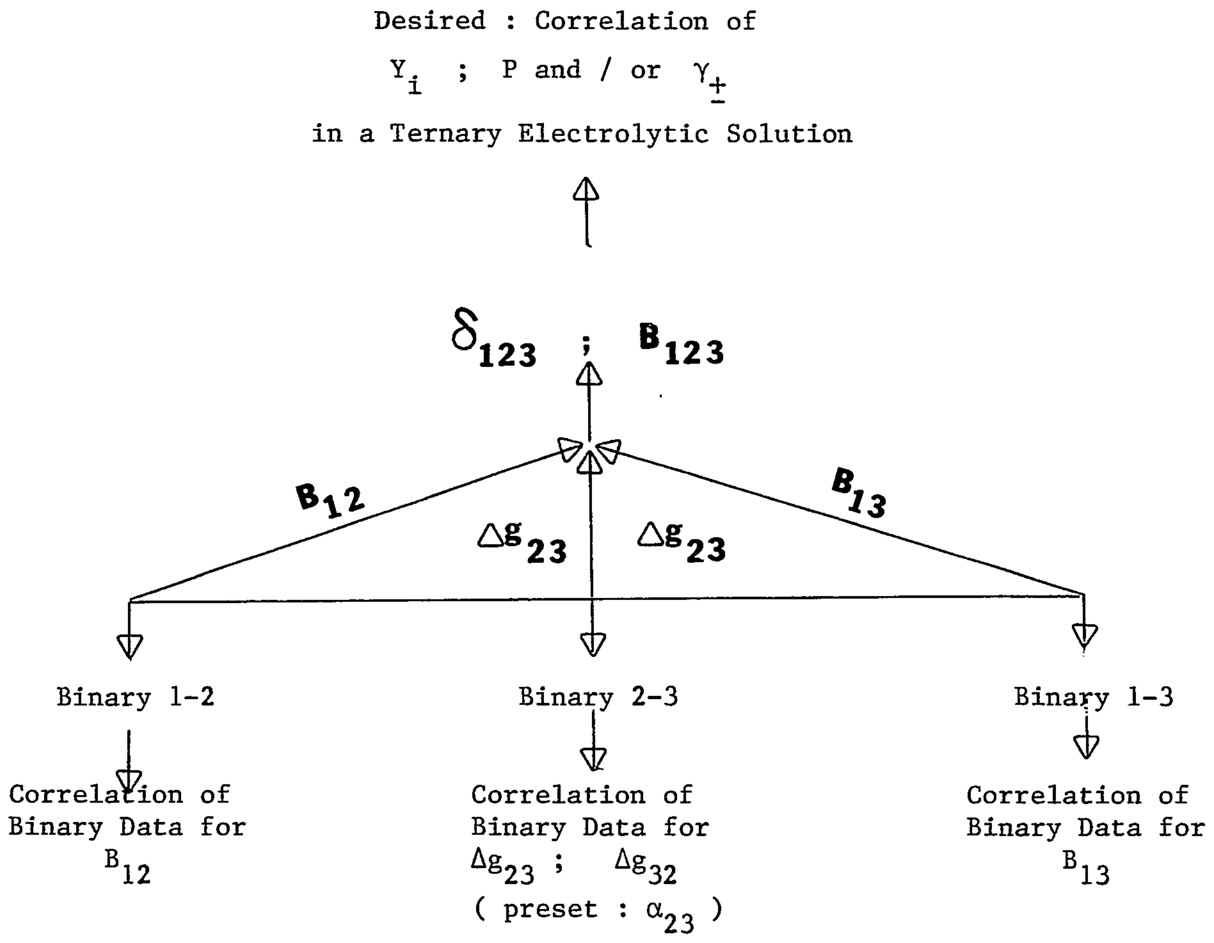


Figure 3.1 A Stepwise Scheme for Correlation for the VLE and Mean Molal Activity Coefficients with Model II

## 3.2 Procedure--Data Reduction

Each binary set is correlated with the appropriate equations for the activity coefficients and the VLE relationships developed in Chapter 1. Binary parameters are then used in the ternary expressions and the ternary isothermal data are correlated. A stepwise scheme for the data correlation is shown in Figure 3.1. A detailed description of the data reduction is given in the following sections.

### A. Solvent-Solvent Binary

The activity coefficient equations for these types of systems are derived by setting $m = 0$ and $N_A = 0$ in equations (3-2) to (3-5). The expressions are the same as equation (2-7). The binary data correlation is the same as discussed in Section 2.2-A.

### B. Electrolyte-Solvent Binary

An aqueous/non-aqueous electrolytic binary is correlated with the one parameter Bromley equation given by equations (C-1), (C-2) and (C-9). A Fibonacci single variable regression program is used to find the best value of the binary adjustable parameter '$B_{12}$' or '$B_{13}$'. Two objective functions, equations (2-9) and (2-10) (Section 2.2-B), with equations (C-1), (C-2), (C-9), (1-19) to (1-21) are used to correlate the binary experimental data.

## C. Electrolyte-Solvent-Solvent Ternary

A ternary mixture requires four binary parameters viz $\Delta g_{23}$, $\Delta g_{32}$ (preset $\alpha_{23}$), $B_{12}$ and $B_{13}$ and two additional ternary parameters.

$$\ln\gamma^*_\pm = \ln\gamma^*_{\pm,\mathrm{Bromley}} + \ln\gamma^*_{\pm,\mathrm{NRTL\text{-}S}} + \ln\gamma^*_{\pm\mathrm{Salt\ Out}} \qquad (3\text{-}7)$$

where,

$$\ln\gamma^*_{\pm,\mathrm{Bromley}} = 2.303[-A_\gamma|Z_+Z_-| \frac{I^{1/2}}{1 + \rho I^{1/2}} + \frac{(0.06 + 0.6B)|Z_+Z_-|I}{(1 + aI)^2} + BI]$$

$$+ 2.303\nu \frac{N_T M_w}{1000} \frac{m}{I} [\frac{0.6}{a^2} |Z_+Z_-| \{\ln(1 + aI) + \frac{1}{(1 + aI)} - 1\} + \frac{I^2}{2}] \frac{\partial B}{\partial N_1}$$

$$+ \ln(0.001\nu m M_w + 1) \qquad (3\text{-}8)$$

where, $\frac{\partial B}{\partial N_1}$ is defined by equation (C-19)

$$\ln\gamma^*_{\pm\mathrm{NRTL\text{-}S}} = \frac{X_2X_3}{RT} [- \frac{Z_{23}}{(X_A\frac{\nu}{\nu_A} + X_3G_{32} + X_2)^2} - \frac{Z_{23}}{(X_A\frac{\nu}{\nu_A} + X_2G_{23} + X_3)^2} + \frac{Z_{32}}{(X_3G_{32} + X_2)^2} + \frac{Z_{23}}{(X_2G_{23} + X_3)^2}] \qquad (3\text{-}9)$$

$$\ln\gamma^{*}_{\pm,\text{Salt Out}} = \delta_{123} \frac{\varepsilon^2}{KTD} \sum_k \frac{\nu_k Z_k}{b_k} (N_2 N_3)^{1/2} \delta' \frac{N_1}{e^{\alpha N_1^{1/2}}} [1 - \frac{\alpha}{4} N_1^{1/2}] \tag{3-10}$$

For the solvents 2 and 3

$$\ln\gamma_i = \ln\gamma_{i,\text{Bromley}} + \ln\gamma_{i,\text{NRTL-S}} + \ln\gamma_{i,\text{Salt Out}} \tag{3-11}$$

where,

$$\begin{aligned}\ln\gamma_{i,\text{Bromley}} = {} & 2.303 \frac{\nu m}{1000} M_{W_i} [A_\gamma \frac{I^{1/2}}{3} \sigma_2(\rho I^{1/2}) |Z_+ Z_-| \\ & - (0.06 + 0.6B)\frac{I}{2} \psi_2(aI) |Z_+ Z_-| + B\frac{I}{2}] \\ & + 2.303\nu m \frac{N_T M_W}{1000}[-I^{1/2} \sigma_2^1(\rho I^{1/2}) |Z_+ Z_-| \frac{\partial A_\gamma}{\partial N_i} \\ & + 0.6 \frac{I}{2} \psi_2^1(aI) |Z_+ Z_-| \frac{\partial B}{\partial N_i} + I \frac{\partial B}{\partial N_i}] \\ & + \ln(0.001\nu m M_W + 1) - 0.001\nu m M_W \end{aligned} \tag{3-12}$$

$\sigma_2(\rho I^{1/2})$, $\psi_2(aI)$, $\sigma_2^1(\rho I^{1/2})$, $\psi_2^1(aI)$ and $\frac{\partial B}{\partial N_i}$ are defined in equations (C-24) to (C-29). B is given by equation (3-3).

$$\begin{aligned}\ln\gamma_{i,\text{NRTL-S}} = {} & \frac{1}{RT}[\frac{X_A X_j \frac{\nu}{\nu_A} Z_{ji} + X_j^2 Z_{ji} G_{ji}}{(X_A \frac{\nu}{\nu_A} + X_j G_{ji} + X_i)^2} \\ & + \frac{X_A X_j \frac{\nu}{\nu_A} Z_{ij} + X_j^2 Z_{ij}}{X_A \frac{\nu}{\nu_A} + X_i G_{ij} + X_j)^2} + X_A X_j \frac{\nu}{\nu_A} \{\frac{Z_{ji}}{(X_j G_{ji} + X_i)^2} \\ & + \frac{Z_{ij}}{(X_i G_{ij} + G_j)^2}\} - 2 X_A X_i X_j \frac{\nu}{\nu_A} \{\frac{Z_{ji}}{(X_j G_{ji} + X_i)^3}\end{aligned}$$

$$+ \frac{Z_{ij}G_{ij}}{(X_iG_{ij} + X_j)^3}\}] \qquad (3\text{-}13)$$

Where,

$$i = 2 \text{ and } j = 3$$

or

$$i = 3 \text{ and } j = 2$$

$$\ln\gamma_{i,\text{Salt Out}} = \frac{\delta_{123}}{e^{\alpha N_1^{1/2}}} \frac{\varepsilon^2}{KTD} \sum_k \frac{\nu_k Z_k^2}{b_k} \frac{N_1^2}{2}$$

$$[\frac{1}{2}(\frac{N_j}{N_i})^{1/2} \delta' - (N_2N_3)^{1/2} \frac{\delta'}{D} \frac{\partial D}{\partial N_i}$$

$$+ (N_2N_3)^{1/2} \frac{\partial \delta'}{\partial N_i}] \qquad (3\text{-}14)$$

Where, $\delta'$ is given by equation (3-6) and $\frac{\partial \delta'}{\partial N_i}$ is defined in equations (C-36) and (C-39).

Note: For the development of equations (3-7) to (3-14), see Appendix-C (Section C.4).

The four binary parameters are obtained by individual binary data correlation. A ternary mixture is correlated for the two ternary parameters, $B_{123}$ and $\delta_{123}$, using the LSQ2 non-linear regression subroutine. Again, as in Model I, three objective function equations, (2-19) to (2-21), have been tried to correlate the experimental data. In all the ternary data reductions, $\Delta g_{23}$ and $\Delta g_{32}$ are preset to their respective values obtained by binary data correlation with $\alpha_{23} = -1.0$.

Equations (3-7) to (3-14) with equations (1-11), (1-12), (1-22) and (1-24) are used to correlate the ternary VLE and $\gamma_{\pm}$ data.

TABLE 3.1 Data Sources *

| System | T (°C) | m | Reference |
|---|---|---|---|
| $NaCl-H_2O$ | 25,50,75,100 | 0.1 - 6.0 | Gibbard et al. (1974) |
| | 25,60,70,80,90,100 | 0.05 - 4.0 | Robinson and Stokes (1955) |
| $KCl-H_2O$ | 25,40,50,60,70,80 | 0.1 - 4.0 | Snipes et al. (1975) |
| $KBr-H_2O$ | 25,60,70,80,90,100 | 0.1 - 4.0 | Robinson and Stokes (1955) |
| $MgSO_4-H_2O$ | 25,40,50,60,70,80 | 0.1 - 2.0 | Snipes et al. (1975) |
| $MgCl_2-H_2O$ | 25,40,50,60,70,80 | 0.1 - 2.0 | Snipes et al. (1975) |
| $Na_2SO_4-H_2O$ | 25,40,50,60,70,80 | 0.1 - 1.6 | Snipes et al. (1975) |

*In addition to the Weast compilation

## 3.3 Results

A list of aqueous electrolyte binary systems used with this model, in addition to the systems presented in Table G.1, are given in Table 3.1. The results of binary and ternary data correlation are discussed below.

### A. Aqueous Electrolyte Binary

Maximum Molality Applicability--Bromley recommended the applicability of his equation [Equations (C-1), (C-2) and (C-9] up to I = 6 for strong electrolytes in water, i.e. nearly completely ionized. This has been demonstrated by combining equations (C-9), (1-20) and (1-21) in the form

$$Y = B_{1i} X \tag{3-15}$$

where,

$$\begin{aligned} Y = {} & (1 - \phi) - 2.303\, A_\gamma |Z_+Z_-| \sigma_2(\rho I^{1/2}) I^{1/2} \\ & + 2.303[0.06\, \frac{\psi_2(aI)}{2}] |Z_+Z_-| I \end{aligned} \tag{3-16}$$

$$X = -2.303[0.6I|Z_+Z_-|\, \frac{\psi_2(aI)}{2} + \frac{I}{2}] \tag{3-17}$$

Figures H.1 and H.2 indicate that reasonably good results are obtained for strong electrolytes up to I = 6, i.e. m = 6 for 1-1 electrolytes (Figure H.1) and m = 2 for 2-1 electrolytes (Figure H.2). On the other hand, very poor results are observed for $MgSO_4$ (Figure H.3) which is incompletely ionized.

Results at 100°C--In the literature a good deal of data at 100°C are available as DP vs m, Weast (1969). Some typical systems are shown in Table H.1. Equation (C-9) with (1-21) was used to calculate the values of $B_{12}$ at 100°C and $\gamma_{\pm}$ values are obtained using equations (C-1) and (C-2). Values of m up to I = 6 were used as above, even though the range of applicability may be somewhat lower here because of the higher temperature. Hence, for 1-1 electrolyte data up to m = 6 (7 points) were used; for 1-2 and 2-1 electrolytes, up to m = 2 (3 points); for 2-2 electrolytes, up to m = 1.5, and since at m = 1.5 is not given, data to m = 2 (I = 8) were used. Finally, for higher electrolytes (3-1, 3-2, etc.) only two points (m = 0.5 and m = 1.0) could be used.

This was considered too limited a data base and these electrolytes were not included in this study. The obtained values of $B_{12}$, along with those at 25°C from Bromley, are presented in Table H.2.

In the case that data are correlated for the maximum m value ($m_{max}$) reported by Weast, the resulting error in DP ($DP'_{max}$) is also included in Table H.2. The larger values of $DP'_{max}$ as compared to those of $DP_{max}$ further support Bromley's suggestion that this equation is applicable only up to I = 6 for aqueous electrolytic mixtures.

The accuracy of the mean molal activity coefficients, calculated using these $B_{12}$ values with equations (C-1) and

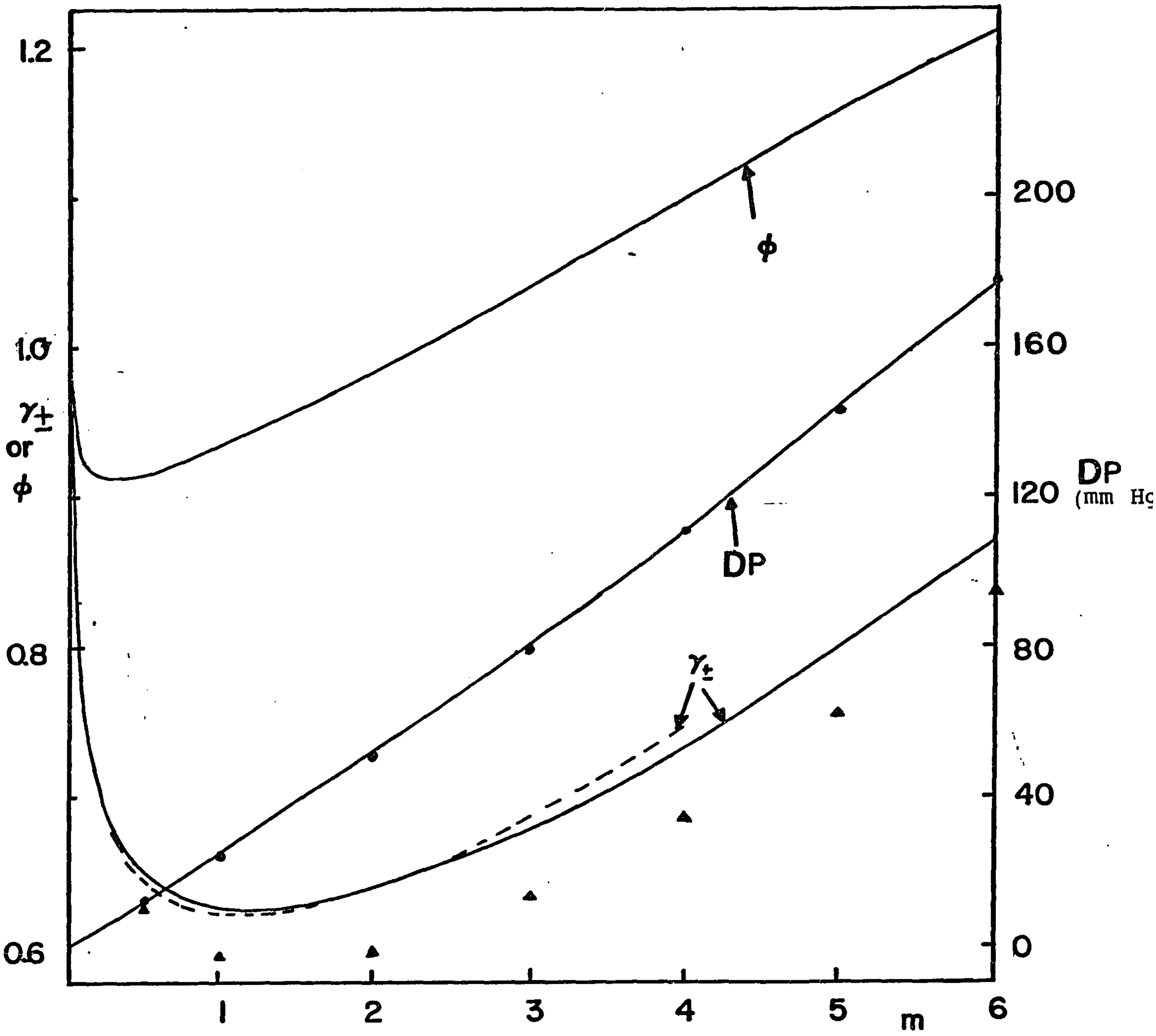


Figure 3.2 Activity and Osmotic Coefficients for the System Water-Sodium Chloride at 100°C

– – – – (Gibbard et al., 1974)

——— (Robinson and Stokes, 1955)

▲ From Weast's Data

● Calculated DP Values, eqn. (C-9), (1-21) and (1-22)

TABLE 3.2 Effect of the Number of Data Points Used in Evaluating $B_{12}$ on the Accuracy of the Calculated $\gamma_{\pm}$ Values (T = 100°C)

| Max m Value | Number of Points | $B_{12}$ | Error % in $\gamma_{\pm}$ | |
|---|---|---|---|---|
| | | | Max | Avg |
| | | NaCl-Water | | |
| 2.0 | 3 | 0.0671 | 10.9 | 4.0 |
| 3.0 | 4 | 0.0595 | 5.3 | 3.5 |
| 4.0 | 5 | 0.0582 | 5.9 | 4.4 |
| 5.0 | 6 | 0.0572 | 6.4 | 5.1 |
| 6.0 | 7 | 0.0567 | 6.7 | 5.4 |
| | | KBr-Water | | |
| 2.0 | 3 | 0.0533 | 6.7 | 2.7 |
| 3.0 | 4 | 0.0479 | 4.9 | 3.5 |
| 4.0 | 5 | 0.0442 | 6.6 | 4.3 |

(C-2), is examined next. Figure 3.2 presents $\gamma_\pm$ values for aqueous NaCl calculated with this approach along with the data from Robinson and Stokes and those of Gibbard et al. (1974). The agreement can be considered reasonably good; maximum error is 6.7%; average error is 5.4%. The other system for which $\gamma_\pm$ data at 100°C are available is aqueous KBr (Robinson and Stokes, 1955). Since this system is not included in the Weast compilation, the $\phi$ values of Robinson and Stokes at m = 0.5, 1, 2, 3 and 4 were used. The results are presented in Figure H.4 and they are of the same quality as those in the NaCl case; maximum error is 6.6%; average error is 4.3%. Since this is not the case for all electrolytes, especially for electrolytes other than 1-1, the effect of the number of data points used on the accuracy of the calculated $\gamma_\pm$ values is examined in Table 3.2. The results obtained by using only three data points (m up to 2) are comparable to those obtained by using all points available, up to m = 6 for NaCl and up to m = 4 for KBr.

*Estimation of DP and $\gamma_\pm$ Values in the Range 25-100°C*--In the typical case, values of DP and $\gamma_\pm$ are needed at temperatures other than 25 or 100°C. Hence, it would be desirable if $B_{12}$ values could be estimated within this temperature range. Bromley recommends two expressions for the temperature dependency of $B_{12}$.

$$B_{12} = B^{*}\ln\left(\frac{T - 243}{T}\right) + \frac{B_1^1}{T} + B_2^1 + B_3^1 \ln T \qquad (3\text{-}18)$$

TABLE 3.3 Values of $B^*$ and $B_1'$ in Equation (3-20) for the Systems in Figures H.5 and H.6

| Electrolyte | $B^*$ | $B_1'$ |
|---|---|---|
| NaCl | 0.05127 | 42.97 |
| KBr | 0.06867 | 43.26 |
| KCl | 0.04361 | 29.164 |
| $Na_2SO_4$ | 0.040945 | 14.763 |
| $MgCl_2$ | 0.01305 | 41.895 |
| $MgSO_4$ | 0.0007 | 6.346 |

and

$$B_{12} = \frac{C^*}{T - 230} + \frac{C_1^{11}}{T} + C_2^{11} + C_3^{11} \ln T \qquad (3\text{-}19)$$

Since $B_{12}$ values are available only at 25°C (Bromley) and 100°C (this study), equations (3-18) and (3-19) were tested in their two adjustable constants form by setting $B_2^1$, $B_3^1$, $C_2^{11}$ and $C_3^{11}$ equal to zero.

$$B_{12}\, T = B_1^1 + B^*\, T \ln \left(\frac{T - 243}{T}\right) \qquad (3\text{-}20)$$

and

$$B_{12}\, T = \frac{C^* T}{T - 230} + C_1^{11} \qquad (3\text{-}21)$$

The equations are written in this linear form so that they can be tested by plotting $B_{12}$ T vs $[T \ln ((T - 243)/T)]$ in equations (3-20) and vs $[T/(T - 230)]$ for equation (3-21). Both expressions give reasonably good results as demonstrated in Figures H.5 and H.6 for equation (3-20). The straight lines were obtained by regressing all the points, excluding those from the Weast data. The values of the constants $B^*$ and $B_1^1$ are reported in Table 3.3.

Use of equation (3-20) for interpolation purposes is demonstrated in Table H.3. The $B_{12}$ values at 70°C were obtained from equation (3-20) with $B^*$ and $B_1^1$ calculated using only the $B_{12}$ (25°C) and the $B_{12}$ (100°C) values. The large error for $MgSO_4$ is due to incomplete dissociation figure H.3. Values of $\gamma_\pm$ at 70°C for the electrolytes of Table 3.3 are given in the references presented in Table 3.1. It should be noted that the $\gamma_{\pm}$ data for KCl, $MgCl_2$, $MgSO_4$ and $Na_2SO_4$ (Snipes et al., 1975) were derived from heat of dilution data, and those for NaCl (Gibbard, 1974) are reported at rounded molalities and temperatures.

## B. Nonaqueous Electrolyte Binary

Maximum Molality Applicability--As shown for the aqueous electrolyte binaries, the Bromley equation in the form of equation (3-15) is used to test the maximum molality range for MeOH electrolyte binaries. The results for the LiBr-MeOH system at 15°C and the LiCl-MeOH system at 60°C (Figures H.7 and H.8) show that the applicability of the Bromley equation is good only up to $I = 3$, for 1-1 electrolytes. For the higher order electrolytes (1-2, 2-1, 2-2, etc.) data are not available. The only data available for higher order electrolytes is for the $CaCl_2$-MeOH system at 25°C. Because of the scattering and unavailability of the experimental data at low molality (Figure H.9), it is not possible to conclude the maximum molality range for this system. Based on 1-1 electrolytes only the molality limit for MeOH system is set $I = 3$. Other nonaqueous binaries could not be tested since this type of data is not available in literature. It would be expected that the molality range would be even lower than $I = 3$ for solvents with dielectric constants less than that of MeOH.

Accuracy of the Binary Data Correlation--The results of some nonaqueous electrolyte binary data correlation are given in Table H.4. The accuracy of data correlation of such systems is less than the accuracy of the corresponding aqueous electrolytic binaries (Table H.5). In a typical case of the system $LiCl-H_2O$ at 60°C, the maximum percent error in DP is 2.0 and the average percent error is 1.0 (Table H.5) whereas for the system LiCl-MeOH at 60°C, the maximum percent error in DP is 15.6% and the average percent error is 7.3 (Table H.4). The correlation of the system $CaCl_2$-MeOH at 25°C, up to m = 2.6 is of poor quality (Table H.4). This is expected for 1-2, 2-1 or higher order electrolytes in MeOH because of the maximum molality limitation.

## C. Isothermal Ternary Data Correlation

The mean molal activity coefficient data of three isothermal ternary systems are correlated with this model (Table H.6), Figure H.9 to H.17. The systems $HCl-H_2O$-MeOH at 25°C and $NaCl-H_2O$-MeOH at 25°C have average percent errors in $\gamma_\pm$ of 1.4 and 7.4, respectively (Figures H.13 to H.17). The correlation of the system $HCl-H_2O$-EtOH at 25°C is good up to m = 2.0 and EtOH concentration (HCl free) <9% (Figures H.10 and H.11). The results are of poor quality for the same system at $x'_{EtOH} = 0.5$, especially when m > 0.5.

The vapor-liquid equilibrium data of five isothermal ternary systems are correlated (Table H.7) with this model. Again, three objective functions [Equations (2-19), (2-20) and (2-21)] are applied for the data reduction. In general, objective function #2 gives the best results. In Table H.7 results are given for the correlation up to $m = 3$ and also for the higher molality range. The overall performance of the model in correlating the ternary VLE data is of good quality within the limited range of molality (Figures H.17 to H.22). The molality applicability decreases to even less than $I = 3$ with an increase in temperature, as in the case of the LiCl-$H_2O$-MeOH system at 60°C, the fit is good only up to $m = 2.0$.

The ternary parameters $\delta_{123}$ and $B_{123}$ obtained by the ternary correlation, indicates that these cannot be considered temperature independent. Therefore this model is not applied to isobaric ternary systems.

## 3.4 Discussion

As already shown, only three DP-m points were used in evaluating $B_{12}$ for 1-2, 2-1 and 2-2 electrolytes. In addition, no experimental $\gamma_{\pm}$ data at 100°C are available for such electrolytes as in the case for 1-1 types, where good results are obtained from three points only (Table 3.2). Figures H.5 and H.6 and Table H.9 demonstrate, however, that the $B_{12}$ values obtained from the Weast data are very close to those obtained by extrapolation of the data in the range from 25 to 80°C. The closeness of the $\gamma_{\pm}$ values obtained from these two $B_{12}$ (100°C) values is depicted in Table H.10 for $MgCl_2$ with a maximum difference of 5.8%. For the $Na_2SO_4$ system, where the fractional difference between the two $B_{12}$ (100°C) values is the largest, the maximum difference in $\gamma_{\pm}$ is 5.7%. Therefore it is suggested that, in addition to the 1-1 electrolytes, reasonably accurate $\gamma_{\pm}$ values can be calculated for 1-2, 2-2, and 2-1 types from $B_{12}$ values obtained using three data points from the Weast compilation.

Table H.3 demonstrates that use of the $B_{12}$ values at 25 and 100°C, along with equation (3-20), can lead to reasonably accurate estimates of $\gamma_{\pm}$ and DP values at intermediate temperatures. However, when the same approach was used to evaluate the derivative $(dB_{12}/dT)$, needed to calculate apparent relative molal enthalpies $(\phi L)$ and relative partial molal enthalpies $(\bar{L}_2)$ for four individual salts, NaCl, KCl, $Na_2SO_4$ and $MgCl_2$

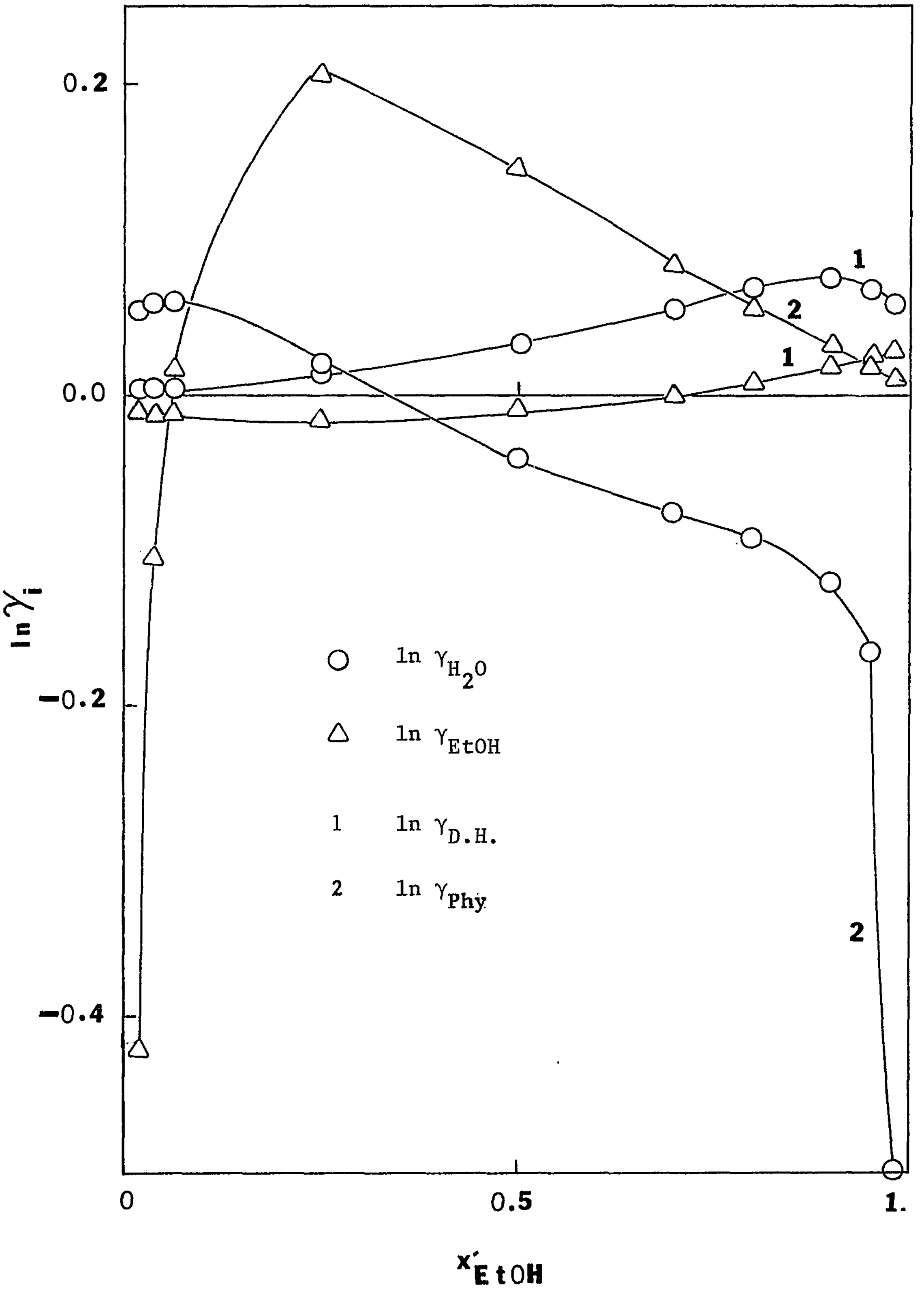


Figure 3.3 Contribution of Different Terms to ln $\gamma_i$ for the System LiCl-$H_2O$-EtOH at 25°C in Model II

with water at 100°C the typical average error was about 50%. This failure becomes apparent from Figures H.5 and H.6 while equation (3-20) is valid for interpolation purposes, it does not provide reliable values for the slope $dB_{12}/dT$. The calculated values for $(\phi L)$ and $(\bar{L}_2)$, however, were in the right direction, but lower than the experimental ones. The expressions used to calculate these quantities are given by Bromley (1973).

When the Bromley equation was applied to nonaqueous electrolytic binaries, the maximum molality range is $\leq 3$, also the binary data reduction is less accurate for such binaries. This is expected since the empirical constants in the original Bromley equation (C-1) were obtained by applying aqueous electrolytic binary data only. However, considering the simplicity of this equation, the results for nonaqueous mixtures are of acceptable quality. The temperature dependency of such systems can also be established by equation (3-20), as shown by Tomasula and Tassios (1980) for the electrolyte-MeOH binaries.

The isothermal ternary data correlation of the VLE and $\gamma_{\pm}$ is of good quality for $m \leq 3.0$. An investigation of the contribution of different terms in a ternary system indicates that the salting in effect of the Debye-Hückel term in the Bromley equation (Figure 3.3) is compensated by the additional salting out term at low EtOH concentration (Figure 3.4) and

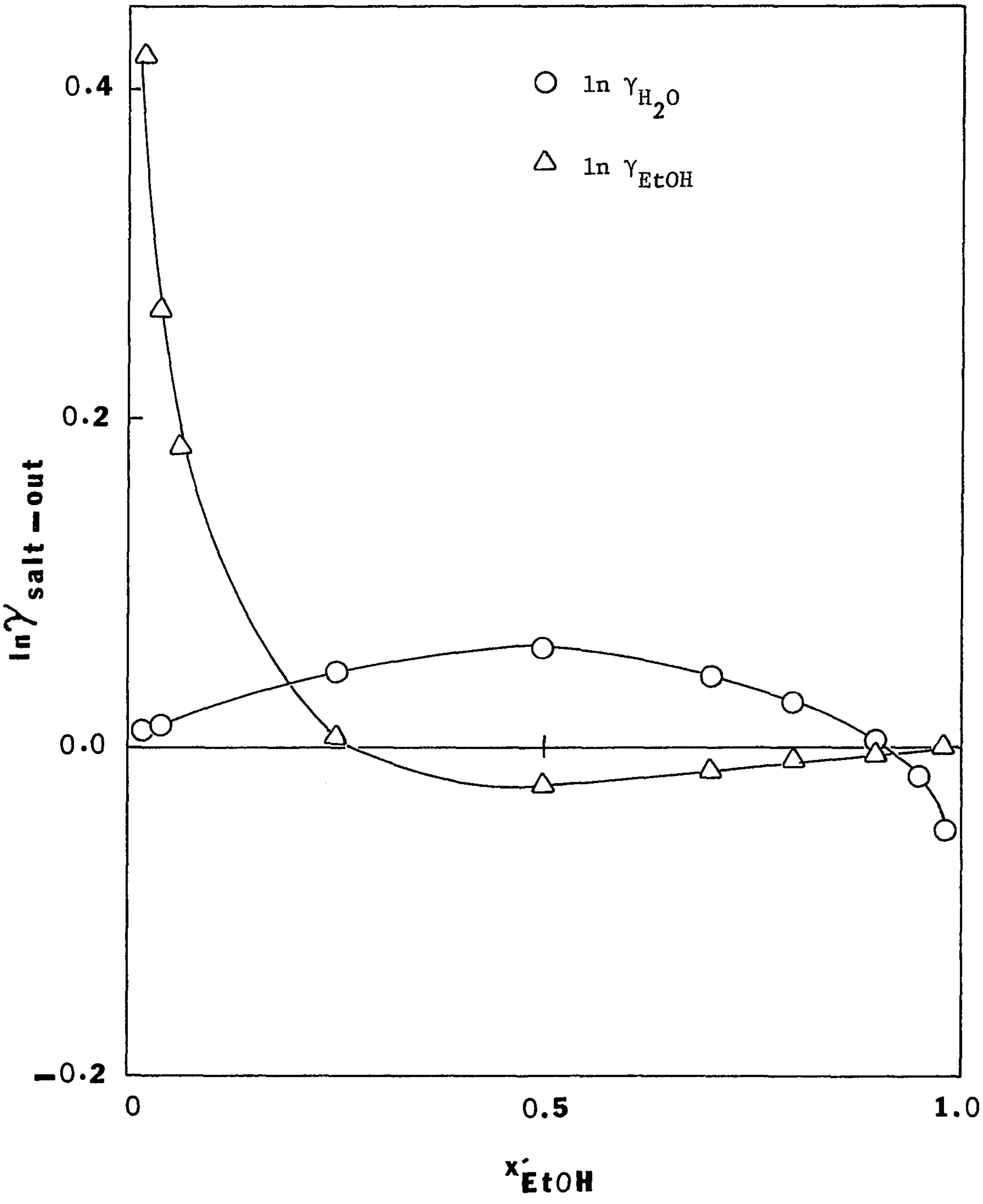


Figure 3.4 Contribution of the Salting-Out Term to ln $\gamma_i$ for the System LiCl-$H_2O$-EtOH at 25°C in Model II

by the additional part of the Bromley equation at higher EtOH concentration (Figure 3.3). It is important to note that for ternary data correlation both binary and ternary experimental data are used.

## 3.5 Conclusions

A method for the correlation of the DP-m data for 53 aqueous electrolytes at 100°C (Weast, 1969), and the evaluation of $\gamma_{\pm}$ values for these electrolytes, is presented. A procedure for the estimation of $\gamma_{\pm}$, $\Delta P$, $\phi L$ and $\bar{L}_2$ in the temperature range of 25-100°C for these electrolytes is also presented. While reasonably good results are obtained for $\gamma_{\pm}$ and $\Delta P$, $\phi L$ and $\bar{L}_2$ values are smaller than the experimental ones by about 50%.

The binary Bromley equation is applied to nonaqueous electrolytic binaries and also has been extended to ternary systems of electrolyte in mixed solvents. The correlation of isothermal nonaqueous binary and ternary data is of good quality; however, the maximum concentration range for such systems is less than the range for aqueous electrolytic binaries.

# CHAPTER 4

# A COMPARATIVE STUDY OF TWO MODELS IN CORRELATING AND PREDICTING BINARY/TERNARY $\gamma_{\pm}$ AND VLE DATA IN ELECTROLYTIC SOLUTIONS

## ABSTRACT

Model I is superior to Model II in correlating binary nonaqueous electrolytic and ternary electrolytic mixtures. However, Model II can be used to predict $\gamma_{\pm}$ using DP vs m data only in a binary mixture more accurately than Model I. Model II is limited only to isothermal ternary data correlation whereas Model I can be applied to predict and/or correlate isothermal or isobaric ternary data.

In principle, the two models presented in Chapters 2 and 3 are similar but consist of different forms of the expressions to represent various interactive forces in the liquid solution. Both the models have the Debye-Hückel equation and an intermediate term also called the transition term represents the change of magnitude of electrostatic forces from the dilute solution to the concentrated solution. The NRTL term has been included in both models, but it represents different molecular interactions in the two models. In Model I the NRTL term describes ion-solvent and solvent-solvent molecular interactions [Equation (2-3)], whereas in Model II ion-solvent interactions are represented by a term: $B \frac{I^2}{2}$ [Equation (3-2)] and the solvent-solvent molecular interactions are by the NRTL-S [Equation (3-4)]. Also, in Model II an additional salting out term is used [Equation (3-5)], which is not needed with Model I.

## A. Binary Data Correlation

Both models simplify to the original NRTL expression [Equation (2-7)] for a solvent-solvent binary. Electrolyte-solvent binary data reduction require two parameters in Model I, i.e. $G_{\pm i}$; $Z_{\pm i}$ or $\Delta g_{Ai}$; $\Delta g_{Bi}$ and one parameter '$B_{1i}$' with Model II. In general, the fit of aqueous electrolyte binaries is better with Model II than Model I, Tables G.4 and H.5. But the correlation of nonaqueous electrolyte binaries shows the reverse trend, Tables G.5 and H.4. However, on the overall analysis of binary data evaluation, it is concluded that both models can be applied successfully. Model I can be used up to I = 6 for electrolyte MeOH binaries and up to even higher molality ranges for aqueous electrolyte binaries, Table 2.3, whereas Model II is limited to I = 3 for MeOH-electrolyte binaries and I = 6 for aqueous electrolyte mixtures. The binary parameters in Model I are considered temperature independent within a 30 to 40°C temperature range, but in Model II, the temperature dependency of the binary parameter '$B_{1i}$' is represented by a two parameter expression, Equation (3-20). This indicates the applicability of Model I to isothermal and isobaric systems without any alterations in the Model itself. The biggest advantage of Model II is that it requires only three data points (DP vs m) to find the optimum value of a single parameter ($B_{1i}$) in a binary mixture which can lead to reliable prediction of $\gamma_\pm$ data for the whole concentration range. The use of three typical data points (DP vs m) with Model I is too small for the evaluation of two parameters in a binary mixture and also the parameters obtained with three points only, cannot be expected to predict $\gamma_\pm$ with reasonable accuracy.

## B. Ternary Data Prediction and Correlation

Model I requires only binary parameters for the ternary VLE and $\gamma_\pm$ data prediction. The binary parameters are obtained by three respective binary data correlation, Tables

2.4 and 2.5. Model II is good only for binary/ternary data correlation. Prediction of a ternary mixture is not possible, because of two ternary parameters '$B_{123}$ and $\delta_{123}$' which should be obtained by ternary data reduction. Also, in Model II binary and ternary parameters ($B_{1i}$, $B_{123}$, $\delta_{123}$) are temperature dependent, hence its applicability is limited to only isothermal data. Model I can be used to correlate binary or ternary data individually whereas with Model II both binary and ternary data are used for ternary data correlation.

Finally, Model I has the possibility of extension to multicomponent systems containing more than two solvents and one electrolyte. In a multicomponent mixture, only binary parameters are required with Model I. The extension of Model II to multicomponent mixtures will be a tedious task.

# APPENDIX A

# EXPRESSIONS FOR THE ACTIVITY COEFFICIENT OF THE SOLVENT AND THE MEAN ACTIVITY COEFFICIENT OF AN ELECTROLYTE IN A BINARY MIXTURE FOR MODEL I

In a binary mixture, the activity coefficients are a combination of an extended form of the Debye-Hückel equation and the modified NRTL equation proposed by Cruz and Renon (1978).

$$\ln\gamma_{\pm} = \ln\gamma_{\pm\,,\ \mathrm{Ext.\ D.H.}} + \ln\gamma^{*}_{\pm,\ \mathrm{NRTL}} \qquad \text{(A-1)}$$

$$\ln\gamma_{i} = \ln\gamma_{i\,,\ \mathrm{Ext.\ D.H.}} + \ln\gamma_{i,\ \mathrm{NRTL}} \qquad \text{(A-2)}$$

Gronwall, LaMer and Sandved (1928) extended the Debye-Hückel equation to higher order terms for symmetrical valence type electrolytes

$$\ln\gamma^{*}_{\pm} = -\frac{(\varepsilon Z)^2}{2DkT}\,\frac{\kappa}{1+\kappa a} + \sum_{m=1}^{\infty}\left(\frac{\varepsilon^2 Z^2}{DkTa}\right)^{2m+1}\left[\frac{1}{2}\,X_{2m+1}(\kappa a) - 2m\,Y_{2m}(\kappa a)\right]$$

(A-3)

where X and Y are functions of ($\kappa a$) and

$$\kappa = \sqrt{\frac{8\pi N\varepsilon^2 Z^2 C}{1000\ DkT}} \qquad \text{(A-4)}$$

The additional higher order terms in equation (A-3) take into account long-range electrostatic forces in the concentrated solution. Further, Gronwall, LaMer and Grieff (1931) extended the above theory to unsymmetrical electrolytes. A semi-empirical extended form of the Debye-Hückel equation is proposed in this work which is analogous to those proposed by Gronwall et al. An additional term with the original D.H. term represents electrostatic forces in concentrated electrolytic solutions.

$$\ln\gamma_{\pm\ \mathrm{Ext.D.H.}} = 2.303\left[-A_{\gamma}\,\frac{I^{1/2}}{1+\rho I^{1/2}} + A_{\gamma}^{2}\,\frac{I}{(1+aI)^{n}}\right]|Z_{+}Z_{-}| \qquad \text{(A-5)}$$

where $\rho$, a and n are adjustable parameters.

The expression for the activity coefficient of the solvent is obtained through the excess Gibbs free energy function, as shown below

$$\frac{G^E}{RT}]_{\text{Ext. D.H.}} = \nu \int_o^{N_1} \ln\gamma_\pm^* \, dN_1 \qquad \text{(A-6)}$$

$$\ln\gamma_\pm^* = \ln\gamma_\pm + \ln(0.001\ \nu m M_w + 1) \qquad \text{(A-7)}$$

$$\ln\gamma_{i\ \text{Ext. D.H.}} = \left.\frac{\partial\ G^E/RT}{\partial N_i}\right|_{T_1 P_1 N_{\ell \neq i}} \qquad \text{(A-7A)}$$

The NRTL part in equations (A-1) and (A-2) for the activity coefficients are the same as given by Cruz-Renon (1978)

$$\ln\gamma_{\pm NRTL}^* = \frac{1}{RT} \frac{\nu_A}{\nu} \left[\frac{X_i^2\ Z_{\pm i}}{(X_A G_{\pm i} + X_i)^2} - Z_{\pm i}\right] \qquad \text{(A-8)}$$

and

$$\ln\gamma_{iNRTL} = \frac{1}{RT} X_A^2 \frac{G_{\pm i}\ Z_{\pm i}}{(X_A G_{\pm i} + X_i)^2} \qquad \text{(A-9)}$$

Equations (A-5) and (A-7A) have three known adjustable parameters, $\rho$, a and n. Equations (A-5) and (A-7A), when combined with the NRTL equations (A-8) and (A-9), have five parameters, $\rho$, a, n, $G_{\pm i}$ and $Z_{\pm i}$ for a binary mixture. Also, it should be noted that the final form of the $\ln\gamma_{i,\text{Ext.D.H.}}$ equation will depend upon the integration of the $\ln\gamma_\pm^*$ term. The integration is accomplished by fixing a value of n, which can be an integer or a noninteger. So the first five parameters were reduced to the two NRTL parameters, $G_{\pm i}$ and $Z_{\pm i}$, by presetting the values of $\rho$, a and n. Secondly, the $\ln\gamma_i$, Ext. D.H. expression is derived by equations (A-6) to (A-7A). Equation (A-5) and the final form of equation (A-7A), when combined with equations (A-8) and (A-9), were used to correlate both binary aqueous electrolyte and nonaqueous electrolyte data. It was found that the best results are obtained (Tables G.4 and G.5) by setting the three adjustable parameters in the extended Debye-Hückel equation to

$$\rho = 1.0$$
$$a = 1.5/|Z_+Z_-| \qquad \text{(A-10)}$$
$$n = 1/2$$

When the parameters of equation (A-10) are substituted in equation (A-5) the following form of the expression for the solvent activity coefficient is obtained

$$\ln\gamma_i,\ \text{Ext. D.H.} = \frac{2.303\ \nu m M_W}{1000}\left[\frac{A_\gamma}{3}\, I^{1/2}\sigma_1(\rho I^{1/2}) + A_\gamma^2\, \frac{I}{2}\, \psi_1(aI)\right] |Z_+Z_-| + \ln(0.001\ \nu m M_W + 1) - 0.001\ \nu m M_W \qquad \text{(A-11)}$$

where

$$\sigma_1(\rho I^{1/2}) = \frac{3}{(\rho I^{1/2})^3}\left[(1+\rho I^{1/2}) - 2\ln(1+\rho I^{1/2}) - \frac{1}{(1+\rho I^{1/2})}\right] \qquad \text{(A-12)}$$

and

$$\psi_1(aI) = \frac{2}{3aI}\left[\frac{2(aI-2)}{aI}(1+aI)^{1/2} + \frac{4}{aI} - \frac{(aI-2)}{(1+aI)^{1/2}} - 2(1+aI)^{1/2}\right] \qquad \text{(A-13)}$$

# APPENDIX B

# A STEPWISE PROCEDURE FOR THE DEVELOPMENT OF TERNARY ACTIVITY COEFFICIENTS FOR MODEL I

## MODEL I:

## Combination of the Extended Debye-Hückel Equation and the Modified NRTL Equation

### B.1--Development of the $\frac{G^{E(\text{ternary})}}{RT}]_{\text{Ext. D.H.}}$ expression

The extended Debye-Hückel part of the mean molal activity coefficient developed in Appendix A for a binary mixture has been extended to a ternary mixture containing one electrolyte and two solvents. This is obtained by modifying the Debye-Hückel constant for the solvent mixture. For a ternary mixture, in equation (A-5), the Debye-Hückel constant is

$$A_\gamma = 1.8246\text{x}10^6\ d^{1/2}\left[\frac{1}{DT}\right]^{3/2} \qquad \text{(B-1)}$$

where

D and d = Dielectric constant and density of a solvent mixture (electrolyte-free)(Appendix D)

The excess Gibbs free energy function for a ternary mixture can be derived by integrating the expression for $\ln\gamma_\pm^*$ for a ternary system. Combination of equations (A-6), (A-7), (A-5) and (B-1) yields

$$\frac{G^{E(\text{ternary})}}{RT}]_{\text{Ext. D.H.}} = \nu\int_0^{N_1}[2.303\{-A_\gamma\frac{I^{1/2}}{(1+\rho I^{1/2})} + A_\gamma^2\frac{I}{(1+aI)^{1/2}}\}$$

$$|Z_+Z_-|]dN_1 + \nu\int_0^{N_1}\ln(0.001\ \nu m M_w + 1)dN_1 \qquad \text{(B-2)}$$

Equation (B-2) can be integrated, term by term, with the following additional equations

$$m = \frac{1000\ N_1}{N_T\ M_w} \tag{B-3}$$

$$N_T = N_2 + N_3 \tag{B-4}$$

$$I = \frac{1}{2}\ m \sum_k \nu_k Z_k^2 = \frac{1}{2}\ m\xi \tag{B-5}$$

$\xi$ = a constant

$$M_w = \frac{N_2}{N_T}\ M_{w2} + \frac{N_3}{N_T}\ M_{w3} \tag{B-6}$$

$$\frac{\partial m}{\partial N_1} = \frac{1000}{N_T M_w} \tag{B-7}$$

$$\frac{\partial I}{\partial m} = \frac{1}{2}\ \xi \tag{B-8}$$

Integration of different terms is as below

$$\nu\int_o^{N_1} \ln(0.001\ \nu m M_w + 1)\,\partial N_1 = \nu\int_o^{m} \ln(0.001\ \nu m M_w + 1)\frac{\partial N_1}{\partial m}\ \partial m$$

$$= \frac{\nu N_T M_w}{1000}\ [\frac{1000}{\nu M_w}\ \{(0.001\ \nu m M_w + 1)$$

$$\ln(0.001\ \nu m M_w + 1) - 0.001\ \nu m M_w\}]$$

$$\nu\int_o^{N_1} \ln(0.001\ \nu m M_w + 1)\,\partial N_1 \equiv N_T[(0.001\ \nu m M_w + 1)\ \ln(0.001\ \nu m M_w + 1)$$

$$-0.001\ \nu m M_w] \tag{B-9}$$

$$\nu \int_0^{N_1} A_\gamma \frac{|Z_+ Z_-|\, I^{1/2}}{1 + \rho I^{1/2}} \partial N_1 = \nu A_\gamma \, |Z_+ Z_-| \int_0^{I} \frac{I^{1/2}}{1 + I^{1/2}} \frac{\partial N_1}{\partial m} \frac{\partial m}{\partial I} \cdot \partial I$$

$$= \nu A_\gamma \frac{N_T M_w}{1000} |Z_+ \quad Z_-| \quad \frac{2}{\xi} \int_0^{I} \frac{I^{1/2}}{1 + \rho I^{1/2}} \partial I$$

$$\nu \int_0^{N_1} A_\gamma \frac{|Z_+ \; Z_-| I^{1/2}}{1 + \rho I^{1/2}} \partial N_1 = \nu A_\gamma \frac{N_T M_w}{1000} |Z_+ \; Z_-| \frac{2}{\xi} \left[\frac{2}{\rho 3} \left\{\frac{1}{2}(1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2}\right\}\right] \qquad \text{(B-10)}$$

$$\nu \int_0^{N_1} A_\gamma^2 \; |Z_+ Z_-| \frac{I}{(1 + aI)^{1/2}} \partial N_1$$

$$= \nu A_\gamma^2 |Z_+ Z_-| \int_0^{I} \frac{I}{(1 + aI)^{1/2}} \frac{\partial N_1}{\partial m} \frac{\partial m}{\partial I} \partial I$$

$$= \nu A_\gamma^2 |Z_+ Z_-| \frac{N_T M_w}{1000} \frac{2}{\xi} \int_0^{I} \frac{I}{(1 + aI)^{1/2}} \partial I$$

$$\nu \int_0^{N_1} A_\gamma^2 |Z_+ Z_-| \frac{I}{(1 + aI)^{1/2}} \partial N_1 = \nu A_\gamma^2 |Z_+ Z_-| \frac{N_T M_w}{1000} \frac{2}{\xi} \left[\frac{2(aI - 2)}{3a^2} (1 + aI)^{1/2} + \frac{4}{3a^2}\right] \qquad \text{(B-11)}$$

Utilizing the change of variables $m/I = 2/\xi$, and combining equations (B-9 to (B-11), results in the excess Gibbs free energy expression, equation (2-2).

## B.2--Development of the $\frac{G^{E(\text{ternary})}}{RT}]_{\text{NRTL}}$ expression

Note: Equations are derived taking into accound that $\gamma_\pm^* \to 1.0$ as $x_1 \to 0.0$ (Assymmetric Convention).

Renon and Prausnitz (1968) proposed an expression for the excess Gibbs free energy in a multicomponent mixture based on the Non-Random Two Liquid Theory. Since the original NRTL equation applies to mixtures following the symmetric convention, it is converted for ternary mixtures utilizing the assymetric convention as indicated below

$$g^{E'}_{NRTL} = \sum_{\ell} x_{\ell} \frac{\sum_{m} X_m Z_{m\ell}}{\sum_{n} X_n G_{n\ell}} \qquad \text{(B-12)}$$

where,

$$Z_{m\ell} = \Delta g_{m\ell}\ G_{m\ell}$$

$$G_{m\ell} = \mathrm{Exp}[-\alpha_{m\ell}\ \frac{\Delta g_{m\ell}}{RT}] \qquad \text{(B-12a)}$$

$$\Delta g_{m\ell} = g_{m\ell} - g_{\ell\ell}$$

$$\alpha_{m\ell} = \alpha_{\ell m} \text{ and } \Delta g_{m\ell} \neq \Delta g_{\ell m}$$

Equation (B-12) can be expanded for a mixture containing electrolyte molecules - 1, cation - A, anion - B, and solvents 2 and 3

$$g^{E'}_{NRTL} = x_A [\frac{x_A Z_{AA} + x_B Z_{BA} + x_1 Z_{1A} + x_2 Z_{2A} + x_3 Z_{3A}}{x_A G_{AA} + x_B G_{BA} + x_1 G_{1A} + x_2 G_{2A} + x_3 G_{3A}}]$$

$$+ x_B [\frac{x_A Z_{AB} + x_B Z_{BB} + x_1 Z_{1B} + x_2 Z_{2B} + x_3 Z_{3B}}{x_A G_{AB} + x_B G_{BB} + x_1 G_{1B} + x_2 G_{2B} + x_3 G_{3B}}]$$

$$+ x_1 [\frac{x_A Z_{A1} + x_B Z_{B1} + x_1 Z_{11} + x_2 Z_{21} + x_3 Z_{31}}{x_A G_{A1} + x_B G_{B1} + x_1 G_{11} + x_2 G_{21} + x_3 G_{31}}]$$

$$+ x_2 [\frac{x_A Z_{A2} + x_B Z_{B2} + x_1 Z_{12} + x_2 Z_{22} + x_3 Z_{32}}{x_A G_{Z2} + x_B G_{B2} + x_1 G_{12} + x_2 G_{22} + x_3 G_{32}}]$$

$$+ x_3 [\frac{x_A Z_{A3} + x_B Z_{B3} + x_1 Z_{13} + x_2 Z_{23} + x_3 Z_{33}}{x_A G_{A3} + x_B G_{B3} + x_1 G_{13} + x_2 G_{23} + x_3 G_{33}}] \qquad \text{(B-13)}$$

Equation (B-13) is simplified by setting $Z_{\ell\ell} = 0.0$ and $G_{\ell\ell} = 1.0$ based on the original development of the equation (B-12). Cruz and Renon (1972) proposed the following additional assumptions for an electrolytic mixture considering that the energy parameter $g_{m\ell}$ increases from low to large numerical values in the following order:

(solvent - ion) < (solvent or electrolyte)-(solvent or electrolyte) << (electrolyte - ion) or (ion - ion of opposite signs) < (ion - ion of the same signs). On the right sign <<, very large values of $g_{m\ell}$ are found, and true local mole fractions are taken equal to zero. Thus

$$Z_{1A} = Z_{1B} = Z_{A1} = Z_{B1} = Z_{AB} = Z_{BA} = 0.0$$

$$G_{1A} = G_{1B} = G_{A1} = G_{B1} = G_{AB} = G_{BA} = 0.0 \qquad \text{(B-14)}$$

For specific ion interaction limitation--

$$G_{AA} = G_{BB} = Z_{AA} = Z_{BB} = 0.0$$

And, also

$$X_{2A} = X_{2B} = X_{3A} = X_{3B} = 1.0$$

$$G_{2A} = G_{2B} = G_{2A} = G_{3B} = 1.0 \qquad \text{(B-15)}$$

where

$$x_{\ell m} = \frac{x_{\ell} G_{\ell m}}{\sum\limits_{n} x_n G_{nm}} \qquad \text{(B-16)}$$

$$Z_{\ell m} = \Delta g_{\ell m} G_{\ell m} \qquad \text{(B-17)}$$

Substitution of equations (B-15) to (B-17) into equation (B-13) yields

$$\begin{aligned} g^{E'}_{NRTL} = {} & x_A [\frac{x_2 \Delta g_{2A} + x_3 \Delta g_{3A}}{x_2 + x_3}] + x_B [\frac{x_2 \Delta g_{2B} + x_3 \Delta g_{3B}}{x_2 + x_3}] \\ & + x_1 [\frac{x_2 Z_{21} + x_3 Z_{31}}{x_1 + x_2 G_{21} + x_3 G_{31}}] \\ & + x_2 [\frac{x_A Z_{A2} + x_B Z_{B2} + x_1 Z_{12} + x_3 Z_{32}}{x_A G_{A3} + x_B G_{B2} + x_1 G_{12} + x_3 G_{32} + x_2}] \\ & + x_3 [\frac{x_A Z_{A3} + x_B Z_{B3} + x_1 Z_{13} + x_2 Z_{23}}{x_A G_{A3} + x_B G_{B3} + x_1 G_{13} + x_2 G_{23} + x_3}] \end{aligned} \qquad \text{(B-18)}$$

$$\begin{aligned} G^{E'}_{NRTL} = (N_T g^{E'}_{NRTL}) = {} & N_A [\frac{N_2 \Delta g_{2A} + N_3 \Delta g_{3A}}{N_2 + N_3}] \\ & + N_B [\frac{N_2 \Delta g_{2B} + N_3 \Delta g_{3B}}{N_2 + N_3}] \\ & + N_1 [\frac{N_2 Z_{21} + N_3 Z_{31}}{N_1 + N_2 G_{21} + N_3 G_{31}}] \\ & + N_2 [\frac{N_A Z_{A2} + N_B Z_{B2} + N_1 Z_{12} + N_3 Z_{32}}{N_A G_{A2} + N_B G_{B2} + N_1 G_{12} + N_3 G_{32} + N_2}] \\ & + N_3 [\frac{N_A Z_{A3} + N_B Z_{B3} + N_1 Z_{13} + N_2 Z_{23}}{N_A G_{A3} + N_B G_{B3} + N_1 G_{13} + N_2 G_{23} + N_3}] \end{aligned} \qquad \text{(B-19)}$$

$$\begin{aligned} RT \ln \gamma_A' &= \frac{\partial G^{E'}}{\partial GN_A}\Bigg|_{T,P,N_\ell \neq A} \\ &= \left[\frac{N_2 \Delta g_{2A} + N_3 \Delta g_{3A}}{N_2 + N_3}\right] \\ &+ N_2\left[\frac{Z_{A2}}{N_A G_{A2} + N_B G_{B2} + N_1 G_{12} + N_3 G_{32} + N_2}\right. \\ &- \left.\frac{(N_A Z_{A2} + N_B Z_{B2} + N_1 Z_{12} + N_3 Z_{32}) G_{A2}}{(N_A G_{A2} + N_B G_{B2} + N_1 G_{12} + N_3 G_{32} + N_2)^2}\right] \\ &+ N_3\left[\frac{Z_{A13}}{N_A G_{A13} + N_B G_{B3} + N_1 G_{13} + N_2 G_{23} + N_3}\right. \\ &- \left.\frac{(N_A Z_{A3} + N_B Z_{B3} + N_1 Z_{13} + N_2 Z_{23}) G_{A3}}{(N_A G_{A3} + N_B G_{B3} + N_1 G_{13} + N_2 G_{23} + N_3)^2}\right] \end{aligned} \qquad \text{(B-20)}$$

$$\begin{aligned} N_A \lim_{\substack{N_A \to 0 \\ N_B \to 0 \\ N_1 \to 0}} RT \ln \gamma_A' &= N_A\left[\frac{N_2 \Delta g_{2A} + N_3 \Delta g_{3A}}{N_2 + N_3}\right] + \frac{N_A N_2 Z_{A2}}{N_3 G_{32} + N_2} \\ &- \frac{N_A N_2 N_3 Z_{32} G_{A2}}{(N_3 G_{32} + N_2)^2} + \frac{N_A N_3 Z_{A3}}{(N_2 G_{23} + N_3)} \\ &- \frac{N_A N_2 N_3 G_{A3} Z_{23}}{(N_2 G_{23} + N_3)^2} \end{aligned} \qquad \text{(B-21)}$$

Similarly

$$\begin{aligned} N_B \lim_{\substack{N_B \to 0 \\ N_A \to 0 \\ N_1 \to 0}} RT \ln \gamma_B' &= N_B\left[\frac{N_2 \Delta g_{2B} + N_3 \Delta g_{3B}}{N_2 + N_3}\right] + \frac{N_B N_2 Z_{B2}}{N_3 G_{32} + N_2} \\ &- \frac{N_B N_2 N_3 Z_{32} G_{B2}}{(N_3 G_{32} + N_2)^2} + \frac{N_B N_3 Z_{B3}}{N_2 G_{23} + N_3} \\ &- \frac{N_B N_2 N_3 G_{B3} Z_{23}}{(N_2 G_{23} + N_3)^2} \end{aligned} \qquad \text{(B-22)}$$

$$G_{NRTL}^{E(ternary)} = G_{NRTL}^{E'} - N_A \lim_{N_A \to 0} RT \ln\gamma_A' - N_B \lim_{N_B \to 0} RT \ln\gamma_B' \qquad \text{(B-23)}$$

Substituting equations (B-19), (B-21) and (B-22) in equation (B-23) results in the following expression for

$$\begin{aligned} G_{NRTL}^{E(ternary)} = {} & N_1 \left[\frac{N_2 Z_{21} + N_3 Z_{31}}{N_1 + N_2 G_{21} + N_3 G_{31}}\right] \\ & + N_2 \left[\frac{N_A Z_{A2} + N_B Z_{B2} + N_1 Z_{12} + N_3 Z_{32}}{N_A G_{A2} + N_B G_{B2} + N_1 G_{12} + N_3 G_{32} + N_2}\right] \\ & + N_3 \left[\frac{N_A Z_{A3} + N_B Z_{B3} + N_1 Z_{13} + N_2 Z_{23}}{N_A G_{A3} + N_B G_{B3} + N_1 G_{13} + N_2 G_{23} + N_3}\right] \\ & - N_2 \left[\frac{N_A Z_{A2} + N_B Z_{B2}}{N_3 G_{32} + N_2}\right] - N_3 \left[\frac{N_A Z_{A3} + N_B Z_{B3}}{N_2 G_{23} + N_3}\right] \\ & + N_2 N_3 Z_{32} \left[\frac{N_A G_{A2} + N_B G_{B2}}{(N_3 G_{32} + N_2)^2}\right] \\ & + N_2 N_3 Z_{23} \left[\frac{N_A G_{A3} + N_B G_{B3}}{(N_2 G_{23} + N_3)^2}\right] \end{aligned} \qquad \text{(B-24)}$$

Considering macroscopic electrical neutrality

$$N_A \nu_B = N_B \nu_A \qquad \text{(B-25)}$$

Substituting equation (B-25) into equation (B-24) gives

$$\begin{aligned} G_{NRTL}^{E(ternary)} = {} & N_1 \left[\frac{N_2 Z_{21} + N_3 Z_{31}}{N_1 + N_2 G_{21} + N_3 G_{31}}\right] \\ & + N_2 \left[\frac{N_A \left(Z_{A2} + \frac{\nu_B}{\nu_A} Z_{B2}\right) + N_1 Z_{12} + N_3 Z_{32}}{N_A \left(G_{A2} + \frac{\nu_B}{\nu_A} G_{B2}\right) + N_1 G_{12} + N_3 G_{32} + N_2}\right] \\ & + N_3 \left[\frac{N_A \left(Z_{A3} + \frac{\nu_B}{\nu_A} Z_{B3}\right) + N_1 Z_{13} + N_2 Z_{23}}{N_A \left(G_{A3} + \frac{\nu_B}{\nu_A} G_{B3}\right) + N_1 G_{13} + N_2 G_{23} + N_3}\right] \end{aligned}$$

$$- N_2\left[\frac{N_A(Z_{A2} + \frac{\nu_B}{\nu_A} Z_{B2})}{N_3G_{32} + N_2}\right] - N_3\left[\frac{N_A(Z_{A3} + \frac{\nu_B}{\nu_A} Z_{B3}}{N_2G_{23} + N_3}\right]$$

$$+ N_2N_3Z_{32}\left[\frac{N_A(G_{A2} + \frac{\nu_B}{\nu_A} G_{B2})}{(N_3G_{32} + N_2)^2}\right]$$

$$+ N_2N_3Z_{23}\left[\frac{N_A(G_{A3} + \frac{\nu_B}{\nu_A} G_{B3})}{(N_2G_{23} + N_3)^2}\right] \qquad \text{(B-26)}$$

Let

$$G_{\pm 2} = G_{A2} + \frac{\nu_B}{\nu_A} G_{B2}$$

$$G_{\pm 3} = G_{A3} + \frac{\nu_B}{\nu_A} G_{B3}$$

$$Z_{\pm 2} = Z_{A2} + \frac{\nu_B}{\nu_A} Z_{B2}$$

$$Z_{\pm 3} = Z_{A3} + \frac{\nu_B}{\nu_A} Z_{B3} \qquad \text{(B-27)}$$

Combining equations (B-25) and (B-27) and setting $N_1 = 0.0$ for the case of complete dissociation, leads to equation (2-3) which is the final expression for $\frac{G^{E(\text{ternary})}}{RT}\Big|_{\text{NRTL}}$ used in this study.

## B.3--Development of the ternary $\ln\gamma_\pm$, $\ln\gamma_2$ and $\ln\gamma_3$ expressions

The total excess Gibbs free energy function in this model is obtained by combining equations (2-2) and (2-3). The activity coefficient expressions are obtained by the appropriate differentiation of the total excess Gibbs free energy expression, equations (1-27) to (1-29). The differentiation of the Debye-Hückel and NRTL terms of the expression have been performed separately as shown below

B.3-I--Debye-Hückel equation--

$$\nu \ln\gamma^*_{\pm \text{Ext.D.H.}} - \frac{\partial}{\partial N_1}\left[\frac{G^{E(\text{ternary})}}{RT}\Big|_{\text{Ext.D.H.}}\right]_{T,P,N_2,N_3} \qquad \text{(B-28)}$$

Since, $\frac{G^E}{RT}\big|_{\text{Ext.D.H.}}$ was obtained by the integration of $\ln\gamma^*_{\pm \text{Ext.D.H.}}$, differentiation of this excess Gibbs free energy function gives the same expression for $\ln\gamma^*_{\pm \text{Ext.D.H.}}$, equation (2-13).

For solvents (2) and (3)

$$\ln\gamma_{2\text{Ext.D.H.}} = \frac{\partial}{\partial N_2}\left[\frac{G^E}{RT}{}_{\text{Ext.D.H.}}\right]_{T,P,N_1,N_3}$$

Equation (2-2) is differentiated term by term by utilizing the change of variables, i.e. $\frac{m}{I} - \frac{2}{\xi}$

$$\text{I term} = \frac{\partial}{\partial N_2}\left[-2.303\nu|Z_+Z_-|\frac{2}{\xi}\,\frac{N_T M_W}{1000}\,A_\gamma\,\frac{2}{\rho_3}\{\frac{1}{2}(1+\rho I^{1/2})^2\right.$$

$$\left.-2(1+\rho I^{1/2}) + \ln(1+\rho I^{1/2}) + \frac{3}{2}\}\right]$$

$$\text{I term} = -2303\,\frac{\nu|Z_+Z_-|}{1000}\,\frac{2}{\xi}[N_T M_W \frac{2}{\rho^3}\{\frac{1}{2}(1+\rho I^{1/2})^2 - 2(1+\rho I^{1/2})$$

$$+ \ln(1+\rho I^{1/2}) + \frac{3}{2}\}\frac{\partial A_\gamma}{\partial N_2} + A_\gamma\,\frac{2}{\rho^3}\{\frac{1}{2}(1+\rho I^{1/2})^2$$

$$- 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \tfrac{3}{2}\} \frac{\partial}{\partial N_2}(N_T M_w)$$

$$+ N_T M_w A_\gamma \frac{2}{\rho 3} \frac{\partial}{\partial I}\{\tfrac{1}{2}(1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2})$$

$$+ \ln(1 + \rho I^{1/2}) + \tfrac{3}{2}\} \frac{\partial I}{\partial m} \frac{\partial m}{\partial N_2}] \tag{B-29}$$

from equations (B-3) and (B-6)

$$\frac{\partial m}{\partial N_2} = \frac{m M_{w2}}{N_T M_w} \tag{B-30}$$

$$\frac{\partial (N_T M_w)}{\partial N_2} = M_{w2} \tag{B-31}$$

Simplifying equation (B-29) and substituting equations (B-30) and (B-31) results in the following expression for term I

$$\text{I term} = 2.303 \frac{\nu m}{1000} |Z_+ Z_-| [A_\gamma I^{1/2} \frac{1}{(\rho I^{1/2})^3}\{(1 + \rho I^{1/2})$$

$$- 2 \ln(1 + \rho I^{1/2}) - \frac{1}{(1 + \rho I^{1/2})}\} - N_T M_w \; I^{1/2}$$

$$\frac{1}{(\rho I^{1/2})^3}\{ \tfrac{1}{2}(1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2})$$

$$+ \tfrac{3}{2}\} \frac{\partial A_\gamma}{\partial N_2}] \tag{B-32}$$

$$\text{II term} = \frac{\partial}{\partial N_2}[2.303 \frac{\nu |Z_+ Z_-|}{1000} \frac{2}{\xi} N_T M_w A_\gamma^2 \{\frac{2(aI - 2)}{3a^2} +$$

$$(1 + aI)^{1/2} + \frac{4}{3a^2}\}]$$

$$= 2.303 \frac{\nu|Z_+Z_-|}{1000} \frac{2}{\xi}[\{\frac{2(aI-2)}{3a^2} + (1+aI)^{1/2} + \frac{4}{3a^2} N_T M_w$$

$$\frac{\partial A_\gamma^2}{\partial N_2} + A_\gamma^2\{\frac{2(aI-2)}{3a^2} + (1+aI)^{1/2} + \frac{4}{3a^2}\}\frac{\partial(N_T M_w)}{\partial N_2}$$

$$+ A_\gamma^2 N_T M_w \frac{\partial}{\partial I}\{\frac{2(aI-2)}{3a^2} + (1+aI)^{1/2} + \frac{4}{3a^2}\}\frac{\partial I}{\partial m}\frac{\partial m}{\partial N_2}]$$

$$\text{II term} = 2.303 \frac{\nu m}{1000} |Z_+Z_-| [M_{w2}A_\gamma^2 \frac{I}{2} \frac{2}{3aI}\{\frac{2(aI-2)(1+aI)^{1/2}}{aI}$$

$$+ \frac{4}{aI} - \frac{(aI-2)}{(1+aI)^{1/2}} - 2(1+aI)^{1/2}\}$$

$$+ N_T M_w \frac{2}{3aI}\{\frac{2(aI-2)(1+aI)^{1/2}}{aI} + \frac{4}{aI}\} I A_\gamma \frac{\partial A_\gamma}{\partial N_2}] \qquad \text{(B-33)}$$

$$\text{III term} = \frac{\partial}{\partial N_2} [N_T\{(0.001\ \nu m M_w + 1)\ln(0.001\ \nu m M_w + 1)$$

$$- 0.001\ \nu m M_w\}]$$

$$\text{III term} = \{(0.001\ \nu m M_w + 1)\ln(0.001\ \nu m M_w + 1) - 0.001\ \nu m M_w \frac{\partial N_T}{\partial N_2}$$

$$+ N_T\{\ln(0.001\ \nu m M_w + 1)\frac{\partial}{\partial N_2}(0.001\ \nu m M_w + 1)$$

$$+ (0.001\ \nu m M_w + 1)\frac{\partial}{\partial N_2}\ln(0.001\ \nu m M_w + 1) - 0.001\nu \frac{\partial}{\partial N_2}(m M_w)\}$$

$$\text{III term} = \ln(0.001\ \nu m M_w + 1) - 0.001\ \nu m M_w \qquad \text{(B-34)}$$

The combination of equations (B-32), (B-33) and (B-34) yields equation (2-16). A similar approach leads to the expression for $\ln\gamma_{3\text{Ext.D.H.}}$

In equation (2-16) $\sigma_1^1(\rho I^{1/2})$ and $\psi_1^1(aI)$ are given by

$$\sigma_1^1(\rho I^{1/2}) = \frac{2}{(\rho I^{1/2})^3}\left[\frac{1}{2}(1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2}\right] \qquad \text{(B-35)}$$

$$\psi_1^1(aI) = \frac{2}{3aI}\left[\frac{2(aI - 2)}{aI}(1 + aI)^{1/2} + \frac{4}{aI}\right] \qquad \text{(B-36)}$$

B.3.II--NRTL equation

$$\nu \ln\gamma_{\pm}^{*} = \frac{\partial}{\partial N_1}\left[\frac{G^{E(\text{ternary})}}{RT}\bigg|_{\text{NRTL}}\right]_{T,P,N_2,N_3}$$

$$\nu \ln\gamma_{\pm}^{*} = \frac{\partial}{\partial N_A}\left[\frac{G^{E(\text{ternary})}}{RT}\bigg|_{\text{NRTL}}\right]_{T,P,N_2,N_3}\frac{\partial N_A}{\partial N_1} \qquad \text{(B-37)}$$

Assuming complete dissociation of the electrolyte

$$N_A = \nu_A N_1 \qquad \text{(B-38)}$$

$$\frac{\partial N_A}{\partial N_1} = \nu_A \qquad \text{(B-39)}$$

Combining equations (B-37) and (B-39) yields

$$\nu \ln \gamma_{\pm}^{*} = \nu_A \ln \gamma_{A,\text{NRTL}} \qquad \text{(B-40)}$$

$\ln \gamma_{\pm}^{*}$ can be obtained by differentiating equation (B-28) with respect to $N_A$

$$\ln\gamma_A = \frac{1}{RT}\left[\frac{N_2(N_A G_{\pm 2} Z_{\pm 2} + N_3 G_{32} Z_{\pm 2} + N_2 Z_{\pm 2} - N_A G_{\pm 2} Z_{\pm 2} - N_3 Z_{32} G_{\pm 2})}{(N_A G_{\pm 2} + N_3 G_{32} + N_2)^2}\right.$$

$$+ \frac{N_3(N_A G_{\pm 3} Z_{\pm 3} + N_2 G_{23} Z_{\pm 3} + N_3 Z_{\pm 3} - N_A G_{\pm 3} Z_{\pm 3} - N_2 Z_{23} G_{\pm 3})}{N_A G_{\pm 3} + N_2 G_{23} + N_3)^2}$$

$$- \left\{\frac{N_2 Z_{\pm 2}}{(N_3 G_{32} + N_2)} + \frac{N_3 Z_{\pm 3}}{(N_2 G_{23} + N_3)}\right\}$$

$$+ N_2N_3 \{\frac{Z_{32}G_{\pm2}}{(N_3G_{32} + N_2)^2} + \frac{Z_{23}G_{\pm3}}{(N_2G_{23} + N_3)^2}\} ] \qquad \text{(B-41)}$$

Combining equations (B-37) and (B-41) and converting moles to the mole fraction leads to equation (2-14).

The activity coefficient of the solvent is obtained by differentiating $\frac{G^E}{RT}|_{NRTL}$ with respect to $N_2$

$$\ln \gamma_{2,NRTL} = \frac{\partial}{\partial N_2}[\frac{G^{E(ternary)}}{RT}|_{NRTL}]_{T,P,N_A,N_B,N_3}$$

$$= \frac{1}{RT}[\frac{N_AZ_{\pm2} + N_3Z_{32}}{(N_AG_{\pm2} + N_3G_{32} + N_2)} - \frac{N_2(N_AZ_{\pm2} + N_3Z_{32})}{(N_AG_{\pm2} + N_3G_{32} + N_2)^2}$$

$$+ \frac{N_3Z_{23}}{(N_AG_{\pm3} + N_2G_{23} + N_3)} - \frac{N_A(N_AZ_{\pm3} + N_2Z_{23})G_{23}}{(N_AG_{\pm3} + N_2G_{23} + N_3)^2}$$

$$- N_A\{\frac{Z_{\pm2}}{N_3G_{32} + N_2} - \frac{N_2Z_{\pm2}}{(N_3G_{32} + N_2)^2} - \frac{N_3Z_{\pm3}G_{23}}{(N_2G_{23} + N_3)^2}\}$$

$$+ N_AN_3 \{\frac{Z_{32}G_{\pm2}}{(N_3G_{32} + N_2)^2} + \frac{Z_{23}G_{\pm3}}{(N_2G_{23} + N_3)^2}\}$$

$$-N_AN_2N_3 \{\frac{2Z_{32}G_{\pm2}}{(N_3G_{32} + N_2)^3} + \frac{2Z_{23}G_{\pm3}G_{23}}{(N_2G_{23} + N_3)^3}\}] \qquad \text{(B-42)}$$

Equation (B-42) can be simplified in the form of equation (2-17). Utilizing a similar approach an expression for $\ln\gamma_{3,NRTL}$ is obtained.

# APPENDIX C

# A STEPWISE PROCEDURE FOR THE DEVELOPMENT OF TERNARY ACTIVITY COEFFICIENT EXPRESSIONS FOR MODEL II

## MODEL II: Combination of the Bromley Equation; The Simplified NRTL Equation and the Salting Out Term

Bromley (1973) presented a generalized analytic correlation for mean activity coefficients of electrolytes in binary aqueous electrolytic solutions.

$$\ln \gamma_{\pm} = 2.303[-A_{\gamma}|Z_+Z_-| \frac{I^{1/2}}{1+\rho I^{1/2}} + \frac{(B_o - B_{1i})^{I}}{(1+aI)^{\eta}} + B_{1i}I + CI^2] \quad \text{(C-1)}$$

where

$A_{\gamma}$ = Debye-Hückel constant (Appendix-L)

$$I = \frac{1}{2} \Sigma\, m_k Z_k^{\,2} \quad \text{(C-1-A)}$$

$\eta$, $\rho$, a, $B_o$, $B_{1i}$ and c: adjustable parameters

On the basis of a comprehensive study using data for $\gamma_{\pm}$, but also osmotic coefficients and other related thermodynamic properties at 25°C, as well as at other temperatures up to 200°C, Bromley concluded that reasonable agreement is obtained by using

$\eta = 2$

$a = 1.5/|Z_+Z_-|$

$c = 0.0$

$\rho = 1.0$

$$(B_o - B_{1i}) = (0.06 + 0.6B_{1i})|Z_+Z_-| \quad \text{(C-2)}$$

in equation (C-1).

Substitution of (C-2) into (C-1) simplifies this equation in terms of only one adjustable parameter '$B_{1i}$' per binary. When the above equation was applied to correlate non-aqueous electrolytic binary with the same constants, the fit was good. Considering the simplicity and success of the above equation in correlating binary systems and the success of the NRTL equation in correlating solvent-solvent binaries, Model II proposes to combine them with an additional ternary salting out term for the correlation of electrolyte (1) - solvent (2) - solvent (3) ternary systems. The following procedure is followed in developing Model II:

C.1: Development of the $\frac{G^{E(\text{ternary})}}{RT}\Big|_{\text{Bromley}}$ expression

Equation (C-1) with (C-2) is first integrated to derive $\frac{G^{E(\text{binary})}}{RT}\Big|_{\text{Bromley}}$, which is then extended to ternary mixtures.

$$\frac{G^{E(\text{binary})}}{RT}\Big|_{\text{Bromley}} = 2.303\nu\Big[\int_0^{N_1}\Big\{-A_\gamma|Z_+Z_-|\frac{I^{1/2}}{1+\rho I^{1/2}}\Big\}dN_1 + \int_0^{N_1}\Big\{\frac{(0.06+0.6B_{1i})\,I}{(1+aI)^2}\Big\}dN_1 + \int_0^{N_1}B_{1i}\;I\;dN_1\Big] + \nu\int_0^{N_1}\ln(0.001\nu m M_w + 1)\,dN_1 \qquad \text{(C-3)}$$

Equation (C-3) can be integrated term by term with equations (B-3) to (B-8)

$$\text{I term} = 2.303\nu\int_0^I -A_\gamma|Z_+Z_-|\frac{I^{1/2}}{1+\rho I^{1/2}}\frac{\partial N_1}{\partial m}\frac{\partial m}{\partial I}\,\partial I$$

$$\text{I term} = -2.303\nu A_\gamma \frac{N_T M_w}{1000} \frac{m}{I}\left[\frac{2}{\rho^3}\left\{\frac{1}{2}(1 + \rho I^{1/2})^2\right.\right.$$

$$\left.\left. - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2}\right\}\right] |Z_+ Z_-| \qquad \text{(C-4)}$$

$$\text{II term} = 2.303\nu \int_o^I \frac{(0.06 + 0.06B_{1i})^I}{(1 + aI)^2} \frac{\partial N_1}{\partial m} \frac{\partial m}{\partial I} \partial I$$

$$\text{II term} = 2.303\nu \frac{N_T M_w}{1000} |Z_+ Z_-| \frac{(0.06 + 0.6B_{1i})}{a^2} \frac{m}{I}[\ln(1 + aI) + \frac{1}{(1 + aI)} - 1]$$

$$\text{(C-5)}$$

$$\text{III term} = 2.303\nu \int_o^I B_{1i}\, I \frac{\partial N_1}{\partial m} \frac{\partial m}{\partial I} \partial I$$

$$\text{III term} = 2.303\nu \frac{N_T M_w}{1000} \frac{m}{I} B_{1i} \frac{I^2}{2} \qquad \text{(C-6)}$$

$$\text{IV term} = \nu \int_o^{N_1} \ln(0.001\nu m M_w + 1) \frac{dN_1}{\partial m} \partial m$$

$$= N_i[(0.001\nu m M_w + 1)\ln(0.001 m M_w + 1)$$

$$- 0.001\nu m M_w] \qquad \text{(C-7)}$$

Combining equations (C-4) to (C-7) leads to the following expression for

$$\frac{G^{E\,(\text{binary})}}{RT}\Bigg|_{\text{Bromley}} = 2.303\nu \frac{N_i M_w}{1000} \frac{m}{I}[-A_\gamma |Z_+ Z_-| \frac{2}{\rho^3}$$

$$\{\frac{1}{2}(1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2})$$

$$+ \frac{3}{2}\} + \frac{(0.06 + 0.6B_{1i})}{a^2} |Z_+ Z_-|$$

$$\{\ln(1 + aI) + \frac{1}{(1 + aI)} - 1\} + \frac{B_{1i} I^2}{2}]$$

$$+ N_i[(0.001\nu m M_w + 1)\ln(0.001\nu m M_w + 1)$$

$$- 0.001\nu m M_w] \qquad \text{(C-8)}$$

In a binary aqueous/nonaqueous electrolyte solution, equation (C-8) can be used to derive the expression for the activity coefficient of the solvent, by equation (1-27)

$$\ln \gamma_{i,\text{Bromley}}^{(\text{binary})} = 2.303 \frac{\nu m}{1000} M_{w_i} [A_\gamma \frac{I^{1/2}}{3} \sigma(\rho I^{1/2}) |Z_+Z_-|$$

$$- (0.06 + 0.6B_{1i}) \frac{I}{2} \psi(aI) |Z_+Z_-| - B \frac{I}{2}]$$

$$+ \ln(0.001\nu m M_w + 1) - 0.001\nu m M_w \qquad \text{(C-9)}$$

Equation (C-8) is modified for a ternary system by the appropriate substitution of B for $B_{1i}$ and the Debye-Hückel constant for mixture. The most important conditions to be satisfied are

$$\lim_{\substack{N_2 \to 0 \\ \text{or} \\ N_3 \to 0}} \frac{G^{E(\text{ternary})}}{RT}\Big|_{\text{Bromley}} = \frac{G^{E(\text{binary})}}{RT}\Big|_{\text{Bromley}} \qquad \text{(C-10)}$$

This requires--

$$\lim_{N_2 \to 0} B = B_{12}$$

$$\lim_{N_2 \to 0} A_\gamma(N_2,N_3,d_2,d_3,D_2,D_3,T) = A_\gamma(d_2,D_2,T)$$

or

$$\lim_{N_3 \to 0} B = B_{13}$$

$$\lim_{N_3 \to 0} A_\gamma(N_2,N_3,d_2,d_3,D_2,D_3,T) = A_\gamma(d_3,D_3,T) \qquad \text{(C-11)}$$

The above constraints lead equation (C-8) to

$$\frac{G^{E(\text{ternary})}}{RT}\Bigg|_{\text{Bromley}}, \text{ equation (3-2)}$$

Note: equation (3-2) involves no solvent-solvent interaction parameters.

## C.2--Development of the $\frac{G^{E(\text{ternary})}}{RT}\Big|_{\text{NRTL-S}}$ Expression

The NRTL equation developed in model I, equation (2-3) is simplified further by considering that the NRTL equation in Model II accounts only for solvent-solvent interactions. Hence, assuming that

$$X_{A2} = X_{B2} = X_{A3} = X_{B3} = 1.0 \qquad \text{(C-12)}$$

in equation (2-3) then,

$$\Delta g_{A2} = \Delta g_{A3} = \Delta g_{B2} = \Delta g_{B} = 0.0$$

$$G_{A2} = G_{B2} = G_{A3} = G_{B3} = 1.0$$

$$G_{\pm 2} = G_{\pm 3} = \frac{\nu}{\nu_A} \qquad \text{(C-13)}$$

$$Z_{A2} = Z_{B2} = Z_{A3} = Z_{B3} = 0.0$$

$$Z_{\pm 2} = Z_{\pm 3} = 0.0 \qquad \text{(C-14)}$$

$$\frac{G^{E(\text{ternary})}}{RT}\Bigg]_{\text{NRTL-S}} = \frac{1}{RT}\Bigg[\frac{N_2N_3Z_{32}}{(N_A\frac{\nu}{\nu_A} + N_2 + N_3G_{32})} + \frac{N_2N_3Z_{23}}{(N_A\frac{\nu}{\nu_A} + N_3 + N_2G_{23})}$$

$$+ \frac{\nu}{\nu_A} N_AN_2N_3\Bigg\{\frac{Z_{32}}{(N_3G_{32} + N_2)^2} + \frac{Z_{23}}{(N_2G_{23} + N_3)^2}\Bigg\}\Bigg] \qquad \text{(C-15)}$$

Equation (C-15) can be converted in terms of mole fractions, equation (3-4).

## C.3--Development of the Salting-Out Term for a Ternary Mixture

It is well known that the addition of an electrolyte in mixed solvents, causes salting-out of one of the solvents. Combination of the Bromley equation and the simplified NRTL equation alone is not enough to account for the salting-out effect, therefore an additional salting-out term was sought. Different theories have been proposed specifically by Debye-McAulay (1925), Butler (1929) and Born (1932), to account for salting-out. In this work, an expression based on the above theories, has been proposed, which requires one ternary salting-out parameter '$\delta_{123}$' and is shown below

$$\frac{g^{E(\text{ternary})}}{RT}\Big|_{\text{salt-out}} = \frac{D' - D}{D^2}\,\frac{\varepsilon^2}{\kappa T}\,\sum_k \frac{\nu_k Z_k^2}{bk}\,\frac{1}{2} \qquad \text{(C-16)}$$

where,

$$D' = D\Big[1 - \frac{\delta_{123}}{e^{\alpha N_1^{1/2}}}\,(X_2' X_3')^{1/2} N_1 (X_2' B_{13} - X_3' B_{12})\, e^{\alpha X_2'}\Big] \qquad \text{(C-17)}$$

$$\alpha = 2.0$$

Combining equations (C-16) and (C-17) leads to the form--

$$\frac{G^{E(\text{ternary})}}{RT}\Big|_{\text{salt-out}} = N_T\,\frac{g^{E(\text{ternary})}}{RT}\Big|_{\text{salt-out}}$$

equation (3-5).

## C.4--Development of the Ternary ln $\gamma_{\pm}$, ln $\gamma_2$ and ln $\gamma_3$ Expressions

The total excess Gibbs free energy function is obtained by combining equations (3-2) to (3-5). The activity coefficient expressions are obtained by the appropriate differentiation of the total Gibbs free energy function. Since the activity coefficients are a combination of three different terms, the differentiation of each term is performed separately, as below

### C.4-I--The Bromley Equation

Combining equations (1-26) (3-2) and (3-3) results in--

$$\nu \ln\gamma^{*(\text{ternary})}_{\pm,\text{Bromley}} = \frac{\partial}{\partial N_1}[2.303\nu \frac{m}{I} \frac{N_T M_w}{1000}\{ \frac{1}{2}(1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2}\} + \frac{(0.06 + 0.06B)}{a^2} \{\ln(1 + aI) + \frac{1}{1 + aI} - 1\} + \frac{B}{2} I^2] + \frac{\partial}{\partial N_1}[N_T\{(0.001\nu m M_w + 1)\ln(0.001\nu m M_w + 1) - 0.001\nu m M_w\}] \quad \text{(C-18)}$$

Equation (C-18) simplifies to the original ln $\gamma^{*}_{\pm,\text{Bromley}}$ equation with an additional term, equation (3-8), where

$$\frac{\partial B}{\partial N_1} = -\frac{3}{2} \alpha B_{123} \frac{1}{N_1^{1/2}} \frac{1}{(1 + \alpha N_1^{1/2})^4} e^{-\alpha X_3'}(X_2' X_3')^{1/4} \quad \text{(C-19)}$$

For solvent 2, equation (3-2) with (3-3) is differentiated term by term

$$\text{I term} = \frac{\partial}{\partial N_2}[-2.303\nu\ \frac{m}{I}\ \frac{N_T M_w}{1000}\ A_\gamma\ \frac{2}{\rho^3}\{\frac{1}{2}(1 + \rho I^{1/2})^2$$

$$- 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2}\}]$$

$$\text{I term} = 2.303\ \frac{\nu m}{1000}[M_{w_2}\ A_\gamma\ I^{1/2}\ \frac{1}{(\rho I^{1/2})^3}\{(1 + \rho I^{1/2})$$

$$- 2\ln(1 + \rho I^{1/2}) - \frac{1}{(1 + \rho I^{1/2})}\} - N_T M_w$$

$$I^{1/2}\ \frac{2}{(\rho I^{1/2})^3}\{\frac{1}{2}(1 + \rho I^{1/2})^2 - 2(1 + \rho I^{1/2})$$

$$+ \ln(1 + \rho I^{1/2}) + \frac{3}{2}\}\frac{\partial A_\gamma}{\partial N_2}] \tag{C-20}$$

$$\text{II term} = \frac{\partial}{\partial N_2}[2.303\nu\ \frac{m}{I}\ \frac{N_T M_w}{1000}\ \frac{(0.06 + 0.06B)}{a^2}$$

$$\{\ln(1 + aI) + \frac{1}{(1 + aI)} - 1\}]$$

$$\text{II term} = +\ 2.303\ \frac{\nu m}{1000}[-M_{w_2}(0.06 + 0.6B)\frac{I}{2}\ \frac{2}{aI}$$

$$\{\frac{(1 + 2aI)}{(1 + aI)^2} - \frac{\ln(1 + aI)}{aI}\} + 0.6\ N_T M_w\ \frac{I}{2}\ \frac{2}{aI}$$

$$\{\frac{\ln(1 + aI)}{aI} - \frac{1}{(1 + aI)}\}\frac{\partial B}{\partial N_2}] \tag{C-21}$$

$$\text{III term} = \frac{\partial}{\partial N_2}[2.303\nu\ \frac{m}{I}\ \frac{N_T M_w}{1000}\ \frac{B}{2}\ I^2]$$

$$\text{III term} = +\ 2.303\ \frac{\nu m}{1000}[-M_{w_2}\ B\ \frac{I}{2} + N_T M_w\ I\ \frac{\partial B}{\partial N_2}] \tag{C-22}$$

$$\text{IV term} = \frac{\partial}{\partial N_2}[(0.001\nu m M_w + 1)\ln(0.001\nu m M_w + 1) - 0.001\nu m M_w]$$

$$\text{IV term} = \ln(0.001\nu m M_w + 1) - 0.001\nu m M_w \tag{C-23}$$

Combining equations (C-20) to (C-23) results in $\ln \gamma_{2,\text{Bromley}}^{(\text{ternary})}$ expression, equation (3-12). Similarly an expression for $\ln \gamma_{3,\text{Bromley}}^{(\text{ternary})}$ can be obtained.

The different terms of equation (3-12) are defined below

$$\sigma_2(\rho I^{1/2}) = \frac{3}{(\rho I^{1/2})^3}[(1 + \rho I^{1/2}) - 2\ln(1 + \rho I^{1/2}) - \frac{1}{(1 + \rho I^{1/2})}] \tag{C-24}$$

$$\sigma_2^1(\rho I^{1/2}) = \frac{2}{(\rho I^{1/2})^3}[\frac{1}{2}(1 + \rho I^{1/2}) - 2(1 + \rho I^{1/2}) + \ln(1 + \rho I^{1/2}) + \frac{3}{2}] \tag{C-25}$$

$$\psi_2(aI) = \frac{2}{aI}[\frac{(1 + 2aI)}{(1 + aI)^2} - \frac{\ln(1 + aI)}{aI}] \tag{C-26}$$

$$\psi_2^1(aI) = \frac{2}{aI}[\frac{\ln(1 + aI)}{aI} - \frac{1}{(1 + aI)}] \tag{C-27}$$

$$\frac{\partial B}{\partial N_2} = (B_{12} - B_{13})\frac{X_2'}{N_T} + \frac{B_{123}}{(1 + \alpha N_1^{1/2})^3}[\{\frac{1}{2}(\frac{X_3'}{X_2'})^{1/2}\frac{1}{X_2'^{1/2}} - (X_2'X_3')^{1/4}\}$$

$$\frac{1}{2}\frac{1}{N_T}e^{-\alpha X_3'} + \alpha\frac{X_3'}{N_T}e^{-\alpha X_3'}(X_2'X_3')^{1/4}] \tag{C-28}$$

$$\frac{\partial B}{\partial N_3} = (B_{13} - B_{12})\frac{X_3'}{N_T} + \frac{B_{123}}{(1 + \alpha N_1^{1/2})^3}[\{\frac{1}{2}(\frac{X_2'}{X_3'})^{1/2}\frac{1}{X_3'^{1/2}} - (X_2'X_3')^{1/4}\}$$

$$\frac{1}{2}\frac{1}{N_T}e^{-\alpha X_3'} - \alpha\frac{X_2'}{N_T}e^{-\alpha X_3'}(X_2'X_3')^{1/4}] \tag{C-29}$$

C.4-II--The NRTL-S equation

Equation (C-15) can be differentiated appropriately to obtain the activity coefficient expression for electrolyte and solvents. Utilizing equations (B-35) to (B-38) with equation (C-15) leads to

$$\ln \gamma^{*(\text{ternary})}_{\pm,\text{NRTL-S}} = \frac{N_2N_3}{RT}\Big[-\frac{Z_{32}}{(N_A\frac{\nu}{\nu_A} + N_2 + N_3G_{32})^2} - \frac{Z_{23}}{(N\frac{\nu}{\nu_A} + N_3 + N_2G_{23})^2} + \frac{Z_{32}}{(N_3G_{32} + N_2)^2} + \frac{Z_{23}}{(N_2G_{23} + N_3)^2}\Big] \qquad \text{(C-30)}$$

Equation (C-30) can be converted in terms of mole fraction, equation (3-8).

$$\ln \gamma^{(\text{ternary})}_{2,\text{NRTL-S}} = \frac{\partial}{\partial N_2}\Big[\frac{G^{E(\text{ternary})}}{RT}\Big|_{\text{NRTL-S}}\Big]$$

$$\ln \gamma^{(\text{ternary})}_{2,\text{NRTL-S}} = \frac{1}{RT}\Big[\frac{N_3Z_{32}(N_A\frac{\nu}{\nu_A} + N_2 + N_3G_{32}) - N_2N_3Z_{32}}{(N_A\frac{\nu}{\nu_A} + N_2 + N_3G_{32})^2} + \frac{N_3Z_{23}(N_A\frac{\nu}{\nu_A} + N_3 + N_2G_{23}) - N_2N_3G_{23}Z_{23}}{N_A\frac{\nu}{\nu_A} + N_3 + N_2G_{23})^2} + \frac{\nu}{\nu_A}N_AN_3\Big\{\frac{Z_{32}}{(N_3G_{32} + N_2)^2} + \frac{Z_{23}}{(N_2G_{23} + N_3)^2}\Big\}$$

$$+ \frac{\nu}{\nu_A} N_A N_2 N_3 \; -\{ \frac{2Z_{32}}{(N_3 G_{32} + N_2)^3} - \frac{2Z_{23}G_{23}}{(N_2 G_{23} + N_3)^2} \}]$$

$$\ln \gamma^{(ternary)}_{2,NRTL-S} = \frac{1}{RT} [ \frac{\nu}{\nu_A} N_A N_3 \{ \frac{Z_{32}}{(N_A \frac{\nu}{\nu_A} + N_2 N_3 G_{32})^2}$$

$$+ \frac{Z_{23}}{(N_A \frac{\nu}{\nu_A} + N_3 + N_2 G_{23})^2} + N_3^2 \{ \frac{G_{32} Z_{32}}{(N_A \frac{\nu}{\nu_A} + N_2 + N_3 G_{32})^2}$$

$$+ \frac{Z_{23}}{(N_A \frac{\nu}{\nu_A} + N_3 + N_2 G_{23})^2} \} +$$

$$\frac{\nu}{\nu_A} N_A N_3 \{ \frac{Z_{32}}{(N_3 G_{32} + N_2)^2} + \frac{Z_{23}}{(N_2 G_{23} + N_3)^2} \}$$

$$- 2 \frac{\nu}{\nu_A} N_A N_2 N_3 \{ \frac{Z_{32}}{(N_3 G_{32} + N_2)^3} + \frac{Z_{23} G_{23}}{(N_2 G_{23} + N_3)^3} \}] \quad (C-31)$$

Using the above approach, an expression for $\ln \gamma^{(ternary)}_{3,NRTL-S}$ can be obtained. These expressions can be rearranged in terms of mole fractions, equation (3-13).

C.3-III--The Salting-Out Term

Equation (3-5) with equation (3-6) is differentiated to obtain the salting-out contribution for the activity coefficients.

$$\ln \gamma^{*(\text{ternary})}_{\pm,\text{salt-out}} = \delta_{123} \frac{\varepsilon^2}{kTD} \sum_k \frac{\nu_k Z_k^2}{b_k} (N_2N_3)^{1/2}\, \delta' \frac{\partial}{\partial N_1}\left[\frac{N_1^2}{2} \frac{1}{e^{\alpha N_1^{1/2}}}\right] \qquad \text{(C-32)}$$

$$\frac{\partial}{\partial N_1}\left[\frac{{}^{2}_{1}}{2} \frac{1}{e^{\alpha N_1^{1/2}}}\right] = \frac{1}{e^{\alpha N_1^{1/2}}}\left[N_1 - \frac{1}{2}\,\alpha\, \frac{1}{N_1^{1/2}} \frac{N_1^2}{2}\right] \qquad \text{(C-33)}$$

Combining equations (C-32) and (C-33) leads to equation (3-1). And

$$\ln \gamma^{(\text{ternary})}_{2,\text{salt-out}} = \delta_{123} \frac{\varepsilon^2}{kT} \sum_k \frac{\nu_k Z_k^2}{b_k} \frac{N_1^2}{2} \frac{1}{e^{\alpha N_1^{1/2}}}\left[\frac{\delta'}{D} \frac{\partial}{\partial N_2}\{(N_2N_3)^{1/2}\}\right.$$

$$\left. + (N_2N_3)^{1/2} \frac{\partial}{\partial N_2}\delta' + \delta'(N_2N_3)^{1/2} \frac{\partial}{\partial N_2}\left(\frac{1}{D}\right)\right] \qquad \text{(C-34)}$$

where,

$$\frac{\partial}{\partial N_2}\{(N_2N_3)^{1/2}\} = \frac{1}{2}\left(\frac{N_3}{N_2}\right)^{1/2} \qquad \text{(C-35)}$$

$$\frac{\partial \delta'}{\partial N_2} = \frac{\partial}{\partial N_2}\left[e^{\alpha X_2'}(X_2'B_{13} - X_3'B_{12})\right]$$

$$= e^{\alpha X_2'}(X_2'B_{13} - X_3'B_{12}) \frac{\partial X_2'}{\partial N_2} + e^{\alpha X_2'} \frac{\partial}{\partial N_2}(X_2'B_{13} - X_3'B_{12})$$

$$\frac{\partial \delta'}{\partial N_2} = \alpha\, e^{\alpha X_2'}(X_2'B_{13} - X_3'B_{12}) \frac{X_3'}{N_T} + (B_{12} + B_{13})e^{\alpha X_2'} \frac{X_3'}{N_T} \qquad \text{(C-36)}$$

$$\frac{\partial}{\partial N_2}\left[\frac{1}{D}\right] = -\frac{1}{D^2} \frac{\partial D}{\partial N_2} \qquad \text{(C-37)}$$

A combination of equations (C-34) to (C-37) results in equation (3-14).

Similarly an expression for $\ln \gamma^{(\text{ternary})}_{3,\text{salt-out}}$ can be obtained with the following additional relationships

$$\frac{\partial}{\partial N_3} [(N_2N_3)^{1/2}] = \frac{1}{2} (\frac{N_2}{N_3})^{1/2} \qquad \text{(C-38)}$$

$$\frac{\partial \delta'}{\partial N_3} = -e^{\alpha X_2'} \frac{X_2'}{N_T} [\alpha(X_2'B_{13} - X_3'B_{12}) + (B_{12} + B_{13})] \qquad \text{(C-39)}$$

$$\frac{\partial}{\partial N_3} [\frac{1}{D}] = - \frac{1}{D^2} \frac{\partial D}{\partial N_3} \qquad \text{(C-40)}$$

# APPENDIX D

# DEBYE-HÜCKEL CONSTANTS, DIELECTRIC CONSTANTS AND DENSITIES OF PURE SOLVENTS AND MIXED SOLVENTS; VAPOR PRESSURE CONSTANTS OF PURE SOLVENTS

The Debye-Hückel constant at the system temperature and pressure is given by

$$A_\gamma = [\frac{2\pi Nd}{1000}]^{1/2} [\frac{\varepsilon^2}{DkT}]^{3/2} \quad \text{(D-1)}$$

or

$$A_\gamma = 1.8246\text{x}10^6 \ d^{1/2} [\frac{1}{DT}]^{3/2} \quad \text{(D-2)}$$

where,

d - density of the solvent

D - dielectric constant of the solvent

The values of the above two properties for the pure solvent or the mixed solvent mixture are presented below

A. Electrolyte-solvent binary (binary 1-2 or 1-3)

$d = d_i$ - pure solvent (2 or 3) liquid density at the system temperature and pressure.

The density data are estimated if experimental data are not available by the following relationship

$$d = \frac{M_w}{V_T^L} \quad \text{(D-3)}$$

$M_w = M_{w_i}$ - molecular weight of the solvent i

$V_T^L = v_i^{\circ L}$ - pure solvent liquid molar volume.

A quadratic equation is used to calculate the pure solvent liquid molar volume, as given in the monograph by Prausnitz et al. (1967)

$$v_i^{\circ L} = a' + b'T + c'T^2 \quad \text{(D-4)}$$

The constants a', b' and c' are obtained, using experimental liquid volume data at three temperatures, by a method used in the monograph. In Table D-1, liquid volume data are listed for the solvents used in this work.

D - $D_i$ - pure component dielectric constant at the system temperature and pressure.

B. Electrolyte (1) - solvent (2) - solvent (3) ternary

d - solvent mixture (electrolyte free) density at the system temperature and pressure.

I - if the experimental solvent mixture data are available, a six-constant polynomial is fitted to get the concentration dependency of the density. The polynomial expression is then used to calculate the density at different temperatures.

$$d = a_1 + a_2X_3' + a_3X_3'^2 + a_4X_3'^3 + a_5X_3'^4 + a_6X_3'^5 \qquad \text{(D-5)}$$

In tables D-2 and D-3, liquid density data for $H_2O$-MeOH at 25°C and $H_2O$-EtOH at 25°C, used in this work are tabulated.

II - if the experimental mixture density data are not available, the solution density is approximated using a linear relationship for the volume equation (D-3). Where,

$$V_T^L = X_2'V_2^{\circ L} + X_3'V_3^{\circ L} \qquad \text{(D-6)}$$

$$M_W = X_2'M_{W2} + X_3'M_{W3} \qquad \text{(D-7)}$$

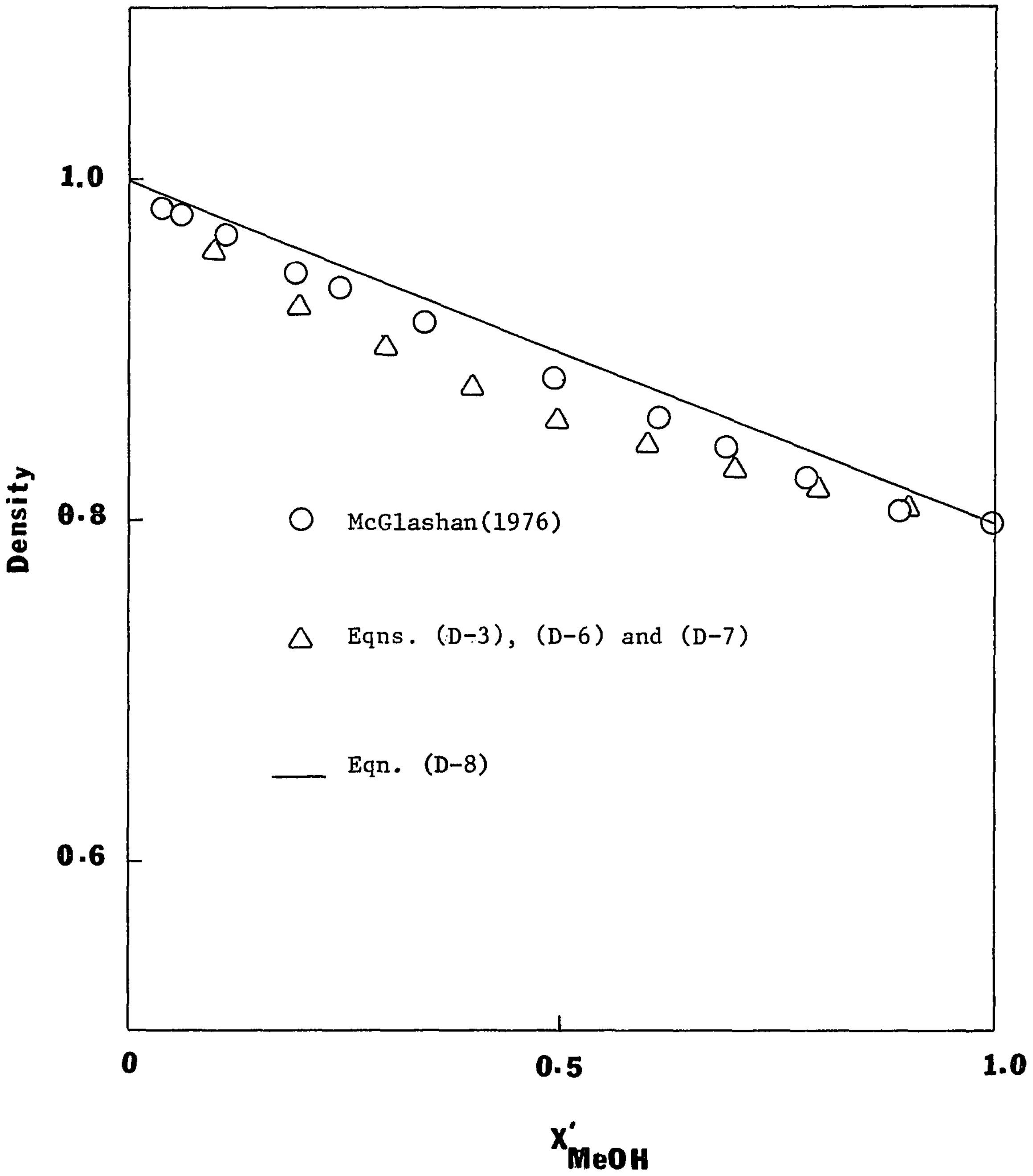


Figure D.1 Comparison of Experimental and Estimated Densities for the System $H_2O$-MeOH at 25°C

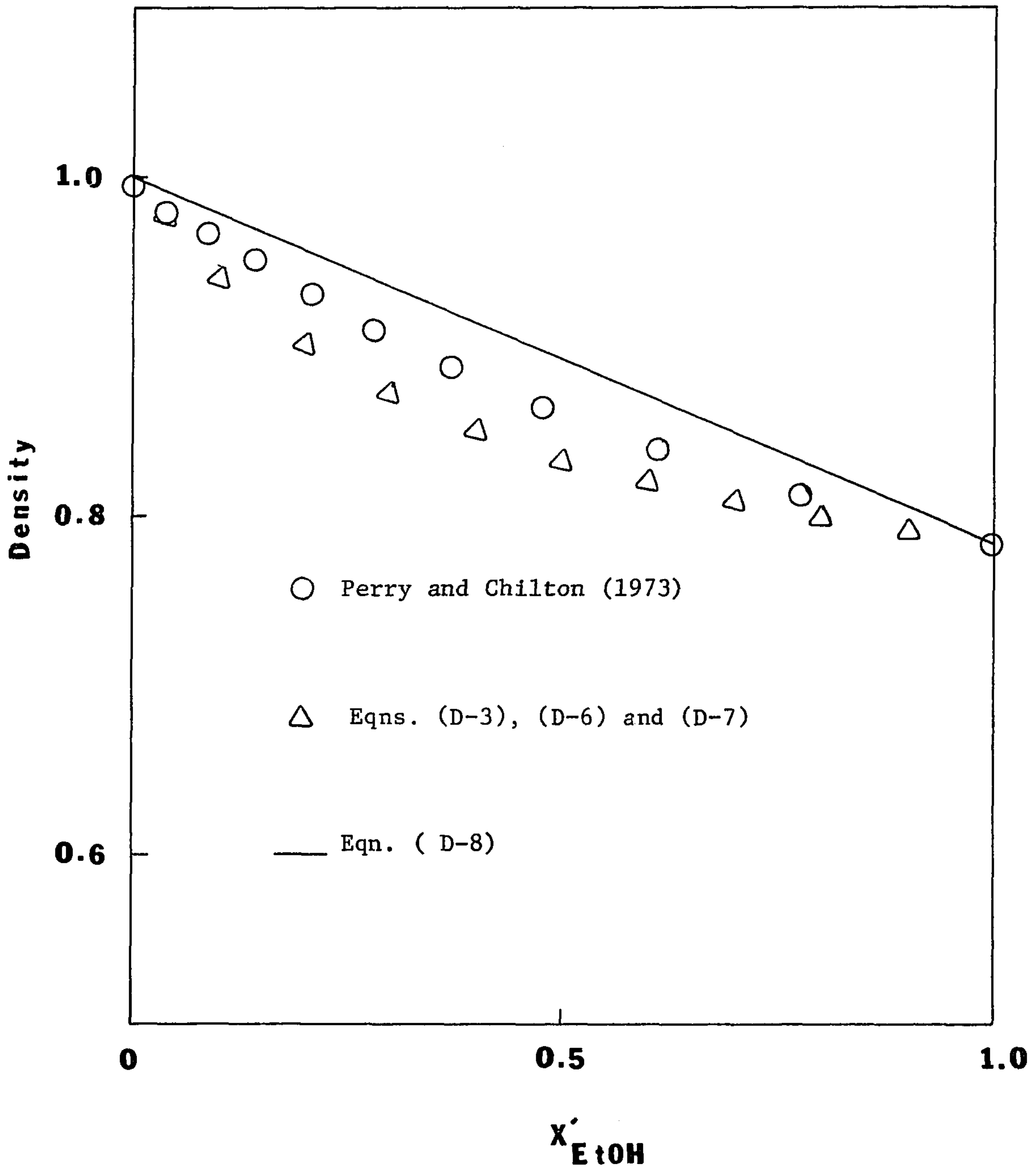


Figure D.2 Comparison of Experimental and Estimated Densities for the System $H_2O$-EtOH at 25°C

$v^{\circ L}_2$ and $v^{\circ L}_3$ are calculated, using equation (D-4) for the pure solvents. Alternatively,

$$d = X'_2 d^\circ_2 + X'_3 d^\circ_3 \qquad \text{(D-8)}$$

The validity of equations (D-3) and (D-8) for the mixture is shown in the figures D.1 and D.2 for the $H_2O$-MeOH system at 25°C and the $H_2O$-EtOH system at 25°C respectively.

D = Dielectric constant of the liquid solvent mixture (electrolyte-free)

III - if the experimental solvent mixture dielectric constant data are available, a six-constant polynomial is fitted to get the concentration dependency of the dielectric constant. The polynomial expression is then used to calculate the dielectric constant at a different concentrations.

$$D = A_1 + A_2X'_3 + A_3X'^2_3 + A_4X'^3_3 + A_5X'^4_3 + A_6X'^5_3 \qquad \text{(D-9)}$$

The data given by Akerlöf (1932) for the mixture dielectric constant have been used in this work. The data at a constant composition has been represented as a function of temperature by

$$\ln D = 2.303\ AD_1 + AD_2\ \ln(T - 293.15) \qquad \text{(D-10)}$$

The constants $AD_1$ and $AD_2$ are listed in the Tables D.4 and D.5 for the mixtures considered in this study.

IV - if the experimental data are not available, the dielectric constant of the solution is approximated using either equation (D-11) or (D-12)

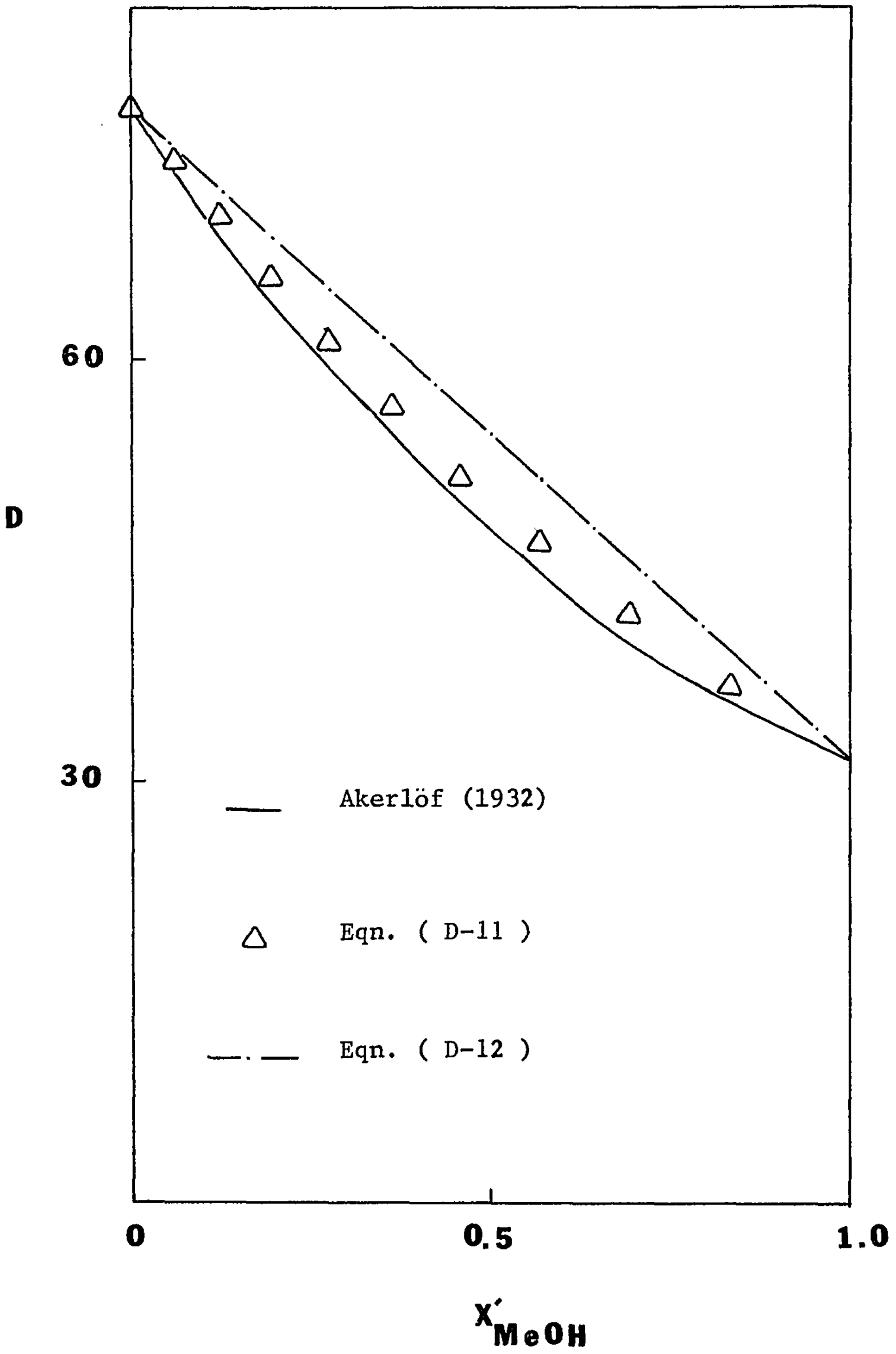


Figure D.3 Comparison of Experimental and Estimated Dielectric Constants of the Mixture $H_2O$-MeOH at 25°C

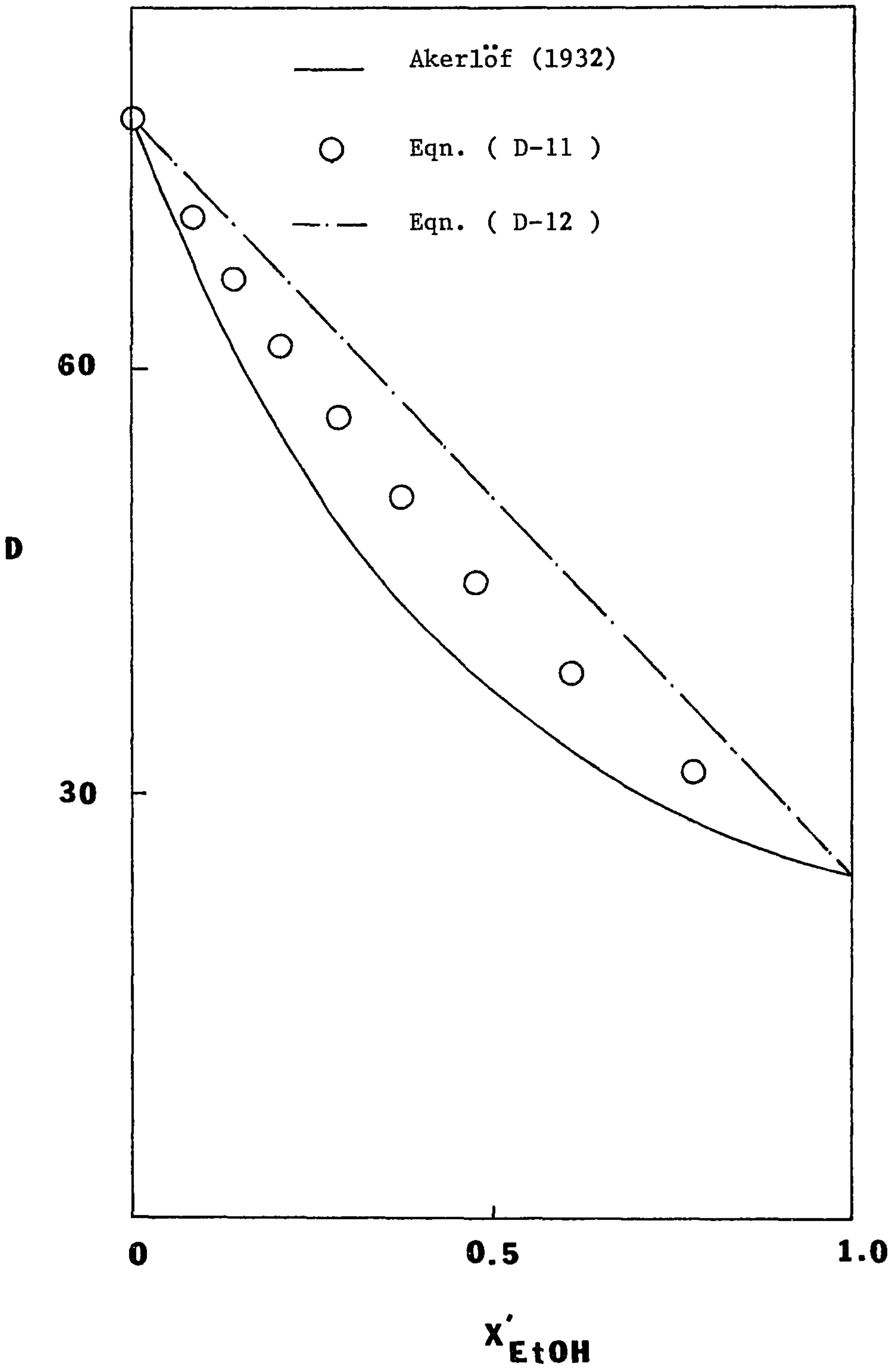


Figure D.4 Comparison of Experimental and Estimated Dielectric Constants of the Mixture $H_2O$-EtOH at 25°C

$$D = D_2 \ \mathrm{Exp}[AX_3'] \qquad \text{(D-11)}$$

where,

$$A = \ln[\frac{D_3}{D_2}] \qquad [\text{Note: } D_3 < D_2]$$

or

$$D = D_2X_2' + D_3X_3' \qquad \text{(D-12)}$$

The experimental dielectric constant data are compared with the expressions (D-11) and (D-12) in figures (D.3) and (D.4) for the $H_2O$-MeOH system at 25°C and the $H_2O$-EtOH system at 25°C respectively.

### Effect of Temperature on $A_\gamma$

The Debye-Hückel constant '$A_\gamma$' is $\alpha \frac{1}{T^{3/2}}$ (equation D-2). Also, the dielectric constant and the density of the solvent are functions of temperature. Therefore $A_\gamma$ is a strong function of temperature.

### Effect of Pressure on $A_\gamma$

This work is limited only to low pressures. At low pressures, the liquid density and the dielectric constant can be considered to be pressure independent. Therefore $A_\gamma$ has no effect of pressure.

### Vapor-Pressure of the Pure Solvent

A six-parameter equation given in the monograph of Prausnitz et al. (1967) has been used to estimate the vapor pressures of the pure components, equation (1-24). Constants $C_1$, $C_2$, $C_3$, $C_4$, $C_5$ and $C_6$ are listed in Table D.6.

## TABLE D.1

### Liquid Molar Volume Data at Three Temperatures

Ref: Prausnitz et al. (1966)

| Solvent | T(°K) | $v^{\circ L}$, cc/gmole |
|---|---|---|
| EtOH | 273.15 | 57.141 |
| | 323.15 | 60.356 |
| | 373.15 | 64.361 |
| MeOH | 273.15 | 39.556 |
| | 373.15 | 44.874 |
| | 473.15 | 57.939 |
| Water | 277.15 | 18.06 |
| | 323.15 | 18.278 |
| | 373.15 | 18.844 |

## TABLE D.2

## Liquid Density Data for the $H_2O$-MeOH System @ 25°C

Ref: McGlashan (1976)

| $x'_{MeOH}$ | d, cc/gmole |
|---|---|
| 0.0 | 0.99707 |
| 0.04085 | 0.98472 |
| 0.06168 | 0.97919 |
| 0.11445 | 0.96649 |
| 0.19739 | 0.94796 |
| 0.24867 | 0.93658 |
| 0.34382 | 0.91534 |
| 0.49446 | 0.88242 |
| 0.61267 | 0.8579 |
| 0.69241 | 0.8421 |
| 0.78454 | 0.82458 |
| 0.89229 | 0.8051 |
| 1.0 | 0.78663 |

## TABLE D.3

## Liquid Density Data for the $H_2O$-EtOH System @ 25°C

Ref: Perry and Chilton (1973)

| $X'_{EtOH}$ | d, cc/gmole |
|---|---|
| 0.0 | 0.99708 |
| 0.0417 | 0.98043 |
| 0.0891 | 0.96639 |
| 0.1436 | 0.95067 |
| 0.2069 | 0.93148 |
| 0.2813 | 0.90985 |
| 0.3699 | 0.88699 |
| 0.4773 | 0.86340 |
| 0.6102 | 0.83911 |
| 0.7788 | 0.81362 |
| 1.00 | 0.78506 |

## TABLE D.4

## Constants for Calculating the Dielectric Constants of Water-EtOH Mixtures at Various Temperatures, Equation (D-10)

---

Ref: Akerlöf (1932)

| $X'_{EtOH}$ | $A_{D1}$ | $A_{D2}$ |
|---|---|---|
| 0.0 | 1.9051 | -0.00205 |
| 0.0417 | 1.8727 | -0.00209 |
| 0.0891 | 1.8367 | -0.00214 |
| 0.1436 | 1.7968 | -0.00221 |
| 0.2069 | 1.752 | -0.0023 |
| 0.2813 | 1.7024 | -0.0024 |
| 0.3699 | 1.6500 | -0.0025 |
| 0.4773 | 1.5926 | -0.00262 |
| 0.6102 | 1.530 | -0.00272 |
| 0.7788 | 1.4625 | -0.00268 |
| 1.00 | 1.3979 | -0.00264 |

# TABLE D.5

## Constants for Calculating the Dielectric Constants of Water-MeOH Mixtures at Various Temperatures, Equation (D-10)

Ref: Akerlöf (1932)

| $X'_{MeOH}$ | $A_{D1}$ | $A_{D2}$ |
|---|---|---|
| 0.0 | 0.19051 | -0.00205 |
| 0.0588 | 1.8799 | -0.00208 |
| 0.1233 | 1.8505 | -0.00212 |
| 0.1942 | 1.8190 | -0.00218 |
| 0.2727 | 1.7865 | -0.00225 |
| 0.3600 | 1.7513 | -0.00234 |
| 0.4576 | 1.7120 | -0.00244 |
| 0.5676 | 1.6658 | -0.00252 |
| 0.6923 | 1.616 | -0.00248 |
| 0.8351 | 1.5648 | -0.00242 |
| 1.00 | 1.5099 | -0.00234 |

## TABLE D.6

Constants for the Vapor Pressure, Equation (D-12)

| Solvent | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | Ref |
|---|---|---|---|---|---|---|---|
| EtOH | 123.9120350 | -8754.0896 | 0.0 | 0.020198435 | 0.0 | -18.1 | Prausnitz et al. (1966) |
| MeOH | 12.3858228 | -3880.50203 | 0.0 | -24.355 | 0.0 | 0.0 | Hala (1969) |
| Water | 70.4346943 | -7362.6981 | 0.0 | 0.006952085 | - | -9.0 | Prausnitz et al. (1966) |

# APPENDIX E

# CALCULATION OF FUGACITY COEFFICIENTS AND POYNTING EFFECT

The following two data points are used for the calculation of $\phi_i^o$, $\hat{\phi}_i^v$, P.E. and $F_i$--

[Ref: Hala (1968)]

| Point # | System | T(°C) | $x_3'$ | $y_3$ | P (mmHg) |
|---|---|---|---|---|---|
| 1 | $H_2O$(2)-MeOH(3) | 60 | 0.0343 | 0.2106 | 183.64 |
| 2 | $H_2O$(2)-MeOH(3) | 60 | 0.7582 | 0.901 | 538.64 |

Pure component second virial coefficients for $H_2O$ and MeOH and the cross-virial coefficient for $H_2O$-MeOH mixture are estimated by Pitzer's correlations, [Smith and VanNess (1973)]

$$B^o = 0.083 - \frac{0.422}{T_r^{1.6}} \tag{E-1}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \tag{E-2}$$

$$B_{ij} = (B^o + \omega B^1) \frac{RT_c}{P_c} \tag{E-3}$$

Pure component liquid molar volumes and pure component vapor pressures are calculated as shown in Appendix D.

The mixture properties necessary to estimate the cross-virial coefficient of the mixtures are calculated by

$$T_{cij} = \sum_{l=2}^{3} y_i T_{ci} \tag{E-4}$$

$$P_{cij} = \sum_{l=2}^{3} y_i P_{ci} \tag{E-5}$$

$$\omega_{ij} = \sum_{1=2}^{3} y_i \omega_i \qquad \text{(E-6)}$$

$$\delta_{23} = 2B_{23} - B_{22} - B_{33} \qquad \text{(E-7)}$$

Applying equations (E-4) to (E-7) with equations (E-1) to (E-3) the cross-properties for the two data points are listed in Table E.2.

The pure component properties listed in Table E.1 and the mixture properties presented in Table E.2 are used in equations (1-5), (1-6), (1-8) and (1-10) to calculate $\phi_i^o$, $(P.E.)_i$, $\hat{\phi}_i^v$ and $F_i$ (see Tables E.3 and E.4 for the two data points).

The values of $F_i$ in Tables E.3 and E.4 for $H_2O$ and MeOH justifies the assumption that, at low pressures, $F_i \simeq 1.0$.

## TABLE E.1

### Pure Component Properties

| Component | $v_i^{oL}$ (cc/gmole) | $P_1^o$ (mmHg) | $B_i^o$ | $B_i^1$ | $\omega_i$ | $B_{ii}$ (cc/gmole) |
|---|---|---|---|---|---|---|
| $H_2O$ | 18.364 | 149.383 | -1.13793 | -2.6577 | 0.348 | -503.4 |
| MeOH | 41.8187 | 634.315 | -0.75793 | -0.91993 | 0.556 | -665.9 |

## TABLE E.2

### Mixture Properties

| Point #1 | $\omega_{23}$ | $B_{23}$ (cc/gmole) | $\delta_{23}$ (cc/gmole) |
|---|---|---|---|
| 1 | 0.3912 | -513.0 | 143.3 |
| 2 | 0.5354 | -622.3 | -75.3 |

## TABLE E.3

### $\phi_i^o$, P.E., $\hat{\phi}_i^v$ and $F_i$ for Data Point #1

| Component | $\phi_i^o$ | $(P.E.)_i$ | $\hat{\phi}_i^v$ | $F_i$ |
|---|---|---|---|---|
| $H_2O$ | 0.99556 | 1.00003 | 0.99562 | 1.0009 |
| MeOH | 0.99413 | 0.99909 | 0.99492 | 1.0075 |

## TABLE E.4

### $\phi_i^o$, P.E., $\hat{\phi}_i^v$ and $F_i$ for Data Point #2

| Component | $\phi_i^o$ | $(P.E.)_i$ | $\hat{\phi}_i^v$ | $F_i$ |
|---|---|---|---|---|
| $H_2O$ | 0.98703 | 1.00034 | 0.98548 | 0.9981 |
| MeOH | 0.98288 | 0.9998 | 0.98288 | 1.0002 |

# APPENDIX F

# COMPUTER PROGRAMS

# CORRELATION AND PREDICTION OF ACTIVITY COEFFICIENTS: TOTAL PRESSURE AND VAPOR PHASE COMPOSITIONS

This appendix contains the following programs:

## F.1 Main Program

Calls subroutines INPDAT, LSQ2, FIBN, TITLE. The main program reads the different indicating markers to perform correlation or prediction of binary or ternary VLE. The comment cards included in this section explain the different options used in this program.

## F.2 INPDAT

Subroutine reads the input data.

## F.3 FITIT [calls POLIFI]

Subroutine fits a polynomial of degree 5.

## F.4 POLIFI

Subroutine makes a least-square fit for FITIT [calls subroutine DETERM].

## F.5 DETERM

Subroutine performs the error analysis for POLIFI.

## F.6 VAPPRE

Subroutine calculates the pure component vapor pressures at the system temperature [Equation (1-24)].

## F.7 TEMPD

Subroutine calculates pure component liquid molar volumes at the system temperature. This also calculates the dielectric-constant of the mixtures. This calls subroutine FITIT to obtain the polynomial constants for the concentration dependence of the dielectric constants at the system temperature.

The following equations are used for the temperature dependence.

For the liquid molar volume

$$V = A + BT + CT^{**}2$$

Where A, B, C - constants. T - temperature of the system.

For the dielectric constant

$$DS = EXP\ [2.303(ADT1 + ADT2\ (T - 293.15))]$$

Where ADT1, ADT2 - Constants for the temperature dependency of a solvent mixture. T - temperature of the system. DS - dielectric constant of the mixture (see Appendix-D).

## F.8 LSQ2

Subroutine applies a search technique to find the best unknown variables that will result in the minimum value of an objective function [number of variables should be greater or equal to 2]. Calls subroutine FN.

### F.9 FN

Subroutine calls different subroutines to calculate the different contributions for the activity coefficients in two models. Finally it calls subroutine MINFUN to set up the objective function. Calls subroutines NRTL1, BROML, ADITON, NRTL2, DEBHUC, VAPPRE, MINFUN.

### F.10 FIBN

Subroutine applies the Fibonacci method to find the one unknown variable that will minimize the non-linear objective function.

### F.11 FUNCT

Subroutine calls different subroutines as in subroutine FN.

### F.12 NRTL1

Subroutine calculates solvent-solvent interaction contributions of the activity coefficients in a ternary mixture using the simplified and the modified form of the NRTL equation in Model #2 [see Chapter 3; Equation (2-4)].

### F.13 BROML

Subroutine calculates ion-ion and ion-solvent interaction contributions of the activity coefficients in a binary or ternary mixture using the Bromley equation in Model #2 [see Chapter 3; Equations (3-8), (3-12) and (C-9)].

### F.14 ADITON

Subroutine calculates salting-out contribution for the activity coefficients in a ternary mixture in Model #2 [see Chapter 3; Equations (3-10) and (3-14)].

### F.15 FUNCB

Subroutine for mixing rule for the Bromley parameter in a ternary mixture [see Chapter 3; Equation (3-3)].

### F.16 FUNCT

Subroutine calculates the Debye-Huckel constant of mixtures and derivatives of the Debye-Huckel constant with respect to the number of moles of solvents [see Appendix-D].

### F.17 NRTL2

Subroutine calculates ion-solvent and solvent-solvent interaction contributions of the activity coefficient in a binary or ternary mixture using the modified NRTL equation in Model #1 [see Chapter 2; Equations (2-7), (2-14) and (2-17)].

### F.18 DEBHUC

Subroutine calculates ion-ion interaction contributions for the activity coefficients in a binary or ternary mixture in Model #1 [see Chapter 2; Equations (2-13) and (2-16)].

### F.19 MINFUN

Subroutine sets up the objective function.

## F.20 TITLE

Subroutine makes tables for output results.

The comment cards included in the programs are assumed to make this program self-explanatory.

```
C    *******************************************************
C
C     MAIN PROGRAM -
C
C     THIS PROGRAM IS TO CORRELATE OR PREDICT EITHER BINARY
C
C     OR TERNARY VLE DATA OR BINARY & TERNARY VLE DATA
C
C     TOGETHER. THE PROGRAM CAN BE USED EITHER FOR ISOBARIC
C
C     OR ISOTHERMAL DATA.
C    ********************************************************
C
C     A BINARY IN THIS WORK IS DEFINED AS A MIXTURE OF
C
C     EITHER TWO SOLVENTS OR ONE ELECTROLYTE AND ONE SOLVENT.
C
C     A TERNARY MIXTURE IS DEFINED AS A MIXTURE OF ONE
C
C     ELECTROLYTE AND TWO SOLVENTS.
C
C    ********************************************************
C
C     THIS PROGRAM IS WRITTEN BY ANIL K. RASTOGI AT THE
C
C     NEW JERSEY INSTITUTE OF TECHNOLOGY AS A PART OF
C
C     DOCTORAL DISSERTATION, YEAR 1981.
C
C    **********************************************************
C
C
C     NSET      - # OF SYSTEM DATA TO BE  USED
C     LL        - TOTAL # OF TRIAL TO  BE USED IN LSQ2
C     EE        - TOLERENCE ERROR FOR THE LSQ2
C
C     NAME(J)   - INFORMATION ABOUT THE SYSTEM ; J=10; 20 CARDS
C     XLIM      - (MAXIMUM  MOLALITY - 1) RANGE OF THE ELECTROLYTE
C     XLLIM     - MINIMUM MOLALITY  RANGE OF THE ELECTROLYTE
C     NAME1,ETC- NAME OF THE SYSTEM TO BE USED
C
C     INDF      - # OF INCREMENTS TO BE GIVEN FOR THE MAXIMUM
C                 MOLALITY RANGE
C     KP        - = 1 EQUATIONS  USED ARE BROOMLEY;SIMPLIFIED NRTL1;
C                 AND SALTINGOUT.(MODEL # 2 IN THE THESIS)
C                 = 2 EQUATIONS USED ARE EXTENDED DEBYE-HUCKEL &
C                 NRTL2.( MODEL # 1 IN THE THESIS )
C
C     NBIN      - (WHEN KP=1)
C                 = 1 PARAMETER B012 REGRESSED
?
```

```
C                 = 2 PARAMETER B013 REGRESSED
C                 = 3 PARAMETER B123 OR DELTA REGRESSED (WHEN M=1)
C                 = 3 PARAMETERS B123 & DELTA REGRESSED (WHEN M=2)
C               - (WHEN KP=2)
C                 = 1 GPN2 & ZPN2 REGRESSED (IF NNRTL=2)
C                 = 1 DGA2 & DGB2 REGRESSED (IF NNRTL=1)
C                 = 2 GPN3 & ZPN3 REGRESSED (IF NNRTL=2)
C                 = 2 DGA3 & DGB3 REGRESSED (IF NNRTL=1)
C                 = 4 DG23 & DG32 REGRESSED
C                 = 5 GPN2,ZPN2,GPN3 & ZPN3 REGRESSED (IF NNRTL=2)
C                 = 5 DGA2,DGB2,DGA3 & DGB3 REGRESSED (IF NNRTL=1)
C
C     NPION     - TYPE OF POSITIVE ION FOR THE CRYSTALLOGRAPHIC RADII
C               = 1 H ION
C               = 2 LI ION
C               = 3 NA ION
C               = 4 CA ION
C     NNION     - TYPE OF NEGATIVE ION FOR THE CRYSTALLOGRAPHIC RADII
C               = 1 BR ION
C               = 2 CL ION
C     NREG      - = 1 VLE DATA ARE PREDICTED
C                 = 2 VLE DATA ARE CORRELATED
C     NDEN      _ = 1 EXPERIMENTAL DATA ARE USED FOR THE DENSITY. A
C                 SIX PARAMETER POLYNOMIAL IS USED FOR THE CONCENTRATI
C                 DEPENDENCY OF THE DENSITY.
C                 = 2 AN APPROXIMATE RELATIONSHIP FOR THE DENSITY IS
C                 USED ( = MW/VS)
C     NBROM     - = 1 DELTA IS FIXED AND B123 IS REGRESSED (M=1)
C                 = 2 B123 IS FIXED AND DELTA IS REGRESSED (M=1)
C     NTYPE     - = 1 DATA OF BINARY 1-2 ARE REGRESSED
C                 = 2 DATA OF BINARY 1-3 ARE REGRESSED
C                 = 3 DATA OF BINARY 2-3 ARE REGRESSED
C                 = 4 DATA OF TERANARY 1-2-3 ARE REGRESSED
C                 = 5 DATA OF TERNARY 1-2-3 & BINARY 1-3 REGRESSED
C                 = 6 DATA OF TERNARY 1-2-3 & BINARY 1-2 REGRESSED
C                 = 7 DATA OF TERNARY 1-2-3 & BINARY 2-3 REGRESSED
C                 = 8 DATA OF TERNARY 1-2-3 & BINARY 1-2 & BINARY 1-3
C                     REGRESSED
C                 = 9 DATA OF TERNARY 1-2-3 & BINARY 1-2 & BINARY 1-3
C                   & BINARY 2-3 REGRESSED
C
C     NMIN      - INTEGER FOR THE DIFFERENT OBJECTIVE FUNCTION
C               = 1 SUM OF ((GCAL-GEXP)/GEXP)**2.  IS MINIMIZED
C               = 2 SUM OF (DP/PEXP)**2. + (DY*10.)**2. IS MINIMIZED
C               = 3 SUM OF ((GCAL-GEXP)/GEXP)**2. + (DY*10.)**2. IS
C                   MINIMIZED
C               = 4 SUM OF ((DPCAL-DPEXP)/DPEXP)**2. IS MINIMIZED FOR
C                   THE BINARY
C
C     ALFA      - ALFA FOR THE NON-ELECTROLYTE BINARY IN THE NRTL
```

```
C                EQUATION
C      DG23,DG32- NON-ELECTROLYTE BINARY PARAMETERS IN THE NRTL
C                EQUATION
C   ALFA2,ALFB2- IONIC ALFAS FOR 1-2 & 1-3 BINARIES (EQ. 2-6  )
C   ALFA3,ALFB3
C
C   DGA2,DGB2, - TEMPERAURE INDEPENDENT PARAMETERS IN THE MODIFIED
C   DGA3,DGB3    NRTL EQUATION FOR THE IONS (EQ. 2-6    )MODEL#1
C
C   GPN2,ZPN2, - IONIC PARAMETERS IN THE MODIFIED NRTL EQUATION
C   GPN3,ZPN3    MODEL # 1 ( EQ. 2-5  )
C
C   BO12,B112, - BROMLEY BINARY TEMPERATURE INDEPENDENT PARAMETRES
C   BO13,B113    MODEL # 2 (CHAPTER 3  )
C
C   B123       - TERNARY ADJUSTABLE PARAMETER FOR THE MIXING RULE IN
C                THE BROMLEY EQUATION
C   DELTA      - TERNARY SALTING OUT PARAMETER FOR THE MODEL # 2
C
C   ALPHA1     - TOLERANCE LIMIT FOR THE FIBBNAUCHI SUBROUTINE
C   AXT1,BXT1  - PARAMETER LIMITS FOR THE FIBBNAUCHI SUBROUTINE
C
C    M         - INTEGER TO SPECIFY # OF PARAMETER TO BE REGRESSED
C              = 1 ONE PARAMETER (BO12 OR BO13 OR B123 OR DELTA)
C              = 2 MORE THAN 1 PARAMETER
C
C    XTX       - INITIAL VALUES OF THE PARAMETERS FOR THE LSQ2
C    DXX       - INCREMENT FOR THE PARAMETERS IN THE LSQ2
C
C
C   *****************************************************************
C
C
C
      COMMON XXMOL(99),XX(3,99),XXF(3,99),GG(3,99),PP(99),YY(3,99),
     % GNRT(3,99),GEL(3,99),GCAL(3,99),AMW(3),ERROR(3,99)
     % ,GDH(3,99),GPHY(3,99),TTT(99),BM(99),GADD(3,99)
     % ,YCAL(3,99),ADD(6),PTC(99)
      COMMON NP,INDF,FNP,FNM,FZP,FZN,FK,ALFA,DG23,DG32,GPN2,
     % GPN3,ZPN2,ZPN3,KP,M,NBIN,NPION,NNION,DELTA
      COMMON NDEN,NNRTL,ALFA2,ALFB2,ALFA3,ALFB3,DGA2,DGB2,
C     DG23,DG32,Z23,Z32 - CAL/gMOLE-K
C
C
C      ***************************************************
C
C
     % DGA3,DGB3,NBROM,NREG,NTYPE,NMIN
      COMMON BO12,B112,BO13,B113,CP2(6),CP3(6),CV2(3),CV3(3),
     % B123,ADT(2,20),NXD,XD(20)
```

```
      DIMENSION YV(3,99),XL(3,99),P(99),XMOL(99),XF(3,99),
     % G(3,99),T(99),PSM(3),DY(99),DP(99)
      REAL *8 NAME(10)
      REAL *8 NAME1,NAME2,NAME3
C
C
C
      DIMENSION XT(6),DX(6),Y(7),X(7,10),XTX(6),DXX(6)
      READ(5,9001)NSET,LL,EE
9001  FORMAT(2I3,F10.1)
      WRITE(6,9002)NSET,LL,EE
9002  FORMAT('1',10X,' # OF DATA SET TO BE USED =',I3,'TRIA
     % I3,'E=',F10.8)
      DO 9110 JAN=1,NSET
      DO 4100 I=1,20
      READ(5,2100)(NAME(J),J=1,10)
      WRITE(6,2100)(NAME(J),J=1,10)
4100  CONTINUE
2100  FORMAT(10A8)
      READ(5,2200)XLIM,XLLIM
      WRITE(6,2200)XLIM,XLLIM
2200  FORMAT(2F10.5)
      READ(5,6080)NAME1,NAME2,NAME3
6080  FORMAT(3A8)
      READ(5,2300)INDF,KP,NBIN,NPION,NNION,NREG,NDEN,NNRTL,
     1 ,NTYPE,NMIN
      WRITE(6,2300)INDF,KP,NBIN,NPION,NNION,NREG,NDEN,NNRTL
     1 ,NTYPE,NMIN
2300  FORMAT(11I2)
      CALL INPDAT(XL,XF,XMOL,T,AMW,FK,FNP,FNM,FZP,FZN,
     % G,NPT,YV,P,NCOMP,ADD,CV2,CV3,CP2,CP3,ADT,NXD,XD)
2400  FORMAT(8F10.5)
      READ(5,2400)ALFA,DG23,DG32,ALFA2,ALFB2,ALFA3,ALFB3
      WRITE(6,2400)ALFA,DG23,DG32,ALFA2,ALFB2,ALFA3,ALFB3
      READ(5,2400)GPN2,ZPN2,GPN3,ZPN3,DGA2,DGB2,DGA3,DGB3
      WRITE(6,2400)GPN2,ZPN2,GPN3,ZPN3,DGA2,DGB2,DGA3,DGB3
      READ(5,2400)B012,B112,B013,B113,B123,DELTA
      WRITE(6,2400)B012,B112,B013,B113,B123,DELTA
      READ(5,9141)ALPHA1,AXT1,BXT1
      WRITE(6,9141)ALPHA1,AXT1,BXT1
9141  FORMAT(F10.7,2F10.4)
      READ(5,2300)M,MM
      WRITE(6,2300)M,MM
      DO 4400 I=1,MM
      READ(5,2600)XTX(I),DXX(I)
      WRITE(6,2600)XTX(I),DXX(I)
4400  CONTINUE
2600  FORMAT(2F10.4)
C
C     INITIALIZATION  FOR THE LSQ2
```

```
C
C
C
        DO 4300 KJ=1,INDF
        DO 4200 JJ=1,7
        DO 4200 JI=1,10
        X(JJ,JI)=0.0
 4200   CONTINUE
C
C
C
        DO 4401 IK=1,MM
        XT(IK)=XTX(IK)
        DX(IK)=DXX(IK)
 4401   CONTINUE
        ALPHA=ALPHA1
        AXT=AXT1
        BXT=BXT1
C
C
C       THIS PART OF THE MAIN PROGRAM SPECIFIES THE TYPE OF
C       DATA TO BE USED. ALSO DATA ARE CONVERTED INTO DIFFERENT
C       SYMBOLS FOR MINIMUM AND MAXIMUM MOLALITY LIMITS.
C
C
        XLIM=XLIM+1.0
        J=0
        WRITE(6,2410)XLIM
 2410   FORMAT('1',5X,'***********MAXIMUM MOLALITY USED=',F10.5)
        DO 4310 I=1,NPT
        GO TO (9901,9902,9003,9004,9005,9006,9007,9008,9000),NTYPE
 9901   IF(XL(3,I).EQ.0.0)GO TO 9000
        GO TO 4310
 9902   IF(XL(2,I).EQ.0.0)GO TO 9000
        GO TO 4310
 9003   IF(XMOL(I).EQ.0.0)GO TO 9000
        GO TO 4310
 9004   IF(XMOL(I).EQ.0.0)GO TO 4310
        IF(XL(2,I).EQ.0.0)GO TO 4310
        IF(XL(3,I).EQ.0.0)GO TO 4310
        GO TO 9000
 9005   IF(XMOL(I).EQ.0.0)GO TO 4310
        IF(XL(3,I).EQ.0.0)GO TO 4310
        GO TO 9000
 9006   IF(XMOL(I).EQ.0.0)GO TO 4310
        IF(XL(2,I).EQ.0.0)GO TO 4310
        GO TO 9000
 9007   IF(XL(2,I).EQ.0.0)GO TO 4310
        IF(XL(3,I).EQ.0.0)GO TO 4310
        GO TO 9000
```

```
9008    IF(XMOL(I).EQ.0.0)GO TO 4310
9000    IF(XMOL(I).LT.XLLIM)GO TO 4310
        IF(XMOL(I).LE.XLIM)GO TO 3100
        GO TO 4310
3100    J=J+1
        NP=J
        YY(2,J)=YV(2,I)
        YY(3,J)=YV(3,I)
        PP(J)=P(I)
        TTT(J)=T(I)
        XXMOL(J)=XMOL(I)
        XX(1,J)=XL(1,I)
        XX(2,J)=XL(2,I)
        XX(3,J)=XL(3,I)
        XXF(2,J)=XF(2,I)
        XXF(3,J)=XF(3,I)
        GG(1,J)=G(1,I)
        GG(2,J)=G(2,I)
        GG(3,J)=G(3,I)
4310    CONTINUE
        IF(KP.LE.1)MO=2
        IF(KP.GT.1)MO=1
C
C
C       PROGRAM FOR THE PREDICTION
C
C
        IF(NREG.GT.1)GO TO 110
        WRITE(6,160)MO
160     FORMAT(//,5X,' VLE DATA ARE PREDICTED USING MODEL #',I3)
        LIC=1
        CALL FN(YYD,XT,LIC)
        GO TO 3300
C
C
C       PROGRRAM FOR THE CORRELATION
C
C
110     WRITE(6,170)KP
170     FORMAT(//,5X,' VLE DATA ARE CORRELATED USING MODEL #',I3)
        IF(M.GT.1)GO TO 3200
        CALL FIBN(ALPHA,AXT,BXT)
        GO TO(240,250,260),NBIN
240     WRITE(6,270)BO12
270     FORMAT(//,10X,' BO12 =',G12.5)
        GO TO 3300
250     WRITE(6,280)BQ13
280     FORMAT(//,10X,' BO13 =',G12.5)
        GO TO 3300
260     GO TO(210,220),NBROM
```

```
210     WRITE(6,290)B123
290     FORMAT(//,10X,'B123 =',G12.5)
        GO TO 3300
220     WRITE(6,300)DELTA
300     FORMAT(//,10X,'DELTA =',G12.5)
        GO TO 3300
3200    L=LL
        E=EE
        M1=M+1
        M3=M+3
        CALL LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
        WRITE(6,2800)(I,XT(I),I=1,M)
2800    FORMAT(///,5X,' FINAL VALUES OF XT(',I2,')=',E15.8)
        WRITE(6,2900)(I,Y(I),I=1,M1)
2900    FORMAT(///,5X,'Y(',I2,')=',E15.8)
C
C
C       FROM HERE MAIN PROGRAM ARRANGES THE OUTPUT
C
C
C
C       GCAL(J,I)     - CALCULATED ACTIVITY COEFFICIENT
C       GG(J,I)       - EXPERIMENTAL ACTIVITY COEFFICIENT
C       ERROR(J,I)    - % ERROR IN ACTIVITY COEFFICIENT
C
C       ALL THE SEPARATE PARTS LISTED BELOW ARE IN THE  LN FORM.
C
C       GDH(J,I)     - DEBYE-HUCKEL PART OF THE ACTVITY COEFFICIENT
C       GPHY(J,I)     - EXTENDED D.H. PART OF THE COULOMBIC TERMS
C                       BESIDES D.H. PART IN THE ACTVITY COEFICIENT
C       GADD(J,I)     - SALTING OUT CONTRIBUTION TO THE ACTVITY COEFFICI
C       GNRT(J,I)     - NRTL CONTRIBUTION TO THE ACTIVITY COEFFICIENT
C
C
C
3300    YSUM=0.0
        PSUM=0.0
        NV=0
        NVP=0
        DO 4530 I=1,NP
        IF(XXMOL(I).EQ.0.0)GO TO 3400
        IF(XX(3,I).EQ.0.0)GO TO 3401
        IF(XX(2,I).EQ.0.0)GO TO 3402
        IF(GG(1,I).EQ.1.0)GO TO 3400
        IF(GG(2,I).EQ.1.0)GO TO 3405
        GO TO 3416
3405    GG(2,I)=1.0 E 58
        GG(3,I)=1.0 E 58
        ERROR(2,I)=1.0 E 58
        ERROR(3,I)=1.0 E 58
```

```
       GO TO 3415
3401   GG(3,I)=1.0 E 58
       ERROR(3,I)=1.0 E 58
       IF(GG(2,I).EQ.1.0)GO TO 3403
       IF(GG(1,I).EQ.1.0)GO TO 3400
       GO TO 3415
3403   GG(2,I)=1.0 E 58
       ERROR(2,I)=1.0 E 58
       GO TO 3415
3402   GG(2,I)=1.0 E 58
       ERROR(2,I)=1.0 E 58
       IF(GG(3,I).EQ.1.0) GO TO 3404
       IF(GG(1,I).EQ.1.0) GO TO 3400
       GO TO 3415
3404   GG(3,I)=1.0 E 58
       ERROR(3,I)=1.0 E 58
       GO TO 3415
3400   GG(1,I)=1.0 E 58
       ERROR(1,I)=1.0 E 58
       IF(XX(2,I).EQ.0.0)GO TO 3415
       IF(XX(3,I).EQ.0.0)GO TO 3415
3416   DP(I)=PTC(I)-PP(I)
       PSUM=PSUM+ABS(DP(I))
       NVP=NVP+1
3410   NV=NV+1
       DY(I)=YCAL(3,I)-YY(3,I)
       YSUM=YSUM+ABS(DY(I))
       WRITE(6,2110)
2110   FORMAT(//,4X,'COMPONENT #',2X,'MOLE-FRACTION',8X, 'YEXP ',8X,'
     % YCAL ',10X,'YCAL-YEXP',7X,'PCAL-PEXP')
2115   FORMAT(8X,I2,5(5X,F12.5))
       DO 4520 J=2,NCOMP
       WRITE(6,2115)J,XX(J,I),YY(J,I),YCAL(J,I),DY(I),DP(I)
4520   CONTINUE
3415   WRITE(6,2120)
2120   FORMAT('-',2X,' COMPONENT #',3X,' MOLALITY ',2X,' LOG NRTL ',
     % 2X,' LOG COULOMBIC ',1X,' LOG PHYSICAL ',1X, ' LOG ADDITION ',
     % 3X,' GAM CAL ',2X,' GAM EXP ', 2X,' % ERROR IN GAMA ')
       DO 4530 J=1,NCOMP
       WRITE(6,2125)J,XXMOL(I),GNRT(J,I),GDH(J,I),GPHY(J,I),GADD(J,I),
     % GCAL(J,I),GG(J,I),ERROR(J,I)
4530   CONTINUE
2125   FORMAT(8X,I2,8X,G10.3,3X,G10.3,5X,G10.3,4X,G10.3,5X,G10.3,4X,
     % G10.3,3X,G10.3,4X,G10.3)
C
C
C      TABLE FOR THE MEAN MOLAL ACTIVITY COEFFICIENT
C
C
       CALL TITLE(NAME1,NAME2,NAME3,ALFA,DG23,DG32,GPN2,GPN3,ZPN2,
```

```
     % ZPN3,B012,B013,B112,B113,B123,DELTA,KP,NTYPE,XX(2,1),
     % XXMOL(1),NNRTL,DGA2,DGA3,DGB2,DGB3,ALFA2,ALFB2,ALFA3,
     % ALFB3)
       WRITE(6,7165)
7165   FORMAT(/,4X,'MOLALITY',5X,'X2',10X,'X3',6X,'MEANMOLALGAM',1X,
     % 'MEANMOLALGAM',2X,'%ERROR')
       WRITE(6,7167)
7167   FORMAT(37X,'EXPERIMENTAL',2X,'CALCULATED')
       GSUM=0.0
       NS=0
       DO 8110 I=1,NP
       IF(ERROR(1,I).GE.1.0 E 58)GO TO 8110
       NS=NS+1
       GSUM=GSUM+ABS(ERROR(1,I))
       WRITE(6,7170)XXMOL(I),XX(2,I),XX(3,I),GG(1,I),GCAL(1,I),
     % ERROR(1,I)
7170   FORMAT(2X,6G12.5)
8110   CONTINUE
       IF(NS.LE.0)NS=1
       GMEAN=GSUM/NS
       WRITE(6,7180)GMEAN
7180   FORMAT(//,6X,'AVG %ERROR IN MEAN MOLAL ACTIVITY COEFFICIENTS
     % ',G12.5)
       WRITE(6,7181)NS
7181   FORMAT(7X,' BASED ON #OF POINTS FOR GAMA SALT=',I3)
C
C
C      TABLE FOR TERNARY Y & P
C
C
       CALL TITLE(NAME1,NAME2,NAME3,ALFA,DG23,DG32,GPN2,GPN3,ZPN2,
     % ZPN3,B012,B013,B112,B113,B123,DELTA,KP,NTYPE,XX(2,1),
     % XXMOL(1),NNRTL,DGA2,DGA3,DGB2,DGB3,ALFA2,ALFB2,ALFA3,
     % ALFB3)
       WRITE(6,7190)
7190   FORMAT(//,2X,'MOLALITY',3X,'X2',10X,'X3',8X,'Y3EXP',8X,'Y3CAL'
     % ,5X,'DY',9X,'DP')
       DO 8220 I =1,NP
       IF(XX(2,I).EQ.0.0) GO TO 8220
       IF(XX(3,I).EQ.0.0) GO TO 8220
       WRITE(6,7195)XXMOL(I),XX(2,I),XX(3,I),YY(3,I),YCAL(3,I)
     % ,DY(I),DP(I)
7195   FORMAT(G10.3,4G12.5,2G10.3)
8220   CONTINUE
       IF(NV.LE.0)NV=1
       IF(NVP.LE.0)NVP=1
       DYAVG=YSUM/NV
       DPAVG=PSUM/NVP
       WRITE(6,7200) DYAVG
7200   FORMAT(///,10X,'AVERAGE DY(YCAL-YEXP)=',G12.5)
?
```

```
      WRITE(6,7201)NV
7201  FORMAT(9X,' BASED ON # OF POINTS FOR Y =',I3)
      WRITE(6,7210)DPAVG
7210  FORMAT(///,10X,'AVERAGE DP(PCAL-PEXP)=',G12.5)
      WRITE(6,7221)NVP
7221  FORMAT(9X,'BASED ON # OF POINTS FOR DP =',I3)
C
C
C     TABLE FOR THE BINARY DELTA P
C
C
      CALL TITLE(NAME1,NAME2,NAME3,ALFA,DG23,DG32,GPN2,GPN3,ZPN2,
     % ZPN3,BO12,BO13,B112,B113,B123,DELTA,KP,NTYPE,XX(2,1),
     % XXMOL(1),NNRTL,DGA2,DGA3,DGB2,DGB3,ALFA2,ALFB2,ALFA3,
     % ALFB3)
      NDP=0
      XDPSUM=0.0
      WRITE(6,8290)
8290  FORMAT(//,2X,'MOLALITY',3X,'XSOLVENT',6X,'DPEXP',6X,'DPCAL',
     % 2X,'% ERROR IN DP')
      DO 8230 I=1,NP
      CALL VAPPRE(CP2,CP3,PSM,TTT(I))
      IF(XX(2,I).EQ.0.0)GO TO 8235
      IF(XX(3,I).EQ.0.0)GO TO 8240
      GO TO 8245
8235  IF(GG(3,I).EQ.1.0)GO TO 8245
      DPEXP=PSM(3)-XX(3,I)*GG(3,I)*PSM(3)
      DPCAL=PSM(3)-XX(3,I)*GCAL(3,I)*PSM(3)
      PDP=(DPCAL-DPEXP)/DPEXP*100.0
      XDP=XX(3,I)
      GO TO 8250
8240  IF(GG(2,I).EQ.1.0)GO TO 8245
      DPEXP=PSM(2)-XX(2,I)*GG(2,I)*PSM(2)
      DPCAL=PSM(2)-XX(2,I)*GCAL(2,I)*PSM(2)
      PDP=(DPCAL-DPEXP)/DPEXP*100.0
      XDP=XX(2,I)
8250  WRITE(6,8255)XXMOL(I),XDP,DPEXP,DPCAL,PDP
8255  FORMAT(2X,G10.3,2G12.5,G10.3,G12.5)
      NDP=NDP+1
      XDPSUM=XDPSUM+ABS(PDP)
      GO TO 8230
8245  NDP=1
8230  CONTINUE
      PDPAVG=XDPSUM/NDP
      WRITE(6,8265)PDPAVG
8265  FORMAT(///,6X,'AVG % ERROR IN DP =',G12.5)
      WRITE(6,8270)NDP
8270  FORMAT(7X,'BASED ON # OF POINTS =',I3)
      IF(KP.GT.1)GO TO 4300
      WRITE(6,9220)
```

```
9220    FORMAT('1',4X,'MOLALITY',5X,'X3',10X,'BMIXTURE')
        WRITE(6,9230)(XXMOL(I),XXF(3,I),BM(I),I=1,NP)
9230    FORMAT(//,4X,G10.3,2G12.5)
4300    CONTINUE
        WRITE(6,7202)
7202    FORMAT('1')
9110    CONTINUE
        STOP
        END
```

```
      SUBROUTINE INPDAT(X,XF,XMOL,T,AMW,FK,FNP,FNM,FZP,
     % FZN,G,NP,Y,P,NCOMP,ADD,CV2,CV3,CP2,CP3,ADT,NXD,XD)
C
C     ******************************************************
C
C      SUBROUTINE INPDAT
C
C      THIS SUBROUTINE READS ALL INPUT VLE DATA AND PURE
C      COMPONENT DATA
C
C     ******************************************************
C
C      NCOMP      - # OF COMPONENTS (= 3 FOR THIS PROGRAM )
C      NP         - # OF DATA POINTS IN A SYSTEM
C      NXD        - # OF SOLUTION DIELECTRIC CONSTANT DATA POINTS
C      NXDD       - # OF SOLUTION DENSITY DATA POINTS
C      CP2,CP3    - PURE COMPONENT VAPOR PRESSURE CONSTANTS FOR THE
C                   COMPONENTS 2 & 3 RESPECTIVELY.
C      AMW(I)     - MOLECULAR WEIGHT OF THE COMPONENT I
C     V21,V22,V23- PURE COMPONENT LIQUID VOLUMES AT DIFFERENT
C     V31,V32,V33  TEMPERATURES
C     CV2(I),     - TEMPERATURE DEPENDENT LIQUID VOLUME CONSTANTS
C     CV3(I)        FOR THE COMPONENT 2 & 3 RESPECTIVELY.
C     ADT(1,I)    - DIELECTRIC CONSTANTS FOR A TEMPERATURE OF THE
C     ADT(2,I)      SOLUTION.
C     XD(I)       - MOLE-FRACTION OF THE SOLVENT(3) IN THE SOLUTION
C                   FOR THE DIELECTRIC CONSTANTS(ELECTROLYTE FREE)
C     FK          - TOTAL # OF IONS OF THE ELECTROLYTE
C     FNP         - # OF POSITIVE IONS IN THE ELECTROLYTE
C     FNM         - # OF NEGATIVE IONS IN THE ELECTROLYTE
C     FZP         - POSITIVE ION VALENCY(ABSOLUTE UNITS)
C     FZN         - NEGATIVE ION VALENCY(ABSOLUTE UNITS)
C     DENS(I)     - DENSITY OF THE SOLUTION(ELECTROLYTE FREE)
C     XDD(I)      - MOLE-FRACTION OF THE SOLVENT(3) IN A SOLUTION
C                   FOR THE DENSITY DENS(I).
C
C     XMOL(I)     - MOLALITY OF THE I TH POINT
C     X(J,I)      - LIQUID MOLE FRACTION ; J DENOTES COMPONENT
C                                          I DENOTES I TH POINT
C     Y(J,I)      - VAPOR PHASE MOLE FRACTION
C     G(J,I)      - EXPERIMENTAL VALUES OF THE ACTIVITY COEFFICIENT
C     P(I)        - TOTAL PRESSURE OF THE SYSTEM
C     T(I)        - TEMPERATURE OF THE SYSTEM
C     XF(J,I)     - SOLVENT MOLE FRACTIONS(ELECTROLYTE FREE)
C     PSM(J)      - PURE COMPONENT VAPOR PRESSURE OF THE COMPONENT
C                   J AT THE SYSTEM TEMPRATURE.
C
C
C    ************************************************************
C
```

```
C
C
       DIMENSION X(3,99),XF(3,99),AMW(3),G(3,99),Y(3,99),P(99),
     % ADD(6),T(99),PSM(3),XMOL(99),DENS(20),XDD(20)
       DIMENSION CV2(3),CV3(3),CP2(6),CP3(6),ADT(2,20),XD(20)
C
C
C
       WRITE(6,1000)
1000   FORMAT('-',5X,'  INPUT DATA      ')
       READ(5,2000)NCOMP,NP,NXD,NXDD
2000   FORMAT(4I2)
       WRITE(6,2000)NCOMP,NP,NXD,NXDD
       READ(5,2100)(CP2(I),I=1,6)
       READ(5,2100)(CP3(I),I=1,6)
       WRITE(6,2100)(CP2(I),I=1,6)
       WRITE(6,2100)(CP3(I),I=1,6)
2100   FORMAT(F12.7,F11.5,F8.3,F13.9,F3.1,F10.5)
       READ(5,2200)(AMW(I),I=1,NCOMP)
2200   FORMAT(6F10.5)
       WRITE(6,2200)(AMW(I),I=1,NCOMP)
       READ(5,2200)V21,T21,V22,T22,V23,T23
       WRITE(6,2200)V21,T21,V22,T22,V23,T23
       READ(5,2200)V31,T31,V32,T32,V33,T33
       WRITE(6,2200)V31,T31,V32,T32,V33,T33
C
C      CALCULATION OF LIQUID MOLAR VOLUME CONSTANTS USING
C      THREE VALUES OF LIQUID MOLAR VOLUME AT THREE
C      DIFFERENT TEMPERATURES.
C
C
       CV2(3)=((T23-T21)*(V22-V21)-(V23-V21)*(T22-T21))/((T22**2.-
     % T21**2.)*(T23-T21)-(T23**2.-T21**2.)*(T22-T21))
       CV2(2)=((V22-V21)-CV2(3)*(T22**2.-T21**2.))/(T22-T21)
       CV2(1)=V21-CV2(2)*T21-CV2(3)*T21**2.0
       CV3(3)=((T33-T31)*(V32-V31)-(V33-V31)*(T32-T31))/((T32**2.-
     % T31**2.)*(T33-T31)-(T33**2.-T31**2.)*(T32-T31))
       CV3(2)=((V32-V31)-CV3(3)*(T32**2.-T31**2.))/(T32-T31)
       CV3(1)=V31-CV3(2)*T31-CV3(3)*T31**2.0
       WRITE(6,5000)
5000   FORMAT(//,5X,' LIQUID MOLAR VOLUME CONSTANTS')
       WRITE(6,5010)CV2(1),CV2(2),CV2(3)
       WRITE(6,5010)CV3(1),CV3(2),CV3(3)
5010   FORMAT(5X,3(G12.5,3X))
5020   FORMAT(5X,6G12.5)
       DO 10 I=1,NXD
       READ(5,2800)ADT(1,I),ADT(2,I),XD(I)
       WRITE(6,2800)ADT(1,I),ADT(2,I),XD(I)
2800   FORMAT(3F10.5)
10     CONTINUE
?
```

```
2300   FORMAT(6F10.5)
       READ(5,2400)FK,FNP,FNM,FZP,FZN
       WRITE(6,2400)FK,FNP,FNM,FZP,FZN
2400   FORMAT(5F10.5)
       DO 50 I=1,NXDD
       READ(5,2300)DENS(I),XDD(I)
       WRITE(6,2300)DENS(I),XDD(I)
50     CONTINUE
       CALL FITIT(NXDD,XDD,DENS,ADD)
       WRITE(6,5020)(ADD(II),II=1,6)
C
C
C      EXPERIMENTAL M-P-T-X-Y-MEAN MOLAL ACTVITY COEFFICIENT DATA
C
C      FOLLOWING INSTRUCTIONS ARE IMPORTANT
C
C     1.IF DATA ARE MOLALITY VS MEAN MOLALITY ACTIVITY
C      COEFFICIENT ONLY, READ P(I)=1.0
C
C     2.IF DATA ARE MOLALITY VS VAPOR PRESSURE ONLY, READ
C      G(1,I)=1.0
C
C     3.IF A BINARY  DATA ARE USED ,READ X AND Y VALUES OF THE
C      OTHER SOLVENT(WHICH IS NOT PRESENT) =0.0
C
C
       DO 4100 I=1,NP
       READ(5,2500)XMOL(I),(X(J,I),Y(J,I),J=2,NCOMP),G(1,I),P(I),T(I)
       WRITE(6,2500)XMOL(I),(X(J,I),Y(J,I),J=2,NCOMP),G(1,I),P(I),T(I
2500   FORMAT(8F10.6)
       CALL VAPPRE(CP2,CP3,PSM,T(I))
       WRITE(6,2501)PSM(2),PSM(3)
2501   FORMAT(1X,G10.3,3X,G10.3)
C
C
C      CALCULATION OF THE EXPERIMENTAL ACTIVITY COEFFICIENT
C      OF SOLVENTS. ASSUMING POYNTING EFFECT = 1.0 &
C      FUGACITY COEFFICIENT = 1.0.
C
C
       SUM=1.0
       DO 4200 K=2,NCOMP
       SUM=SUM-X(K,I)
4200   CONTINUE
       X(1,I)=SUM/FK
       XSUM=0.0
       DO 4300 K=2,NCOMP
       XSUM=XSUM+X(K,I)
       IF(P(I).EQ.1.0)GO TO 3100
       IF(X(K,I).EQ.0.0)GO TO 3100
?
```

```
          G(K,I)=Y(K,I)*P(I)/X(K,I)/PSM(K)
          GO TO 4300
 3100     G(K,I)=1.0
 4300     CONTINUE
          DO 4400 K=2,NCOMP
          XF(K,I)=X(K,I)/XSUM
 4400     CONTINUE
 4100     CONTINUE
          WRITE(6,2601)
 2601     FORMAT('-',18X,' X1 ',10X,' X2 ',12X,' X3 ',9X,' GAMA1 ',8X,
        % ' GAMA2 ',8X,' GAMA3 ')
          DO 4500 I=1,NP
          WRITE(6,2600)X(1,I),X(2,I),X(3,I),G(1,I),G(2,I),G(3,I)
 2600     FORMAT(10X,6F15.6)
 4500     CONTINUE
          RETURN
          END
```

```
      SUBROUTINE FITIT(NPOINT,X1,AGAMA,A)
C
C     THIS PROGRAM FITS A POLYNOMIAL OF DEGREE 5
C
      DIMENSION SIGMAY(20),X1(20),AGAMA(20),A(6),DELTAY(20),YCAL(20)
      IF(NPOINT.LE.3) GO TO 99
C
      DO 2 I=1,NPOINT
      SIGMAY(I)=0.
2     CONTINUE
      NCODE=0
      MAXORD=5
      IF(NPOINT.LE.4) MAXORD=2
      IF(MAXORD.GT.6) MAXORD=6
      NNK=1
      DO 3 K=5,NNK
      K1=K+1
C
      CALL POLIFI(X1,AGAMA,SIGMAY,NPOINT,K1,0,A,CHISQR)
C
      ERROR=0.0
      DO 4 J=1,NPOINT
      SUM=A(1)
      DO 5 I=2,K1
      SUM=SUM+A(I)*X1(J)**(I-1)
5     CONTINUE
      YCAL(J)=SUM
      DELTAY(J)=YCAL(J)-AGAMA(J)
4     ERROR=ERROR+DELTAY(J)**2
      ERROR=ERROR/NPOINT
C
3     CONTINUE
C
99    RETURN
      END
?
```

```
      SUBROUTINE POLIFI(X,Y,SIGMAY,NPTS,NTERMS,MODE,A,CHISQR)
C
C     EXTRACTED FROM: BEVINGTON,P. R., 'DATA REDUCTION AND
C     ERROR ANALYSIS FOR THE PHYSICAL SCIENCES', MCGRAW HILL,1969
C
C     SUBROUTINE POLIFIT PURPOSE
C
C     MAKE A LEAST-SQUARES FIT TO DATA WITH A POLYNOMIAL CURVE
C     Y = A(1) + A(2)*X + A(3)*X**2 + A(4)*X**3 + ...
C
C     DESCRIPTION OF PARAMETERS
C     X    -ARRAY OF DATA POINTS FOR INDEPENDENT VARIABLE
C     Y    -ARRAY OF DATA POINTS FOR DEPENDENT VARIABLE
C     SIGMAY - ARRAY OF STANDARD DEVIATIONS FOR Y DATA POINTS
C     NPTS   -NUMBER OF PAIRS OF DATA POINTS
C     NTERMS -NUMBER OF COEFFICIENTS(DEGREE OF POLYNOMIAL + 1)
C     MODE  -DETERMINANTS METHOD OF WEIGHTING LEAST-SQUARES FIT
C             +1 (INSTRUMENTAL) WEIGHT(I)=1./SIGMAY(I)**2
C              0 (NO WEIGHTING) WEIGHT =1.
C             -1 (STATISTICAL) WEIGHT(I) = 1./Y(I)
C     A  - ARRAY OF COEFFICIENTS OF POLYNOMIAL
C     CHISQR - REDUCED CHI SQUARE FOR FIT
C
C      SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C       DELTERM (ARRAY,NORDER)
C       EVALUATES THE DETERMINANTS OF A SYMMETRIC TWO-DIMENSIONAL
C       MATRIX OF NORDER
C
      DOUBLE PRECISION SUMX,SUMY,XTERM,YTERM,ARRAY,CHISQ
      DIMENSION X(20), Y(20), SIGMAY(20), A(6)
      DIMENSION SUMX(20),SUMY(20),ARRAY(8,8)
C
C     ACCUMULATE WEIGHTING SUMS
C
11    NMAX = 2*NTERMS - 1
      DO 13 N=1, NMAX
13    SUMX(N) = 0.
      DO 15 J=1, NTERMS
15    SUMY(J)= 0.
      CHISQ =0.
21    DO 50 I=1, NPTS
      XI=X(I)
      YI= Y(I)
31    IF (MODE) 32,37,39
32    IF(YI) 35,37,33
33    WEIGHT = 1./YI
      GO TO 41
35    WEIGHT = 1./(-YI)
      GO TO 41
37    WEIGHT = 1.
```

```
         GO TO 41
   39    WEIGHT = 1. / SIGMAY(I)**2
   41    XTERM=WEIGHT
         DO 44 N=1,NMAX
         SUMX(N) = SUMX(N) + XTERM
   44    XTERM = XTERM * XI
   45    YTERM = WEIGHT*YI
         DO 48 N=1, NTERMS
         SUMY(N)=SUMY(N) + YTERM
   48    YTERM = YTERM *XI
   49    CHISQ = CHISQ + WEIGHT*YI**2
   50    CONTINUE
   C
   C     CONSTRUCT MATRICES AND CALCULATE COEFFICIENTS
   C
   51    DO 54 J=1, NTERMS
         DO 54 K=1, NTERMS
         N = J + K - 1
   54    ARRAY(J,K) = SUMX(N)
         DELTA = DETERM (ARRAY,NTERMS)
         IF(DELTA) 61,57,61
   57    CHISQR = 0.
         DO 59 J=1, NTERMS
   59    A(J) = 0.
         GO TO 80
   61    DO 70 L=1, NTERMS
   62    DO 66 J=1, NTERMS
         DO 65 K=1,NTERMS
         N = J+K-1
   65    ARRAY(J,K)=SUMX(N)
   66    ARRAY(J,L)=SUMY(J)
   70    A(L)=DETERM(ARRAY,NTERMS)/DELTA
   C
   C     CALCULATES CHI SQUARE
   C
   71    DO 75 J=1, NTERMS
         CHISQ = CHISQ - 2.*A(J)*SUMY(J)
         DO 75 K=1, NTERMS
         N=J+K-1
   75    CHISQ=CHISQ+A(J)*A(K)*SUMX(N)
   76    FREE=NPTS-NTERMS
   77    CHISQR=CHISQ/FREE
   80    RETURN
         END
```

```
      FUNCTION DETERM(ARRAY,NORDER)
C
C     EXTRACTED FROM: BEVINGTON,P. R., 'DATA REDUCTION AND
C     ERROR ANALYSIS FOR THE PHYSICAL SCIEINCES',MCGRAW HILL,1969
C
C     FUNCTION DETERM
C
C     PURPOSE
C     CALCULATES THE DETERMINANT OF A SQUARE MATRIX
C
C     USAGE
C     DET = DETERM(ARRAY,NORDER)
C
C     DESCRIPTION OF PARAMETERS
C       ARRAY  -MATRIX
C       NORDER -ORDER OF DETERMINANT (DEGREE OF MATRIX)
C
C     SUBROUTINE AND FUNCTION SUBPROGRAMS REQUIRED
C     NONE
C
C     COMMENTS
C     THIS SUBPROGRAM DESTROYS THE INPUT MATRIX ARRAY
C
      DOUBLE PRECISION ARRAY,SAVE
      DIMENSION ARRAY(8,8)
10    DETERM =1.
11    DO 50 K=1, NORDER
C
C      INTERCHANGE COLUMNS IF DIAGNOL ELEMENT IS ZERO
C
      IF(ARRAY(K,K)) 41,21,41
21    DO 23 J=K, NORDER
      IF(ARRAY(K,J)) 31,23,31
23    CONTINUE
      DETERM = 0.
      GO TO 60
31    DO 34 I=K, NRODER
      SAVE = ARRAY(I,J)
      ARRAY(I,J)=ARRAY(I,K)
34    ARRAY(I,K)=SAVE
      DETERM = -DETERM
C
C     SUBTRACT ROW K FROM LOWER ROWS TO GET DIAGONAL MATRIX
C
41    DETERM = DETERM*ARRAY(K,K)
      IF(K - NORDER) 43,50,50
43    K1=K+1
      DO 46 I=K1, NORDER
      DO 46 J=K1,NORDER
46    ARRAY(I,J)=ARRAY(I,J)-ARRAY(I,K)*ARRAY(K,J)/ARRAY(K,K)

50    CONTINUE
60    RETURN
      END
```

```
      SUBROUTINE VAPPRE(CP2,CP3,PSM,T)
C
C
C    ****************************************************************
C
C     SUBROUTINE VAPPRE
C
C     THIS SUBROUTINE CALCULATES PURE COMPONENT VAPOR-PRESSURES
C
C     OF THE SOLVENTS AT THE SYSTEM TEMPERATURE.
C
C    ****************************************************************
C
C
C
      DIMENSION CP2(6),CP3(6),PSM(3)
      PSM(2)=(EXP(CP2(1)+CP2(2)/(CP2(3)+T)+CP2(4)*T+
     % CP2(5)*T**2.+CP2(6)*ALOG(T)))*760.
      PSM(3)=(EXP(CP3(1)+CP3(2)/(CP3(3)+T)+CP3(4)*T+
     % CP3(5)*T**2.+CP3(6)*ALOG(T)))*760.
      RETURN
      END
?
```

```
      SUBROUTINE TEMPD(CV2,CV3,NXD,XD,ADT,AD,VO,T)
C
C    **************************************************************
C
C     SUBROUTINE TEMPD
C
C     THIS SUBROUTINE CALCULATES THE TEMPERATURE DEPENDENCY OF
C
C     THE LIQUID MOLAR VOLUME AND DIELECTRIC CONSTANT.
C
C
C
C     CALLS SUBROUTINE FITIT FOR CONCENTRATION DEPENDENCE
      OF DIELECTRIC CONSTANT.
C
C
C    *****************************************************************
C
C
C
      DIMENSION CV2(3),CV3(3),XD(20),ADT(2,20),AD(6),VO(3),DSXD(20)
      VO(2)=CV2(1)+CV2(2)*T+CV2(3)*T**2.0
      VO(3)=CV3(1)+CV3(2)*T+CV3(3)*T**2.0
      DO 10 I=1,NXD
      DSXD(I)=EXP(2.303*(ADT(1,I)+ADT(2,I)*(T-293.15)))
10    CONTINUE
      CALL FITIT(NXD,XD,DSXD,AD)
      RETURN
      END
?
```

```
      SUBROUTINE LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
C
C
C     *****************************************************************
C
C      SUBROUTINE LSQ2
C
C      NON-LINEAR REGRESSION SUBROUTINE CALLS SUBROUTINE FN FOR
C
C      THE OBJECTIVE FUNCTION.
C
C
C     *****************************************************************
C
C
C
       DIMENSION XT(6),DX(6),X(7,10),Y(7),JJ(3),A(3,3)
      IL=0
      IH=0
      LIC=0
      IF(L.LE.0) GO TO 50
      IHC=M1+1
      EN=M
      EN=EN*1.5
      L1=L
      L=-L
      L2=(3*M)/2+5
      K3=2
       IF(M.GE.3)K3=3
      K4=K3-1
      G=K3*2
      G=1.0/G
      DO 100 I=1,M
100   X(I,1)=XT(I)
      CALL FN(Y(1),XT,LIC)
      DO 106 J=2,M1
      XT(J-1)=XT(J-1)+DX(J-1)
      DO 104 I=1,M
104   X(I,J)=XT(I)
      CALL FN(Y(J),XT,LIC)
      XT(J-1)=X(J-1,1)
106    CONTINUE
      L2C=0
      FLG=1.0
      GO TO 50
108   LIC=LIC+1
      IF(LIC.GE.L1)GO TO 400
50    YL=1.0E38
      YH=-YL
      Y2=YH
?
```

```
      Y3=YL
      DO 110 J=1,M1
      IF(Y(J).LT.YH)GO TO 1091
      Y2=YH
      I2=IH
      YH=Y(J)
      IH=J
      GO TO 109
1091   IF(Y(J).LT.Y2)GO TO 109
      Y2=Y(J)
      I2=J
109   IF(Y(J).GT.YL)GO TO 1101
      Y3=YL
      I3=IL
      IL=J
      YL=Y(J)
      GO TO 110
1101   IF(Y(J).GT.Y3)GO TO 110
      Y3=Y(J)
      I3=J
110    CONTINUE
      L2C=L2C+1
      IF(L2C.LT.L2)GO TO 111
      L2C=0
      JJ(1)=IL
      JJ(2)=I2
       JJ(3)=I3
      DO 60 K1=1,K3
      J1=JJ(K1)
      DO 60 K2=K1,K3
      J2=JJ(K2)
      S=0.0
      DO 55 I=1,M
55    S=S+(X(I,J1)-X(I,IH))*(X(I,J2)-X(I,IH))
60     A(K1,K2)=S
      D=A(1,1)*A(2,2)-A(1,2)**2
      GO TO (62,61),K4
61     D1=A(1,1)*A(2,3)-A(1,2)*A(1,3)
      IF(A(1,1).EQ.0.0)A(1,1)=1.0E-5
      D=((A(1,1)*A(3,3)-A(1,3)**2)*D-D1*D1)/(A(1,1)*9.0)
62     IF(D.EQ.0.0)GO TO 65
      IF(D.LE.0.0)D=ABS(D)
      D=(D/4.0)**G
      IF(D.LT.E)GO TO 65
      FLG=1.0
      GO TO 111
65     IF(FLG.LT.0.0)GO TO 400
      FLG=-1.0
111    DO 115 I=1,M
      XT(I)=0.0
```

```
      DO 112 J=1,M1
      IF(J.NE.IH)XT(I)=XT(I)+X(I,J)
112   CONTINUE
115     XT(I)=(3.0*XT(I)+X(I,I2)-X(I,IL))/EN-X(I,IH)
121    CALL FN(YT,XT,LIC)
      IF(YT.GE.Y2)GO TO 167
      IHC=M1+1
      IF(YT.GE.YL)GO TO 140
      YTT=YT
      DO 135 I=1,M
135    XT(I)=1.5*XT(I)-0.5*X(I,IH)
      CALL FN(YT,XT,LIC)
      IF(YT.LE.YL)GO TO 140
      DO 138 I=1,M
138    X(I,IH)=(2.0*XT(I)+X(I,IH))/3.0
      Y(IH)=YTT
      GO TO 108
140    DO 142 I=1,M
142    X(I,IH)=XT(I)
      Y(IH)=YT
      GO TO 108
167    IHC=IHC-1
      IF(IHC.EQ.0)GO TO 300
      IF(YT.GE.YH)GO TO 173
       DO 168 I=1,M
      XS=XT(I)
      XT(I)=X(I,IH)
168    X(I,IH)=XS
173    DO 174 I=1,M
174    XT(I)=0.75*X(I,IH)+0.25*XT(I)
       CALL FN(YT,XT,LIC)
      IF(YT.GT.YH)GO TO 180
      Y(IH)=YT
      DO 175 I=1,M
175   X(I,IH)=XT(I)
      GO TO 108
180   DO 185 J=1,M1
      IF(J.EQ.IL)GO TO 185
      DO 182 I=1,M
      XT(I)=(X(I,J)+X(I,IL))/2.0
182   X(I,J)=XT(I)
      CALL FN(Y(J),XT,LIC)
185   CONTINUE
      GO TO 108
300   IHC=2*M1
      IF(M.GE.3)GO TO 350
      S=0.0
      DO 302 I=1,M
      X(I,M+2)=X(I,IH)-X(I,IL)
      X(I,M+3)=X(I,IH)-X(I,I3)
```

```
302    S=S+X(I,M+2)**2
303    S=SQRT(S)
       IF(S.EQ.0.0)S=1.0E-5
304    U=-X(2,M+2)/S
       X(2,M+2)=X(1,M+2)/S
       X(1,M+2)=U
       S=X(1,M+2)*X(1,M+3)+X(2,M+2)*X(2,M+3)
       DO 305 I=1,M
305    X(I,M+2)=X(I,M+2)*S
306    DO 307 I=1,M
307    XT(I)=X(I,IH)+X(I,M+2)
       CALL FN(YT,XT,LIC)
       DO 309 I=1,M
309    XT(I)=X(I,IH)-X(I,M+2)
       CALL FN(YTT,XT,LIC)
       IF(YTT.LE.YT)GO TO 320
       DO 311 I=1,M
311    XT(I)=X(I,IH)+X(I,M+2)
       YTT=YT
320    Y(IH)=YTT
       DO 321 I=1,M
321    X(I,IH)=XT(I)
       GO TO 108
350    DO 352 I=1,M
       XT(I)=X(I,IH)-X(I,IL)
       X(I,M+2)=X(I,IH)-X(I,I2)
352    X(I,M+3)=X(I,IH)-X(I,I3)
       S=0.0
       S1=0.0
       DO 355 I=1,M
       S=S+XT(I)**2
355    S1=S1+X(I,M+3)**2
       S=SQRT(S)
       S1=SQRT(S1)
       S2=0.0
       DO 357 I=1,M
       IF(S.EQ.0.0)S=1.0E-5
       XT(I)=XT(I)/S
       S2=S2+XT(I)*X(I,M+2)
       IF(S1.EQ.0.0)S1=1.0E-5
357    X(I,M+3)=X(I,M+3)/S1
       DO 360 I=1,M
360    X(I,M+2)=X(I,M+2)-XT(I)*S2
       S1=0.0
       DO 362 I=1,M
362    S1=S1+X(I,M+2)**2
       S1=SQRT(S1)
       DO 365 I=1,M
       IF(S1.EQ.0.0)S1=1.0E-5
365    X(I,M+2)=X(I,M+2)/S1
```

```
      S1=0.0
      S2=0.0
      DO 367 I=1,M
      S1=S1+XT(I)*X(I,M+3)
  367 S2=S2+X(I,M+2)*X(I,M+3)
      DO 370 I=1,M
  370 X(I,M+2)=S*(S1*XT(I)+S2*X(I,M+2)-X(I,M+3))
      GO TO 306
  400 S=Y(1)
      Y(1)=Y(IL)
      Y(IL)=S
      DO 402 I=1,M
      XT(I)=X(I,IL)
      X(I,IL)=X(I,1)
  402 X(I,1)=XT(I)
      WRITE(6,772) LIC
  772 FORMAT('-','LIC=',I5)
      RETURN
      END
```

```
      SUBROUTINE FN(YY,XT,LIC)
C
C     ************************************************************
C
C      SUBROUTINE FN
C
C
C     ***********************************************************
C
C      THIS SUBROUTINE IS CALLED BY SUBROUTINE LSQ2. THIS
C
C      SUBROUTINE ESTABLISHES THE OBJECTIVE FUNCTION BY CALLING
C
C      SUBROUTINE MINFUN.
C
C     ***********************************************************
C
C      GCAL(J,I)    - CALCULATED ACTIVITY COEFFICIENT
C      GADD(J,I)    - LN OF THE SALTING OUT CONTRIBUTION TO THE
C                     ACTVITY COEFFICIENT.
C      GEL(J,I)     - LN OF DEBYE HUCKEL CONTRIBUTION AND THE
C                     ADDITIONAL TERMS FOR THE COULOMBIC INTERACTION
C                     TO THE ACTVITY COEFFICIENT.
C      GNRT(J,I)    - LN OF THE NRTL CONTRIBUTION TO THE ACTVITY
C                     COEFFICIENT.
C      PTC(I)       - CALCULATED TOTAL PRESSURE OF THE SYSTEM
C      YCAL(J,I)    - CALCULATED VAPOR PHASE COMPOSITION.
C
C
C     ************************************************************
C
C
      COMMON XMOL(99),X(3,99),XF(3,99),GG(3,99),P(99),YV(3,99),GNRT(
     % 3,99),GEL(3,99),GCAL(3,99),AMW(3),ERROR(3,99),GDH(3,99)
     % ,GFHY(3,99),T(99),BMM(99),GADD(3,99),YCAL(3,99),ADD(6)
     % ,PTC(99)
      COMMON NP,INDF,FNP,FNM,FZP,FZN,FK,ALFA,DG23,DG32,
     % GPN2,GPN3,ZP2,ZP3,KP,M,NBIN,NPION,NNION,DELTA
      COMMON NDEN,NNRTL,ALFA2,ALFB2,ALFA3,ALFB3,DGA2,DGB2,
     % DGA3,DGB3,NBROM,NREG,NTYPE,NMIN
      COMMON B012,B112,B013,B113,CP2(6),CP3(6),CV2(3),CV3(3),
     % B123,ADT(2,20),NXD,XD(20)
      DIMENSION XT(6),PSM(3)
      IF(NREG.LE.1)GO TO 1070
      GO TO (1040,1050,1060,1080,1085),NBIN
1040  GO TO(10,20),NNRTL
10    DGA2=XT(1)
      DGB2=XT(2)
      GO TO 1070
20    IF(XT(1).LT.0.0)XT(1)=0.0
?
```

```
          GFN2=XT(1)
          ZP2=XT(2)
          GO TO 1070
  1050    GO TO(30,40),NNRTL
  30      DGA3=XT(1)
          DGB3=XT(2)
          GO TO 1070
  40      IF(XT(1).LT.0.0)XT(2)=0.0
          GFN3=XT(1)
          ZP3=XT(2)
          GO TO 1070
  1060    DELTA=XT(2)
          B123=XT(1)
          GO TO 1070
  1080    DG23=XT(1)
          DG32=XT(2)
          GO TO 1070
  1085    GO TO (50,60),NNRTL
  50      DGA2=XT(1)
          DGB2=XT(2)
          DGA3=XT(3)
          DGB3=XT(4)
          GO TO 1070
  60      IF(XT(1).LT.0.0)XT(1)=0.0
          IF(XT(3).LT.0.0)XT(3)=0.0
          GFN2=XT(1)
          ZFN2=XT(2)
          GFN3=XT(3)
          ZFN3=XT(4)
  1070    IF(KP.GT.1) GO TO 3100
          CALL NRTL1(X,T,GNRT,FK,FNP,NP,ALFA,DG23,DG32)
          CALL BROML(XMOL,XF,AMW,FNP,FNM,FK,FZP,FZN,T,GEL,
        % NP,B123,GDH,GPHY,BMM,ADD,NDEN,CV2,CV3,NXD,XD,ADT,B012,B112
        % ,B013,B113)
          CALL ADITON(XF,T,AMW,XMOL,FK,FZP,FZN,FNP,FNM,GADD,
        % DELTA,NPION,NNION,NP,ADD,NDEN,CV2,CV3,NXD,XD,ADT,
        % B012,B112,B013,B113)
          GO TO 3200
  3100    CALL NRTL2(X,T,GNRT,FK,FNP,NP,GFN2,GFN3,ZP2,ZP3,ALFA,DG23,
        % DG32,FNM,NNRTL,ALFA2,ALFB2,ALFA3,ALFB3,DGA2,DGB2,
        % DGA3,DGB3)
          CALL DEBHUC(XMOL,XF,X,FK,FNP,FNM,FZP,FZN,GEL,AMW,
        % T,NP,GDH,GPHY,ADD,NDEN,CV2,CV3,NXD,XD,ADT)
          DO 8010 IJ=1,NP
          GADD(1,IJ)=0.0
          GADD(2,IJ)=0.0
          GADD(3,IJ)=0.0
  8010    CONTINUE
  3200    YS=0.0
          DO 4000 I=1,NP
```

```
       IF(XF(2,I).EQ.0.0)GO TO 1000
       IF(XF(3,I).EQ.0.0)GO TO 1010
       GO TO 1020
1000   GNRT(2,I)=0.0
       GEL(2,I)=0.0
       GADD(2,I)=0.0
       GADD(1,I)=0.0
       GO TO 1020
1010   GNRT(3,I)=0.0
       GEL(3,I)=0.0
       GADD(3,I)=0.0
       GADD(1,I)=0.0
1020   AMS = XF(2,I)*AMW(2)+XF(3,I)*AMW(3)
       CALL VAPPRE(CP2,CP3,PSM,T(I))
       GCAL(1,I)=EXP(GNRT(1,I)+GEL(1,I)+GADD(1,I)-ALOG(0.001*FK*AMS*
     % XMOL(I)+1.0))
       GCAL(2,I)=EXP(GNRT(2,I)+GEL(2,I)+GADD(2,I))
       GCAL(3,I)=EXP(GNRT(3,I)+GEL(3,I)+GADD(3,I))
       PTC(I)=X(2,I)*GCAL(2,I)*PSM(2)+X(3,I)*GCAL(3,I)*PSM(3)
       YCAL(2,I)=X(2,I)*GCAL(2,I)*PSM(2)/PTC(I)
       YCAL(3,I)=X(3,I)*GCAL(3,I)*PSM(3)/PTC(I)
       ERROR(1,I)=(GG(1,I)-GCAL(1,I))/GG(1,I)*100.
       ERROR(2,I)=(GG(2,I)-GCAL(2,I))/GG(2,I)*100.
       ERROR(3,I)=(GG(3,I)-GCAL(3,I))/GG(3,I)*100.
       IF(XMOL(I).EQ.0.0)ERROR(1,I)=0.0
       IF(X(2,I).EQ.0.0)ERROR(2,I)=0.0
       IF(X(3,I).EQ.0.0)ERROR(3,I)=0.0
       IF(GG(1,I).EQ.1.0)ERROR(1,I)=0.0
       IF(GG(2,I).EQ.1.0)ERROR(2,I)=0.0
       IF(GG(3,I).EQ.1.0)ERROR(3,I)=0.0
       DIF1=ABS(ERROR(1,I)/100.)
       DIF2=ABS(ERROR(2,I)/100.)
       DIF3=ABS(ERROR(3,I)/100.)
       DIF4=ABS(YCAL(3,I)-YV(3,I))
       DIF5=ABS((PTC(I)-P(I))/P(I))
       IF(NMIN.GT.3)GO TO 2000
       GO TO 2010
2000   IF(X(2,I).EQ.0.0)GO TO 2020
       IF(X(3,I).EQ.0.0)GO TO 2030
2020   DIF3=ABS((P(I)-PTC(I))/(PSM(3)-P(I)))
       IF(P(I).EQ.1.0)DIF3=0.0
       GO TO 2010
2030   DIF2=ABS((P(I)-PTC(I))/(PSM(2)-P(I)))
       IF(P(I).EQ.1.0)DIF2=0.0
2010   CALL MINFUN(NTYPE,NMIN,DIF1,DIF2,DIF3,DIF4,DIF5,Y,X(2,I),
     % X(3,I))
       YS=YS+Y
4000   CONTINUE
       YY=YS
       IF(LIC/20*20.NE.LIC)GO TO 301
```

```
        WRITE(6,302)LIC
  302   FORMAT(10X,' TRIAL # USED = ',I4)
        WRITE(6,303)YY,(XT(I),I=1,M)
  303   FORMAT(///,5X,' YY= ',F15.7,5X,' XT VALUES ',6F15.6)
  301   RETURN
        END
```

```
      SUBROUTINE FIBN(ALPHA,A,B)
C
C    ************************************************************
C
C     SUBROUTINE FIBN
C
C     THIS SUBROUTINE USES THE FIBONACCI METHOD TO FIND THE
C
C     MINIMUM VALUE OF A NON LINEAR FUCTION.
C
C    ************************************************************
C
C
      DIMENSION FIB(50)
C
C     SUBROUTINE FOR FIBONACCI PROCEDURE
C
      DEL=B-A
      WRITE(6,001)
001   FORMAT(///,10X,35HFIBONACCI SINGLE-VARIABLE PROCEDURE )
C
C     DEFINE THE FIRST THREE FIBONACCI NUMBERS
C
      FIBO=1.0
      FIB(1)=1.0
      FIB(2)=2.0
C
C     CALCULATE THE REMAINING FIBONACCI NUMBERS
C
5     BB=1.0/ALPHA
      IF(BB-2.)10,10,11
10    GO TO 14
11    CONTINUE
      JJ=2
12    JJ=JJ+1
      FIB(JJ)=FIB(JJ-1)+FIB(JJ-2)
      CC=FIB(JJ)
      IF(CC-BB)13,15,15
13    GO TO 12
14    WRITE(6,002)
002   FORMAT(///,10X,' ACCURACY SPECIFIED IN FUNC NOT SUFFICIENT.',
     % //,10X,' PROGRAM RESET ALPHA,ALPHA=0.01')
      ALPHA=0.01
      GO TO 5
C
C     FIRST STEP IN THE TABLEAU
15    I=0
      KK=JJ-2
      IK=JJ-2
      BL=B-A
?
```

```
            ALL=FIB(IK)*BL/FIB(JJ)
            W=A+ALL
            V=B-ALL
            CALL FUNC(W,T)
            CALL FUNC(V,U)
            JK=1
            WRITE(6,003)
      003   FORMAT(//,1X,1HK,5X,2HLK,12X,2HAK,13X,2HBK,12X,3HLLK,9X,1HX,
          % 8X,1HY)
            WRITE (6,004)JK,BL,A,B,ALL,W,T
      004   FORMAT(/,I3,6G11.4)
      006   FORMAT(41X,E12.4,2X,E12.4)
      C
      C     SUCCEEDING STEPS IN THE TABLEAU
      C
            IK=IK-1
            JJ=JJ-1
            DO 70 I=1,KK
            IF(U-T)20,20,22
      20    A=A+ALL
            BL=B-A
            W=V
            CALL FUNC(W,T)
            ALL=FIB(IK)*BL/FIB(JJ)
            V=B-ALL
            CALL FUNC(V,U)
            II=I+1
            IK=IK-1
            JJ=JJ-1
            IF(IK-1)28,29,29
      28    IK=1
      29    CONTINUE
            WRITE(6,004)II,BL,A,B,ALL,W,T
            WRITE(6,006)V,U
            GO TO 70
      22    B=B-ALL
            BL=B-A
            V=W
            CALL FUNC(V,U)
            ALL=FIB(IK)*BL/FIB(JJ)
            W=A+ALL
            CALL FUNC(W,T)
            II=I+1
            IK=IK-1
            JJ=JJ-1
            IF(IK-1)30,31,31
      30    IK=1
      31    CONTINUE
            WRITE(6,004)II,BL,A,B,ALL,V,U
            WRITE(6,006)W,T
```

```
      GO TO 70
70    CONTINUE
C
C     CALCULAT1ON OF THE FINAL RANGE OF THE DEPENENT VARIABLE
C
      EPS=0.001*W
      DL=W+EPS
      CALL FUNC(DL,YL)
      IF(YL-T)80,80,81
80    CALL FUNC (B,BF)
      WRITE(6,007)W,B
007   FORMAT(///,25HTHE FINAL FEASIBLE REGION ,2X,2HX=,E15.4,2X,2HX=,
     % E15.4)
      WRITE(6,008)T,BF
008   FORMAT(/   ,20HWITH FUNCTION VALUES,7X,2HY=,E10.4,2X,2HY=,E10.4)
      GO TO 87
81    CALL FUNC(A,AF)
      WRITE(6,009)W,A
009   FORMAT(///   ,25HTHE FINAL FEASIBLE REGION,2X,2HX=,E15.4,2X,2HX=
     % E15.4)
      WRITE(6,017)T,AF
017   FORMAT(/    ,20HWITH FUNCTION VALUES,7X,2HY=,E10.4,2X,2HY=,E10.4
87    ACC=(W-A )/(DEL)
      WRITE(6,018)ACC
018   FORMAT(/   ,    15HTHE ACCURACY IS,12X,E10.4)
      WRITE(6,019)ALPHA
019     FORMAT(/       ,'THE REQUIRED ACCURACY WAS =',E10.4)
C
      RETURN
      END
```

```
      SUBROUTINE FUNC(XT,YY)
C
C
C     ****************************************************************
C
C      SUBROUTINE FUNC
C
C     ****************************************************************
C
C      THIS SUBROUTINE ESTABLISHES THE OBJECTIVE FUNCTION
C
C      SIMILAR TO SUBROUTINE FN. THIS IS CALLED BY
C
C      SUBROUTINE FIBN. ALL SYMBOLS ARE SAME AS IN
C
C      SUBROUTINE FN.
C
C     ****************************************************************
C
C
C
      COMMON XMOL(99),X(3,99),XF(3,99),GG(3,99),P(99),YV(3,99),GNRT(
     % 3,99),GEL(3,99),GCAL(3,99),AMW(3),ERROR(3,99),GDH(3,99)
     % ,GPHY(3,99),T(99),BMM(99),GADD(3,99),YCAL(3,99),ADD(6)
     % ,PTC(99)
      COMMON NP,INDF,FNP,FNM,FZP,FZN,FK,ALFA,DG23,DG32,
     % GPN2,GPN3,ZPN2,ZPN3,KP,M,NBIN,NPION,NNION,DELTA
      COMMON NDEN,NNRTL,ALFA2,ALFB2,ALFA3,ALFB3,DGA2,DGB2,
     % DGA3,DGB3,NBROM,NREG,NTYPE,NIMN
      COMMON B012,B112,B013,B113,CP2(6),CP3(6),CV2(3),CV3(3),
     % B123,ADT(2,20),NXD,XD(20)
      DIMENSION PSM(3)
      GO TO (1040,1050,1060),NBIN
1040  B012=XT
      DELTA=0.0
      B112=0.0
      B123=0.0
      GO TO 1070
1050  B013=XT
      DELTA=0.0
      B113=0.0
      B123=0.0
      GO TO 1070
1060  GO TO(10,20),NBROM
10    B123=XT
      GO TO 1070
20    DELTA=XT
1070  IF(KP.GT.1) GO TO 3100
      CALL NRTL1(X,T,GNRT,FK,FNP,NP,ALFA,DG23,DG32)
      CALL BROML(XMOL,XF,AMW,FNP,FNM,FK,FZP,FZN,T,GEL,
?
```

```
     % NP,B123,GDH,GPHY,BMM,ADD,NDEN,CV2,CV3,NXD,XD,ADT,B012,B112
     % ,B013,B113)
      CALL ADITON(XF,T,AMW,XMOL,FK,FZP,FZN,FNP,FNM,GADD,
     % DELTA,NPION,NNION,NP,ADD,NDEN,CV2,CV3,NXD,XD,ADT,
     % B012,B112,B013,B113)
      GO TO 3200
 3100 CALL NRTL2(X,T,GNRT,FK,FNP,NP,GPN2,GPN3,ZPN2,ZPN3,ALFA,DG23,
     % DG32,FNM,NNRTL,ALFA2,ALFB2,ALFA3,ALFB3,DGA2,DGB2,DGA3,DGB3)
      CALL DEBHUC(XMOL,XF,X,FK,FNP,FNM,FZP,FZN,GEL,AMW,
     % T,NP,GDH,GPHY,ADD,NDEN,CV2,CV3,NXD,XD,ADT)
      DO 8010 IJ=1,NP
      GADD(1,IJ)=0.0
      GADD(2,IJ)=0.0
      GADD(3,IJ)=0.0
 8010 CONTINUE
 3200 YS=0.0
      DO 4000 I=1,NP
      IF(XF(2,I).EQ.0.0)GO TO 1000
      IF(XF(3,I).EQ.0.0)GO TO 1010
      GO TO 1020
 1000 GNRT(2,I)=0.0
      GEL(2,I)=0.0
      GNRT(1,I)=0.0
      GADD(2,I)=0.0
      GADD(1,I)=0.0
      GO TO 1020
 1010 GNRT(3,I)=0.0
      GEL(3,I)=0.0
      GNRT(1,I)=0.0
      GADD(3,I)=0.0
      GADD(1,I)=0.0
 1020 AMS = XF(2,I)*AMW(2)+XF(3,I)*AMW(3)
      GCAL(1,I)=EXP(GNRT(1,I)+GEL(1,I)+GADD(1,I)-ALOG(0.001*FK*AMS*
     % XMOL(I)+1.0))
      GCAL(2,I)=EXP(GNRT(2,I)+GEL(2,I)+GADD(2,I))
      GCAL(3,I)=EXP(GNRT(3,I)+GEL(3,I)+GADD(3,I))
      CALL VAPPRE(CP2,CP3,PSM,T(I))
      PTC(I)=X(2,I)*PSM(2)*GCAL(2,I)+X(3,I)*PSM(3)*GCAL(3,I)
      YCAL(2,I)=X(2,I)*PSM(2)*GCAL(2,I)/PTC(I)
      YCAL(3,I)=X(3,I)*PSM(3)*GCAL(3,I)/PTC(I)
      ERROR(1,I)=(GG(1,I)-GCAL(1,I))/GG(1,I)*100.
      ERROR(2,I)=(GG(2,I)-GCAL(2,I))/GG(2,I)*100.
      ERROR(3,I)=(GG(3,I)-GCAL(3,I))/GG(3,I)*100.
      IF(XMOL(I).EQ.0.0)ERROR(1,I)=0.0
      IF(X(2,I).EQ.0.0)ERROR(2,I)=0.0
      IF(X(3,I).EQ.0.0)ERROR(3,I)=0.0
      IF(GG(1,I).EQ.1.0)ERROR(1,I)=0.0
      IF(GG(2,I).EQ.1.0)ERROR(2,I)=0.0
      IF(GG(3,I).EQ.1.0)ERROR(3,I)=0.0
      DIF1=ABS(ERROR(1,I)/100.)
```

```
          DIF2=ABS(ERROR(2,I)/100.)
          DIF3=ABS(ERROR(3,I)/100.)
          DIF4=ABS(YCAL(3,I)-YV(3,I))
          DIF5=ABS((PTC(I)-P(I))/P(I))
          IF(NMIN.GT.3)GO TO 2000
          GO TO 2010
 2000     IF(X(2,I).EQ.0.0)GO TO 2030
          IF(X(3,I).EQ.0.0)GO TO 2020
 2020     DIF3=ABS((P(I)-PTC(I))/(PSM(3)-P(I)))
          IF(P(I).EQ.1.0)DIF3=0.0
          GO TO 2010
 2030     DIF2=ABS((P(I)-PTC(I))/(PSM(2)-P(I)))
          IF(P(I).EQ.1.0)DIF2=0.0
 2010     CALL MINFUN(NTYPE,NMIN,DIF1,DIF2,DIF3,DIF4,DIF5,Y,X(2,I)
        % ,X(3,I))
          YS=YS+Y
 4000     CONTINUE
          YY=YS
          RETURN
          END
```

```
      SUBROUTINE NRTL1(X,T,GNRT,FK,FNP,NP,ALFA,DG23,DG32)
C
C
C    ***************************************************************
C
C     SUBROUTINE NRTL1
C
C     THIS SUBROUTINE CALCULATES SOLVENT-SOLVENT INTERACTION
C
C     FOR A TERNARY MIXTURE IN MODEL # 2.
C
C    ****************************************************************
C
C
      DIMENSION XA(99),X(3,99),GNRT(3,99),T(99)
      R=1.987
      DO 4001 I=1,NP
      G32=EXP(-ALFA*DG32/R/T(I))
      Z32=DG32*G32
      G23=EXP(-ALFA*DG23/R/T(I))
      Z23=DG23*G23
      XA(I)=FNP*X(1,I)
      FNT1=(FK*XA(I)/FNP+X(2,I)+X(3,I)*G32)**2.
      FNT2=(FK*XA(I)/FNP+X(3,I)+X(2,I)*G23)**2.
      FNT3=X(2,I)+X(3,I)*G32
      FNT4=X(3,I)+X(2,I)*G23
      GNRT(1,I)=(-Z32/FNT1-Z23/FNT2+Z32/(FNT3**2.)+Z23/(FNT4**2.))*
     % X(2,I)*X(3,I)/R/T(I)
      AT2=XA(I)*X(3,I)*FK*(Z32/FNT1+Z23/FNT2+Z32/(FNT3**2.)+
     % Z23/(FNT4**2.))/(FNP*R*T(I))
      AT3=XA(I)*X(2,I)*FK*(Z32/FNT1+Z23/FNT2+Z32/(FNT3**2.)+Z23
     % /(FNT4**2.))/(FNP*R*T(I))
      BT3=X(2,I)**2.*(Z32/FNT1+Z23*G23/FNT2)/(R*T(I))
      BT2=X(3,I)**2.*(G32*Z32/FNT1+Z23/FNT2)/(R*T(I))
      CT2=-2.*FK*X(2,I)*X(3,I)*XA(I)*(Z32/(FNT3**3.)+G23*Z23
     % /(FNT4**3.))/(FNP*R*T(I))
      CT3=-2.*FK*X(2,I)*X(3,I)*XA(I)*(Z32*G32/(FNT3**3.)+
     %  Z23/(FNT4**3.))/(FNP*R*T(I))
      GNRT(2,I)=AT2+BT2+CT2
      GNRT(3,I)=AT3+BT3+CT3
4001    CONTINUE
      RETURN
      END
?
```

```
      SUBROUTINE BROML(XMOL,XF,AMW,FNP,FNM,FK,FZP,FZN,T,GBM,
     % NP,B123,GDH,GPHY,BM,ADD,NDEN,CV2,CV3,NXD,XD,ADT,BO12,
     % B112,BO13,B113)
C
C
C     ******************************************************
C
C      SUBROUTINE BROML
C
C      THIS SUBROUTINE CALCULATES ION-ION INTERACTION &
C
C      ION-SOLVENT INTERACTION ACCORDING TO THE BROMLEY
C
C      EQUATION, IN  MODEL # 2.
C
C     ******************************************************
C
C      GDH(J,I)    - CONTRIBUTION OF THE DEBYE-HUCKEL TERM
C      GPHY(J,I)   - CONTRIBUTION OF THE B TERMS IN THE EQUATION
C                    (i.e. ION-SOLNENT INTERACTION )
C      GBM(J,I)    - COMBINATION OF THE ABOVE TWO TERMS
C
C
C      THIS SUBTOUTINE CALLS  SUBROUTINES FUNCT & FUNCB.
C
C     ********************************************************
C
C
      DIMENSION XMOL(99),XF(3,99),AMW(3),T(99)
      DIMENSION SIG(99),SAI(99),SIG1(99),SAI1(99),GBM(3,99),
     % AI(99),F2(99),F3(99),BM(99),VO(3),AD(6)
     % ,GDH(3,99),GPHY(3,99)
      DIMENSION ADD(6),CV2(3),CV3(3),XD(20),ADT(2,20)
      ROW=1.0
      DO 4001 I=1,NP
      IF(XMOL(I).EQ.0.0)GO TO 2010
      B12=BO12*ALOG((T(I)-243.)/T(I))+B112/T(I)
      B13=BO13*ALOG((T(I)-243.)/T(I))+B113/T(I)
      CALL TEMPD(CV2,CV3,NXD,XD,ADT,AD,VO,T(I))
      AA=1.5/(FZP*FZN)
      AI(I)=(FNP*FZP**2.+FNM*FZN**2.)*XMOL(I)/2.
      XT1=1.+ROW*AI(I)**0.5
      XT2=AA*AI(I)
      XT3=1.+XT2
      XT4=1.+2.*XT2
      AMS=XF(2,I)*AMW(2)+XF(3,I)*AMW(3)
      TNS=1000./AMS
      XT5=(ROW*AI(I)**0. 5)**3.
      XT6=0.001*FK*XMOL(I)
      XT7=XT6*AMS+1.
```

```
          IF(XF(2,I).EQ.0.0)GO TO 1000
          IF(XF(3,I).EQ.0.0)GO TO 1010
          CALL FUNCT(XF(2,I),XF(3,I),T(I),TNS,F2(I),F3(I),
        % ADB,FD2,FD3,AD,DS,ADD,V0,NDEN,AMW)
          CALL FUNCB(XF(2,I),XF(3,I),B12,B13,BM(I)
        % ,FB2,FB3,TNS,B123,AI(I),FNF,FNM,FZP,FZN,AMS,AMW(2),AMW(3)
        % ,FB1,XMOL(I))
          GO TO 1020
 1000     BM(I)=B13
          D30=AD(1)+AD(2)*XF(3,I)+AD(3)*XF(3,I)**2.+AD(4)*XF(3,I)**3.
        % +AD(5)*XF(3,I)**4.+AD(6)*XF(3,I)**5.
          D03=AMW(3)/V0(3)
          ADB3=1.8246*10.**(6.0)*(D03**0.5)*((D30*T(I))**(-1.5))
          FB1=0.0
          FB2=0.0
          FB3=0.0
          F2(I)=0.0
          F3(I)=0.0
          FD2=0.0
          FD3=0.0
          ADB=ADB3
          GO TO 1020
 1010     BM(I)=B12
          D20=AD(1)+AD(2)*XF(3,I)+AD(3)*XF(3,I)**2.0+AD(4)*XF(3,I)**3.
        % +AD(5)*XF(3,I)**4.+AD(6)*XF(3,I)**5.
          D02=AMW(2)/V0(2)
          ADB2=1.8246*10.**(6.0)*(D02**0.5)*((D20*T(I))**(-1.5))
          FB1=0.0
          FB2=0.0
          FB3=0.0
          F2(I)=0.0
          F3(I)=0.0
          FD2=0.0
          FD3=0.0
          ADB=ADB2
 1020     SIG(I)=3.*(XT1-1./XT1-2.*ALOG(XT1))/XT5
          SAI(I)=2.*(-ALOG(XT3)/XT2+XT4/(XT3**2.))/XT2
          SIG1(I)=2.*(XT1**2./2.-2.*XT1+ALOG(XT1)+1.5)/XT5
          SAI1(I)=0.6*2.0*FZP*FZN*(ALOG(XT3)/XT2-1./XT3)/XT2+1.0
          YBT1=XT6*2.303*ADB*SIG(I)*AI(I)**(0.5)/3.*(FZP*FZN)
          YBT2=2.303*FZP*FZN*XT6*(0.06+0.6*BM(I))*SAI(I)*AI(I)/2.
          YBT3=2.303*XT6*BM(I)*AI(I)/2.
          YBT4=2.303*XT6*TNS*AMS*SIG1(I)*AI(I)**(0.5)*(FZP*FZN)
          YBT5=FB3
          YBT7=FB2
          YBT6=2.303*XT6*AMS*TNS*AI(I)/2.0
          FT1=-YBT2-YBT3
          FT5=XT6*AMS
          FT6=ALOG(XT7)
          FT7=FT6-FT5
```

```
      GDH(1,I)=-2.303*ADB*FZP*FZN*AI(I)**0.5/XT1
      GDH(2,I)=YBT1*AMW(2)-YBT4*F2(I)
      GDH(3,I)=YBT1*AMW(3)-YBT4*F3(I)
      GPHY(1,I)=((0.06+ 0.6*BM(I))*AI(I)/(XT3**2.)
     % *FZP*FZN+BM(I)*AI(I))*2.303+2.303*XMOL(I)*AI(I)*TNS*AMS*SAI1(I)
     % *FB1/2.0/1000.0
      GPHY(2,I)=FT1*AMW(2)+YBT7*YBT6*SAI1(I)
      GPHY(3,I)=FT1*AMW(3)+YBT5*YBT6*SAI1(I)
      GBM(1,I)=GDH(1,I)+GPHY(1,I)+ALOG(XT7)
      GBM(2,I)=GDH(2,I)+GPHY(2,I)+FT7
      GBM(3,I)=GDH(3,I)+GPHY(3,I)+FT7
      GO TO 4001
2010  GBM(1,I)=0.0
      GBM(2,I)=0.0
      GBM(3,I)=0.0
      GDH(1,I)=0.0
      GDH(2,I)=0.0
      GDH(3,I)=0.0
      GPHY(1,I)=0.0
      GPHY(2,I)=0.0
      GPHY(3,I)=0.0
4001  CONTINUE
      RETURN
      END
```

```
      SUBROUTINE ADITON(XF,T,AMW,XMOL,FK,FZP,FZN,FNP,FNM,
C
C
C    ************************************************************
C
C     SUBROUTINE ADITON
C
C     THIS SUBROUTINE CALCULATES THE SALTING OUT CONTRIBUTION IN A
C
C     A TERNARY MIXTURE IN MODEL # 2. DELTA IS THE SALTING OUT
C
C     PARAMETER.
C
C    ************************************************************
C
C
C
     % GADD,DELTA,NPION,NNION,NP,ADD,NDEN,CV2,CV3,NXD,XD,ADT,BO12
     % ,B112,BO13,B113)
      DIMENSION XMOL(99),XF(3,99),T(99),AMW(3),AD(6),GADD(3,99)
      DIMENSION RP(6),RN(6),VO(3),ADT(2,20),CV2(3),CV3(3),ADD(6)
       DIMENSION XD(20)
C      RP(1)  = H ION
C      RP(2)   = LI ION
C      RP(3)  = NA ION
C      RP(4)  = CA ION
C      RN(1)  = BR ION
C      RN(2)  = CL ION
      RP(1)=2.08*10.**(-8.0)
      RP(2)=0.60*10.**(-8.0)
      RP(3)=0.95*10.**(-8.0)
       RP(4)=0.99*10.**(-8.0)
      RN(1)=1.95*10.**(-8.0)
      RN(2)=1.81*10.**(-8.0)
      CONST=1.6710383*10.**(-3.0)
      DO 10 I=1,NP
       ALFA=2.0
       AN1=XMOL(I)
       IF(XF(2,I).EQ.0.0)GO TO 20
       IF(XF(3,I).EQ.0.0)GO TO 20
      AMS=XF(2,I)*AMW(2)+XF(3,I)*AMW(3)
      TNS=1000./AMS
       CALL TEMPD(CV2,CV3,NXD,XD,ADT,AD,VO,T(I))
       B12=BO12*ALOG((T(I)-243.)/T(I))+B112/T(I)
       B13=BO13*ALOG((T(I)-243.)/T(I))+B113/T(I)
       CONST1=FNP*FZP**2./RP(NPION)+FNM*FZN**2./RN(NNION)
       CALL FUNCT(XF(2,I),XF(3,I),T(I),TNS,F2,F3,
     % ADB,FD2,FD3,AD,DS,ADD,VO,NDEN,AMW)
       TN3=XF(3,I)*TNS
       TN2=XF(2,I)*TNS
?
```

```
          D=EXP(-ALFA*AN1**0.5)
          A=(TN2*TN3)**0.5
          B=XF(2,I)*B13-XF(3,I)*B12
          C=EXP(2.0*XF(2,I))
          AX=(1.0-ALFA*XMOL(I)/(4.0*AN1**0.5))
          GADD(1,I)=DELTA*D*CONST*CONST1*A*B*C*XMOL(I)*AX/(FK*T(I)*DS)
          GADD(2,I)=DELTA*D*CONST*CONST1*(XMOL(I)**2.0)*((TN3/TN2)**0.5
        % *B*C/2.0-A*B*C*FD2/DS+(B12+B13)*XF(3,I)*A*C/TNS+A*B*C*2.0*
        % XF(3,I)/TNS)/(DS*T(I)*2.0)
          GADD(3,I)=DELTA*D*CONST*CONST1*(XMOL(I)**2.0)*((TN2/TN3)**0.5
        % *B*C/2.0-A*B*C*FD3/DS-(B12+B13)*XF(2,I)*A*C/TNS-A*B*C*2.0*
        % XF(2,I)/TNS)/(DS*T(I)*2.0)
          GO TO 10
   20     GADD(1,I)=0.0
          GADD(2,I)=0.0
          GADD(3,I)=0.0
   10     CONTINUE
          RETURN
          END
```

```
      SUBROUTINE FUNCB(X2,X3,B12,B13,BM,FB2,FB3,TNS,B123,
     % AI,FNP,FNM,FZP,FZN,AMS,AMW2,AMW3,FB1,XMOL)
C
C    **************************************************************
C
C     SUBROUTINE FUNCB
C
C     THIS SUBROUTINE CALCULATES THE MIXTURE TERNARY BROMLEY
C
C     CONSTANT 'BM' . B123 IS THE TERNARY ADJUSTABLE PARAMETER.
C
C    ***************************************************************
C
C
C
      AN1=XMOL
      D23=B123
      A=(X2*X3)**0.25
      ALFA=2.0
      D=(1.0+ALFA*AN1**0.5)**3.0
      D1=((1.0+ALFA*AN1**0.5)**4.0)*(AN1**0.5)
      B=EXP(-ALFA*X3)
      FDBN2=ALFA*X3*B/TNS
      FDBN3=-ALFA*X2*B/TNS
      FDAN2=(((X3/X2)**0.25/(X2**0.5))/2.0-A)/TNS/2.0
      FDAN3=(((X2/X3)**0.25/(X3**0.5))/2.0-A)/TNS/2.0
      BM=B12*X2+B13*X3+D23*A*B/D
      FB2=(B12-B13)*X3/TNS+D23*(A*FDBN2+B*FDAN2)/D
      FB3=(B13-B12)*X2/TNS+D23*(A*FDBN3+B*FDAN3)/D
      FB1=-3.0*ALFA*D23*A*B/(2.0*D1)
      RETURN
      END
```

```
      SUBROUTINE FUNCT(XF2,XF3,T,TNS,F2,F3,ADB
     % ,FD2,FD3,AD,DS,ADD,VO,NDEN,AMW)
C
C
C      ************************************************************
C
C       SUBROUTINE FUNCT
C
C       THIS SUBROUTINE CALCULATES THE DEBYE-HUCKEL CONSTANT
C
C       AND THE SLOPE OF D.H. CONSTANT WITH RESPECT TO # OF
C
C       MOLES OF SOLVENTS IN A TERNARY MIXTURE.
C
C       IF   NDEN = 1 EXPERIMENTAL CONCENTRATION DEPENDENT DATA
C                     ARE USED FOR DENSITIES.
C
C       IF   NDEN = 2 APPROXIMATE RELATIONSHIP IS USED FOR DENSITIES
C
C      ******************************************************************
C
C
      DIMENSION AD(6),ADD(6),VO(3),AMW(3)
      DS=AD(1)+AD(2)*XF3+AD(3)*XF3**2.+AD(4)*XF3**3.+AD(5)*XF3**4.
     % +AD(6)*XF3**5.
      FT1=AD(2)+2.*AD(3)*XF3+3.*AD(4)*XF3**2.+4.*AD(5)*XF3**3.
     % +5.*AD(6)*XF3**4.0
      FD2=-FT1*XF3/TNS
      FD3=FT1*XF2/TNS
      GO TO(10,20),NDEN
10    DSS=ADD(1)+ADD(2)*XF3+ADD(3)*XF3**2.+ADD(4)*XF3**3.+
     % ADD(5)*XF3**4.+ADD(6)*XF3**5.0
      FDT1=ADD(2)+2.0*ADD(3)*XF3+3.0*ADD(4)*XF3**2.+4.0*ADD(5)*
     % XF3**3.+5.*ADD(6)*XF3**4.
      DDS2=-FDT1*XF3/TNS
      DDS3=FDT1*XF2/TNS
      GO TO 30
20    AMWW=AMW(2)*XF2+AMW(3)*XF3
      VS=VO(2)*XF2+VO(3)*XF3
      DSS=AMWW/VS
      DDS2=((AMW(2)-AMW(3))-AMWW*(VO(2)-VO(3))/VS)*XF3/TNS/VS
      DDS3=((AMW(3)-AMW(2))-AMWW*(VO(3)-VO(2))/VS)*XF2/TNS/VS
30    ADB=1.8246*10.**(6.0)*(DSS**0.5)*((DS*T)**(-1.5))
      F2=ADB*(DDS2/DSS/2.-3.*FD2/2./DS)
      F3=ADB*(DDS3/DSS/2.-3.0*FD3/2./DS)
      RETURN
      END
?
```

```
      SUBROUTINE NRTL2(X,T,GNRT,FK,FNP,NP,GPN2,GPN3,ZP2,ZP3,ALFA,
     % DG23,DG32,FNM,NNRTL,ALFA2,ALFB2,ALFA3,ALFB3,
     % DGA2,DGB2,DGA3,DGB3)
C
C
C     ***********************************************************
C
C     SUBROUTINE NRTL2
C
C     THIS SUBROUTINE CALCULATES ION-SOLVENT AND SOLVENT-
C
C     SOLVENT INTERACTIONS OF THE ACTIVTY COEFFICIENTS IN
C
C     MODEL # 1.
C
C     THIS SUBROUTINE IS USED FOR BOTH BINARY & TERNARY MIXTURES
C
C
C     *************************************************************
C
C
C     DG23,DG32,Z23,Z32 - CAL/gMOLE-K
C
C     ZP2,ZP3 - K Joules/ gMOLE
C
C     DGA2,DGB2,DGA3,DGB3 - K Joules/gMOLE-K
C
C     *************************************************************
C
C
C
      DIMENSION X(3,99),XA(99),GNRT(3,99),T(99)
      R=1.987
      R1=8.3143*10.**(-3.0)
      DO 4001 I=1,NP
      GO TO(10,20),NNRTL
10    GPN2=EXP(-ALFA2*DGA2/R1/T(I))+FNM*EXP(-ALFB2*DGB2
     % /R1/T(I))/FNP
      ZP2=DGA2*EXP(-ALFA2*DGA2/R1/T(I))+FNM*DGB2*EXP(-ALFB2*DGB2
     % /R1/T(I))/FNP
      GPN3=EXP(-ALFA3*DGA3/R1/T(I))+FNM*EXP(-ALFB3*DGB3
     % /R1/T(I))/FNP
      ZP3=DGA3*EXP(-ALFA3*DGA3/R1/T(I))+FNM*DGB3*EXP(-ALFB3*DGB3/
     % R1/T(I))/FNP
20    ZPN2=ZP2*238.862
      ZPN3=ZP3*238.862
      G32=EXP(-ALFA*DG32/R/T(I))
      Z32=DG32*G32
      G23=EXP(-ALFA*DG23/R/T(I))
      Z23=DG23*G23
?
```

```
      XA(I)=X(1,I)*FNP
      DT1=(XA(I)*GPN3+X(2,I)*G23+X(3,I))**2.0
      DT2=(XA(I)*GPN2+X(3,I)*G32+X(2,I))**2.0
      DT3=X(3,I)*G32+X(2,I)
      DT4=X(2,I)*G23+X(3,I)
      TT1=ZPN2*GPN2*XA(I)**2.+XA(I)*X(3,I)*ZPN2*G32+XA(I)*X(3,I)
     % *Z32*GPN2+Z32*G32*X(3,I)**2.
      TT2=XA(I)*X(3,I)*Z23*GPN3+Z23*X(3,I)**2.
     % -XA(I)*X(3,I)*ZPN3*G23
      TT3=X(2,I)*(X(3,I)*G32*ZPN2+X(2,I)*ZPN2-X(3,I)*Z32*GPN2)
     TT4=X(3,I)*(X(2,I)*G23*ZPN3+X(3,I)*ZPN3-X(2,I)*Z23*GPN3)
      TT5=ZPN3*GPN3*XA(I)**2.+XA(I)*ZPN3*G23*X(2,I)+XA(I)
     % *X(2,I)*Z23*GPN3+Z23*G23*X(2,I)**2.
      TT6=XA(I)*X(2,I)*Z32*GPN2+Z32*X(2,I)**2.-XA(I)*
     % X(2,I)*ZPN2*G32
      GNRT(1,I)=(TT3/DT2+TT4/DT1-X(2,I)*ZPN2/DT3-X(3,I)*ZPN3/DT4
     % +X(2,I)*X(3,I)*Z32*GPN2/(DT3**2.)+X(2,I)*X(3,I)*Z23*GPN3/
     % (DT4**2.))*FNP/R/T(I)/FK
      TT7=(Z32*GPN2-ZPN2*G32)/(DT3**2.)+(Z23*GPN3+ZPN3*G23)
     % /(DT4**2.)
      TT8=2.*XA(I)*X(2,I)*X(3,I)*(Z32*GPN2/(DT3**3.)+Z23*GPN3*G23/
     % (DT4**3.))
      TT9=2.*XA(I)*X(2,I)*X(3,I)*(G32*Z32*GPN2/(DT3**3.)+Z23*GPN3
     % /(DT4**3.))
      TT10=(Z32*GPN2+ZPN2*G32)/(DT3**2.)+(Z23*GPN3-G23
     % *ZPN3)/(DT4**2.)
      GNRT(2,I)=(TT1/DT2+TT2/DT1+XA(I)*X(3,I)*TT7-TT8)/R/T(I)
      GNRT(3,I)=(TT5/DT1+TT6/DT2+XA(I)*X(2,I)*TT10-TT9)/R/T(I)
 4001 CONTINUE
      RETURN
       END
```

```
      SUBROUTINE DEBHUC(XMOL,XF,X,FK,FNP,FNM,FZP,FZN,GEL,
     % AMW,T,NP,GDH,GPHY,ADD,NDEN,CV2,CV3,NXD,XD,ADT)
C
C     ************************************************************
C
C     SUBROUTINE DEBHUC
C
C     THIS SUBROUTINE CALCULATES ION-ION INTERACTION USING
C
C     THE EXTENDED DEBYE-HUCKEL EQUATION, IN MODEL # 1.
C
C
C     GDH(J,I)     - D.H CONTRIBUTION IN EQUATION
C     GPHY(J,I)    - EXTENDED PART OF THE D.H EQUATION
C     GEL(J,I)     - COMBINATION OF ABOVE TWO TERMS
C
C
C    **************************************************************
C
C
C
      DIMENSION VO(3),XF(3,99),X(3,99),XMOL(99),GEL(3,99),GDH(3,99),
     % GPHY(3,99),AI(99),AMW(3),T(99),AD(6)
      DIMENSION F2(99),F3(99)
      DIMENSION SIG(99),SIG1(99),SAI(99),SAI1(99)
      DIMENSION ADD(6),CV2(3),CV3(3),XD(20),ADT(2,20)
      AA=1.5/(FZP*FZN)
      DO 4001 I=1,NP
      IF(XMOL(I).EQ.0.0)GO TO 2010
      AMS=XF(2,I)*AMW(2)+XF(3,I)*AMW(3)
      TNS=1000./AMS
      CALL TEMPD(CV2,CV3,NXD,XD,ADT,AD,VO,T(I))
      IF(XF(2,I).EQ.0.0)GO TO 1000
      IF(XF(3,I).EQ.0.0)GO TO 1010
      CALL FUNCT(XF(2,I),XF(3,I),T(I),TNS,F2(I),F3(I),
     % ADB,FD2,FD3,AD,DS,ADD,VO,NDEN,AMW)
      GO TO 1020
1000  F2(I)=0.0
      F3(I)=0.0
      D30=AD(1)+AD(2)*XF(3,I)+AD(3)*XF(3,I)**2.+AD(4)*XF(3,I)
     1 **3.+AD(5)*XF(3,I)**4.+AD(6)*XF(3,I)**5.
      GO TO (10,20),NDEN
10    D03=ADD(1)+ADD(2)+ADD(3)+ADD(4)+ADD(5)+ADD(6)
      GO TO 30
20    D03=AMW(3)/VO(3)
30    FD2=0.0
      FD3=0.0
      ADB=1.8246*10.**(6.0)*(D03**0.5)*((D30*T(I))**(-1.5))
      GO TO 1020
1010  F2(I)=0.0
?
```

```
            F3(I)=0.0
            D20=AD(1)+AD(2)*XF(3,I)+AD(3)*XF(3,I)**2.+AD(4)*XF(3,I)
          1 **3.+AD(5)*XF(3,I)**4.+AD(6)*XF(3,I)**5.
            GO TO (40,50),NDEN
 40         DO2=ADD(1)
            GO TO 60
 50         DO2=AMW(2)/VO(2)
 60         FD2=0.0
            FD3=0.0
            ADB=1.8246*10.**(6.0)*(DO2**0.5)*((D20*T(I))**(-1.5))
 1020       AI(I)=XMOL(I)*(FNP*FZP**2.+FNM*FZN**2.)/2.
            XT1=0.001*FK*XMOL(I)*AMS
            XT2=ALOG(XT1+1.)
            ROW=1.0
            FT1=ROW*AI(I)**0.5
            FT2=1.+FT1
            FT3=AA*AI(I)
            FT4=1.+FT3
            SIG(I)=3.*(FT2-2.*ALOG(FT2)-1./FT2)/(FT1**3.)
            SIG1(I)=2.*(FT2**2./2.-2.*FT2+ALOG(FT2)+1.5)/(FT1**3.)
            SAI(I)=2.*(2.*(FT3-2.)*((1.+FT3)**0.5)/FT3+4./FT3-(FT3-2.)/
          % ((1.+FT3)**0.5)-2.*((1.+FT3)**0.5))/3./FT3
            SAI1(I)=2.*(2.*(FT3-2.)*((1.+FT3)**0.5)/FT3+4./FT3)/3./FT3
            GEL(1,I)=-2.303*ADB*FZP*FZN*AI(I)**0.5/FT2+2.303*AI(I)
          % *FZP*FZN*ADB**2.0/(FT4**0.5)+XT2
            TT1=2.303*FK*XMOL(I)*ADB*SIG(I)*AI(I)**0.5/3./1000.
            TT2=2.303*FK*XMOL(I)*TNS*AMS*AI(I)**0.5*SIG1(I)/1000.
            TT3=2.303*FK*XMOL(I)*AI(I)*SAI(I)*ADB**2./2./1000.
            TT4=2.303*FK*XMOL(I)*TNS*AMS*AI(I)*ADB*SAI1(I)/1000.
            GEL(2,I)=((TT1+TT3)*AMW(2)+(TT4-TT2)*F2(I))*FZP*FZN+
          % XT2-XT1
            GEL(3,I)=((TT1+TT3)*AMW(3)+(TT4-TT2)*F3(I))*FZP*FZN+
          % XT2-XT1
            GDH(1,I)=-2.303*ADB*FZP*FZN*AI(I)**0.5/FT2
            GDH(2,I)=(TT1*AMW(2)-TT2*F2(I))*FZP*FZN
            GDH(3,I)=(TT1*AMW(3)-TT2*F3(I))*FZP*FZN
            GPHY(1,I)=2.303*AI(I)*FZP*FZN*ADB**2./(FT4**0.5)
            GPHY(2,I)=(TT3*AMW(2)+TT4*F2(I))*FZP*FZN
            GPHY(3,I)=(TT3*AMW(3)+TT4*F3(I))*FZP*FZN
            GO TO 4001
 2010       GEL(1,I)=0.0
            GEL(2,I)=0.0
            GEL(3,I)=0.0
            GDH(1,I)=0.0
            GDH(2,I)=0.0
            GDH(3,I)=0.0
            GPHY(1,I)=0.0
            GPHY(2,I)=0.0
            GPHY(3,I)=0.0
 4001       CONTINUE
```

```
      RETURN
      END
```

```
      SUBROUTINE MINFUN(NTYPE,NMIN,DIF1,DIF2,DIF3,DIF4,DIF5,
     % Y,X2,X3)
C
C
C     ************************************************************
C
C      SUBROUTINE MINFUN
C
C      THIS SUBROUTINE SETS UP DIFFERENT OBJECTIVE FUNCTIONS USING
C
C      A SYMBOL 'NMIN'. THE EXPLANATION HAS BEEN GIVEN IN
C
C      MAIN PROGRAM.
C
C     *************************************************************
C
C
      GO TO(10,10,10,20,20,20,20,20,20,20),NTYPE
 10   DIF4=0.0
      DIF5=0.0
      GO TO 60
 20   GO TO(30,40,50,40),NMIN
 30   DIF4=0.0
      DIF5=0.0
      GO TO 60
 40   IF(X2.EQ.0.0)GO TO 70
      IF(X3.EQ.0.0)GO TO 70
      DIF1=0.0
      DIF2=0.0
      DIF3=0.0
      DIF4=DIF4*10.0
      GO TO 60
 70   DIF4=0.0
      DIF5=0.0
      GO TO 60
 50   IF(X2.EQ.0.0)GO TO 80
      IF(X3.EQ.0.0)GO TO 80
      DIF5=0.0
      DIF4=DIF4*10.0
      GO TO 60
 80   DIF4=0.0
      DIF5=0.0
 60   Y=DIF1**2.+DIF2**2.+DIF3**2.+DIF4**2.+DIF5**2.
      RETURN
      END
?
```

```
         SUBROUTINE TITLE(NAME1,NAME2,NAME3,ALFA,DG23,DG32,GPN2,
        % GPN3,ZPN2,ZPN3,BO12,BO13,B112,B113,B123,DELTA,KP,NTYPE,
        % XX2,XMOL,NNRTL,DGA2,DGA3,DGB2,DGB3,ALFA2,ALFB2,ALFA3,
        % ALFB3)
      C
      C
      C      ***************************************************************
      C
      C        SUBROUTINE TITLE
      C
      C        THIS SUBROUTINE MAKES TITLES FOR FINAL TABULAR RESULTS
      C
      C
      C      ***************************************************************
      C
      C
      C
         REAL *8 NAME1,NAME2,NAME3
         WRITE(6,7100)
      7100   FORMAT('1',30X,'TABLE#')
         WRITE(6,7110)NAME1,NAME2,NAME3
      7110   FORMAT(//,15X,'SYSTEM:',3A8)
         WRITE(6,7130)
      7130   FORMAT(/,25X,' ** VALUES OF THE PARAMETERS **')
         GO TO(9041,9041,9061,9061,9061,9061,9061,9061,9061),NTYPE
      9041   IF(KP.GT.1)GO TO 9065
         WRITE(6,120)
         IF(XX2.EQ.0.0)GO TO 9070
         WRITE(6,9082)BO12,B112
      9082   FORMAT(/,10X,'BO12= ',G12.5,' B112= ',G12.5)
         GO TO 9052
      9070   WRITE(6,9081)BO13,B113
      9081   FORMAT(/,10X,'BO13= ',G12.5,' B113 =',G12.5)
      110    FORMAT(/,10X, ' EXTENDED DEBYE-HUCKEL + MODIFIED NRTL')
      120    FORMAT(/,10X,'BROMLEY - BINARY - EXPRESSION')
      130    FORMAT(/,5X,'BROMLEY &  SIMPLIFIED MODIFIED NRTL &',
        % ' SALTING-OUT EQUATIONS')
         GO TO 9052
      9065   WRITE(6,110)
         IF(XX2.EQ.0.0)GO TO 9075
         GO TO(10,20),NNRTL
      20     WRITE(6,9084)GPN2,ZPN2
      9084   FORMAT(/,10X,' GPN2 =',G12.5,3X,'ZPN2=',G12.5)
         GO TO 9052
      10     WRITE(6,100)ALFA2,ALFB2,DGA2,DGB2
      100    FORMAT(/,3X,'ALFA2=',G12.5,'ALFB2=',G12.5,'DGA2=',
        % G12.5,'DGB2=',G12.5)
         GO TO 9052
      9075   GO TO(30,40),NNRTL
      30     WRITE(6,150)ALFA3,ALFB3,DGA3,DGB3
      ?
```

```
150     FORMAT(/,3X,'ALFA3=',G12.5,'ALFB3=',G12.5,'DGA3=',
     %  G12.5,'DGB3=',G12.5)
        GO TO 9052
40      WRITE(6,9086)GPN3,ZPN3
9086    FORMAT(/,10X,'GPN3=',G12.5,3X,'ZPN3=',G12.5)
        GO TO 9052
9061    WRITE(6,7140)ALFA,DG23,DG32
7140    FORMAT(/,3X,' NONELECTROLYTE BINARY : ALFA=',G12.5,
     %  'DG23=',G12.5,'DG32=',G12.5)
        IF(XMOL.EQ.0.0)GO TO 9052
        IF(KP.GT.1)GO TO 9051
        WRITE(6,130)
        WRITE(6,7150)BO12,B112,BO13,B113
7150    FORMAT(/,5X,'BO12=',G10.3,'B112=',G10.3,'BO13=',G10.3
     %  ,'B113=',G10.3)
        WRITE(6,200)B123,DELTA
200     FORMAT(/,15X,' B123=',G12.5,'DELTA =',G12.5)
        GO TO 9052
9051    WRITE(6,110)
        GO TO(70,80),NNRTL
70      WRITE(6,100)ALFA2,ALFB2,DGA2,DGB2
        WRITE(6,150)ALFA3,ALFB3,DGA3,DGB3
        GO TO 9052
80      WRITE(6,7160)GPN2,ZPN2,GPN3,ZPN3
7160    FORMAT(/,6X,'GPN2=',G12.5,'ZPN2=',G12.5,'GPN3=',
     %  G12.5,'ZPN3=',G12.5)
9052    RETURN
        END
```

## INPUT DATA SEQUENCE

| Card # | Variables | Format |
|---|---|---|
| 1 | NSET,LL,EE | 2I3,F10.1 |
| 2-21 | INFORMATION | 8A10 |
| 22 | XLIM,XLLIM | 2F10.5 |
| 23 | NAME1,NAME2,NAME3 (name of the system) | 3A8 |
| 24 | INDF,KP,NBIN,NPION,NNION,NREG,NDEN, NNRTL,NBROM,NTYPE,NMIN | 11I2 |
| 25 | NCOMP,NP,NXD,NXDD | 4I2 |
| 26 | CP2(I), I=1,6 | |
| 27 | CP3(I), I=1,6<br>(pure component vapor pressure constants) | F12.7,F11.5,F8.3, F3.1,F10.5 |
| 28 | AMW(I), I=1,3 | 6F10.5 |
| 29 | V21,T21,V22,T22,V23,T23 | |
| 30 | V31,T31,V32,T32,V33,T33 | 6F10.6 |
| 31-(30+NXD) | ADT(1,I),ADT(2,I),XD(I) (total # of data are nxd)(if NXD = 11, card #31-41) | 3F10.5 |
| 42 | FK,FNP,FNM,FZP,FZN | 5F10.5 |
| 43-(42+NXDD) | DENS(I),XDD(I) (only two data on a card,total # NXDD)(if NXDD=13, card #43-55) | 6F10.5 |
| 56-(55+NP) | XMOL(I), X(J,I),Y(J,I),J=2,3),G(1,I), P(I),T(I)(8 data on a card, total card = NP)(IF NP=34, card #56-89) | 8F10.6 |
| 90 | ALFA,DG23,DG32,ALFA2,ALFB2,ALFA3, ALFB3 | 8F10.5 |
| 91 | GPN2,ZPN2,GPN3,ZPN3,DGA2,DGB2,DGA3, DGB3 | 8F10.5 |
| 92 | BO12,B112,BO13,B113,B123,DELTA | 8F10.5 |
| 93 | ALPHA1,AXT1,BXT1 | F10.7,2F10.4 |

| | | |
|---|---|---|
| 94 | M,MM | 2I2 |
| 95-(94+MM) | XTX(I),BXX(I)(two data on a card, total cards = MM)(if MM=4 cards 95-98) | 2F10.4 |

SAMPLE INPUT

```
0014000.0000010
  *********************************************
  *  FILE NAME - LICLH2O.MEOHAT25.COMBINED
  *
  *
  *
  *
  *   BINARY 1-3: SKABICHVESKKI
  *
  *   TERNARY 1-2-3: CIPARIS
  *
  *
  *
  *
  *
  *
  *
  *
  *****************************************


   3.000000000.0
  LICL - H2O - MEOH
 1 2 5 2 2 1 1 2 1 4 2
 3341113
0070.4346943-7362.698100000.000000.0069520850.0  -9.0
0012.3858228-3880.50203 -24.355000.0000000000.0  00.000
  42.4     18.0     32.0
  18.06    277.13     18.278   323.15     18.844   373.15
  39.556   273.15     44.874   373.15     57.939   473.15
   1.9051   -0.00205   0.0
   1.8799   -0.00208   0.0588
   1.8505   -0.00212   0.1233
   1.8190   -0.00218   0.1942
   1.7865   -0.00225   0.2727
   1.7513   -0.00234   0.3600
   1.7120   -0.00244   0.4576
   1.6658   -0.00252   0.5676
   1.6160   -0.00248   0.6923
   1.5648   -0.00242   0.8351
   1.5099   -0.00234   1.0
    2.000     1.000     1.000     1.00    1.0
   0.99707  00.0
   0.98472  00.04085
   0.97919  00.06168
   0.96649  00.11445
```

```
47.        0.94796  00.19739
48.        0.93658  00.24867
49.        0.91534  00.34382
50.        0.88242  00.49446
51.        0.85790  00.61267
52.        0.84210  00.69241
53.        0.82458  00.78454
54.        0.80510  00.89229
55.        0.78663  01.0
56.       1.0       0.815184  0.395     0.146118  0.605     1.0       47.3      298.15
57.       1.0       0.672192  0.235     0.285347  0.765     1.0       65.3      298.15
58.       1.0       0.505166  0.14      0.447977  0.86      1.0       80.0      298.15
59.       1.0       0.284199  0.07      0.66313   0.93      1.0       96.3      298.15
60.       1.0       0.039517  0.007     0.901372  0.993     1.0      115.3      298.15
61.       0.328     0.0       0.0       0.979440  1.0       1.0      125.0818  298.15
62.       1.340     0.0       0.0       0.921014  1.0       1.0      116.4291  298.15
63.       1.933     0.0       0.0       0.889908  1.0       1.0      109.5579  298.15
64.       2.560     0.0       0.0       0.859225  1.0       1.0      101.9232  298.15
65.       2.971     0.0       0.0       0.840234  1.0       1.0       96.1972  298.15
66.       3.667     0.0       0.0       0.809921  1.0       1.0       85.3814  298.15
67.       0.100000  0.996413  1.000000  0.000000  0.000000  0.790000 23.675820298.149900
68.       0.200000  0.992852  1.000000  0.000000  0.000000  0.757000 23.595910298.149900
69.       0.300000  0.989316  1.000000  0.000000  0.000000  0.744000 23.514770298.149900
70.       0.400000  0.985805  1.000000  0.000000  0.000000  0.740000 23.431860298.149900
71.       0.500000  0.982318  1.000000  0.000000  0.000000  0.739000 23.347740298.149900
72.       0.600000  0.978857  1.000000  0.000000  0.000000  0.743000 23.261910298.149900
73.       0.700000  0.975420  1.000000  0.000000  0.000000  0.748000 23.174160298.149900
74.       0.800000  0.972006  1.000000  0.000000  0.000000  0.755000 23.084890298.149900
75.       0.900000  0.968617  1.000000  0.000000  0.000000  0.764000 22.994150298.149900
76.       1.000000  0.965251  1.000000  0.000000  0.000000  0.774000 22.901130298.149900
77.       1.2       0.958589  1.0       0.0       0.0       0.796    22.711330298.15
78.       1.4       0.952018  1.0       0.0       0.0       0.823    22.513356298.15
79.       1.6       0.945537  1.0       0.0       0.0       0.853    22.309082298.15
80.       1.8       0.939144  1.0       0.0       0.0       0.885    22.098690298.15
81.       2.0       0.932836  1.0       0.0       0.0       0.921    21.880828298.15
82.       2.5       0.917431  1.0       0.0       0.0       1.026    21.301025298.15
83.       3.0       0.902527  1.0       0.0       0.0       1.156    20.675445298.15
84.       3.5       0.888099  1.0       0.0       0.0       1.317    19.999737298.15
85.       4.0       0.874126  1.0       0.0       0.0       1.510    19.282137298.15
86.       4.5       0.860585  1.0       0.0       0.0       1.741    18.531818298.15
87.       5.0       0.847457  1.0       0.0       0.0       2.02     17.750526298.15
88.       5.5       0.834724  1.0       0.0       0.0       2.34     16.949615298.15
89.       6.0       0.822368  1.0       0.0       0.0       2.72     16.134811298.15
90.       -1.00000-150.900000336.470000000.20000  00.000000000.20000  00.0
91.       12.66600 068.1660  075.8180 -11.239000135.11000  -4.12000 -17.800000134.9
92.       -0.07341  0.00000   -0.170760000.00000 -18.800000000.016
```

```
93.      00.0000005   -1.0000001.0
94.        4 4
95.        0012.666000000.01
96.          68.166000000.10
97.      00075.818000000.1
98.         -11.239000000.1
```

## SAMPLE OUTPUT

```
             # OF DATA SET TO BE USED =  1TRIAL #400E=0.00000100
 *********************************************
 *  FILE NAME - LICLH20.MEOHAT25.COMBINED
 *
 *
 *
 *
 *   BINARY 1-3: SKABICHVESKKI
 *
 *   TERNARY 1-2-3: CIPARIS
 *
 *
 *
 *
 *
 *
 *
 *
 *****************************************


  3.00000   0.0
1 2 5 2 2 1 1 2 1 4 2
      INPUT DATA
3341113
 70.4346924-7362.69531   0.0    0.0069520850.0  -9.00000
 12.3858223-3880.50195 -24.355  0.0         0.0   0.0
 42.39999  18.00000  32.00000
 18.06000 277.12988  18.27800 323.14990  18.84399 373.14990
 39.55600 273.14990  44.87399 373.14990  57.93900 473.14990


    LIQUID MOLAR VOLUME CONSTANTS
     22.887       -0.36416E-01    0.68557E-04
     64.510       -0.19716        0.38735E-03
  1.90510  -0.00205   0.0
  1.87990  -0.00208   0.05880
  1.85050  -0.00212   0.12330
  1.81900  -0.00218   0.19420
  1.78650  -0.00225   0.27270
  1.75130  -0.00234   0.36000
  1.71200  -0.00244   0.45760
  1.66580  -0.00252   0.56760
  1.61600  -0.00248   0.69230
  1.56480  -0.00242   0.83510
  1.50990  -0.00234   1.00000
```

```
2.00000   1.00000   1.00000   1.00000   1.00000
 0.99707   0.0
 0.98472   0.04085
 0.97919   0.06168
 0.96649   0.11445
 0.94796   0.19739
 0.93658   0.24867
 0.91534   0.34382
 0.88242   0.49446
 0.85790   0.61267
 0.84210   0.69241
 0.82458   0.78454
 0.80510   0.89229
 0.78663   1.00000
   0.99662    -0.29616     0.37569    -0.84751     0.88645    -0.32857
1.000000  0.815184  0.395000  0.146118  0.605000  1.000000 47.299988298.149902
 23.8          127.
1.000000  0.672192  0.235000  0.285347  0.765000  1.000000 65.299988298.149902
 23.8          127.
1.000000  0.505166  0.140000  0.447977  0.860000  1.000000 80.000000298.149902
 23.8          127.
1.000000  0.284199  0.070000  0.663130  0.930000  1.000000 96.299988298.149902
 23.8          127.
1.000000  0.039517  0.007000  0.901372  0.993000  1.000000115.299988298.149902
 23.8          127.
0.328000  0.0       0.0       0.979440  1.000000  1.000000125.081787298.149902
 23.8          127.
1.339999  0.0       0.0       0.921014  1.000000  1.000000116.429092298.149902
 23.8          127.
1.933000  0.0       0.0       0.889908  1.000000  1.000000109.557892298.149902
 23.8          127.
2.559999  0.0       0.0       0.859225  1.000000  1.000000101.923187298.149902
 23.8          127.
2.971000  0.0       0.0       0.840234  1.000000  1.000000 96.197189298.149902
 23.8          127.
3.667000  0.0       0.0       0.809921  1.000000  1.000000 85.381393298.149902
 23.8          127.
0.100000  0.996413  1.000000  0.0       0.0       0.790000 23.675812298.149658
 23.8          127.
0.200000  0.992852  1.000000  0.0       0.0       0.757000 23.595901298.149658
 23.8          127.
0.300000  0.989316  1.000000  0.0       0.0       0.744000 23.514755298.149658
 23.8          127.
0.400000  0.985805  1.000000  0.0       0.0       0.740000 23.431854298.149658
 23.8          127.
0.500000  0.982318  1.000000  0.0       0.0       0.739000 23.347733298.149658
```

```
  23.8        127.
0.600000  0.978857  1.000000  0.0       0.0       0.743000 23.261902298.149658
  23.8        127.
0.700000  0.975420  1.000000  0.0       0.0       0.748000 23.174149298.149658
  23.8        127.
0.800000  0.972006  1.000000  0.0       0.0       0.755000 23.084885298.149658
  23.8        127.
0.900000  0.968617  1.000000  0.0       0.0       0.764000 22.994141298.149658
  23.8        127.
1.000000  0.965251  1.000000  0.0       0.0       0.774000 22.901123298.149658
  23.8        127.
1.200000  0.958589  1.000000  0.0       0.0       0.796000 22.711319298.149902
  23.8        127.
1.400000  0.952018  1.000000  0.0       0.0       0.823000 22.513351298.149902
  23.8        127.
1.599999  0.945537  1.000000  0.0       0.0       0.853000 22.309067298.149902
  23.8        127.
1.799999  0.939144  1.000000  0.0       0.0       0.885000 22.098679298.149902
  23.8        127.
2.000000  0.932836  1.000000  0.0       0.0       0.921000 21.880814298.149902
  23.8        127.
2.500000  0.917431  1.000000  0.0       0.0       1.025999 21.301010298.149902
  23.8        127.
3.000000  0.902527  1.000000  0.0       0.0       1.155999 20.675430298.149902
  23.8        127.
3.500000  0.888099  1.000000  0.0       0.0       1.316999 19.999725298.149902
  23.8        127.
4.000000  0.874126  1.000000  0.0       0.0       1.509999 19.282135298.149902
  23.8        127.
4.500000  0.860585  1.000000  0.0       0.0       1.740999 18.531815298.149902
  23.8        127.
5.000000  0.847457  1.000000  0.0       0.0       2.020000 17.750519298.149902
  23.8        127.
5.500000  0.834724  1.000000  0.0       0.0       2.339999 16.949600298.149902
  23.8        127.
6.000000  0.822368  1.000000  0.0       0.0       2.719999 16.134796298.149902
  23.8        127.
               X1             X2             X3            GAMA1          GAMA2          GAMA3
            0.019349       0.815184       0.146118       1.000000       0.964812       1.539131
            0.021231       0.672192       0.285347       1.000000       0.961010       1.375829
            0.023429       0.505166       0.447977       1.000000       0.933306       1.206968
            0.026336       0.284199       0.663130       1.000000       0.998487       1.061386
            0.029556       0.039517       0.901372       1.000000       0.859773       0.998246
            0.010280       0.0            0.979440       1.000000       1.000000       1.003643
            0.039493       0.0            0.921014       1.000000       1.000000       0.993479
            0.055046       0.0            0.889908       1.000000       1.000000       0.967524
```

```
                0.070387         0.0              0.859225         1.000000         1.000000         0.932243
                0.079883         0.0              0.840234         1.000000         1.000000         0.899757
                0.095039         0.0              0.809921         1.000000         1.000000         0.828483
                0.001794         0.996413         0.0              0.790000         1.000259         1.000000
                0.003574         0.992852         0.0              0.757000         1.000459         1.000000
                0.005342         0.989316         0.0              0.744000         1.000582         1.000000
                0.007098         0.985805         0.0              0.740000         1.000606         1.000000
                0.008841         0.982318         0.0              0.739000         1.000552         1.000000
                0.010572         0.978857         0.0              0.743000         1.000399         1.000000
                0.012290         0.975420         0.0              0.748000         1.000136         1.000000
                0.013997         0.972006         0.0              0.755000         0.999784         1.000000
                0.015692         0.968617         0.0              0.764000         0.999338         1.000000
                0.017375         0.965251         0.0              0.774000         0.998766         1.000000
                0.020706         0.958589         0.0              0.796000         0.997357         1.000000
                0.023991         0.952018         0.0              0.823000         0.995487         1.000000
                0.027232         0.945537         0.0              0.853000         0.993216         1.000000
                0.030428         0.939144         0.0              0.885000         0.990546         1.000000
                0.033582         0.932836         0.0              0.921000         0.987413         1.000000
                0.041285         0.917431         0.0              1.025999         0.977389         1.000000
                0.048737         0.902527         0.0              1.155999         0.964350         1.000000
                0.055951         0.888099         0.0              1.316999         0.947989         1.000000
                0.062937         0.874126         0.0              1.509999         0.928585         1.000000
                0.069708         0.860585         0.0              1.740999         0.906494         1.000000
                0.076271         0.847457         0.0              2.020000         0.881726         1.000000
                0.082638         0.834724         0.0              2.339999         0.854786         1.000000
                0.088816         0.822368         0.0              2.719999         0.825920         1.000000
 -1.00000-150.89999 336.46997   0.20000   0.0        0.20000   0.0
 12.66600  68.16599  75.81799 -11.23900 135.10999  -4.12000 -17.79999 134.89999
 -0.07341   0.0      -0.17076   0.0     -18.79999   0.01600
0.0000005   -1.0000    1.0000
4 4
  12.6660    0.0100
  68.1660    0.1000
  75.8180    0.1000
 -11.2390    0.1000
    ***********MAXIMUM MOLALITY USED=    4.00000

    VLE DATA ARE PREDICTED USING MODEL #1

  COMPONENT #   MOLE-FRACTION        YEXP            YCAL           YCAL-YEXP        PCAL-PEXP
      2            0.81518         0.39500         0.39209         0.00291          6.00903
      3            0.14612         0.60500         0.60791         0.00291          6.00903
  COMPONENT #     MOLALITY     LOG NRTL    LOG COULOMBIC   LOG PHYSICAL   LOG ADDITION     GAM CAL     GAM EXP    % ERROR IN GAMA
      1             1.00        -4.22         -0.724          0.576           0.0         0.127E-01   0.100E 59     0.100E 59
```

```
    2        1.00       0.810E-01     0.107E-01    -0.145E-01     0.0          1.08      0.965        -11.9
    3        1.00       0.557        -0.158E-01     0.148E-01     0.0          1.74       1.54        -13.2


COMPONENT #  MOLE-FRACTION     YEXP          YCAL           YCAL-YEXP      PCAL-PEXP
    2         0.67219        0.23500       0.24449        -0.00949       5.62950
    3         0.28535        0.76500       0.75551        -0.00949       5.62950
COMPONENT #    MOLALITY    LOG NRTL    LOG COULOMBIC   LOG PHYSICAL   LOG ADDITION    GAM CAL     GAM EXP    % ERROR IN GAMA
    1            1.00      -3.60        -0.883          0.856          0.0          0.265E-01   0.100E 59    0.100E 59
    2            1.00      0.947E-01    0.193E-01     -0.305E-01       0.0             1.09      0.961         -13.0
    3            1.00      0.389       -0.155E-01      0.165E-01       0.0             1.48       1.38         -7.27

COMPONENT #  MOLE-FRACTION     YEXP          YCAL           YCAL-YEXP      PCAL-PEXP
    2         0.50517        0.14000       0.14603        -0.00603       7.16751
    3         0.44798        0.86000       0.85397        -0.00603       7.16751
COMPONENT #    MOLALITY    LOG NRTL    LOG COULOMBIC   LOG PHYSICAL   LOG ADDITION    GAM CAL     GAM EXP    % ERROR IN GAMA
    1            1.00      -2.59        -1.11           1.35           0.0          0.951E-01   0.100E 59    0.100E 59
    2            1.00      0.922E-01    0.347E-01     -0.668E-01       0.0             1.06      0.933         -13.7
    3            1.00      0.267       -0.128E-01      0.143E-01       0.0             1.31       1.21         -8.20

COMPONENT #  MOLE-FRACTION     YEXP          YCAL           YCAL-YEXP      PCAL-PEXP
    2         0.28420        0.07000       0.06173         0.00827       6.08536
    3         0.66313        0.93000       0.93827         0.00827       6.08536
COMPONENT #    MOLALITY    LOG NRTL    LOG COULOMBIC   LOG PHYSICAL   LOG ADDITION    GAM CAL     GAM EXP    % ERROR IN GAMA
    1            1.00      -0.814       -1.48           2.41           0.0             1.12     0.100E 59    0.100E 59
    2            1.00      0.354E-01    0.659E-01     -0.166           0.0            0.936      0.998          6.24
    3            1.00      0.144       -0.150E-02     -0.118E-01       0.0             1.14       1.06         -7.26

COMPONENT #  MOLE-FRACTION     YEXP          YCAL           YCAL-YEXP      PCAL-PEXP
    2         0.03952        0.00700       0.00622         0.00078      -9.29149
    3         0.90137        0.99300       0.99378         0.00078      -9.29149
COMPONENT #    MOLALITY    LOG NRTL    LOG COULOMBIC   LOG PHYSICAL   LOG ADDITION    GAM CAL     GAM EXP    % ERROR IN GAMA
    1            1.00       1.64        -1.97           4.24           0.0             50.1     0.100E 59    0.100E 59
    2            1.00      -0.109        0.105         -0.347          0.0            0.703      0.860          18.3
    3            1.00      -0.246E-02   0.247E-01      -0.105          0.0            0.919      0.998          7.99
```

```
                              TABLE#

              SYSTEM:  LICL - H2O - MEOH

                        ** VALUES OF THE PARAMETERS **

  NONELECTROLYTE BINARY : ALFA= -1.0000    DG23= -150.90    DG32=  336.4

         EXTENDED DEBYE-HUCKEL + MODIFIED NRTL

    GPN2=  12.666    ZPN2=  68.166    GPN3=  75.818    ZPN3= -11.239

 MOLALITY   X2           X3          Y3EXP        Y3CAL       DY          DP
 1.00      0.81518     0.14612     0.60500     0.60791     0.291E-02   6.01
 1.00      0.67219     0.28535     0.76500     0.75551    -0.949E-02   5.63
 1.00      0.50517     0.44798     0.86000     0.85397    -0.603E-02   7.17
 1.00      0.28420     0.66313     0.93000     0.93827     0.827E-02   6.09
 1.00      0.39517E-01 0.90137     0.99300     0.99378     0.779E-03  -9.29


        AVERAGE DY(YCAL-YEXP)= 0.54953E-02
        BASED ON # OF POINTS FOR Y =  5


        AVERAGE DP(PCAL-PEXP)=  6.8366
       BASED ON # OF POINTS FOR DP =  5
?
```

# APPENDIX G

# TABLES AND FIGURES FOR MODEL I

TABLE G.1 Binary Data Sources

| # | System | T(°C) or P(atm) | 'm' Range | Type of Data | # of Data Points | Reference |
|---|---|---|---|---|---|---|
| 1 | $CaCl_2$-$H_2O$ | 25 | 0.1-6.0 | m vs $\gamma_\pm$ and P | 23 | Robinson & Stokes (1955) |
| 2 | HCl-$H_2O$ | 25 | 0.1-2.0 | m vs $\gamma_\pm$ & $\gamma_{solvent}$ | 15 | Robinson & Stokes (1955) |
| 3 | LiCl-$H_2O$ | 25 | 0.1-6.0 | m vs $\gamma_\pm$ and P | 27 | Robinson & Stokes (1955) |
| 4 | LiCl-$H_2O$ | 60 | 0.88-9.0 | m vs P | 17 | Hala (1969) |
| 5 | NaBr-$H_2O$ | 25 | 0.1-4.0 | m vs $\gamma_\pm$ and P | 19 | Robinson & Stokes (1955) |
| 6 | NaBr-$H_2O$ | 40 | 4.0 | m vs P | 4 | Ciparis (1966) |
| 7 | NaCl-$H_2O$ | 25,60,70<br>80,90,100 | 0.1-4.0 | m vs $\gamma_\pm$ and P | 11 | Robinson & Stokes (1955) |
| 8 | $CaCl_2$-MeOH | 25 | 0.3-2.6 | m vs P | 7 | Eric (1979) |
| 9 | HCl-MeOH | 25 | 0.002-0.56 | m vs $\gamma_\pm$ | 22 | Harned & Owen (1958) |
| 10 | HCl-EtOH | 25 | 0.005-0.1 | m vs $\gamma_\pm$ | 8 | Janz & Taniguichi (1957) |
| 11 | LiBr-MeOH | 15,25 | 0.3-6.6 | m vs P |  | Skabichevskii (1969) |
| 12 | LiCl-MeOH | 25 | 0.33-3.67 | m vs P | 6 | Skabichevskii (1969) |
| 13 | LiCl-MeOH | 60 | 0.33-7.4 | m vs P | 12 | Hala (1969) |
| 14 | NaBr-MeOH | 25 | 0.56-1.56 | m vs P | 9 | Eric (1979) |
| 15 | NaCl-MeOH | 25 | 0.0001-0.1 | m vs $\gamma_\pm$ | 7 | Convington (1973) |

TABLE G.1 Binary Data Sources (Cont'd.)

| # | System | T(°C) or P(atm) | 'm' Range | Type of Data | # of Data Points | Reference |
|---|---|---|---|---|---|---|
| 16 | $H_2O$-MeOH | 25 | 0.0 | X-y-P-T | 8 | Ciparis (1966) |
| 17 | $H_2O$-MeOH | 40 | 0.0 | X-y-P-T | 6 | Ciparis (1966) |
| 18 | $H_2O$-EtOH | 25 | 0.0 | X-y-P-T | 10 | Ciparis (1966) |
| 19 | $H_2O$-MeOH | 1 atm | 0.0 | X-y-P-T | 34 | Rebolleda (1958) |

TABLE G.2 Ternary Data Sources

| # | System | T or P | 'm' Range | Type of Data | # of Data Points | Reference |
|---|---|---|---|---|---|---|
| 1 | $HCl-H_2O-EtOH$ | 25°C | 0.006-2.5 | $m-X-\gamma_{\pm}$ | 44 | Harned & Owen (1958) |
| 2 | $HCl-H_2O-MeOH$ | 25°C | 0.02-0.5 | $m-X-\gamma_{\pm}$ | 24 | Akerlof (1930) |
| 3 | $HCl-H_2O-MeOH$ | 25°C | 0.001-2.0 | $m-X-\gamma_{\pm}$ | 24 | Harned & Owen (1958) |
| 4 | $LiCl-H_2O-EtOH$ | 25°C | 0.5-4.0 | m-X-y-P-T | 31 | Ciparis (1966) |
| 5 | $LiCl-H_2O-MeOH$ | 25°C | 0.02-1.0 | $m-X-\gamma_{\pm}$ | 45 | Akerlof (1930) |
| 6 | $LiCl-H_2O-MeOH$ | 25°C | 1.0 | m-X-y-P-T | 5 | Ciparis (1966) |
| 7 | $LiCl-H_2O-MeOH$ | 60°C | 0.58-14.1 | m-X-y-P-T | 25 | Hala (1969) |
| 8 | $NaBr-H_2O-MeOH$ | 25°C | 1.0-7.1 | m-X-y-P-T | 16 | Ciparis (1966) |
| 9 | $NaBr-H_2O-MeOH$ | 40°C | 1.0-6.2 | m-X-y-P-T | 10 | Ciparis (1966) |
| 10 | $NaCl-H_2O-MeOH$ | 25°C | 0.02-0.5 | $m-X-\gamma_{\pm}$ | 35 | Akerlof (1930) |
| 11 | $KCl-H_2O-MeOH$ | 1 atm | 0.012-2.0 | m-X-y-P-T | 33 | Rousseau et al. (1975) |
| 12 | $LiCl-H_2O-MeOH$ | 1 atm | 0.085-3.8 | m-X-y-P-T | 24 | Rousseau et al. (1975) |
| 13 | $NaBr-H_2O-MeOH$ | 1 atm | 0.076-3.8 | m-X-y-P-T | 23 | Rousseau et al. (1975) |
| 14 | $NaF-H_2O-MeOH$ | 1 atm | 0.012-0.95 | m-X-y-P-T | 24 | Rousseau et al. (1975) |

## TABLE G.3 Solvent-Solvent Binary Data Correlation

| System | # of Points | T or P | $\alpha_{23}$ | $\Delta g_{23}$ | $\Delta g_{32}$ | $\Delta Y$ Max | $\Delta Y$ Avg | $\Delta P$ (mmHg) Max | $\Delta P$ (mmHg) Avg |
|---|---|---|---|---|---|---|---|---|---|
| $H_2O$-MeOH | 8 | 25°C | 0.3 | 806.03 | -321.46 | 0.013 | 0.004 | 2.0 | 1.4 |
| $H_2O$-MeOH | 8 | 25°C | -1.0 | -150.9 | 836.76 | 0.012 | 0.0038 | 2.1 | 1.4 |
| $H_2O$-MeOH | 6 | 40°C | 0.3 | 1453.1 | -498.7 | 0.0146 | 0.0066 | 7.8 | 3.4 |
| $H_2O$-MeOH | 6 | 40°C | -1.0 | -364.7 | 493.7 | 0.0226 | 0.0086 | 3.5 | 2.2 |
| $H_2O$-MeOH | 12 | 60°C | 0.3 | 431.65 | 43.59 | 0.01 | 0.0057 | - | 4.1 |
| $H_2O$-MeOH | 12 | 60°C | -1.0 | 140.3 | 235.9 | 0.011 | 0.0057 | - | 4.2 |
| $H_2O$-EtOH | 10 | 25°C | 0.3 | 894.5 | -62.9 | 0.049 | 0.012 | 2.2 | 0.7 |
| $H_2O$-EtOH | 10 | 25°C | -1.0 | 105.7 | 383.87 | 0.054 | 0.013 | 2.6 | 0.8 |
| $H_2O$-MeOH | 34 | 1 atm | 0.3 | 627.6 | -54.5 | 0.0086 | 0.003 | 13.1 | 5.6 |
| $H_2O$-MeOH | 34 | 1 atm | -1.0 | 97.077 | 312.5 | 0.007 | 0.0026 | 13.0 | 5.4 |

TABLE G.4 Aqueous Electrolytic Binary Data Correlation with Two Objective Functions, Equations (2-9) & (2-10)

| | | | | Objective Function #1 | | | | | | Objective Function #2 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| System | # of Points | Max 'm' | T (°C) | $G_{\pm 2}$ | $Z_{\pm 2}$ | % Error in $\gamma_{\pm}$ | | % Error in DP | | $G_{\pm 2}$ | $Z_{\pm 2}$ | % Error in $\gamma_{\pm}$ | | % Error in DP | |
| | | | | | | Max | Avg | Max | Avg | | | Max | Avg | Max | Avg |
| $CaCl_2$-$H_2O$ | 21 | 5.0 | 25 | 37.755 | 13.545 | 24.2 | 7.6 | 7.7 | 4.3 | 36.411 | 13.766 | 25.9 | 7.5 | 7.8 | 4.1 |
| HCl-$H_2O$ | 15 | 2.0 | 25 | 0.094 | -32.79 | 5.4 | 2.4 | - | - | - | - | - | - | - | - |
| LiCl-$H_2O$ | 22 | 4.0 | 25 | 0.209 | -19.1 | 16.6 | 6.4 | 11.7 | 3.3 | 0.056 | -81.532 | 15.1 | 6.5 | 11.1 | 3.3 |
| LiCl-$H_2O$ | 11 | 6.0 | 60 | 0.0515 | -279.7 | - | - | 10.4 | 5.1 | 0.0353 | -287.85 | - | - | 8.4 | 4.7 |
| NaBr-$H_2O$ | 19 | 4.0 | 25 | 37.37 | 1.2447 | 4.1 | 1.1 | 3.2 | 1.0 | 36.949 | 1.261 | 4.3 | 1.1 | 3.3 | 1.0 |
| NaBr-$H_2O$ | 4 | 10.3 | 40 | 0.05 | -109.4 | - | - | 9.4 | 4.6 | 0.0266 | -108.23 | - | - | 7.7 | 4.7 |
| NaCl-$H_2O$ | 10 | 1.0 | 25 | 12.63 | 3.136 | 0.3 | 0.14 | 1.0 | 0.4 | 12.638 | 3.173 | 0.37 | 0.17 | 0.9 | 0.3 |

TABLE G.5 Nonaqueous Electrolytic Binary Data with Two Objective Functions, Equations (2-9) and (2-10)

| System | # of Points | Max 'm' | T (°C) | Objective Function #1 | | | | | | Objective Function #2 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $G_{\pm 3}$ | $Z_{\pm 3}$ | % Error in $\gamma_\pm$ | | % Error in DP | | $G_{\pm 2}$ | $Z_{\pm 2}$ | % Error in $\gamma_\pm$ | | % Error in DP | |
| | | | | | | Max | Avg | Max | Avg | | | Max | Avg | Max | Avg |
| $CaCl_2$-MeOH | 7 | 3.0 | 25 | 5.2817 | 537.62 | - | - | 31.0 | 10.0 | 5.6848 | 518.76 | - | - | 16.3 | 11.4 |
| HCl-EtOH | 8 | 0.1 | 25 | 117.0 | 12.35 | 8.7 | 6.0 | - | - | - | - | - | - | - | - |
| HCl-MeOH | 22 | 0.56 | 25 | 10.8 | 39.7 | 0.7 | 0.4 | - | - | - | - | - | - | - | - |
| LiCl-EtOH | 4 | 4.0 | 25 | 3.67 | 151.5 | - | - | 28.6 | 10.8 | 4.1 | 144.19 | - | - | 15.3 | 6.5 |
| LiCl-MeOH | 6 | 4.0 | 25 | 5.2 | 60.0 | - | - | 13.7 | 4.8 | 6.1745 | 56.382 | - | - | 7.0 | 3.3 |
| LiCl-MeOH | 11 | 6.0 | 60 | 3.403 | 106.21 | - | - | 37.7 | 13.5 | 5.09 | 91.208 | - | - | 17.5 | 7.3 |
| NaBr-MeOH | 9 | 1.6 | 25 | 6.449 | 54.747 | - | - | 4.6 | 2.0 | 6.876 | 54.598 | - | - | 3.9 | 1.9 |
| NaCl-MeOH | 7 | 0.1 | 25 | 380.8 | 4.26 | 2.7 | 1.8 | - | - | - | - | - | - | - | - |

TABLE G.6 Aqueous Electrolytic Binary Data Correlation with Temperature Independent Parameters Using Objective Function #2, Equation (2-10) and Presetting $\alpha_{A2} = 0.2$; $\alpha_{B2} = 0.0$

| System | # of Points | Max 'm' | T (°C) | $\Delta g_{A2}$ | $\Delta g_{B2}$ | % Error in $\gamma_\pm$ |  | % Error in DP |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Max | Avg | Max | Avg |
| $CaCl_2$-$H_2O$ | 17 | 3.0 | 25 | -42.589 | 668.8 | 7.1 | 4.2 | 5.0 | 2.8 |
| HCl-$H_2O$* | 15 | 2.0 | 25 | 77.553 | -3.3056 | 5.5 | 2.4 | - | - |
| LiCl-$H_2O$ | 19 | 4.0 | 25 | 61.958 | -5.0817 | 15.8 | 6.6 | 11.6 | 3.3 |
| LiCl-$H_2O$ | 11 | 6.0 | 60 | 81.743 | -11.592 | - | - | 8.6 | 5.0 |
| NaBr-$H_2O$ | 4 | 10.3 | 40 | 98.318 | -3.2249 | - | - | 7.8 | 4.9 |
| NaBr-$H_2O$ | 19 | 4.0 | 25 | -24.258 | 174.11 | 9.4 | 4.0 | 8.1 | 2.3 |
| NaCl-$H_2O$ | 17 | 4.0 | 25 | -32.396 | 444.79 | 3.4 | 1.2 | 3.3 | 1.0 |

*For the system HCl-$H_2O$ binary objective function #1 [Equation (2-9)] is used.

TABLE G.7 Nonaqueous Electrolytic Binary Data Correlation with Temperature Independent Parameters Using Objective Function #2, Equation (2-10) and Presetting $\alpha_{A3} = 0.2$; $\alpha_{B3} = 0.0$

| System | # of Points | Max 'm' | T (°C) | $\Delta G_{A3}$ | $\Delta G_{B3}$ | % Error in $\gamma_{\pm}$ |  | % Error in DP |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Max | Avg | Max | Avg |
| $CaCl_2$-MeOH | 7 | 3.0 | 25 | -16.156 | 289.16 | - | - | 16.3 | 9.3 |
| HCl-EtOH | 8 | 0.1 | 25 | -58.994 | 6897.7 | 8.7 | 6.0 | - | - |
| HCl-MeOH | 22 | 0.56 | 25 | -28.306 | 317.33 | 0.66 | 0.4 | - | - |
| LiCl-EtOH | 3 | 4.0 | 25 | -14.056 | 187.82 | - | - | 15.3 | 12.3 |
| LiCl-MeOH | 6 | 4.0 | 25 | -20.384 | 161.93 | - | - | 7.0 | 3.4 |
| LiCl-MeOH | 11 | 6.0 | 60 | -19.497 | 170.92 | - | - | 17.5 | 7.3 |
| NaBr-MeOH | 9 | 1.6 | 25 | -21.556 | 177.28 | - | - | 4.1 | 1.9 |
| NaCl-MeOH | 7 | 0.1 | 25 | -10.262 | 210.86 | 11.3 | 6.6 | - | - |
| LiBr-MeOH | 8 | 6.64 | 15 | -20.198 | 158.28 | - | - | 2.9 | 1.5 |
| LiBr-MeOH | 8 | 6.64 | 30 | -23.999 | 216.56 | - | - | 14.0 | 5.7 |

TABLE G.8 Binary Data Correlation with Temperature Independent Parameters Using Objective Function #2, Equation (2-10) and Presetting $\alpha_{Ai} = 0.2$; $\alpha_{Bi} = -1.0$

| System | # of Points | Max 'm' | T (°C) | $\Delta g_{Ai}$ | $\Delta g_{Bi}$ | % Error in $\gamma_\pm$ |  | % Error in DP |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Max | Avg | Max | Avg |
| LiCl-$H_2O$ | 19 | 4.0 | 25 | -2.8668 | -12.27 | 16.1 | 6.6 | 11.6 | 3.4 |
| NaBr-$H_2O$ | 4 | 10.3 | 40 | -2.1801 | -13.616 | - | - | 7.7 | 5.0 |
| LiCl-EtOH | 2 | 1.0 | 25 | 20.872 | 6.102 | - | - | 26.6 | 22.5 |
| LiCl-MeOH | 6 | 3.7 | 25 | 20.285 | 5.32 | - | - | 16.6 | 9.7 |
| NaBr-MeOH | 9 | 1.6 | 25 | 19.938 | 5.2467 | - | - | 6.9 | 5.7 |
| LiCl-MeOH | 11 | 6.0 | 60 | 23.133 | 6.3664 | - | - | 42.7 | 27.4 |

TABLE G.9 Binary Data Correlation with Temperature Independent Parameters Using Objective Function #2, Equation (2-10) and Presetting $\alpha_{Ai} = -1.0$; $\alpha_{Bi} = -1.0$

| System | # of Points | Max 'm' | T (°C) | $\Delta g_{Ai}$ | $\Delta g_{Bi}$ | % Error in DP | |
|---|---|---|---|---|---|---|---|
| | | | | | | Max | Avg |
| LiCl-EtOH | 2 | 1.0 | 25 | 6.1822 | -27.801 | 27.5 | 25.3 |
| LiCl-MeOH | 6 | 3.7 | 25 | 5.4454 | -32.375 | 17.7 | 10.5 |
| NaBr-MeOH | 9 | 1.6 | 25 | 5.3709 | -32.753 | 7.3 | 3.9 |
| LiCl-MeOH | 11 | 6.0 | 60 | 6.479 | -51.103 | 43.6 | 28.3 |
| $CaCl_2$-MeOH | 7 | 2.6 | 25 | -50.83 | 7.1956 | 275.7 | 205.0 |

TABLE G.10 Prediction of Binary Data at One Temperature Using the Parameters of Another Temperature, Presetting $\alpha_{Ai} = 0.2$ and $\alpha_{Bi} = 0.0$

| System | # of Points | Max 'm' | T (°C) | of T (°C) | Parameters Used |  | % Error in $\gamma_{\pm}$ |  | % Error in DP |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | $\Delta g_{Ai}$ | $\Delta g_{Bi}$ | Max | Avg | Max | Avg |
| LiCl-$H_2O$ | 19 | 6.0 | 25 | 60 | 81.743 | -11.592 | 24.3 | 11.2 | 14.3 | 5.2 |
| LiCl-$H_2O$ | 11 | 6.0 | 60 | 25 | 61.958 | -5.0817 | - | - | 13.0 | 5.8 |
| NaBr-$H_2O$ | 19 | 4.0 | 25 | 40 | 98.318 | -3.2249 | 33.5 | 20.5 | 9.4 | 6.8 |
| NaBr-$H_2O$ | 4 | 10.3 | 40 | 25 | 163.29 | 12.545 | - | - | 25.1 | 11.6 |
| LiBr-MeOH | 8 | 6.6 | 15 | 30 | -23.999 | 216.56 | - | - | 23.4 | 13.8 |
| LiBr-MeOH | 8 | 6.6 | 30 | 15 | -20.198 | 158.28 | - | - | 30.4 | 9.4 |
| LiCl-MeOH | 9 | 6.0 | 25 | 60 | -19.497 | 170.9 | - | - | 62.0 | 42.0 |
| LiCl-MeOH | 11 | 6.0 | 60 | 25 | -20.384 | 161.8 | - | - | 39.6 | 35.1 |

TABLE G.11 Isothermal Ternary $\gamma_\pm$ Data Correlation for the Four Parameters: $G_{\pm 2}$, $Z_{\pm 2}$, $G_{\pm 3}$ and $Z_{\pm 3}$, Presetting the Solvent-Solvent Binary Parameters Corresponding to $\alpha_{23}$ = -1.0

| System | # of Points | Max 'm' | T (°C) | $\alpha_{23}$ | $\Delta g_{23}$ | $\Delta g_{32}$ | $G_{\pm 2}$ | $Z_{\pm 2}$ | $G_{\pm 3}$ | $Z_{\pm 3}$ | % Error in $\gamma_\pm$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | Max | Avg |
| $HCl-H_2O-EtOH$ | 44 | 2.5 | 25 | -1.0 | 105.8 | 383.8 | 19.677 | 1.789 | 9.460 | 84.647 | 10.0 | 2.0 |
| $HCl-H_2O-MeOH$ | 48 | 2.0 | 25 | -1.0 | -150.9 | 336.5 | 19.677 | 1.789 | 7.63 | 40.14 | 18.4 | 2.2 |
| $LiCl-H_2O-MeOH$ | 45 | 1.0 | 25 | -1.0 | -150.9 | 336.5 | 28.32 | 3.141 | 21.875 | 24.882 | 22.8 | 7.7 |
| $NaCl-H_2O-MeOH$ | 35 | 1.0 | 25 | -1.0 | -150.9 | 336.5 | 38.981 | 4.216 | 44.11 | 14.638 | 27.0 | 6.1 |

TABLE G.12 A Comparative Study of the Three Objective Functions [Equations (2-19), (2-20), (2-21)] in Correlating Ternary Isothermal VLE Data with the Four Parameters [$G_{\pm2}$, $Z_{\pm2}$, $G_{\pm3}$, $Z_{\pm3}$], Presetting $\Delta g_{23}$ and $\Delta g_{32}$ from Table G.3 Corresponding to $\alpha_{23} = -1.0$

| System | Max 'm' | T (°C) | ΔY |  | ΔP (mmHg) |  |
|---|---|---|---|---|---|---|
|  |  |  | Max | Avg | Max | Avg |
| <u>Objective Function #1</u> |  |  |  |  |  |  |
| LiCl-$H_2O$-EtOH | 1.0 | 25 | 0.035 | 0.011 | 5.6 | 2.2 |
| LiCl-$H_2O$-MeOH | 1.0 | 25 | 0.022 | 0.012 | 8.0 | 4.8 |
| NaBr-$H_2O$-MeOH | 6.2 | 40 | 0.023 | 0.012 | 11.5 | 5.1 |
| NaBr-$H_2O$-MeOH | 7.1 | 25 | 0.047 | 0.017 | 15.0 | 8.8 |
| LiCl-$H_2O$-MeOH | 6.0 | 60 | 0.04 | 0.015 | 33.2 | 13.8 |
| <u>Objective Function #2</u> |  |  |  |  |  |  |
| LiCl-$H_2O$-EtOH | 1.0 | 25 | 0.034 | 0.009 | 3.1 | 1.2 |
| LiCl-$H_2O$-MeOH | 1.0 | 25 | 0.009 | 0.0055 | 9.3 | 6.8 |
| NaBr-$H_2O$-MeOH | 6.2 | 40 | 0.022 | 0.01 | 17.7 | 5.6 |
| NaBr-$H_2O$-MeOH | 7.1 | 25 | 0.02 | 0.0088 | 11.4 | 4.8 |
| LiCl-$H_2O$-MeOH | 6.0 | 60 | 0.023 | 0.009 | 54.3 | 11.7 |
| <u>Objective Function #3</u> |  |  |  |  |  |  |
| LiCl-$H_2O$-EtOH | 1.0 | 25 | 0.035 | 0.01 | 6.1 | 2.3 |
| LiCl-$H_2O$-MeOH | 1.0 | 25 | 0.011 | 0.0066 | 10.2 | 5.6 |
| NaBr-$H_2O$-MeOH | 6.2 | 40 | 0.022 | 0.011 | 15.2 | 5.4 |
| NaBr-$H_2O$-MeOH | 7.1 | 25 | 0.021 | 0.0092 | 11.3 | 5.0 |
| LiCl-$H_2O$-MeOH | 6.0 | 60 | 0.025 | 0.0097 | 50.3 | 11.6 |

TABLE G.13 Values of the Parameters Obtained with the Three Objective Functions for Isothermal Ternary VLE Data

| System | T (°C) | $G_{\pm 2}$ | $Z_{\pm 2}$ | $G_{\pm 3}$ | $Z_{\pm 3}$ |
|---|---|---|---|---|---|
| Objective Function #1 | | | | | |
| LiCl-$H_2O$-EtOH | 25 | 6.3977 | 76.681 | 0.1946 | 1346.3 |
| LiCl-$H_2O$-MeOH | 25 | 5.4754 | 124.08 | 0.0 | 930.92 |
| NaBr-$H_2O$-MeOH | 40 | 23.21 | 20.24 | 3.653 | 52.82 |
| NaBr-$H_2O$-MeOH | 25 | 22.76 | 1.56 | 0.2243 | 316.1 |
| LiCl-$H_2O$-MeOH | 60 | 22.32 | 0.025 | 1.5917 | 131.0 |
| Objective Function #2 | | | | | |
| LiCl-$H_2O$-EtOH | 25 | 12.666 | 68.166 | 0.1983 | 2076.1 |
| LiCl-$H_2O$-MeOH | 25 | 12.666 | 68.166 | 75.818 | -11.239 |
| NaBr-$H_2O$-MeOH | 40 | 20.762 | 21.419 | 3.4156 | 55.672 |
| NaBr-$H_2O$-MeOH | 25 | 13.657 | 13.023 | 0.1382 | 601.16 |
| LiCl-$H_2O$-MeOH | 60 | 15.463 | 5.1261 | 0.2639 | 531.88 |
| Objective Function #3 | | | | | |
| LiCl-$H_2O$-EtOH | 25 | 13.644 | 53.324 | 0.1282 | 2122.4 |
| LiCl-$H_2O$-MeOH | 25 | 13.644 | 53.324 | 59.022 | -11.455 |
| NaBr-$H_2O$-MeOH | 40 | 21.205 | 20.357 | 3.364 | 53.684 |
| NaBr-$H_2O$-MeOH | 25 | 14.979 | 11.67 | 0.1367 | 604.9 |
| LiCl-$H_2O$-MeOH | 60 | 17.929 | 4.017 | 0.2525 | 634.78 |

TABLE G.14 A Comparative Study of the Three Objective Functions [Equations (2-19), (2-20), (2-21)] in Correlating Ternary Isobaric VLE Data with the Four Parameters [$\Delta g_{A2}$, $\Delta g_{B2}$, $\Delta g_{A3}$ & $\Delta g_{B3}$] Presetting $\Delta g_{23}$ and $\Delta g_{32}$ Corresponding to $\alpha_{23} = -1.0$ [Table G.3] and $\alpha_{A2} = 0.2$; $\alpha_{B2} = 0.0$; $\alpha_{A3} = 0.2$; $\alpha_{B3} = 0.0$

| System | Max 'm' | P (mmHg) | ΔY Max | ΔY Avg | ΔP (mmHg) Max | ΔP (mmHg) Avg |
|---|---|---|---|---|---|---|
| Objective Function #1 | | | | | | |
| LiCl-$H_2O$-MeOH | 3.8 | 760.0 | 0.04 | 0.0135 | 39.0 | 15.7 |
| NaBr-$H_2O$-MeOH | 3.8 | 760.0 | 0.053 | 0.021 | 35.1 | 14.9 |
| KCl-$H_2O$-MeOH | 2.0 | 760.0 | 0.055 | 0.016 | 34.3 | 14.4 |
| NaF-$H_2O$-MeOH | 1.0 | 760.0 | 0.051 | 0.01 | 35.6 | 13.9 |
| Objective Function #2 | | | | | | |
| LiCl-$H_2O$-MeOH | 3.8 | 760.0 | 0.036 | 0.0136 | 39.7 | 16.2 |
| NaBr-$H_2O$-MeOH | 3.8 | 760.0 | 0.052 | 0.02 | 35.1 | 13.1 |
| KCl-$H_2O$-MeOH | 2.0 | 760.0 | 0.056 | 0.0155 | 38.9 | 15.7 |
| NaF-$H_2O$-MeOH | 1.0 | 760.0 | 0.051 | 0.01 | 35.5 | 15.6 |
| Objective Function #3 | | | | | | |
| LiCl-$H_2O$-MeOH | 3.8 | 760.0 | 0.036 | 0.0136 | 40.0 | 16.1 |
| NaBr-$H_2O$-MeOH | 3.8 | 760.0 | 0.051 | 0.02 | 53.3 | 19.1 |
| KCl-$H_2O$-MeOH | 2.0 | 760.0 | 0.056 | 0.0155 | 35.3 | 14.9 |
| NaF-$H_2O$-MeOH | 1.0 | 760.0 | 0.051 | 0.01 | 34.4 | 15.0 |

TABLE G.15 Values of the Parameters Obtained with the Three Objective Functions for Isobaric VLE Data

| System | P (mmHg) | $\Delta g_{A2}$ | $\Delta g_{B2}$ | $\Delta g_{A3}$ | $\Delta g_{B3}$ |
|---|---|---|---|---|---|
| <u>Objective Function #1</u> | | | | | |
| LiCl-$H_2O$-MeOH | 760 | 142.84 | -19.8 | -35.0 | 319.10 |
| NaBr-$H_2O$-MeOH | 760 | 0.0506 | 12.009 | 99.65 | -303.26 |
| KCl-$H_2O$-MeOH | 760 | 105.8 | -44.06 | -40.16 | 340.5 |
| NaF-$H_2O$-MeOH | 760 | -11.81 | 40.08 | 4916.8 | -2559.8 |
| <u>Objective Function #2</u> | | | | | |
| LiCl-$H_2O$-MeOH | 760 | 125.35 | -26.6 | -33.52 | 334.05 |
| NaBr-$H_2O$-MeOH | 760 | -5.695 | 23.0 | 111.3 | -320.36 |
| KCl-$H_2O$-MeOH | 760 | 124.21 | -79.67 | -41.151 | 446.55 |
| NaF-$H_2O$-MeOH | 760 | 104.95 | -176.71 | 12394.0 | -2932.0 |
| <u>Objective Function #3</u> | | | | | |
| LiCl-$H_2O$-MeOH | 760 | 153.03 | -24.3 | -35.571 | 336.4 |
| NaBr-$H_2O$-MeOH | 760 | 65.9 | -21.77 | 89.295 | -454.8 |
| KCl-$H_2O$-MeOH | 760 | 50.72 | -50.618 | -40.88 | 432.38 |
| NaF-$H_2O$-MeOH | 760 | 21.952 | -79.58 | 3674.4 | -2767.1 |

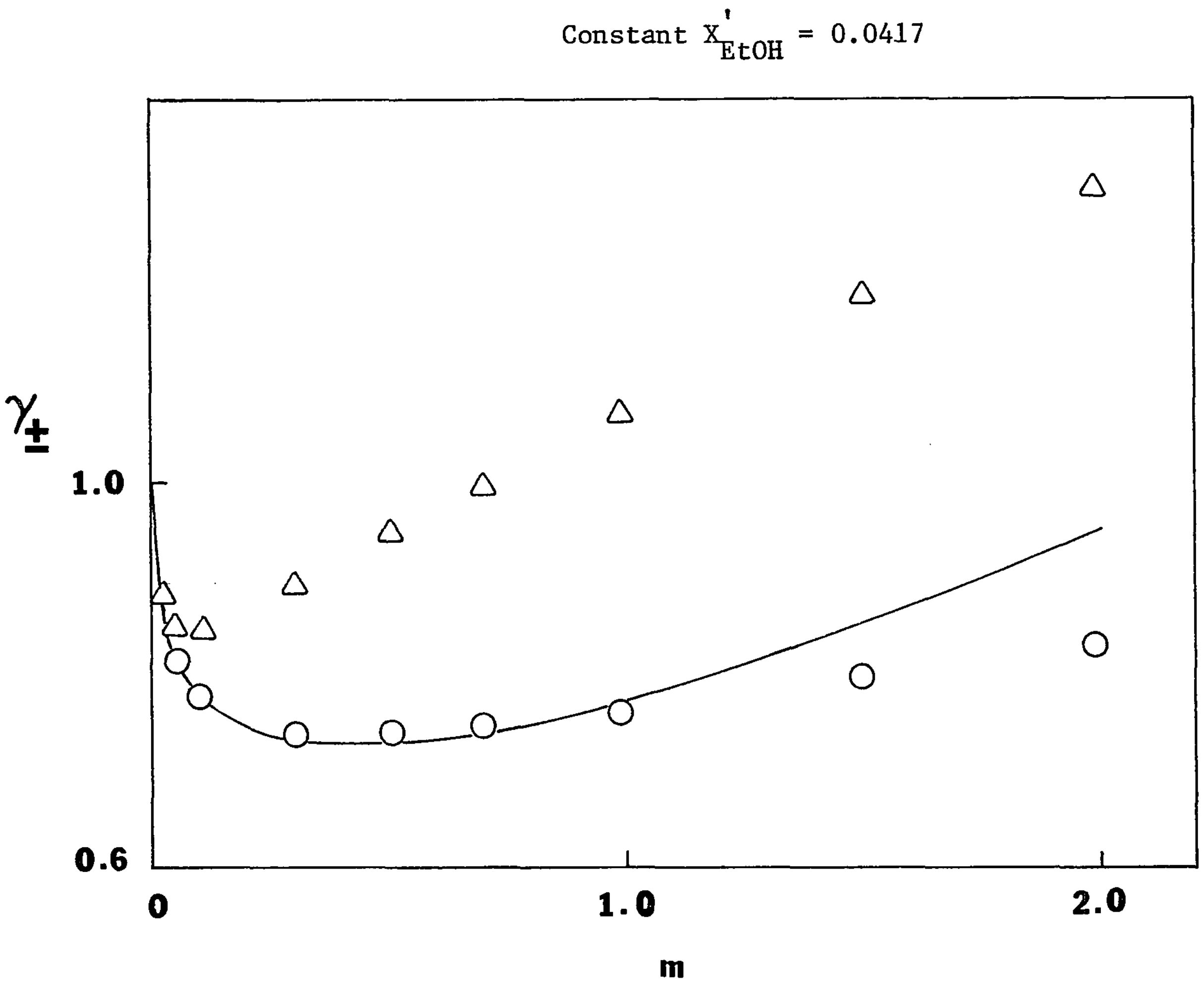


Figure G.1 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System $HCl-H_2O-EtOH$ at 25°C and Constant $X'_{EtOH} = 0.0417$. ___ Experimental, Harned and Owen(1958) ; ○ Correlated ( $\alpha_{23}=-1.0$ ) ; △ Predicted ( $\alpha_{23}=-1.0$ )

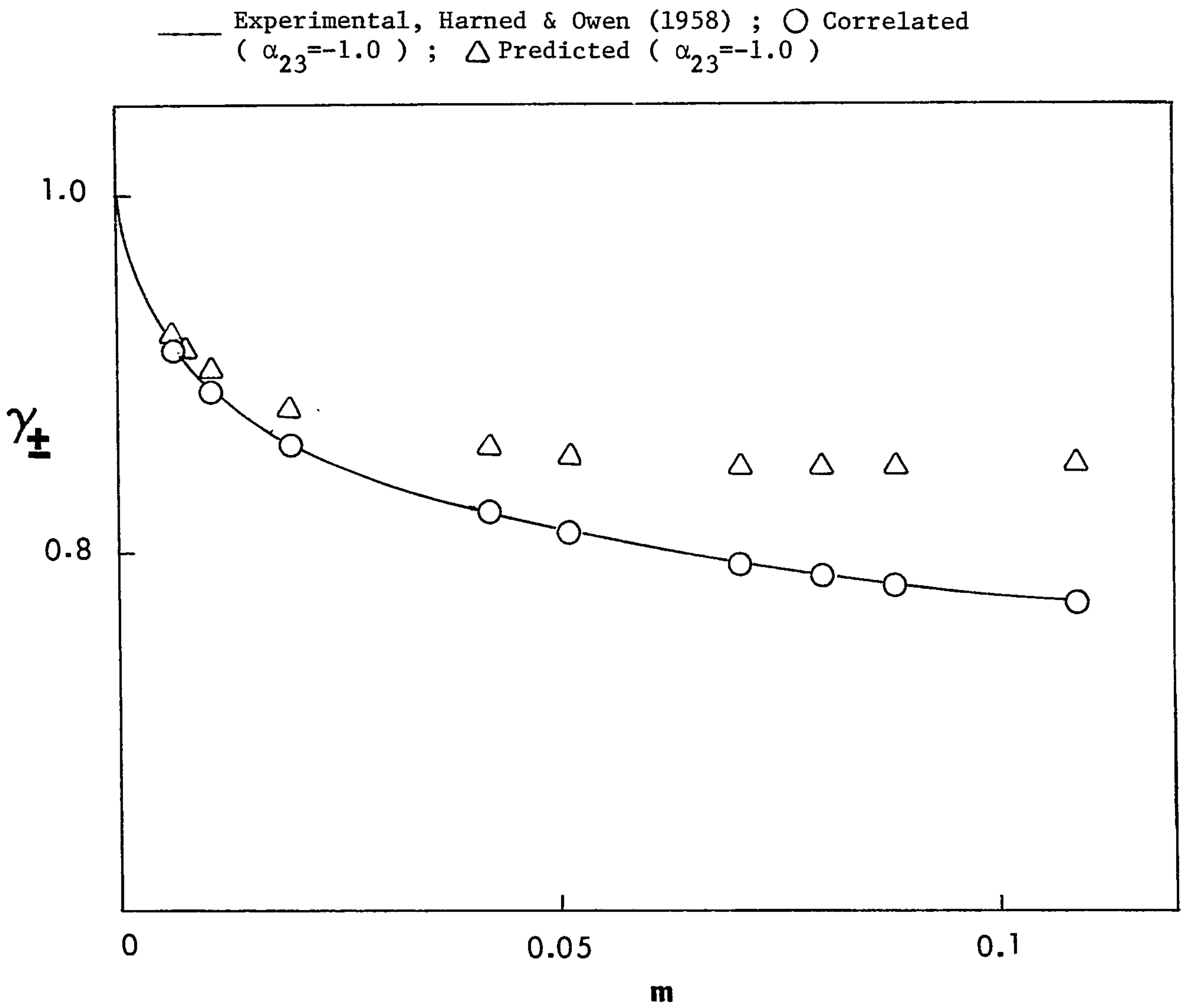


Figure G.1A Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I up to m = 0.2 for the System $HCl$-$H_2O$-$EtOH$ at 25°C and Constant $X'_{EtOH}$= 0.0417

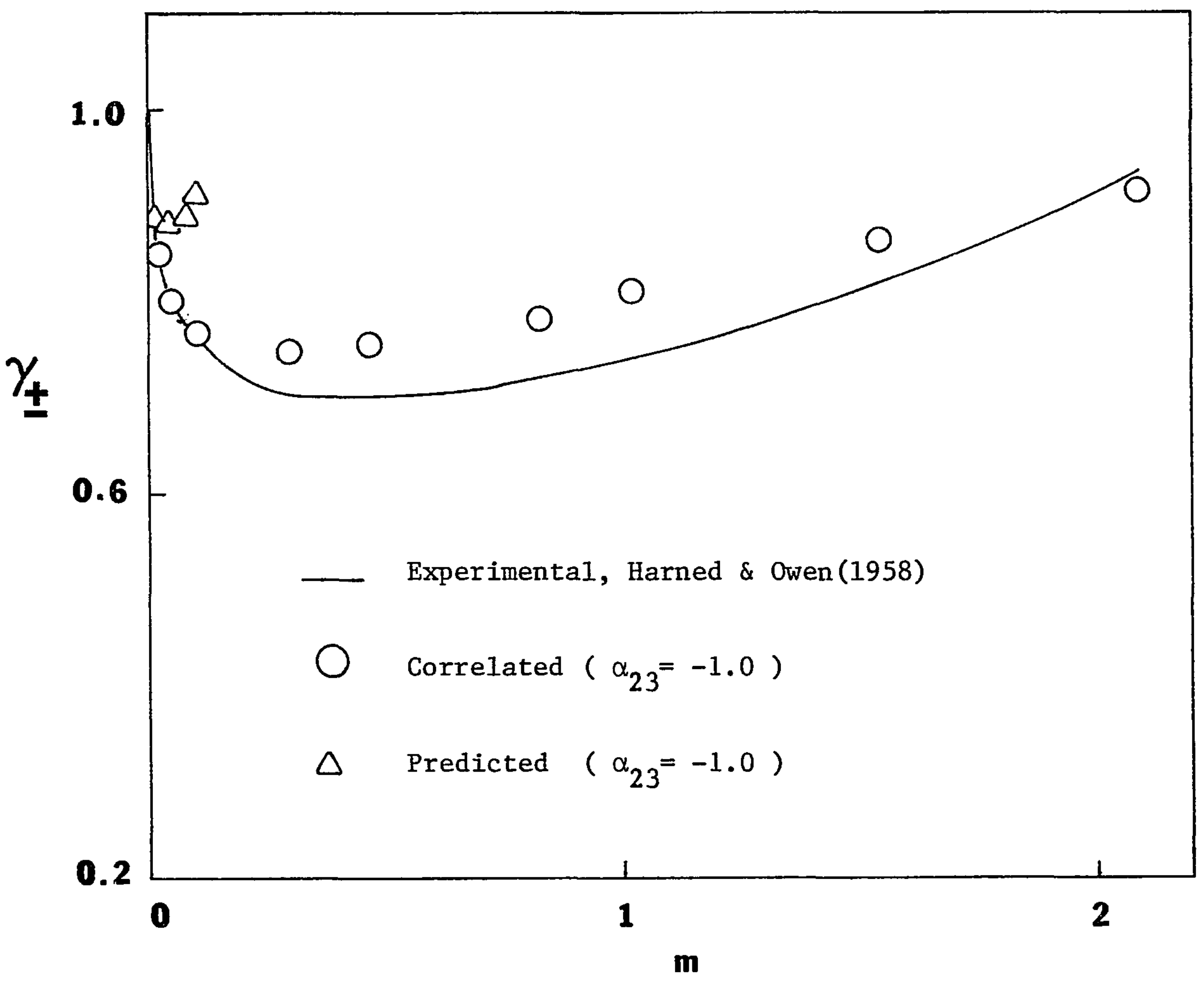


Figure G.2 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System $HCl-H_2O-EtOH$ at 25°C and Constant $X'_{EtOH}$ = 0.0891

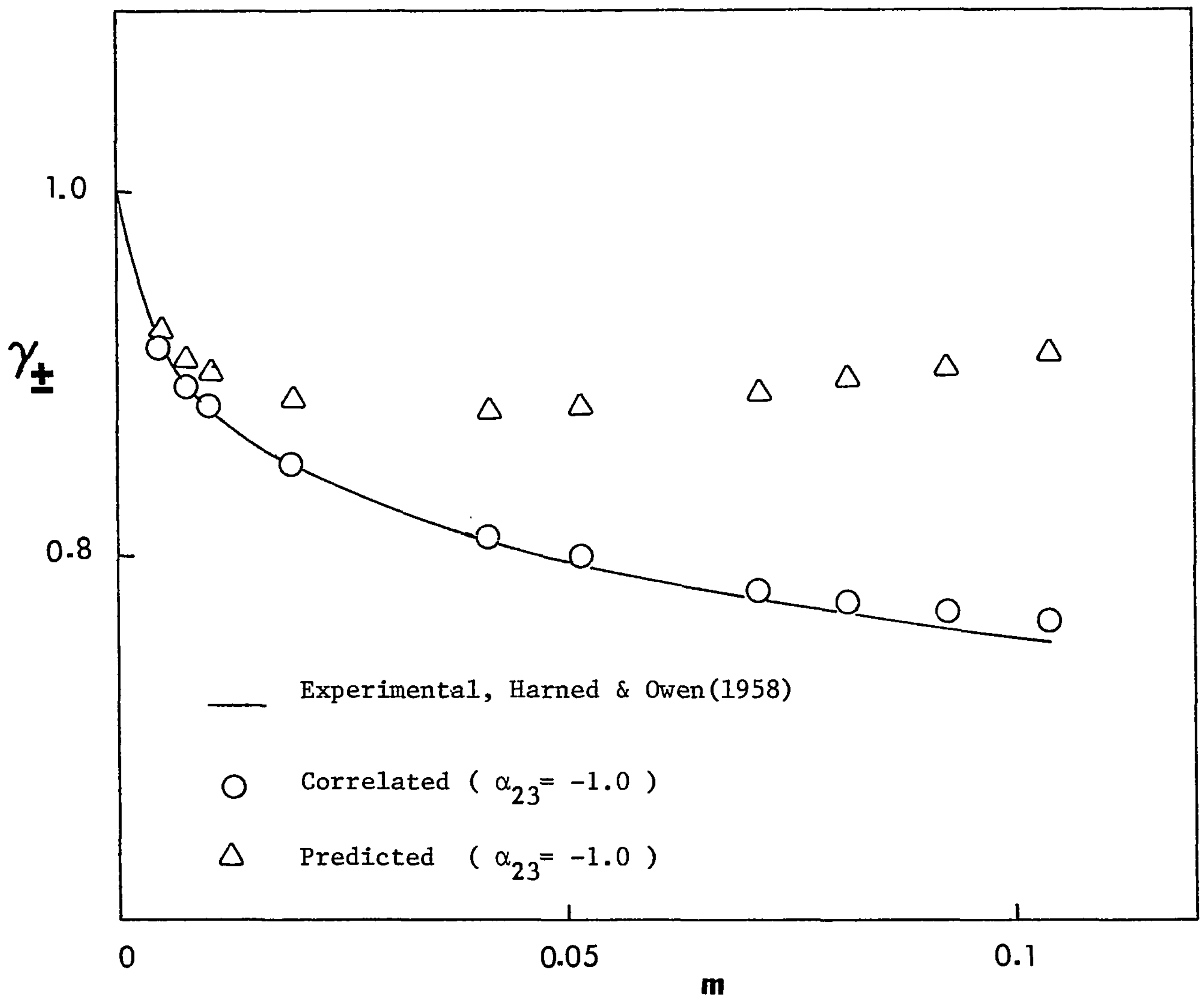


Figure G.2A Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I up to m = 0.2 for the System HCl-$H_2O$-EtOH at 25°C and Constant $X'_{EtOH}$ = 0.0891

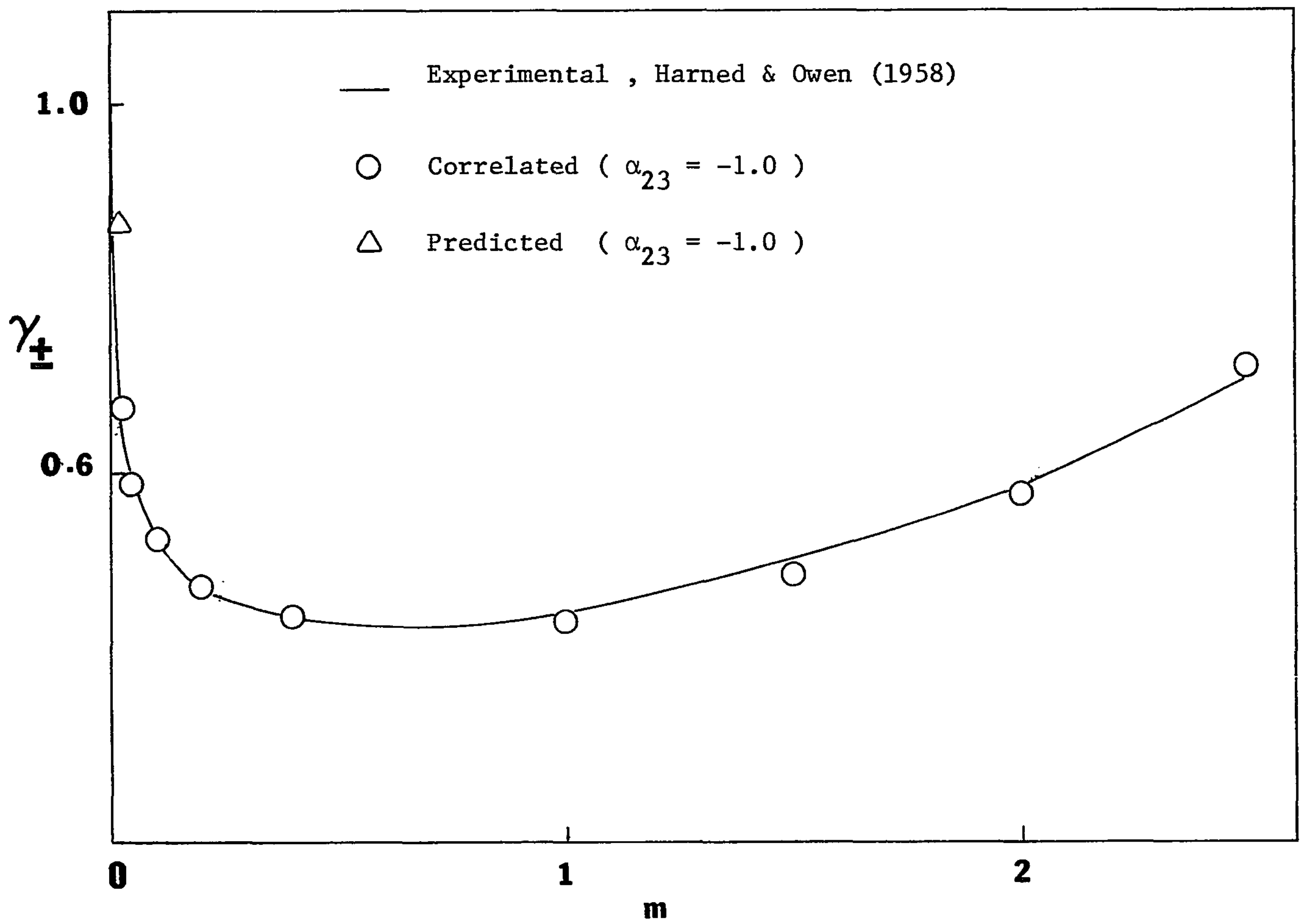


Figure G.3 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-$H_2O$-EtOH at 25°C and Constant $X'_{EtOH} = 0.5$

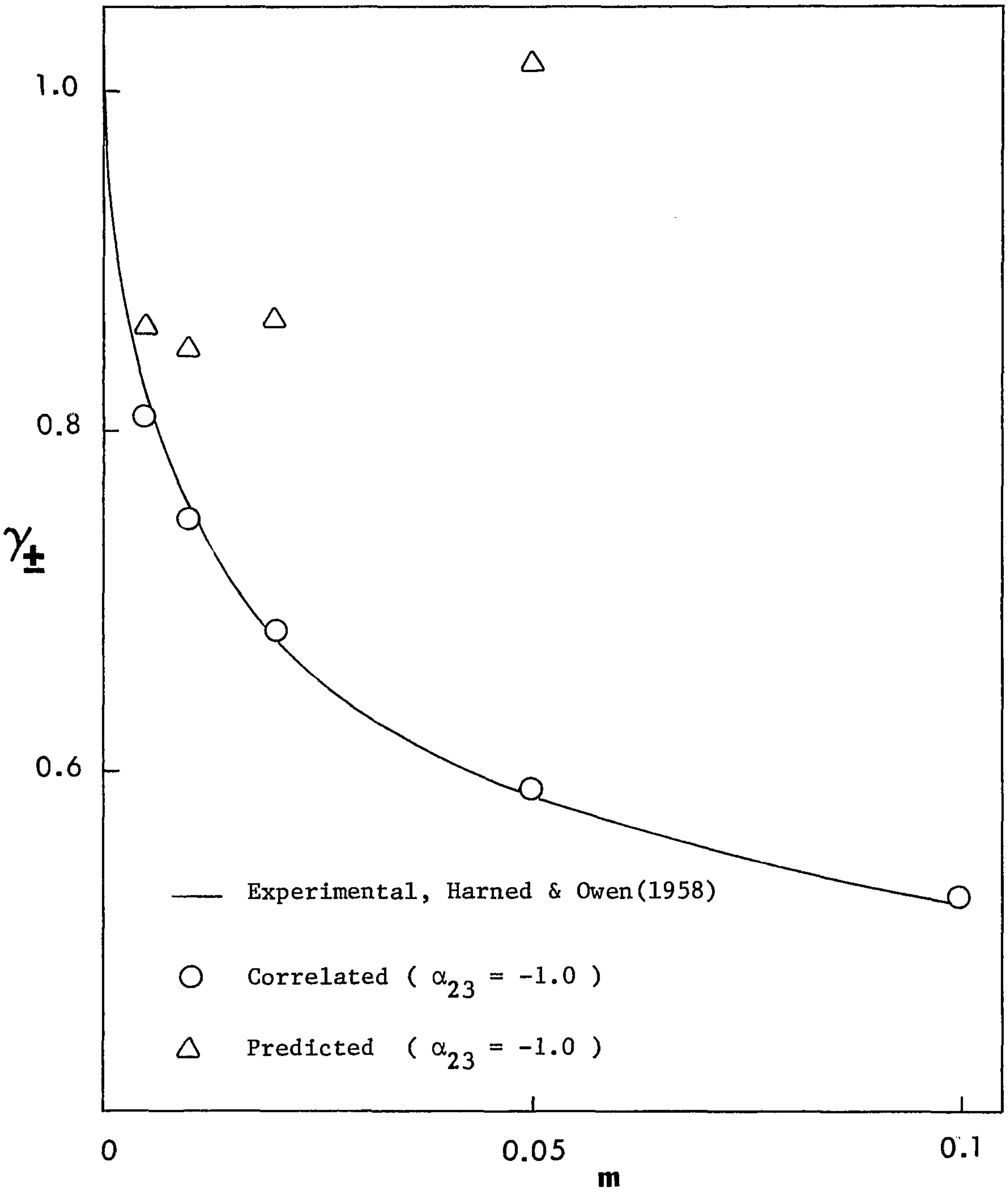


Figure G.3A Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I up to m = 0.2 for the System HCl-$H_2O$-EtOH at 25°C and Constant $X'_{EtOH}$ = 0.5

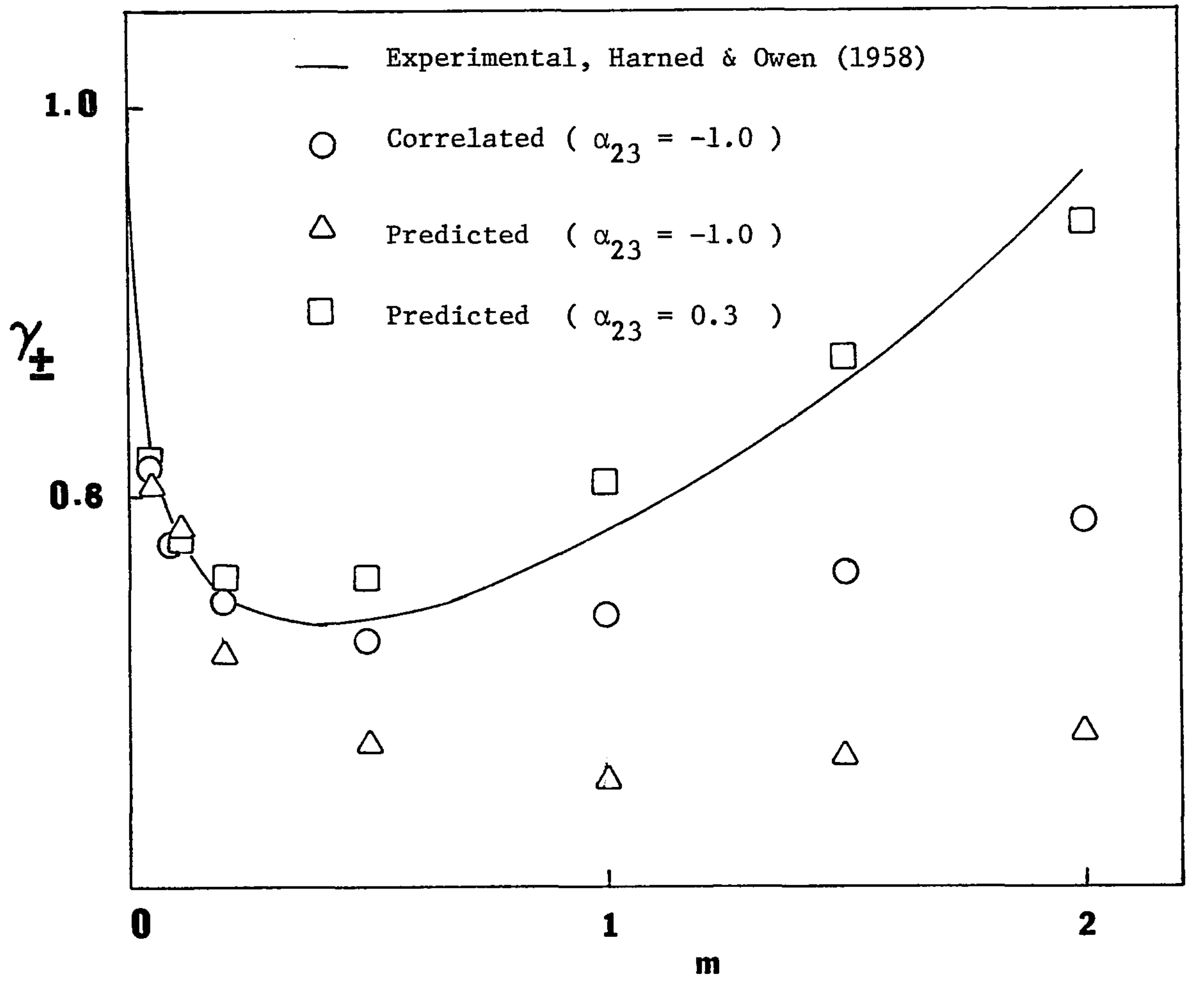


Figure G.4 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System $HCl-H_2O-MeOH$ at 25°C and Constant $X'_{MeOH}$ = 0.0584

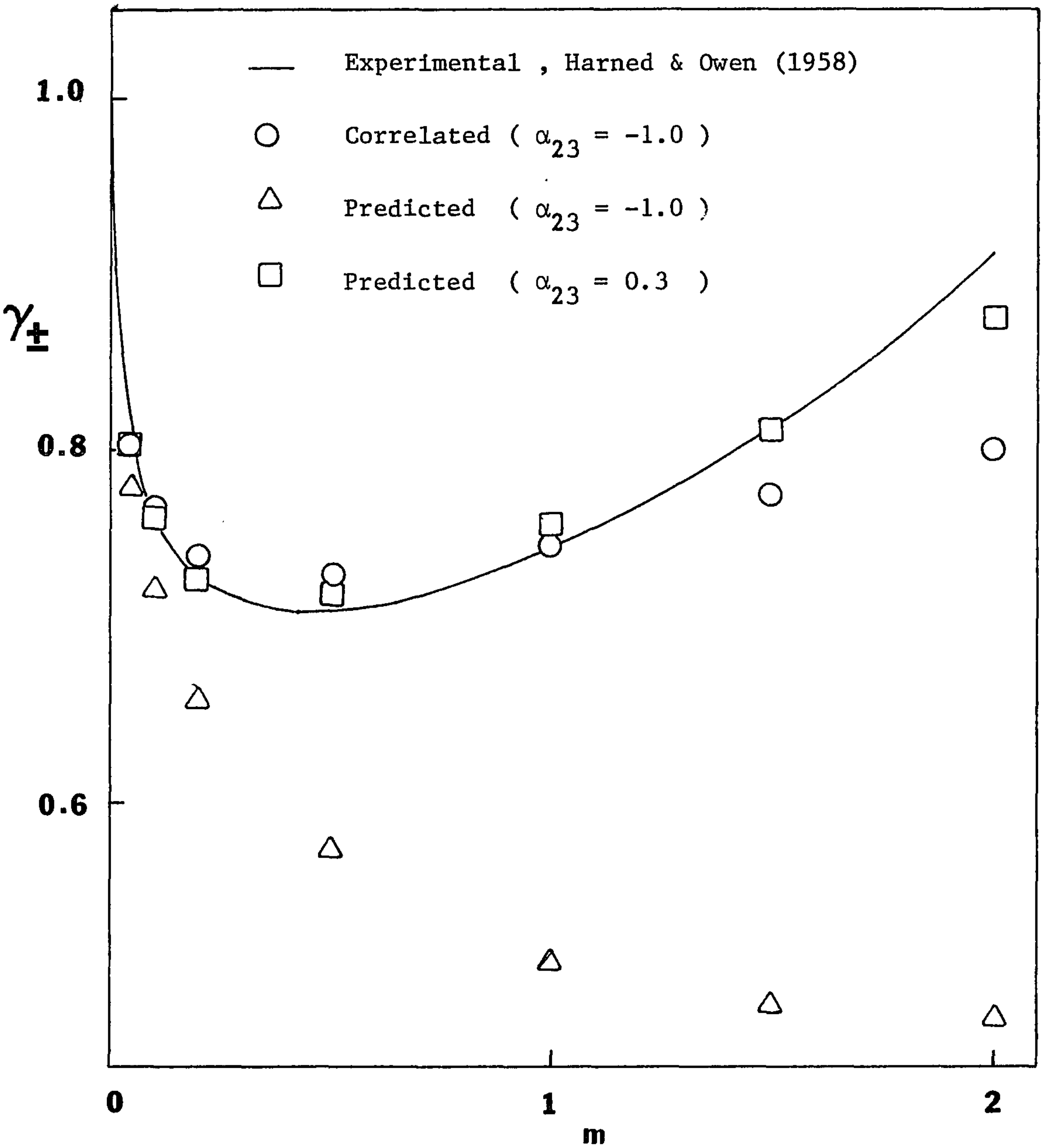


Figure G.5 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System HCl-$H_2O$-MeOH at 25°C and Constant $X'_{MeOH}$ = 0.1233

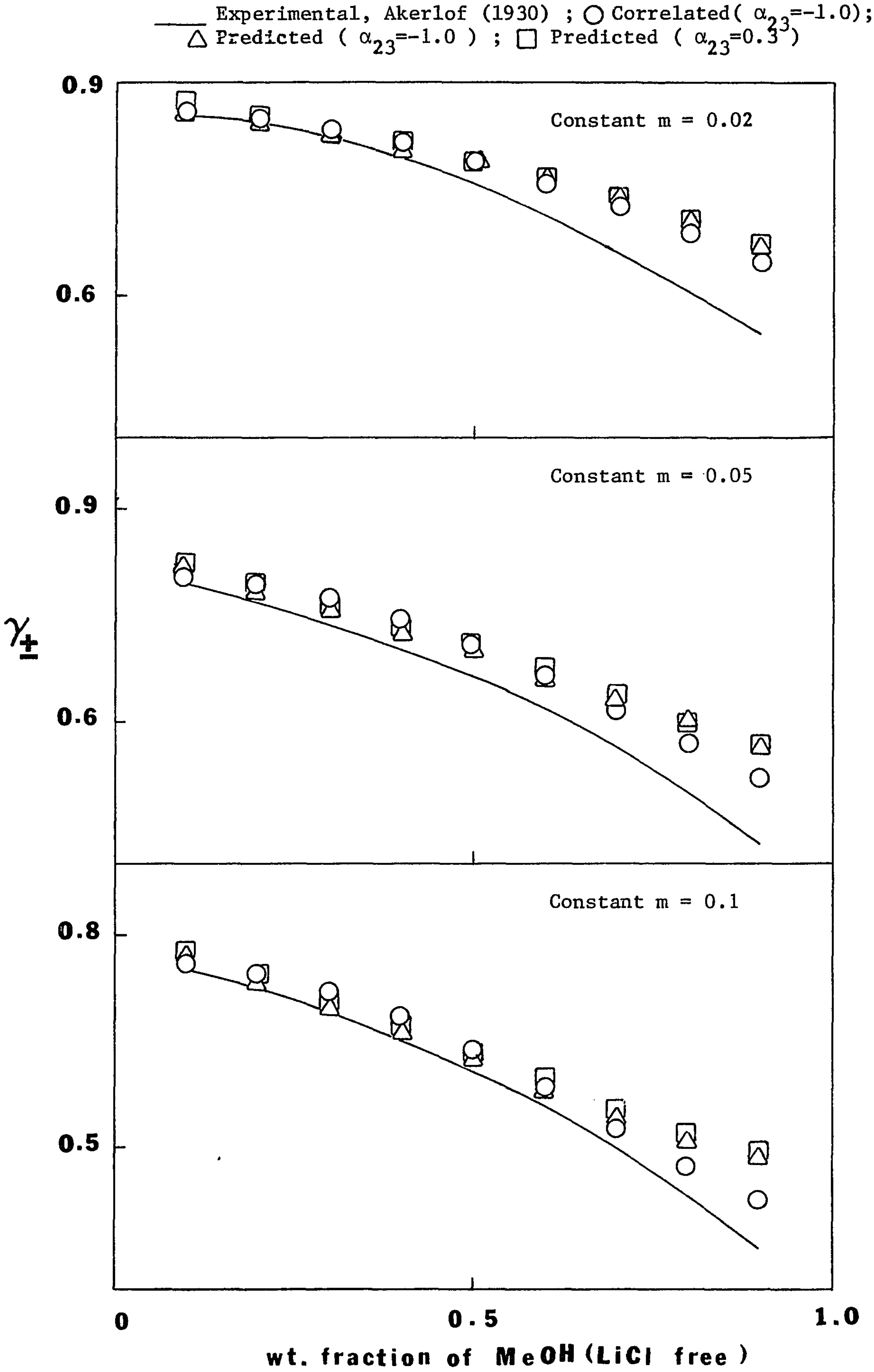


Figure G.6 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System LiCl-$H_2O$-MeOH at 25°C

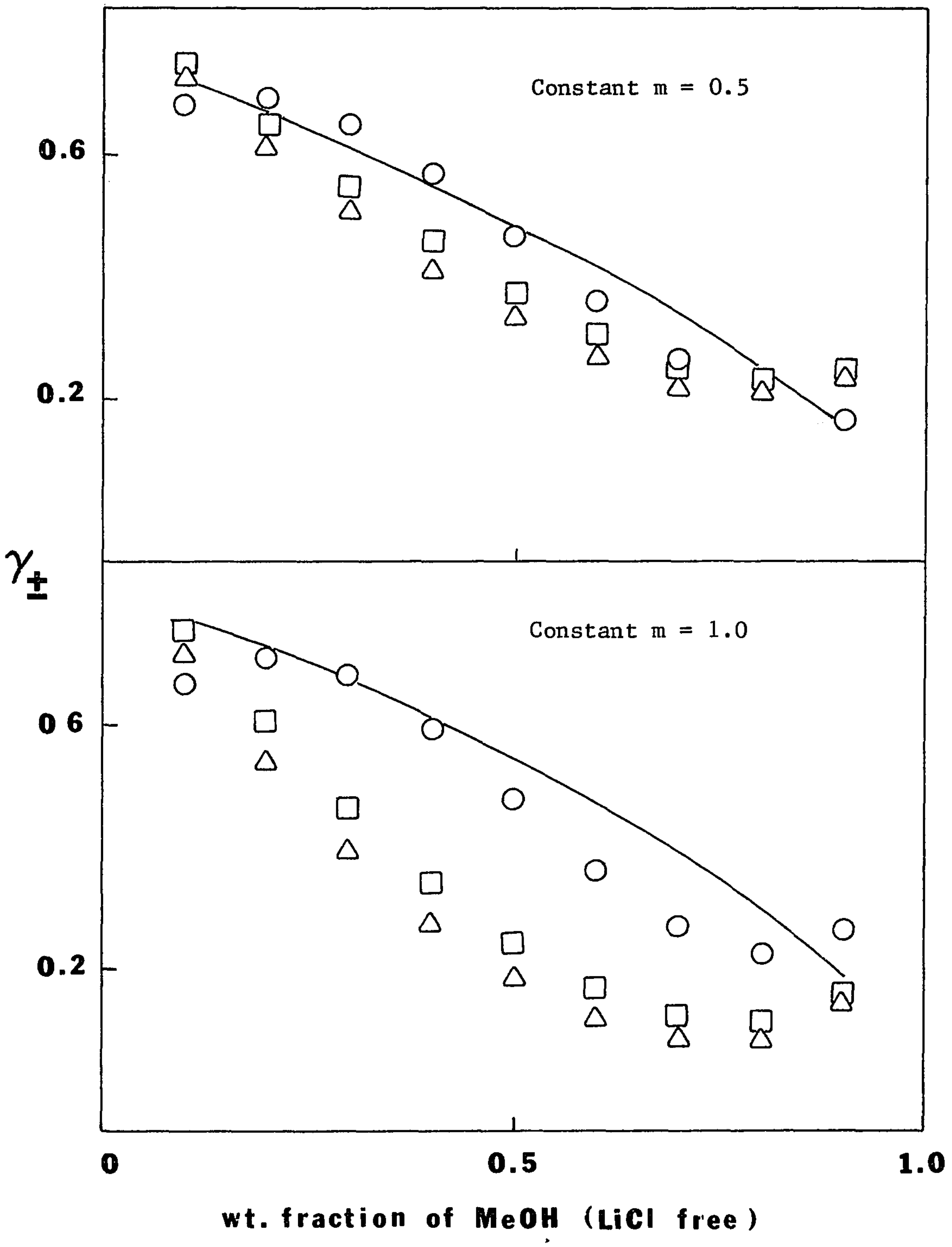


Figure G.7 Comparison of Experimental Mean Molal Activity Coefficients with those Predicted and Correlated by Model I for the System LiCl-$H_2O$-MeOH at 25°C and Constant m = 0.5, 1.0. ___ Experimental, Akerlof(1930) ; ○ Correlated ( $\alpha_{23}$= -1.0) ; △ Predicted ( $\alpha_{23}$= -1.0) ; □ Predicted ( $\alpha_{23}$= 0.3)

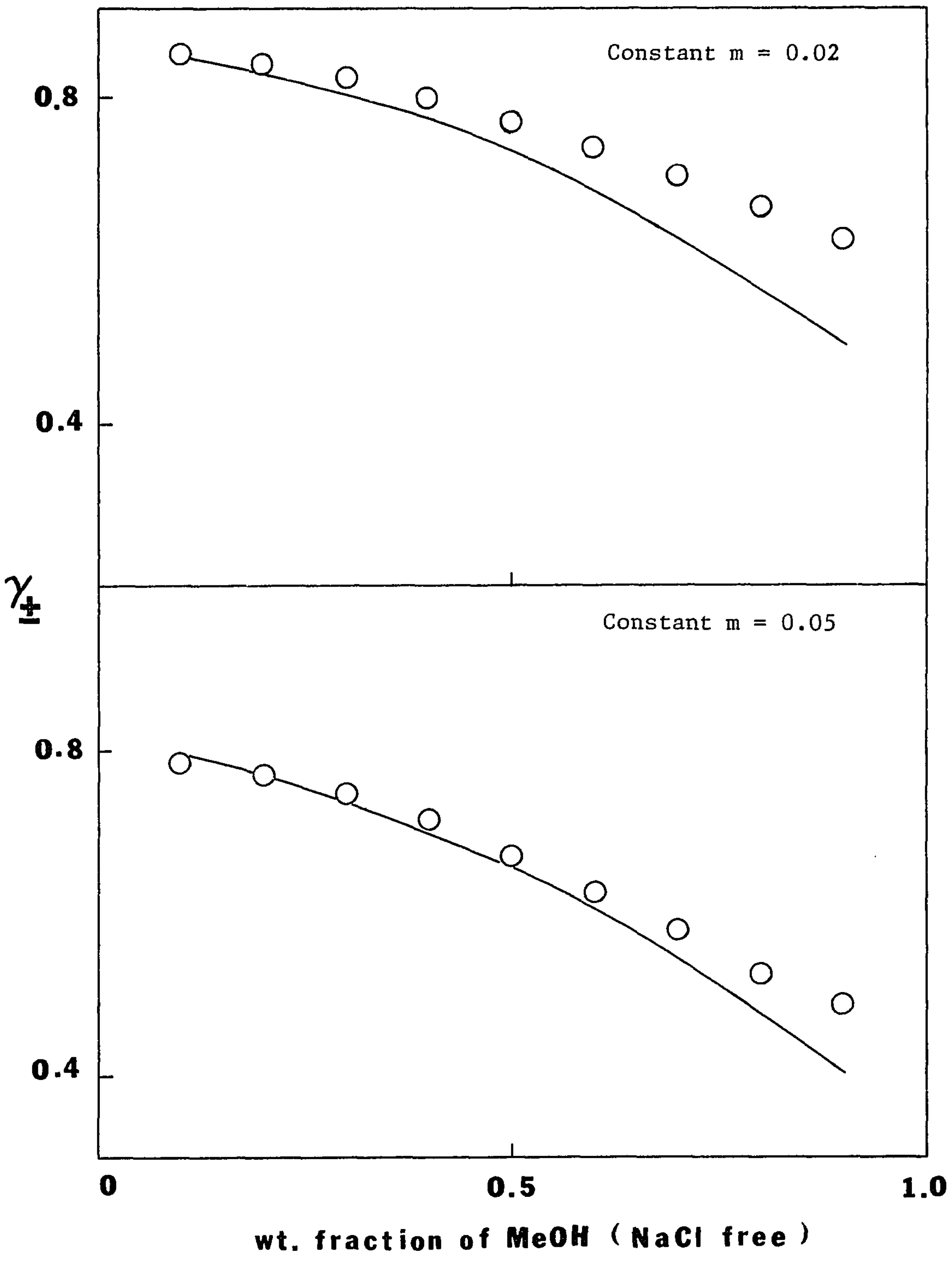


Figure G.8 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated for the System NaCl - $H_2O$ - MeOH at 25°C and Constant m = 0.02 , 0.05

—— Experimental, Akerlof (1930) ; ○ Correlated ( $\alpha_{23}$=-1.0)

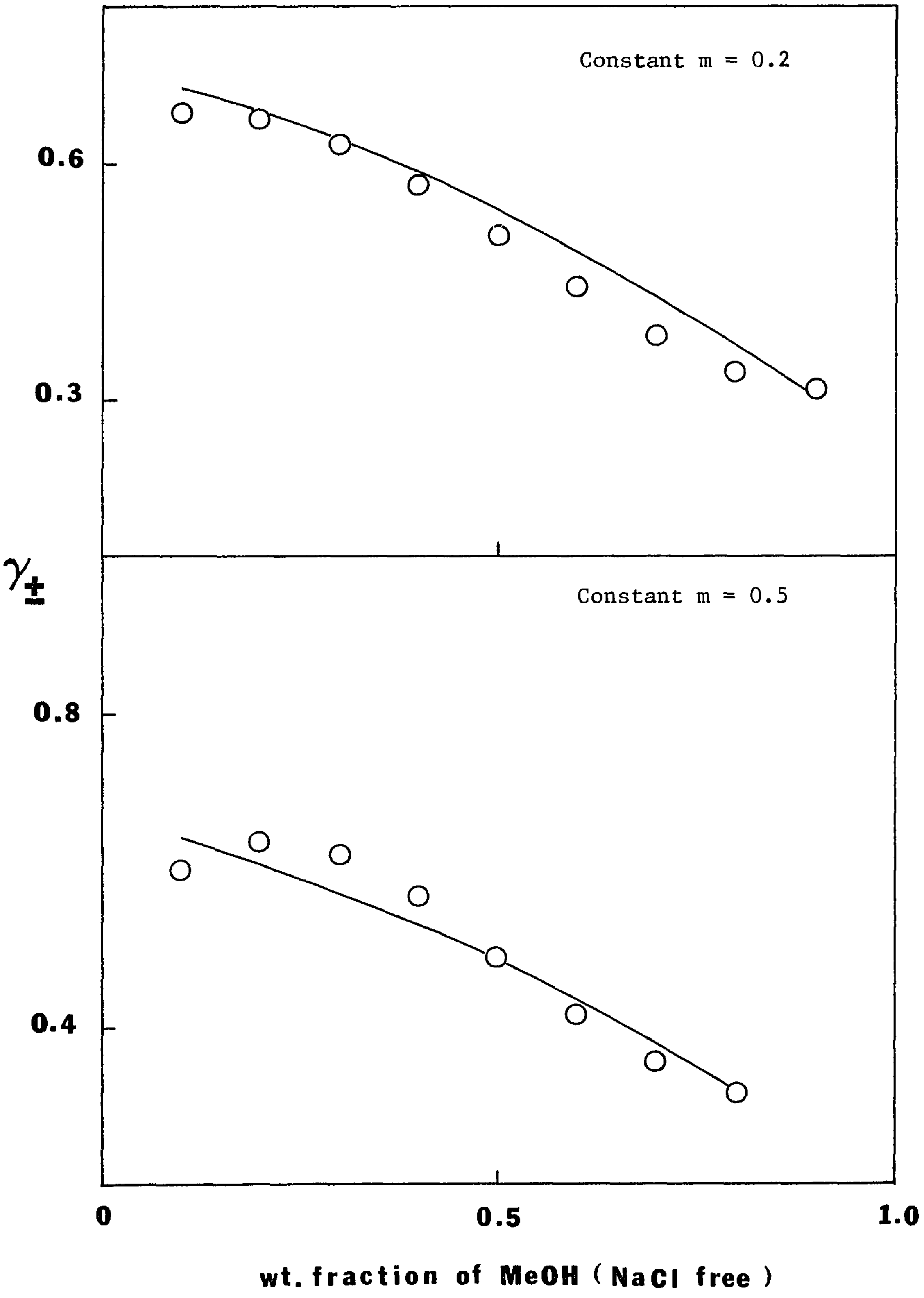


Figure G.9 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated for the System NaCl-$H_2O$-MeOH at 25°C and Constant m = 0.2 , 0.5.

___ Experimental , Akerlof (1930) ; ○ Correlated ( $\alpha_{23}$=-1.0)

Figure G.10 Comparison of Experimental Vapor Phase Compositions with those Predicted and Correlated by Model I for the System LiCl-$H_2O$-EtOH at 25°C and Constant m = 0.5

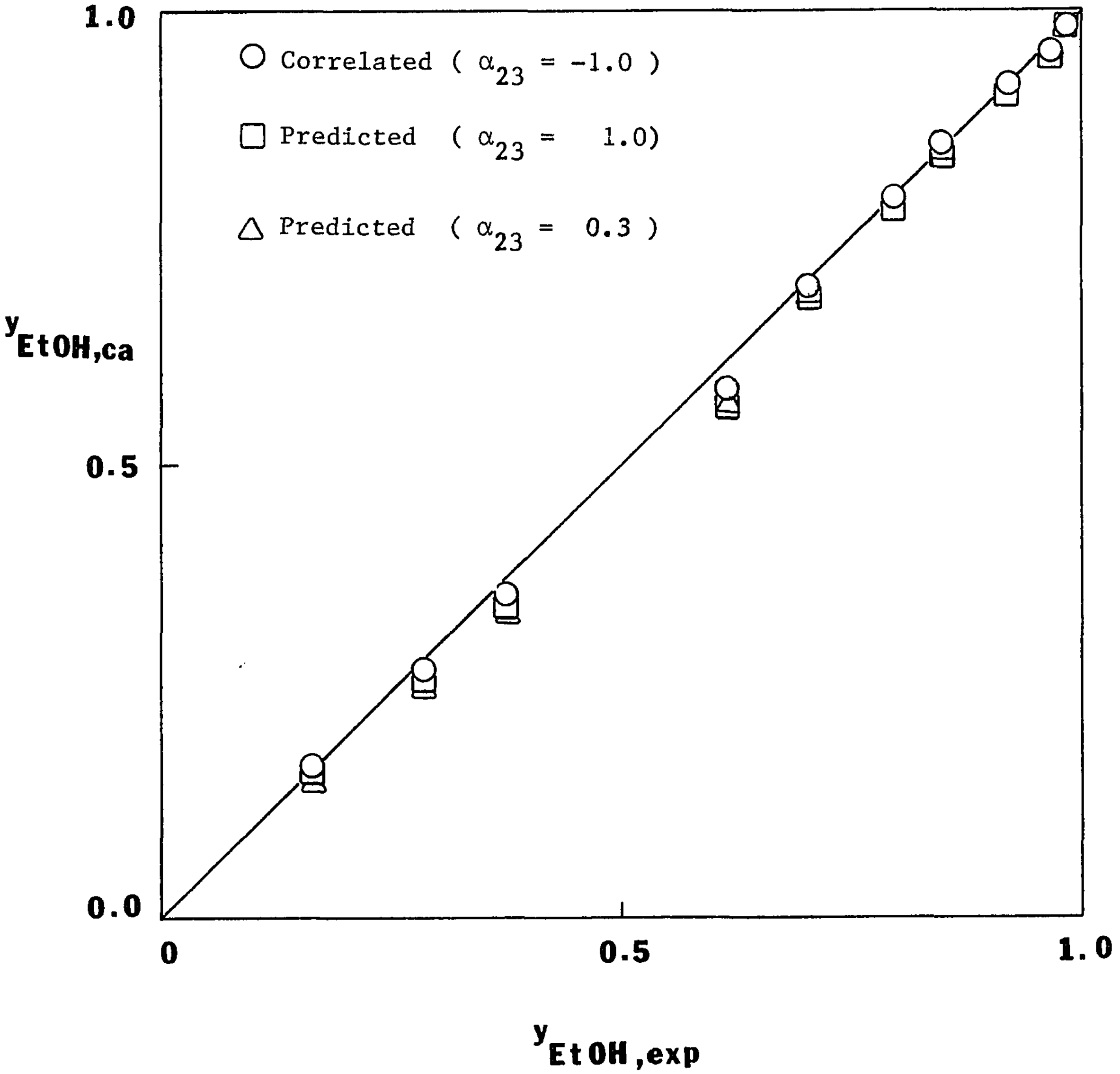


Figure G.11 Comparison of Experimental with Predicted and Correlated Vapor-Phase Compositions Using Model I for the System LiCl-$H_2O$-EtOH at 25°C and Constant m = 1.0

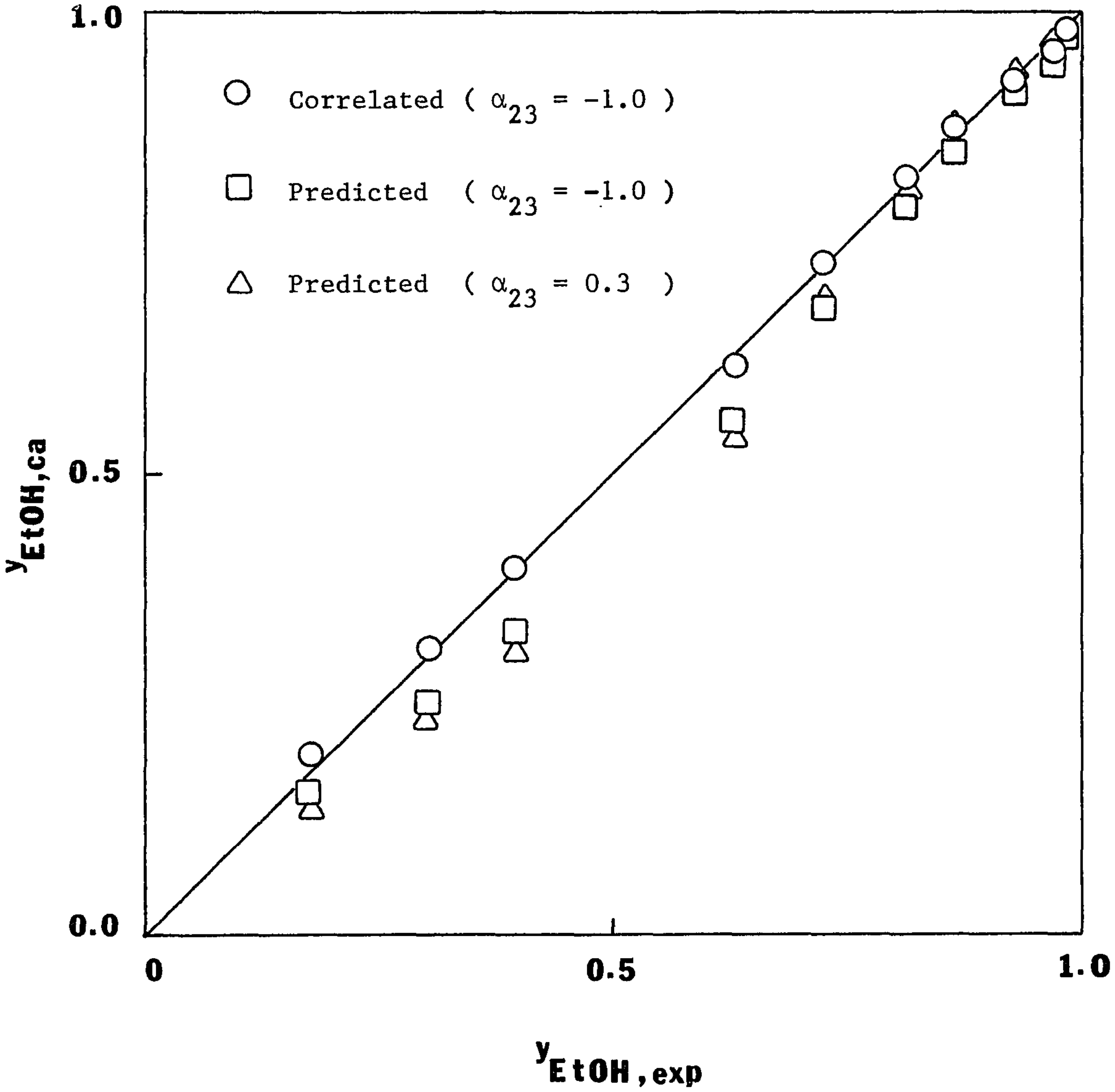
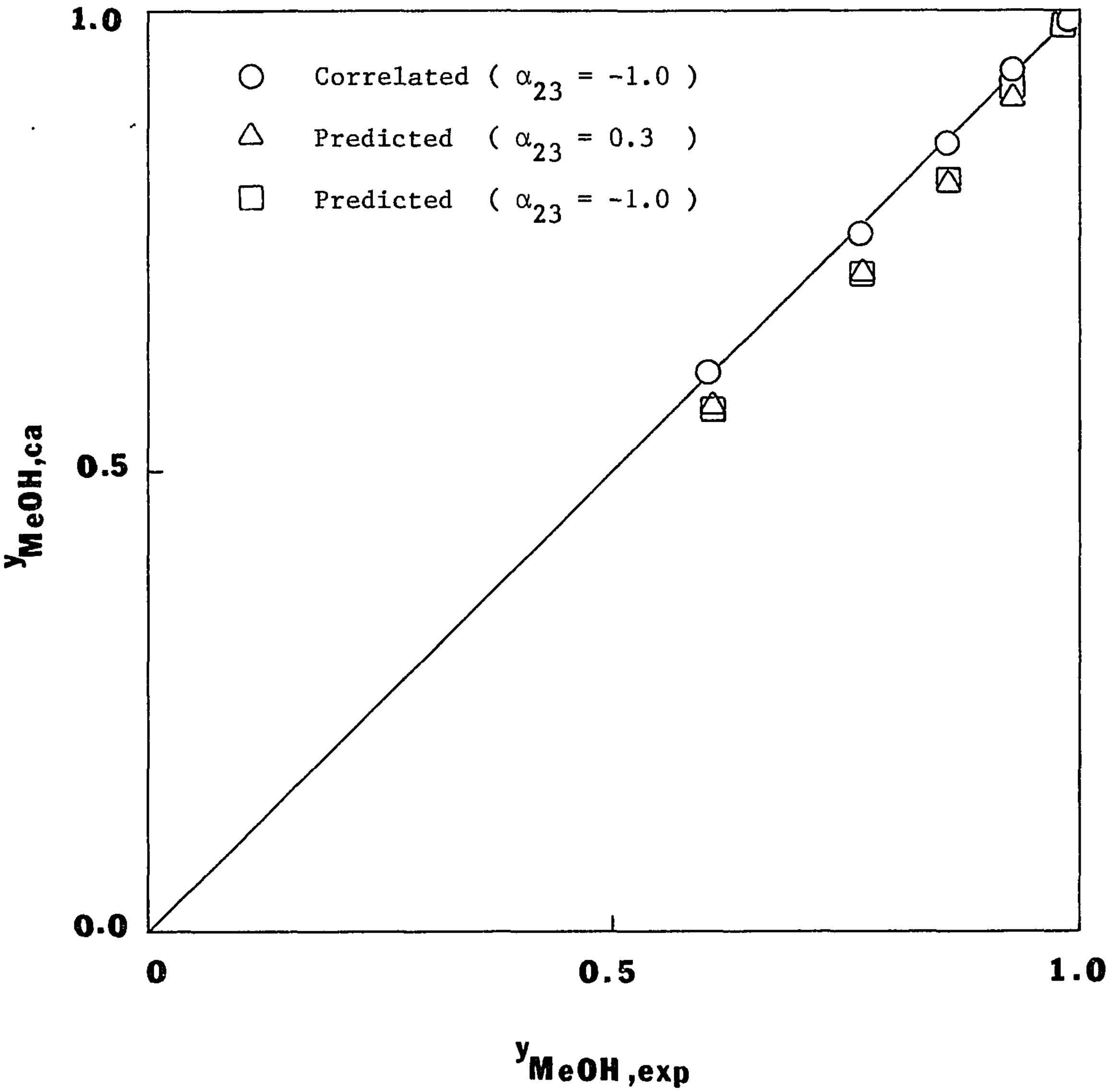


Figure G.12 Comparison of Experimental with Predicted and Correlated Vapor-Phase Compositions Using Model I for the System LiCl-$H_2O$-MeOH at 25°C and Constant m = 1.0



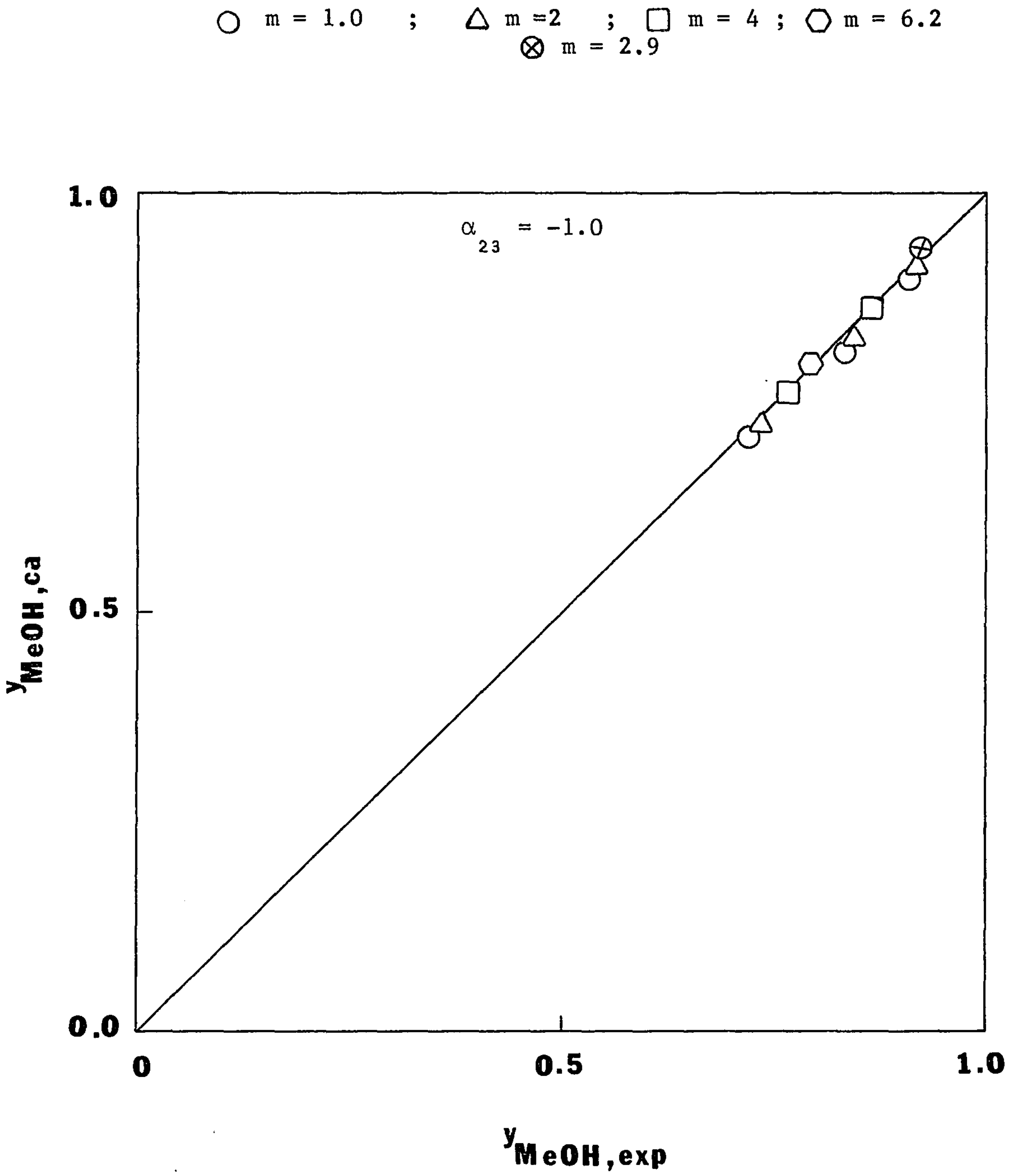
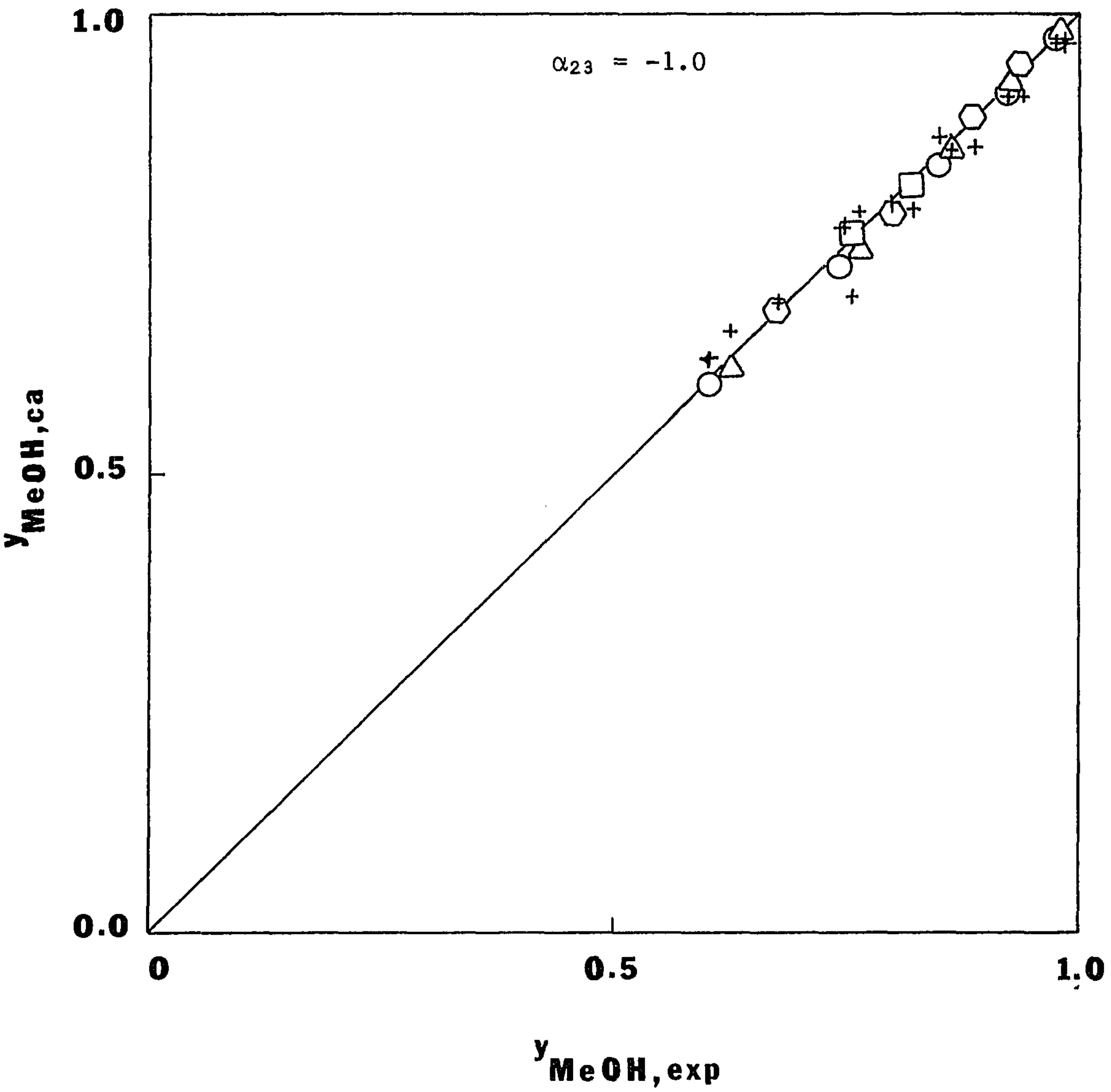


Figure G.13 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System NaBr-$H_2O$-MeOH at 40°C



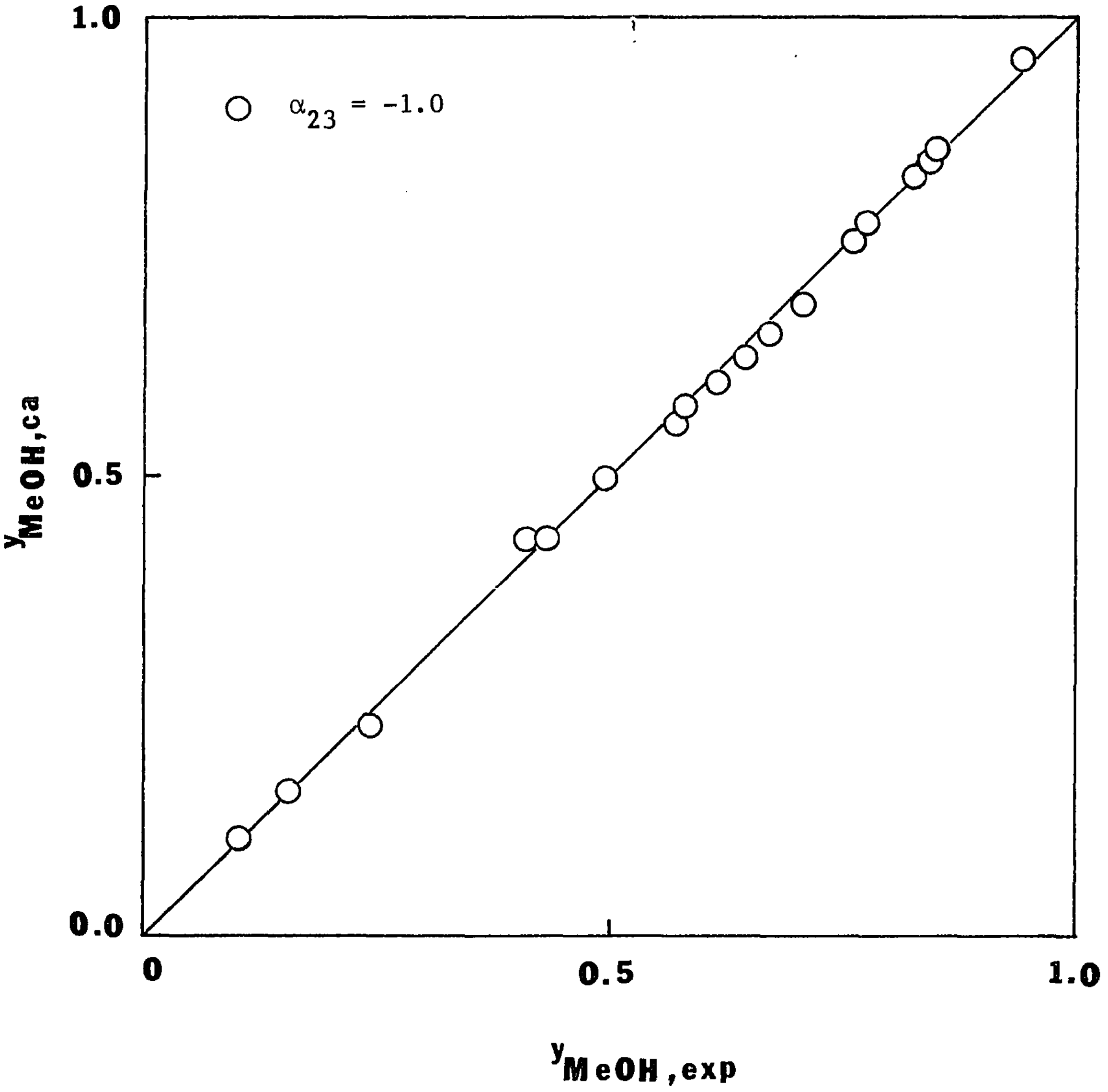
○ m = 1 ; △ $1 < m \leqslant 2$ ; ⬡ $2 < m \leqslant 4$ ; □ $m > 4$

\+ Evans et.al. (1979)

Figure G.14 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System NaBr-$H_2O$-MeOH at 25°C

Figure G.15 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System LiCl-$H_2O$ at 60°C

m = 0.58 - 5.6



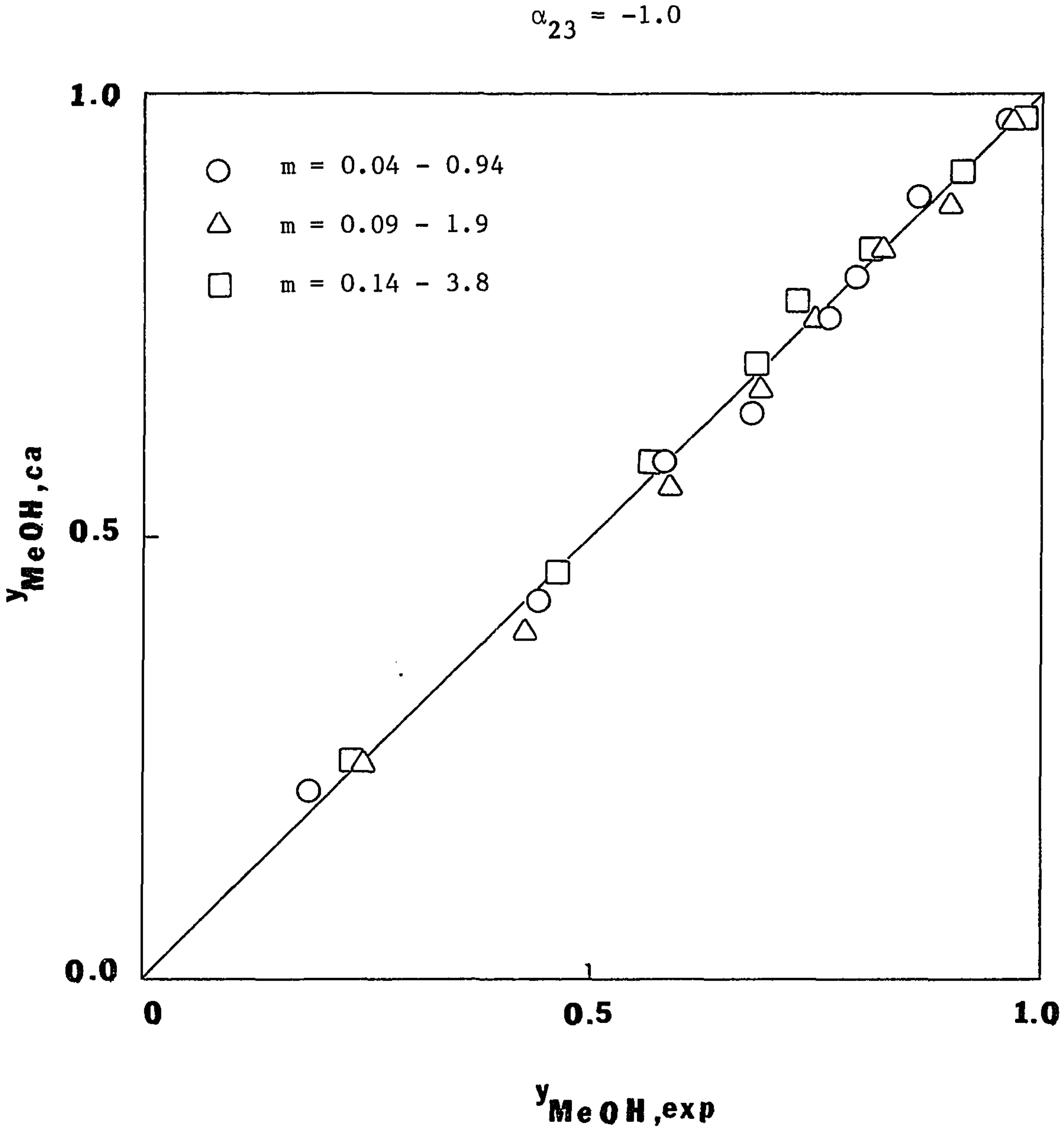


Figure G.16 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System LiCl-$H_2O$-MeOH at P = 1 atm

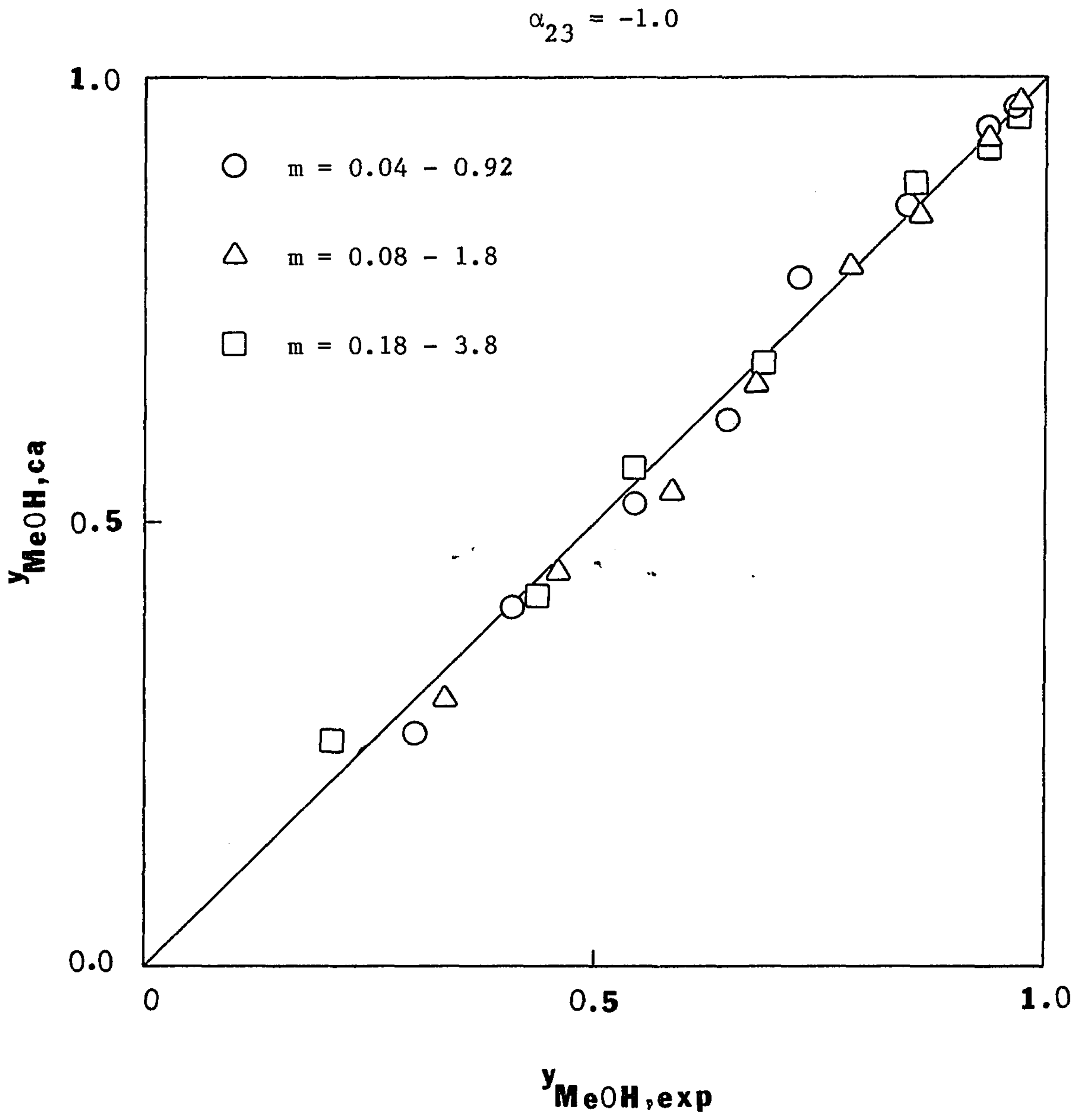


Figure G.17 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System NaBr-$H_2O$-MeOH at P = 1 atm

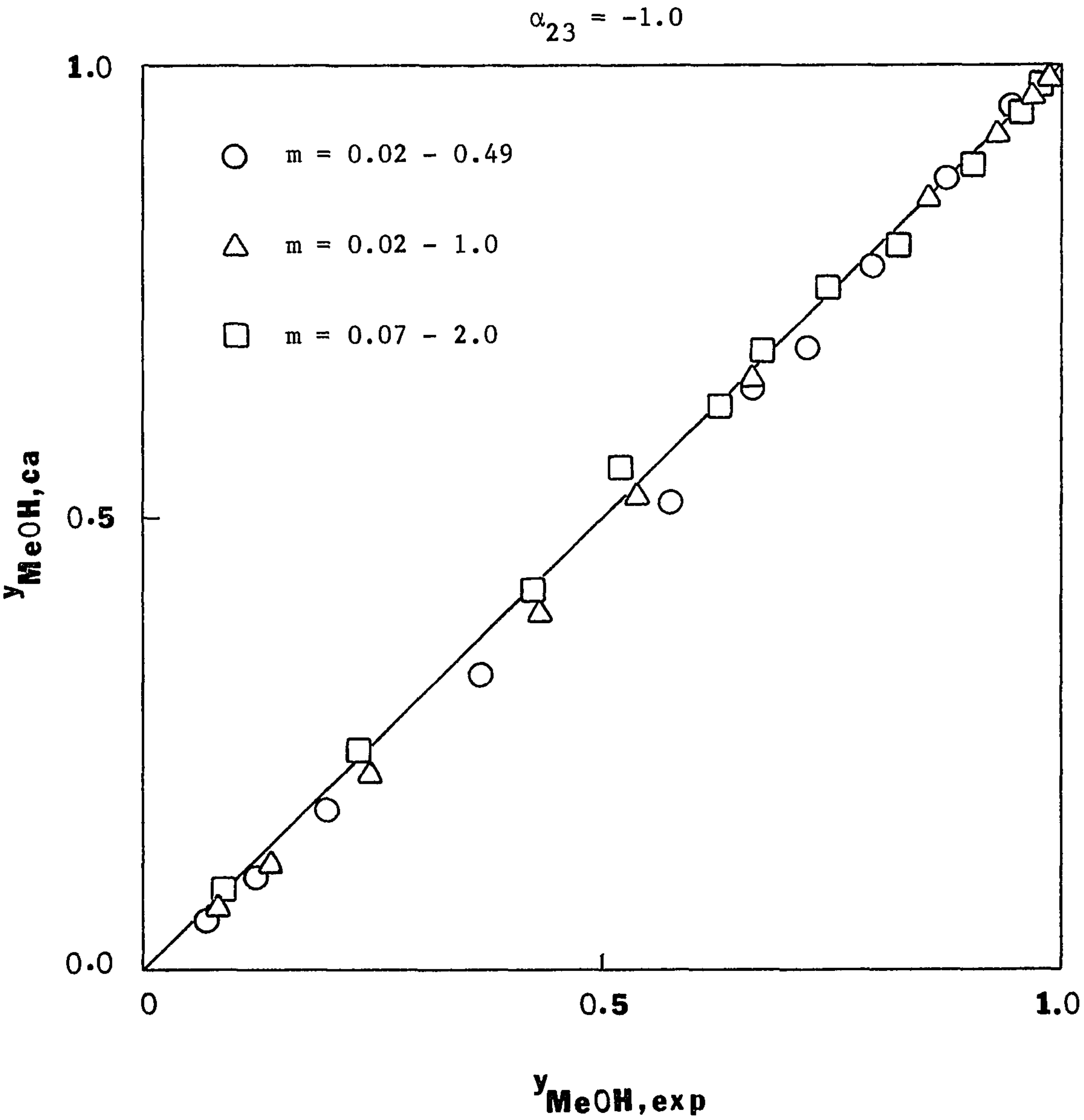


Figure G.18 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System KCl-$H_2O$-MeOH at P = 1 atm

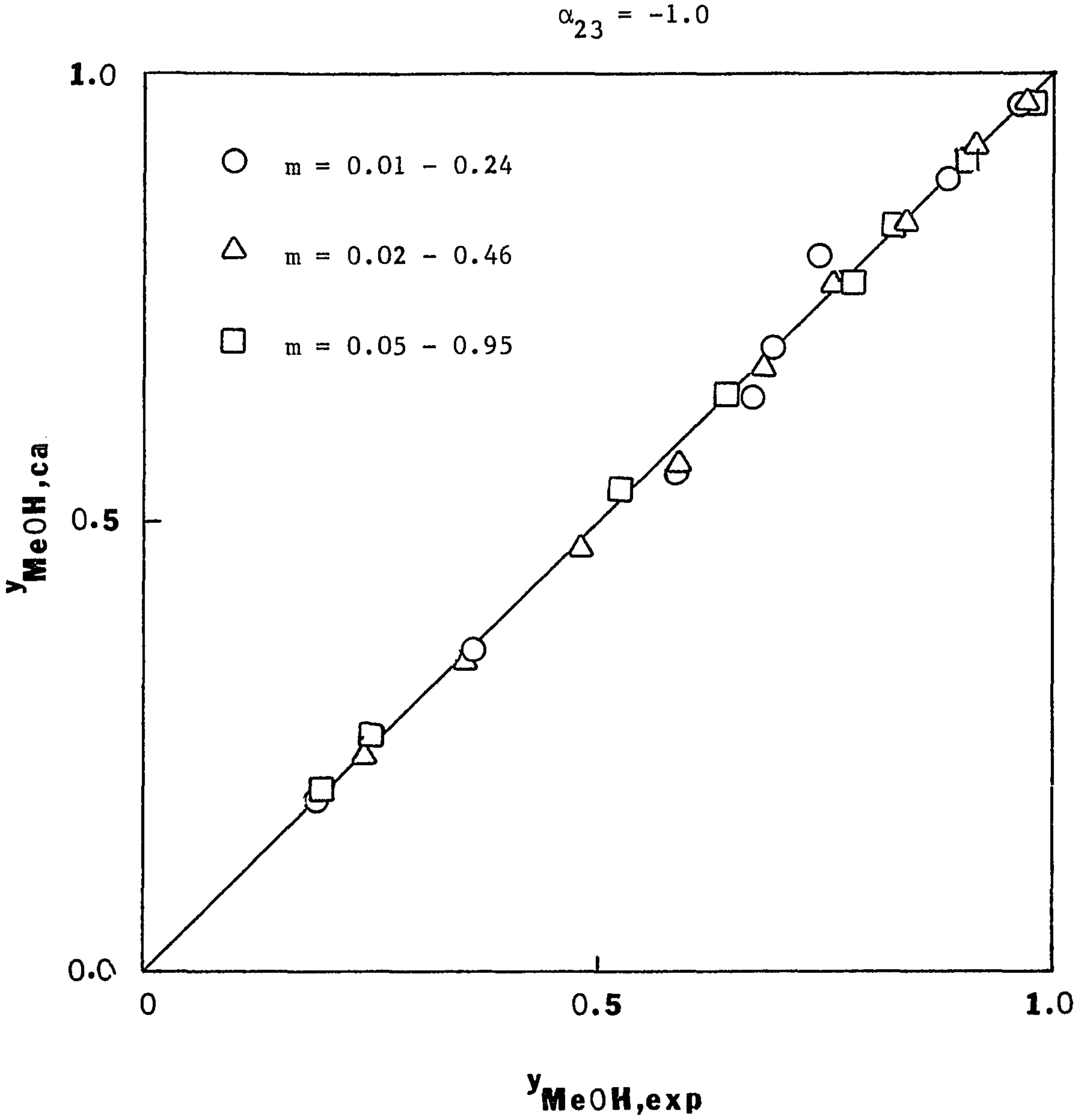
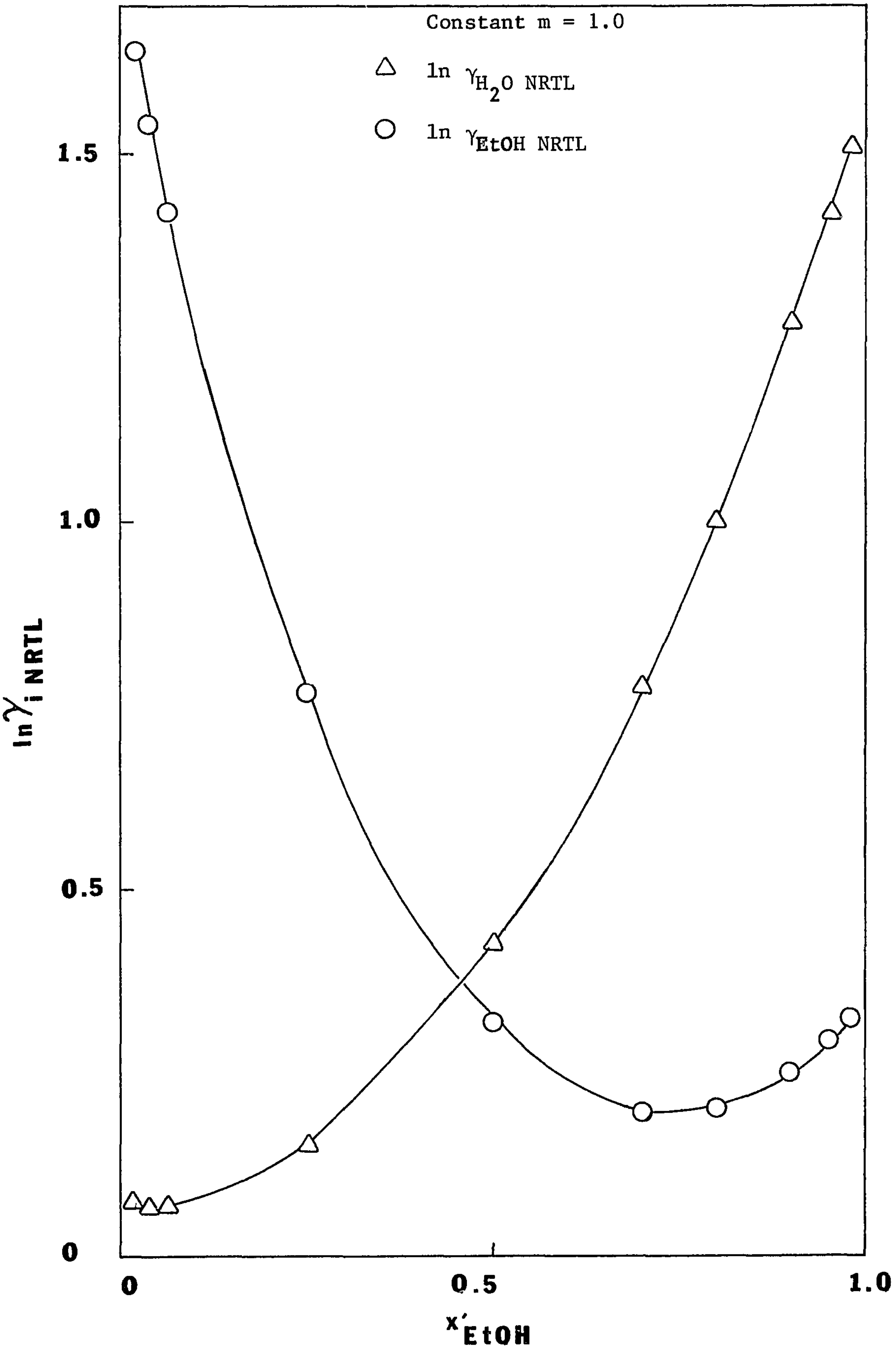


Figure G.19 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model I for the System NaF-$H_2O$-MeoH at P = 1 atm

Figure G.20 Contribution of the NRTL Term to ln $\gamma_i$ for the System LiCl-$H_2O$-EtOH at 25 C in Model I



# APPENDIX H

# TABLES AND FIGURES FOR MODEL II

TABLE H.1 Typical m-$\bar{D}P$ Data from the Weast Compilation

| Electrolyte \ m | 0.5 | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 |
|---|---|---|---|---|---|---|---|
| | DP (mm Hg) | | | | | | |
| KCl | 12.2 | 24.4 | 48.8 | 74.1 | 100.9 | 128.5 | 152.2 |
| $MgCl_2$ | 16.8 | 39.0 | 100.5 | | | | |
| $Na_2SO_4$ | 12.6 | 25.0 | 48.9 | | | | |
| $MgSO_4$ | 6.5 | 12.0 | 24.5 | | | | |

TABLE H.2 . Values of $B_{12}$ and Quality of Correlation of the Weast Data

| Electrolyte | max m | $\overline{\mathrm{DP}}$ | $\mathrm{DP}_{\max}$ | $\mathrm{DP}'_{\max}$ | $B_{12}(100°\mathrm{C})$ | $B_{12}(25°\mathrm{C})$ |
|---|---|---|---|---|---|---|
| KBr* | 4.0 | 0.6 | 1.0 | 1.0 | 0.0442 | 0.0296 |
| KCl | 6.0 | 1.1 | 2.1 | 2.1 | 0.0311 | 0.0240 |
| KI | 10.0 | 1.7 | 3.6 | 9.3 | 0.0537 | 0.0428 |
| $KNO_3$ | 10.0 | 0.8 | 1.2 | 2.7 | -0.0256 | -0.0862 |
| KOH | 10.0 | 3.6 | 6.0 | 9.8 | 0.1176 | 0.1131 |
| LiBr | 10.0 | 1.6 | 2.9 | 3.8 | 0.1325 | 0.1527 |
| LiCl | 10.0 | 0.7 | 2.3 | 3.6 | 0.1089 | 0.1283 |
| LiI | 10.0 | 1.0 | 1.3 | 15.4 | 0.1645 | 0.1815 |
| $LiNO_3$ | 10.0 | 2.5 | 4.8 | 11.2 | 0.0742 | 0.0938 |
| LiOH | 2.0 | 2.6 | 5.1 | 5.1 | 0.3064 | -0.0097 |
| NaBr | 8.0 | 1.5 | 3.0 | 5.2 | 0.0832 | 0.0749 |
| NaCl | 6.0 | 0.4 | 1.1 | 1.1 | 0.0567 | 0.0574 |
| NaI | 10.0 | 2.2 | 5.8 | 12.5 | 0.1129 | 0.0994 |
| $NaNO_3$ | 10.0 | 0.9 | 1.2 | 6.2 | 0.0074 | -0.0128 |
| NaOH | 10.0 | 1.0 | 2.1 | 2.5 | 0.0508 | 0.0747 |
| $NH_4Br$ | 10.0 | 1.4 | 3.1 | 6.7 | 0.0235 | -0.0066 |
| $NH_4Cl$ | 10.0 | 1.0 | 2.1 | 6.8 | 0.0154 | 0.0200 |

TABLE H.2 (Cont'd.)

| Electrolyte | max m | $\overline{DP}$ | $DP_{max}$ | $DP'_{max}$ | $B_{12}$(100°C) | $B_{12}$(25°C) |
|---|---|---|---|---|---|---|
| $NH_4I$ | 10.0 | 1.8 | 2.8 | 10.9 | 0.0361 | 0.0210 |
| $NH_4NO_3$ | 10.0 | 1.0 | 1.6 | 2.9 | -0.0051 | -0.0358 |
| $BaBr_2$ | 4.0 | 0.6 | 1.2 | 8.3 | 0.0773 | 0.0852 |
| $BaCl_2$ | 2.0 | 1.3 | 2.8 | 2.8 | 0.0501 | 0.0638 |
| $Ba(NO_3)_2$ | 1.0 | 0.4 | 0.6 | 0.6 | -0.0021 | -0.0545 |
| $Ba(OH)_2$ | 2.0 | 0.6 | 0.9 | 0.9 | -0.0275 | -0.024 |
| $CaBr_2$ | 5.0 | 2.2 | 3.4 | 4.4 | 0.1083 | 0.1179 |
| $CaCl_2$ | 5.0 | 0.6 | 1.1 | 4.9 | 0.0853 | 0.0948 |
| $Ca(NO_3)_2$ | 5.0 | 0.9 | 1.8 | 26.3 | 0.0436 | 0.0461 |
| $CdBr_2$ | 4.0 | 3.4 | 4.7 | 8.3 | -0.0341 | -0.1701 |
| $CdCl_2$ | 5.0 | 2.7 | 3.7 | 9.7 | -0.0336 | -0.1448 |
| $CdI_2$ | 3.0 | 4.5 | 6.7 | 8.7 | -0.0411 | -0.2497 |
| $Cd(NO_3)_2$ | 2.0 | 0.9 | 2.1 | 2.1 | 0.0505 | 0.0719 |
| $CoCl_2$ | 4.0 | 0.7 | 1.4 | 5.9 | 0.0593 | 0.1016 |
| $Co(NO_3)_2$ | 6.0 | 1.0 | 2.2 | 13.7 | 0.0730 | 0.0912 |
| $MgBr_2$ | 4.0 | 0.4 | 1.1 | 3.8 | 0.1260 | 0.1419 |
| $MgCl_2$ | 5.0 | 0.8 | 1.0 | 5.0 | 0.0951 | 0.1129 |

TABLE H.2 (Cont'd.)

| Electrolyte | max m | $\overline{DP}$ | $DP_{max}$ | $DP'_{max}$ | $B_{12}$(100°C) | $B_{12}$(25°C) |
|---|---|---|---|---|---|---|
| $Mg(NO_3)_2$ | 3.0 | 0.8 | 1.7 | 2.4 | 0.0975 | 0.1014 |
| $MnCl_2$ | 5.0 | 0.6 | 0.9 | 9.0 | 0.0457 | 0.0869 |
| $NiCl_2$ | 4.0 | 0.5 | 0.7 | 2.5 | 0.0674 | 0.1039 |
| $Pb(NO_3)_2$ | 3.0 | 1.0 | 1.4 | 1.6 | -0.0163 | -0.0606 |
| $SrBr_2$ | 4.0 | 0.7 | 1.7 | 1.8 | 0.0977 | 0.1038 |
| $SrCl_2$ | 5.0 | 0.6 | 1.2 | 10.5 | 0.0773 | 0.0847 |
| $Sr(NO_3)_2$ | 4.0 | 0.7 | 0.9 | 3.4 | 0.0221 | 0.0138 |
| $ZnCl_2$ | 6.0 | 4.1 | 6.2 | 12.9 | -0.0167 | 0.0364 |
| $Zn(NO_3)_2$ | 4.0 | 0.6 | 0.9 | 5.3 | 0.0814 | 0.1002 |
| $K_2CO_3$ | 8.0 | 0.4 | 0.9 | 5.3 | 0.0298 | 0.0372 |
| $K_2CrO_4$ | 2.0 | 0.7 | 1.5 | 1.5 | 0.0141 | -0.0003 |
| $Li_2SO_4$ | 3.0 | 0.4 | 1.1 | 1.2 | 0.0072 | 0.0207 |
| $Na_2CO_3$ | 4.0 | 0.8 | 1.2 | 5.1 | -0.0086 | 0.0089 |
| $Na_2HPO_4$ | 6.0 | 0.8 | 1.3 | 8.0 | -0.0200 | -0.0265 |
| $Na_2SO_4$ | 3.0 | 0.8 | 1.2 | 1.5 | -0.0086 | -0.0204 |
| $(NH_4)_2SO_4$ | 6.0 | 1.5 | 2.6 | 4.7 | -0.0135 | -0.0287 |
| $CdSO_4$ | 2.0 | 0.8 | 2.0 | 2.0 | -0.0029 | -0.0371 |

TABLE H.2 (Cont'd.)

| Electrolyte | max m | $D\bar{P}$ | $DP_{max}$ | $DP'_{max}$ | $B_{12}(100°C)$ | $B_{12}(25°C)$ |
|---|---|---|---|---|---|---|
| $MgSO_4$ | 3.0 | 0.2 | 0.3 | 2.8 | 0.0107 | -0.0153 |
| $NiSO_4$ | 2.0 | 1.5 | 2.3 | 2.3 | 0.0029 | -0.0298 |
| $ZnSO_4$ | 4.0 | 0.9 | 1.4 | 4.4 | 0.0037 | -0.0240 |

*Data for KBr are from Robinson and Stokes (1955) because they are not reported by Weast.

TABLE H.3 Quality of Results with the $B_{12}$ Value at 70°C Obtained by Interpolation of the $B_{12}$(25°C) and $B_{12}$(100°C) Values in Equation (3-20)

| Electrolyte | $B_{12}$(70°C) | Abs. % Error in $\gamma_{\pm}$ | | DP | |
|---|---|---|---|---|---|
| | | Max | Avg | Max | Avg |
| KBr | 0.0421 | 4.7 | 3.3 | 0.3 | 0.1 |
| KCl | 0.0303 | 3.8 | 2.9 | 0.3 | 0.1 |
| NaCl | 0.0619 | 4.3 | 3.2 | 0.2 | 0.1 |
| $Na_2SO_4$ | -0.0090 | 2.9 | 1.6 | 0.2 | 0.1 |
| $MgCl_2$ | 0.1119 | 8.8 | 6.3 | 0.7 | 0.4 |
| $MgSO_4$ | 0.0182 | 34.0 | 29.3 | 0.5 | 0.3 |

TABLE H.4 Nonaqueous Electrolytic Binary Data Correlation with the Bromley Equation

| System | # of Points | Max 'm' | T (°C) | $B_{13}$ | % Error in $\gamma_{\pm}$ |  | % Error in DP |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Max | Avg | Max | Avg |
| $CaCl_2$-MeOH | 7 | 2.6 | 25 | 0.15541 | - | -- | 75.2 | 27.4 |
| HCl-EtOH | 8 | 0.1 | 25 | -0.44655 | 16.0 | 10.8 | - | - |
| HCl-MeOH | 22 | 0.56 | 25 | 0.40686 | 1.7 | 0.6 | - | - |
| LiCl-EtOH | 3 | 4.0 | 25 | 0.41205 | - | - | 13.5 | 7.8 |
| LiCl-MeOH | 6 | 4.0 | 25 | 0.28811 | - | - | 8.8 | 3.6 |
| LiCl-MeOH | 11 | 6.0 | 60 | 0.25195 | - | - | 15.6 | 7.3 |
| NaBr-MeOH | 9 | 1.6 | 25 | 0.30629 | - | - | 9.9 | 4.1 |
| NaCl-MeOH | 7 | 0.1 | 25 | -0.3223 | 10.7 | 6.2 | - | - |

TABLE H.5 Aqueous Electrolytic Binary Data Correlation with the Bromley Equation

| System | # of Points | Max 'm' | T (°C) | $B_{12}$ | % Error in $\gamma_\pm$ | | % Error in DP | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Max | Avg | Max | Avg |
| $CaCl_2$-$H_2O$ | 21 | 5.0 | 25 | 0.1000 | 11.0 | 5.5 | 3.6 | 2.10 |
| HCl-$H_2O$ | 15 | 2.0 | 25 | 0.13963 | 0.9 | 0.6 | - | - |
| LiCl-$H_2O$ | 19 | 4.0 | 25 | 0.12366 | 2.5 | 0.9 | 2.0 | 0.5 |
| LiCl-$H_2O$ | 11 | 6.0 | 60 | 0.12049 | - | - | 1.9 | 0.9 |
| NaBr-$H_2O$ | 4 | 10.3 | 40 | 0.06607 | - | - | 13.0 | 5.5 |
| NaBr-$H_2O$ | 19 | 4.0 | 25 | 0.07376 | 0.5 | 0.1 | 1.1 | 0.2 |
| NaCl-$H_2O$ | 10 | 1.0 | 25 | 0.05586 | 0.1 | 0.04 | 1.0 | 0.3 |

TABLE H.6 Isothermal Ternary $\gamma_\pm$ Data Correlation with Model II

| System | # of Points | Max 'm' | T (°C) | Ternary Parameters $B_{123}$ | $\delta_{123}$ | % Error in $\gamma_\pm$ Max | Avg |
|---|---|---|---|---|---|---|---|
| $HCl-H_2O-EtOH$ | 25 | 0.1 | 25 | -4.283 | -0.0245 | 13.8 | 2.4 |
|  | 44 | 2.5 | 25 | -4.283 | -0.0245 | 92.1 | 13.1 |
| $HCl-H_2O-MeOH$ | 48 | 2.0 | 25 | 0.57215 | -0.0498 | 11.6 | 1.4 |
| $NaCl-H_2O-MeOH$ | 35 | 0.5 | 25 | -11.967 | -0.0286 | 28.0 | 7.4 |

TABLE H.7 A Comparative Study of the Three Objective Functions [Equations (2-19), (2-20), (2-21)] in Correlating Ternary Isothermal VLE Data with Model II

| System | Max 'm' | T (°C) | $\Delta Y$ | | $\Delta P$ (mmHg) | |
|---|---|---|---|---|---|---|
| | | | Max | Avg | Max | Avg |
| Objective Function #1 | | | | | | |
| LiCl-$H_2O$-EtOH | 1.0 | 25 | 0.034 | 0.0145 | 4.7 | 2.0 |
| LiCl-$H_2O$-MeOH | 1.0 | 25 | 0.015 | 0.0087 | 11.7 | 9.0 |
| NaBr-$H_2O$-MeOH | 3.0 | 40 | 0.035 | 0.0165 | 9.0 | 3.6 |
| | 6.2 | 40 | 0.026 | 0.014 | 8.0 | 4.4 |
| NaBr-$H_2O$-MeOH | 3.0 | 25 | 0.028 | 0.01 | 4.9 | 1.9 |
| | 7.1 | 25 | 0.066 | 0.015 | 3.9 | 1.5 |
| LiCl-$H_2O$-MeOH | 2.0 | 60 | 0.054 | 0.026 | 16.8 | 7.4 |
| | 3.0 | 60 | 0.05 | 0.028 | 12.6 | 6.6 |
| Objective Function #2 | | | | | | |
| LiCl-$H_2O$-EtOH | 1.0 | 25 | 0.023 | 0.009 | 8.9 | 3.3 |
| LiCl-$H_2O$-MeOH | 1.0 | 25 | 0.011 | 0.007 | 4.4 | 3.1 |
| NaBr-$H_2O$-MeOH | 3.0 | 40 | 0.021 | 0.012 | 11.4 | 3.9 |
| | 6.2 | 40 | 0.021 | 0.011 | 11.4 | 4.6 |
| NaBr-$H_2O$-MeOH | 3.0 | 25 | 0.013 | 0.0064 | 5.0 | 2.0 |
| | 7.1 | 25 | 0.042 | 0.0096 | 12.7 | 4.5 |
| LiCl-$H_2O$-MeOH | 2.0 | 60 | 0.038 | 0.018 | 40.0 | 27.7 |
| | 3.0 | 60 | 0.036 | 0.02 | 46.4 | 30.2 |
| Objective Function #3 | | | | | | |
| LiCl-$H_2O$-EtOH | 1.0 | 25 | 0.025 | 0.01 | 8.0 | 3.0 |
| LiCl-$H_2O$-MeOH | 1.0 | 25 | 0.011 | 0.008 | 10.2 | 8.0 |
| NaBr-$H_2O$-MeOH | 3.0 | 40 | 0.02 | 0.012 | 13.2 | 3.8 |
| | 6.2 | 40 | 0.02 | 0.011 | 12.1 | 4.8 |
| NaBr-$H_2O$-MeOH | 3.0 | 25 | 0.014 | 0.007 | 5.1 | 2.0 |
| | 7.1 | 25 | 0.048 | 0.011 | 10.5 | 3.4 |
| LiCl-$H_2O$-MeOH | 2.0 | 60 | 0.042 | 0.019 | 31.0 | 19.6 |
| | 3.0 | 60 | 0.036 | 0.02 | 46.4 | 30.2 |

TABLE H.8 Values of the Parameters Obtained with Three Objective Functions for Model II

| System | Max 'm' | T (°C) | Ternary Parameters | |
|---|---|---|---|---|
| | | | $B_{123}$ | $\delta_{123}$ |
| <u>Objective Function #1</u> | | | | |
| LiCl-$H_2O$-EtOH | 1.0 | 25 | -117.68 | 0.0604 |
| LiCl-$H_2O$-MeOH | 1.0 | 25 | -145.85 | -0.0612 |
| NaBr-$H_2O$-MeOH | 3.0 | 40 | -60.53 | -0.182 |
| | 6.2 | 40 | -68.105 | -0.1582 |
| NaBr-$H_2O$-MeOH | 3.0 | 25 | -93.462 | -0.1135 |
| | 7.1 | 25 | -81.45 | -0.11248 |
| LiCl-$H_2O$-MeOH | 2.0 | 60 | -21.409 | 0.0282 |
| | 3.0 | 60 | -32.164 | 0.03745 |
| <u>Objective Function #2</u> | | | | |
| LiCl-$H_2O$-EtOH | 1.0 | 25 | -152.94 | 0.0899 |
| LiCl-$H_2O$-MeOH | 1.0 | 25 | -64.026 | -0.1587 |
| NaBr-$H_2O$-MeOH | 3.0 | 40 | -59.76 | -0.1246 |
| | 6.2 | 40 | -64.96 | -0.113 |
| NaBr-$H_2O$-MeOH | 3.0 | 25 | -93.2 | -0.0235 |
| | 7.1 | 25 | -99.38 | -0.0102 |
| LiCl-$H_2O$-MeOH | 2.0 | 60 | -72.477 | 0.0759 |
| | 3.0 | 60 | -80.63 | 0.0847 |
| <u>Objective Function #3</u> | | | | |
| LiCl-$H_2O$-EtOH | 1.0 | 25 | -145.91 | 0.08379 |
| LiCl-$H_2O$-MeOH | 1.0 | 25 | -133.37 | -0.0573 |
| NaBr-$H_2O$-MeOH | 3.0 | 40 | -51.02 | -0.1674 |
| | 6.2 | 40 | -62.74 | -0.1292 |
| NaBr-$H_2O$-MeOH | 3.0 | 25 | -93.997 | -0.0507 |
| | 7.1 | 25 | -95.00 | -0.0483 |
| LiCl-$H_2O$-MeOH | 2.0 | 60 | -59.4 | 0.0639 |
| | 3.0 | 60 | -68.70 | 0.0724 |

TABLE H.9 $B_{12}$ Values Obtained from Weast's Data and Equation (3-20) with B* and $B_1'$ Values from Table 3.3

| Electrolyte | $B_{12}$ from Weast Data | $B_{12}$ from Eqn (3-20) |
|---|---|---|
| NaCl | 0.0567 | 0.0612 |
| KBr | 0.0462 | 0.0436 |
| KCl | 0.0311 | 0.0322 |
| $Na_2SO_4$ | -0.0086 | -0.0036 |
| $MgCl_2$ | 0.0951 | 0.1017 |
| $MgSO_4$ | 0.0107 | 0.0163 |

TABLE E.10 $\gamma_{\pm}$ Values for $MgCl_2$ Using $B_{12}$ Values from Weast's Data and Equation (3-20)

| molality | $\gamma_{\pm}$ from Weast Data | $\gamma_{\pm}$ from Eqn (3-20) |
|---|---|---|
| 0.2 | 0.4034 | 0.4071 |
| 0.4 | 0.3737 | 0.3796 |
| 0.6 | 0.3713 | 0.3792 |
| 0.8 | 0.3820 | 0.3924 |
| 1.0 | 0.4018 | 0.4150 |
| 1.2 | 0.4292 | 0.4458 |
| 1.4 | 0.4636 | 0.4842 |
| 1.6 | 0.5050 | 0.5304 |
| 1.8 | 0.5537 | 0.5848 |
| 2.0 | 0.6103 | 0.6482 |

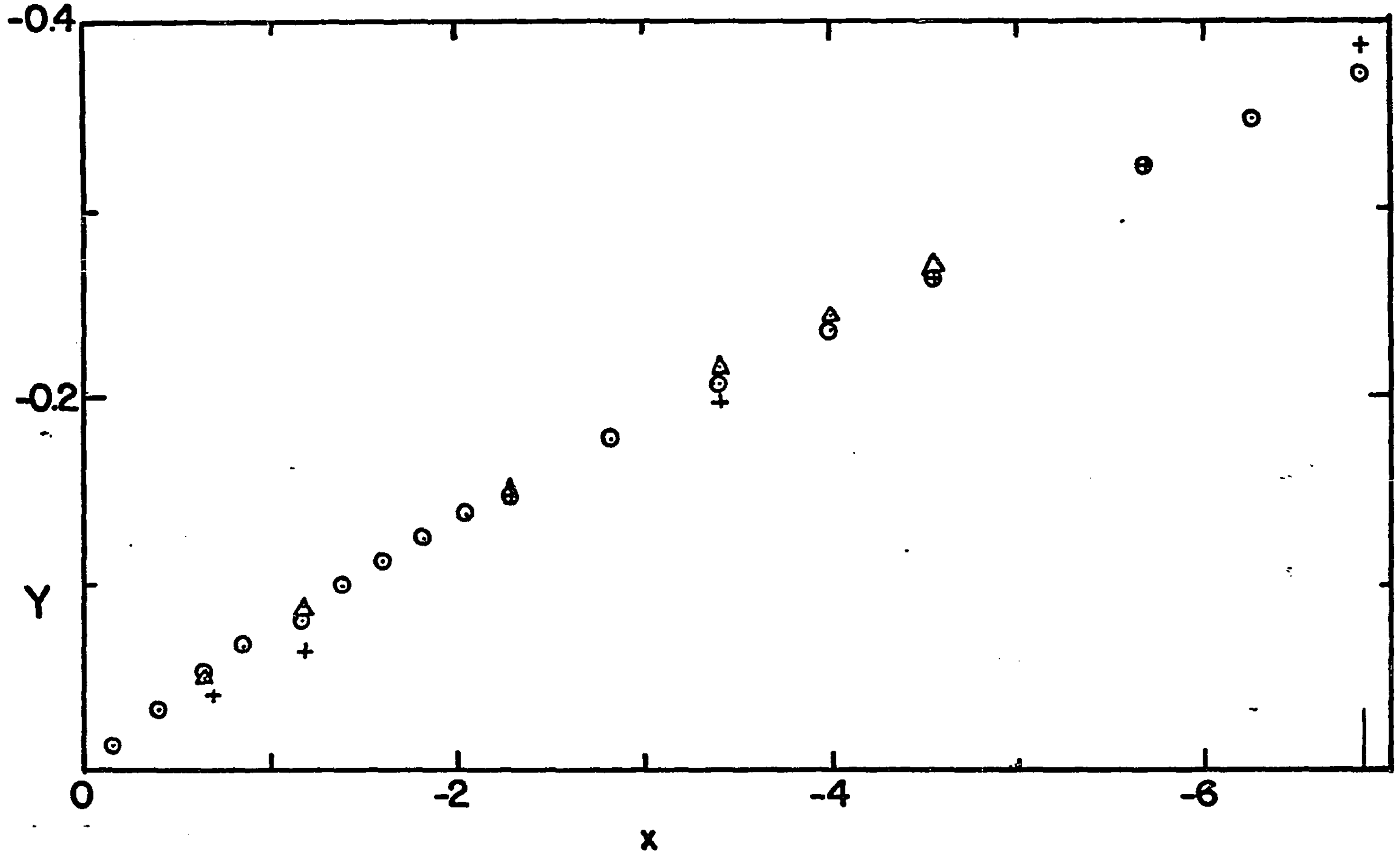


Figure H.1 Test of the Bromley Equation

System: NaCl-Water at 100°C

| | |
|---|---|
| + | Weast (1969) |
| △ | Robinson and Stokes (1955) |
| ⊙ | Gibbard et al., (1974) |
| Y,x | are defined in equation (3-15) |

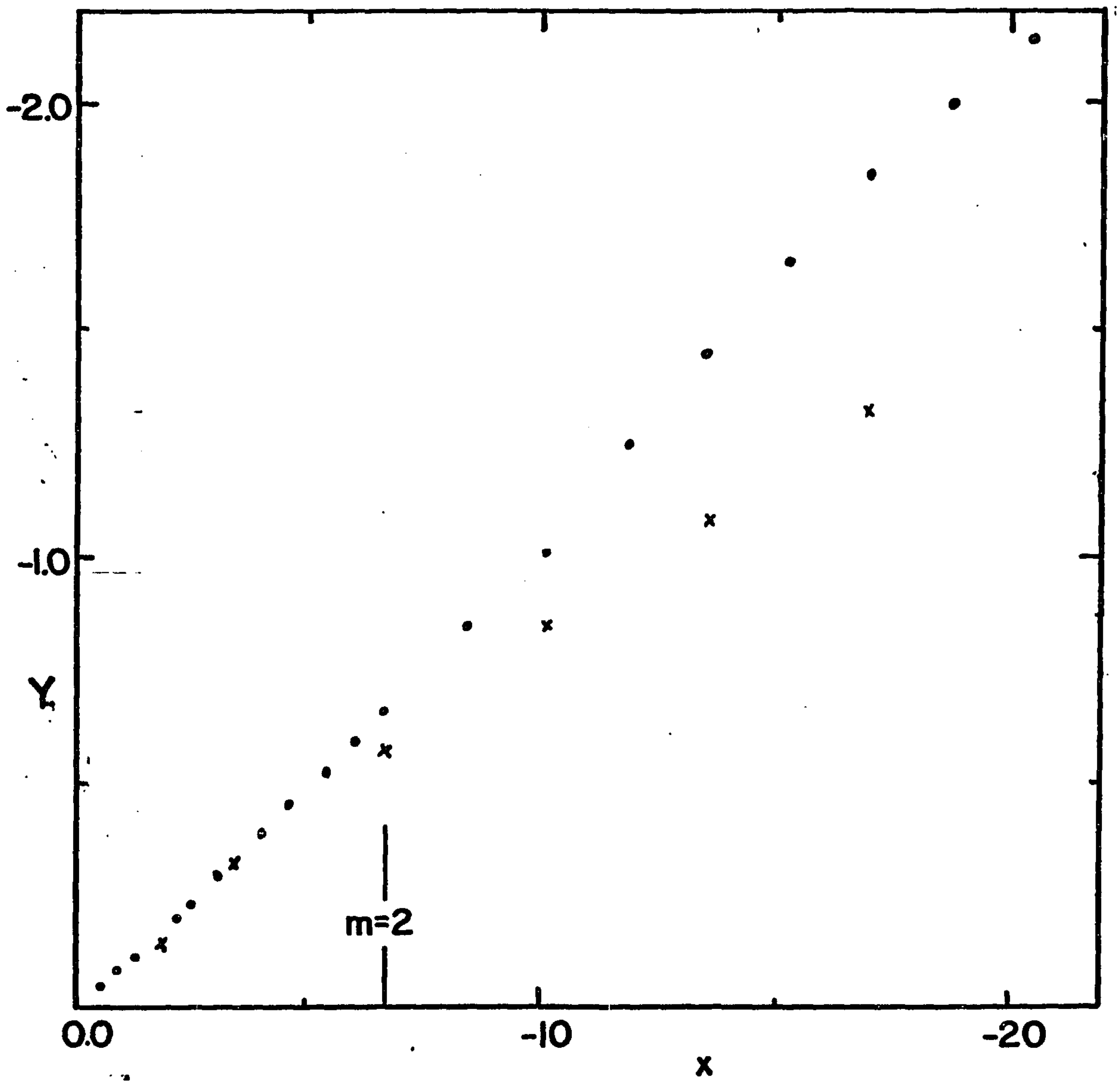


Figure H.2 Test of the Bromley Equation

System: $CaCl_2$-$H_2O$

● Robinson and Stokes (25°C)

× Weast (100°C)

Y,x are defined in equation (3.15)

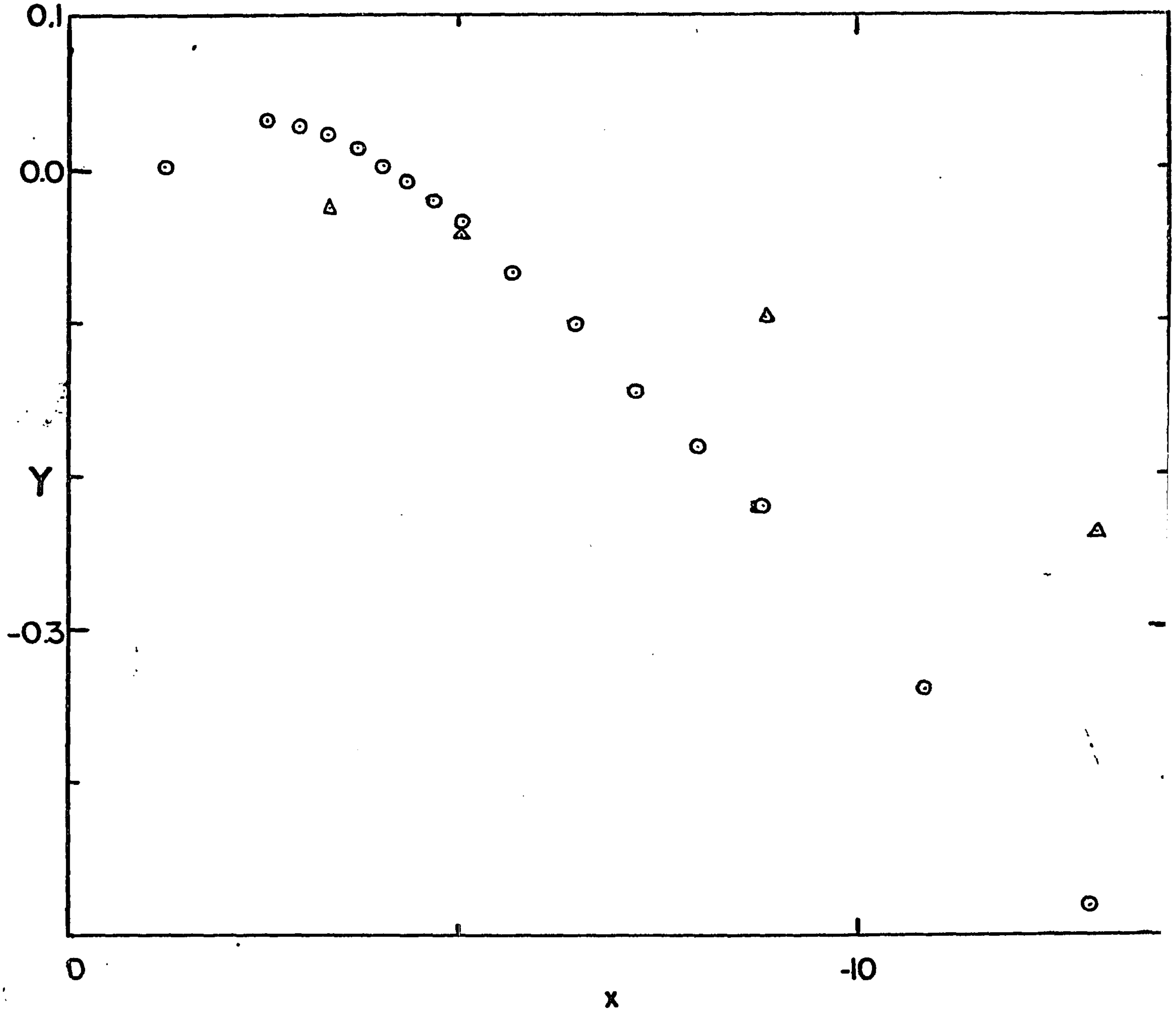


Figure H.3 Test of the Bromley Equation

System: $MgSO_4$

⊙ Robinson and Stokes (25°C)

△ Weast (100°C)

Y,x are defined in equation (3-15)

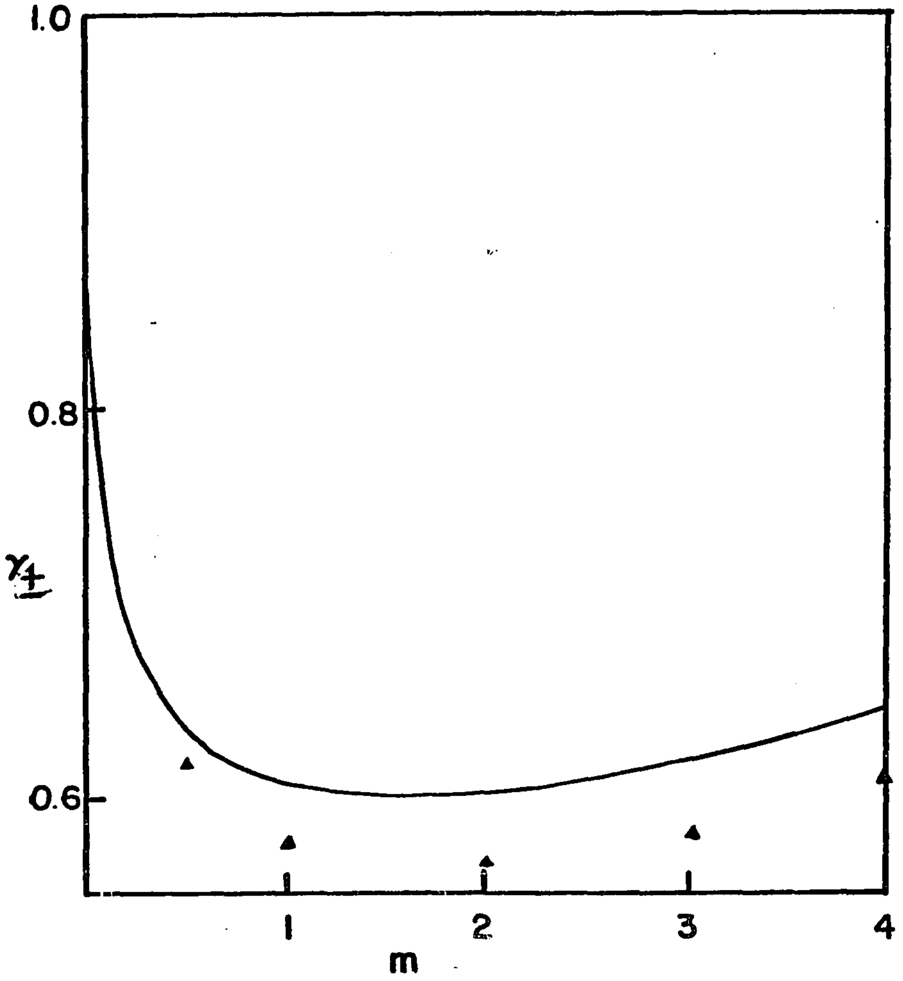


Figure H.4 Activity Coefficients as a function of concentration for the System KBr-Water at 100°C

——— Robinson and Stokes

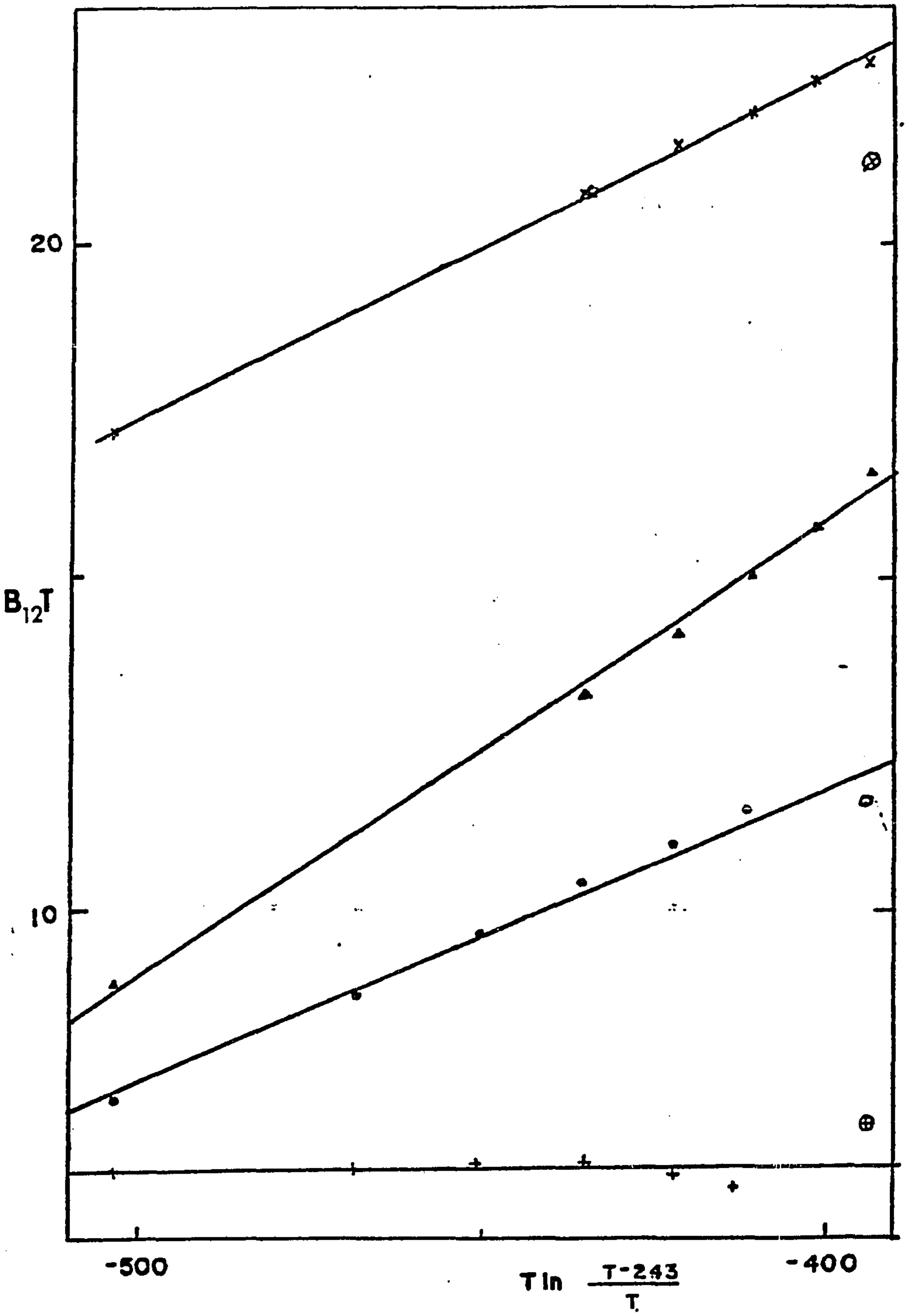


Figure H.5 Test of Temperature Dependency of $B_{12}$ Equation ( 3-20)

| | |
|---|---|
| ● | KCl (Snipes et al., 1975) |
| ⊙ | KCl (Weast, 1969) |
| ▲ | KBr (Robinson and Stokes, 1955) |
| + | $MgSO_4$ (Snipes, et al., 1975) |
| ⊕ | $MgSO_4$ (Weast, 1969) |
| × | NaCl (Robinson and Stokes, 1955) |
| ⊗ | Weast (1969) |

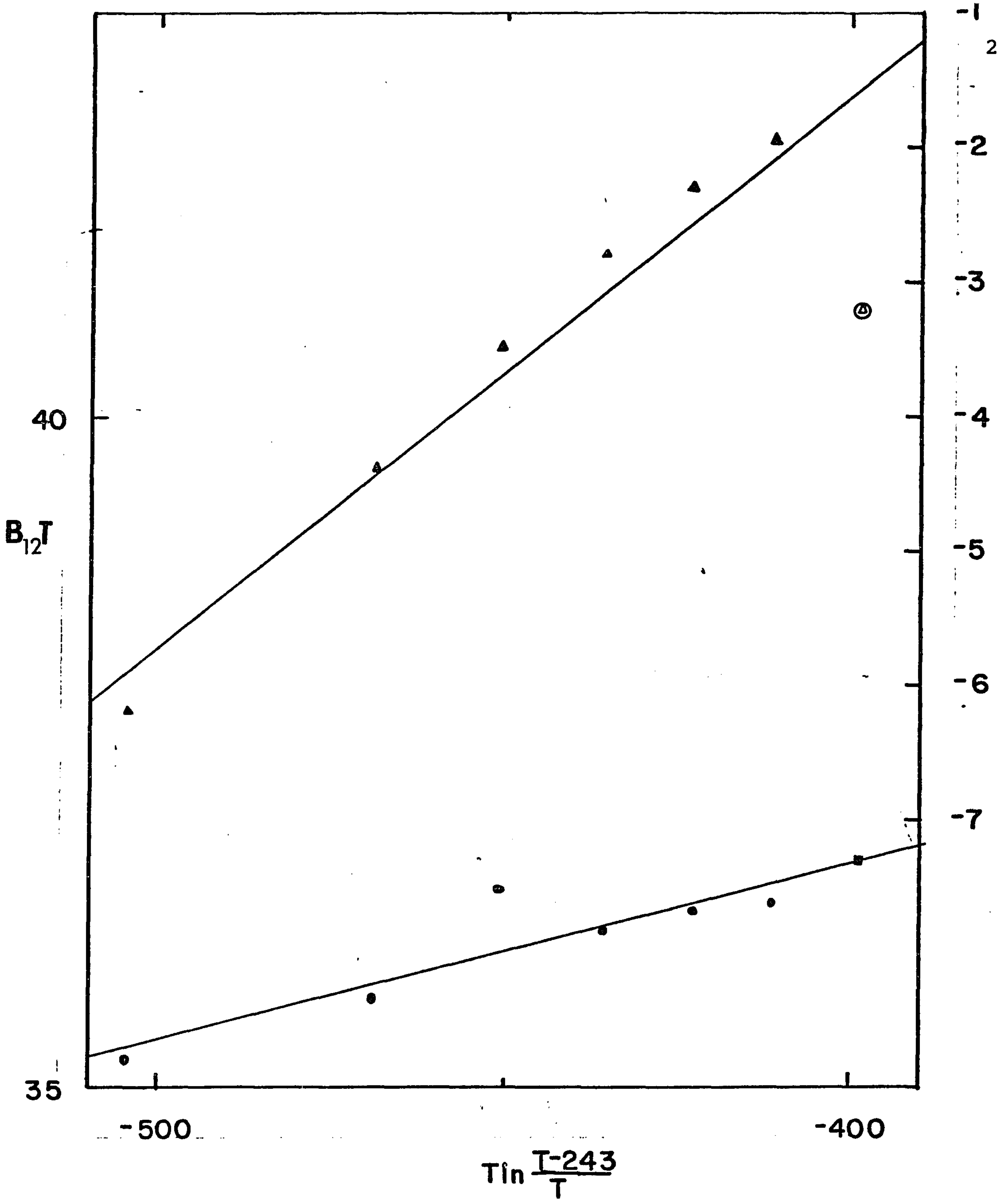


Figure H.6 Test of Temperature Dependency of $B_{12}$ Equation (3-20)

● MgCl$_2$ (Snipes et al., 1975)

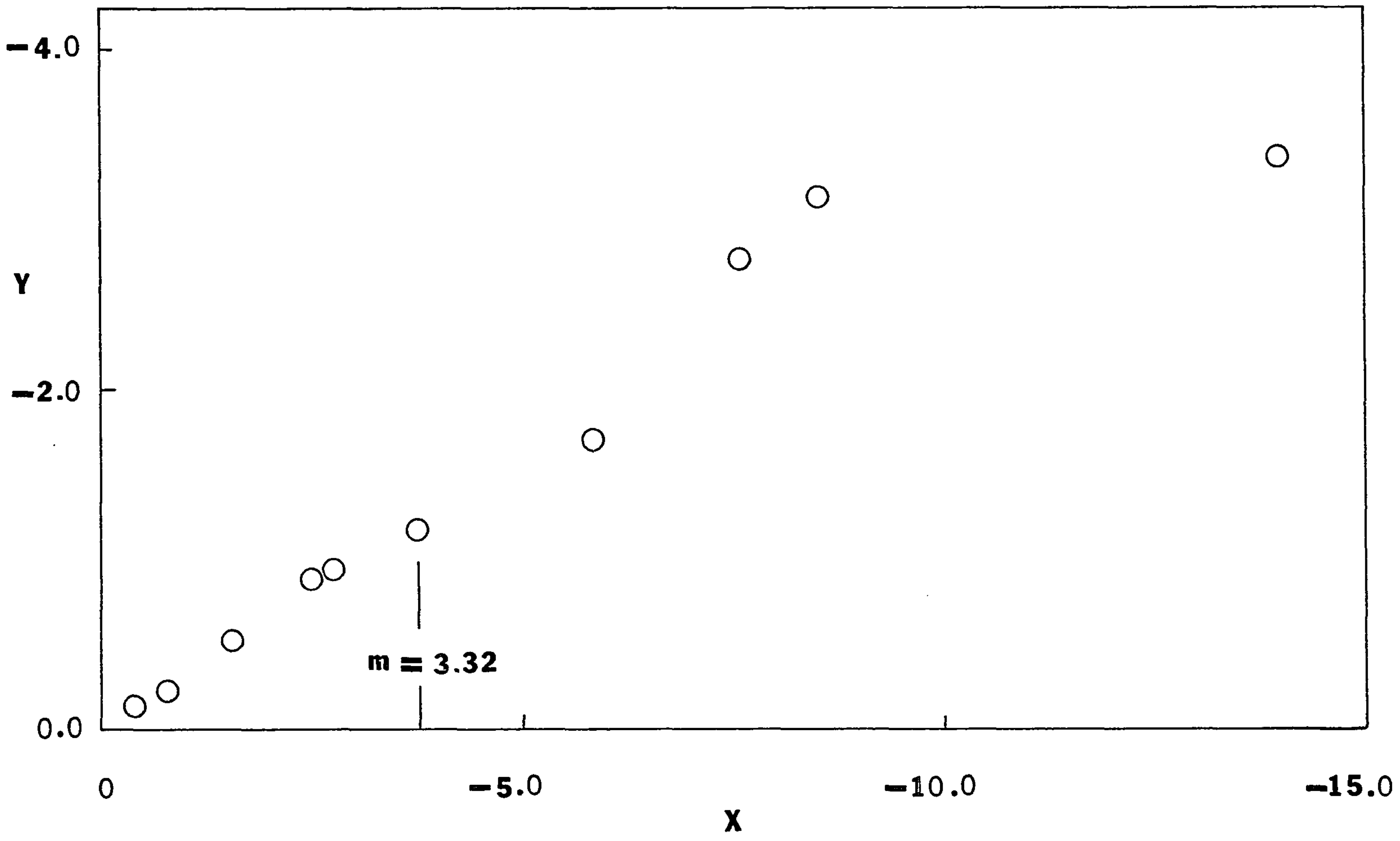
■ MgCl$_2$ (Weast, 1969)

▲ Na$_2$SO$_4$ (Snipes et al., 1975)

△ Na$_2$SO$_4$ (Weast, 1969)

Figure H.7 Test of the Bromley Equation , System : LiBr-MeOH at 25°C

Y,x are defined in equation (3-15)



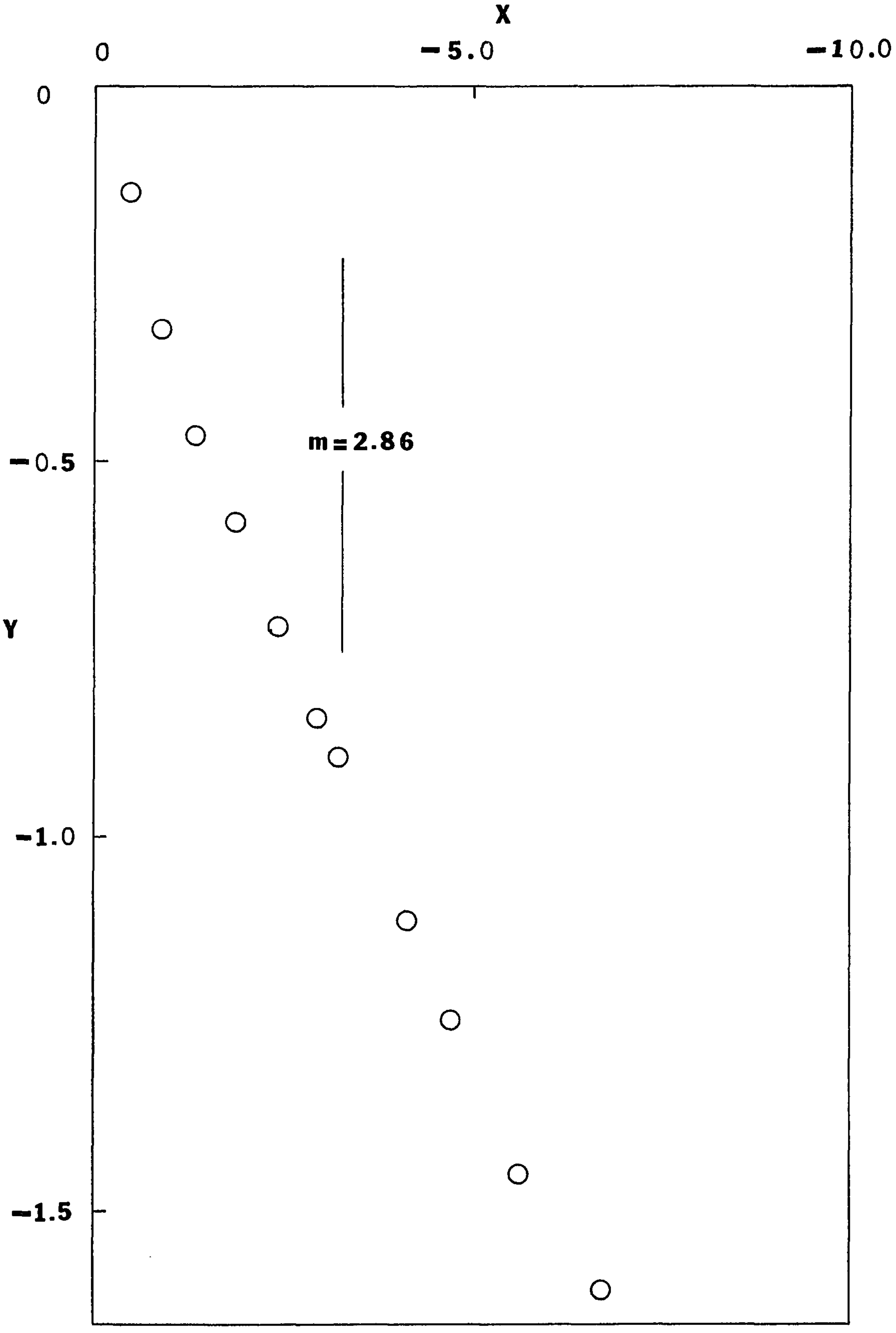


Figure H.8 Test of the Bromley Equation, System : LiCl-MeOH at 60°C

Y,x are defined in equation (3-15)

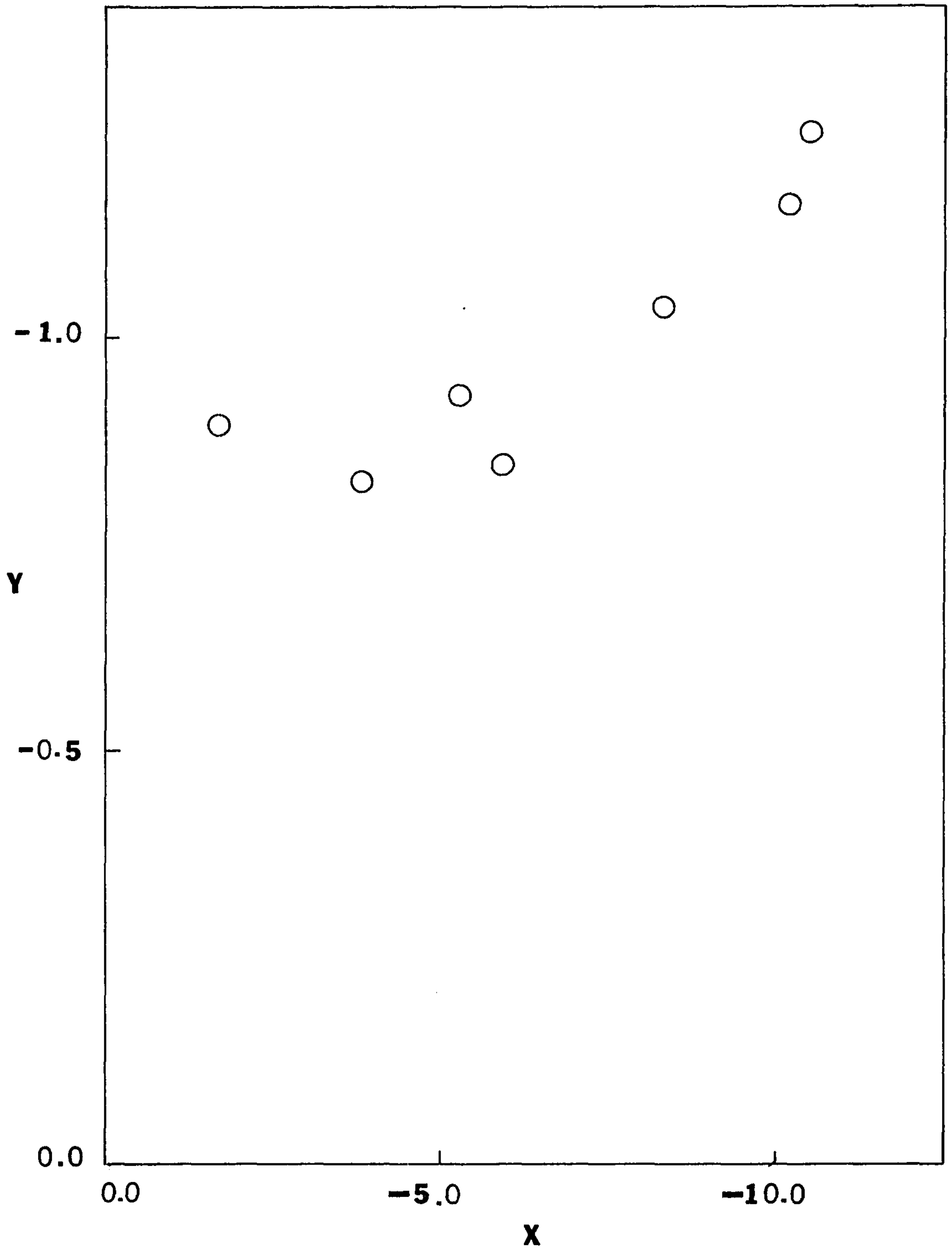


Figure H.9 Test of the Bromley Equation, System : $CaCl_2$-MeOH at 25°C

Y,x are defined in equation (3-15)

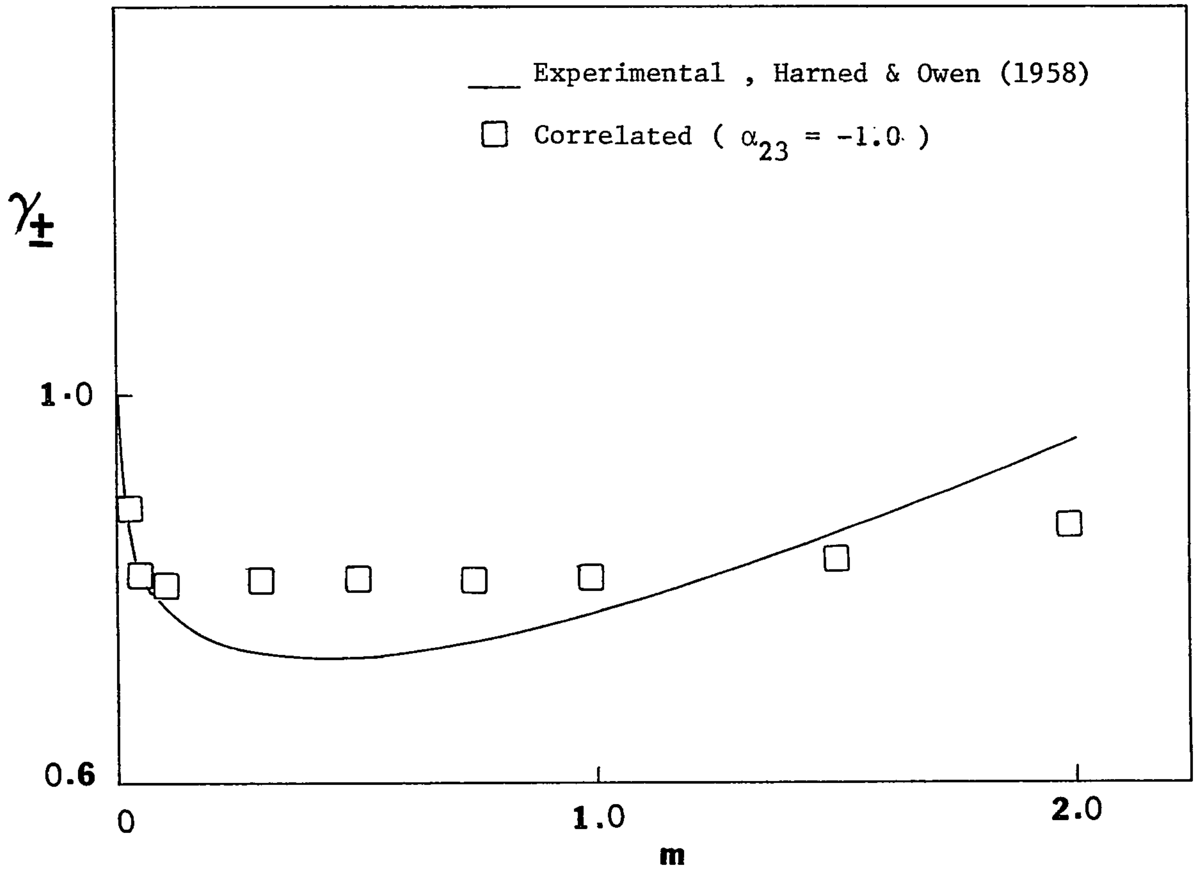


Figure H.10 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System $HCl-H_2O-EtOH$ at 25 C and Constant $X'_{EtOH} = 0.0417$

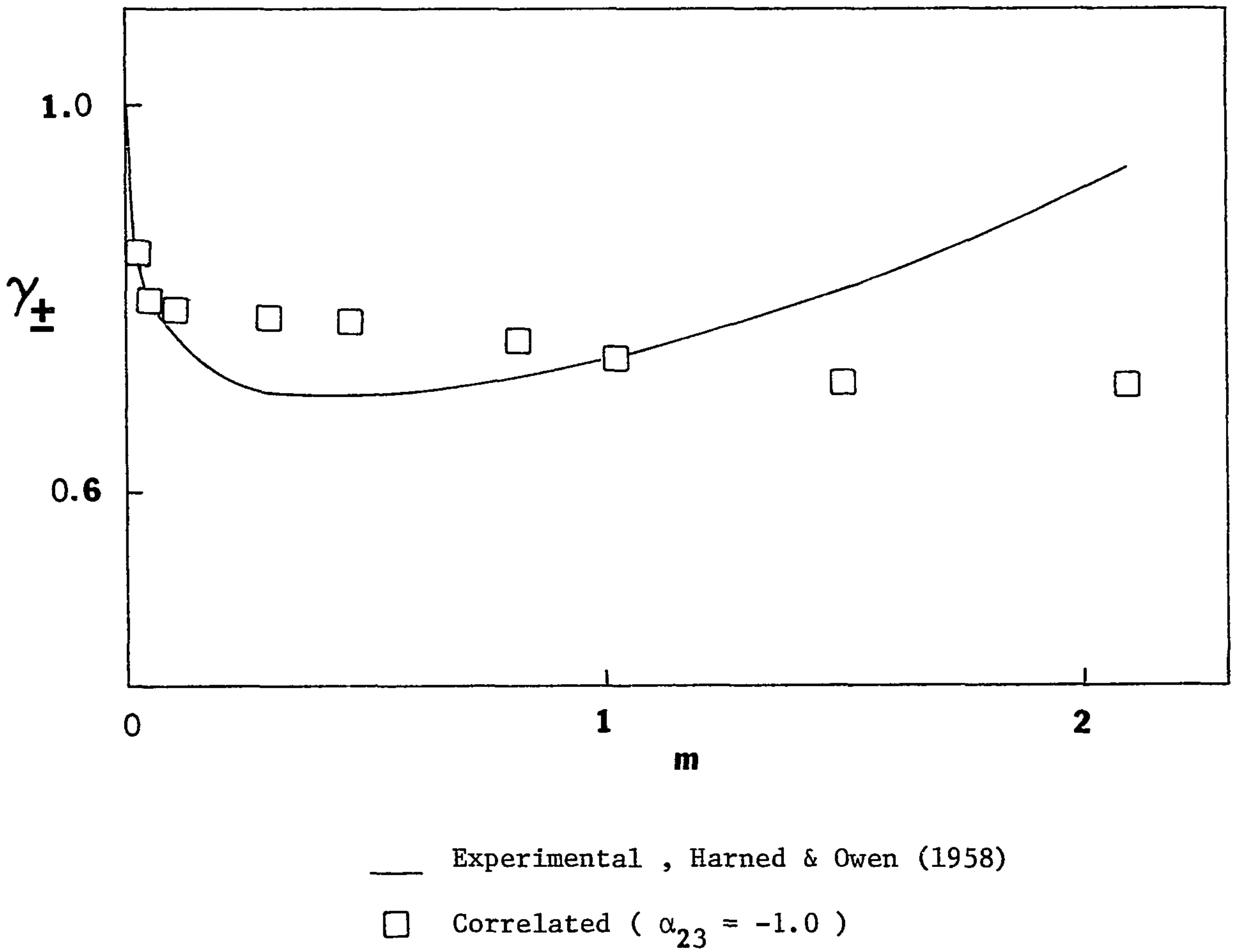


Figure H.11 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System $HCl-H_2O-EtOH$ at 25°C and Constant $X'_{EtOH}=0.0891$

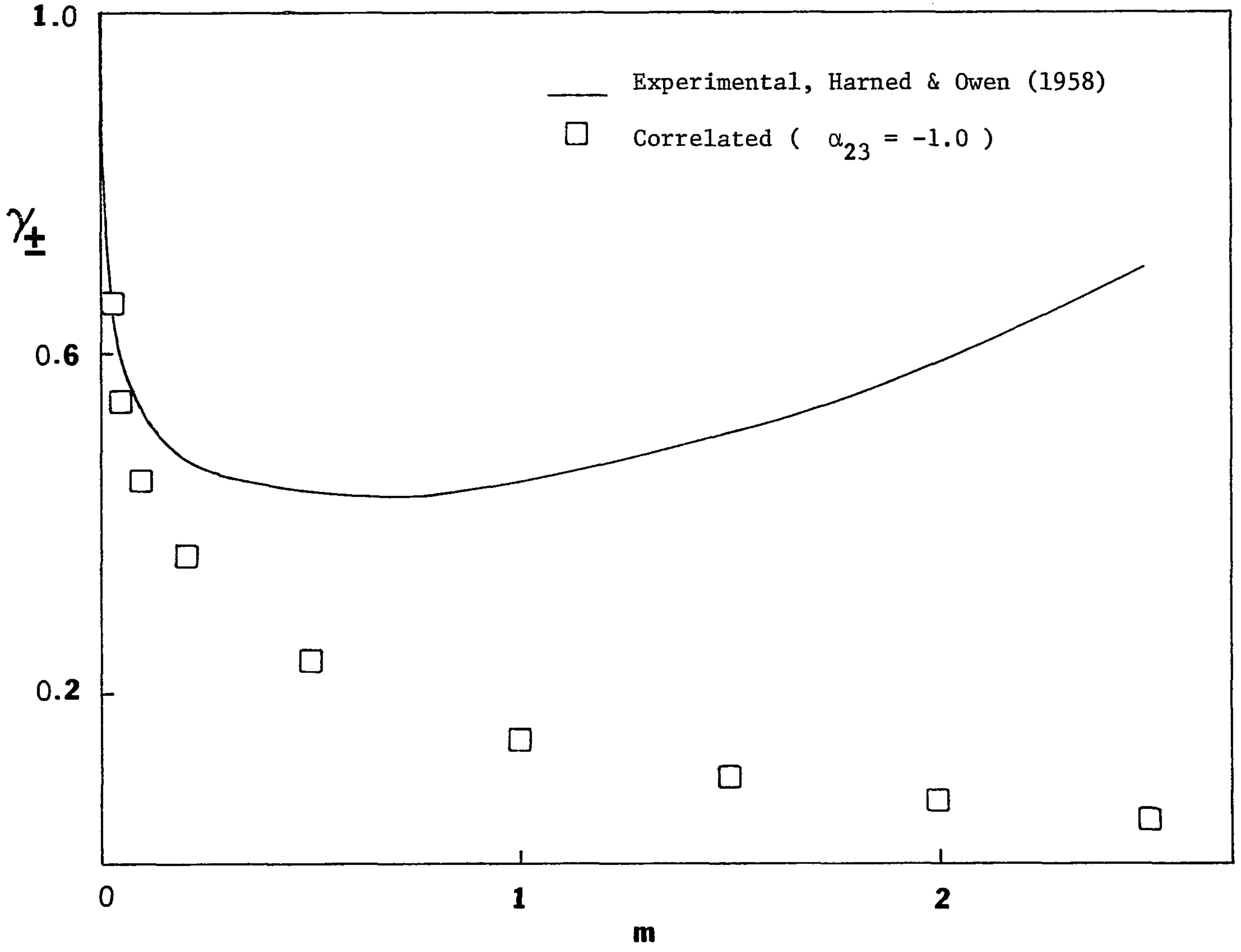


Figure H.12 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-$H_2O$-EtOH at 25°C and Constant $X'_{EtOH} = 0.5$

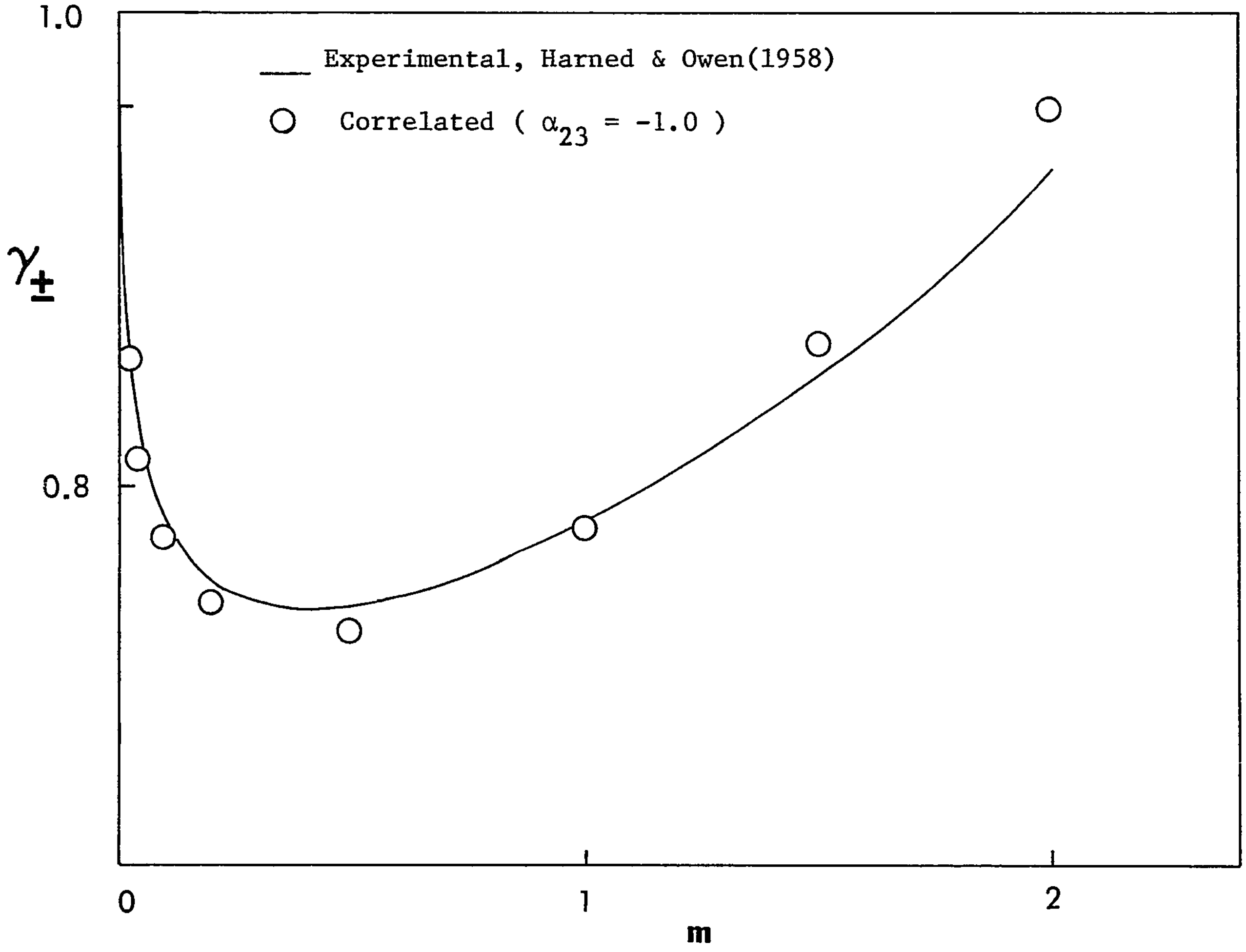


Figure H.13 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System $HCl-H_2O-MeOH$ at 25°C and Constant $X'_{MeOH}$ = 0.0584

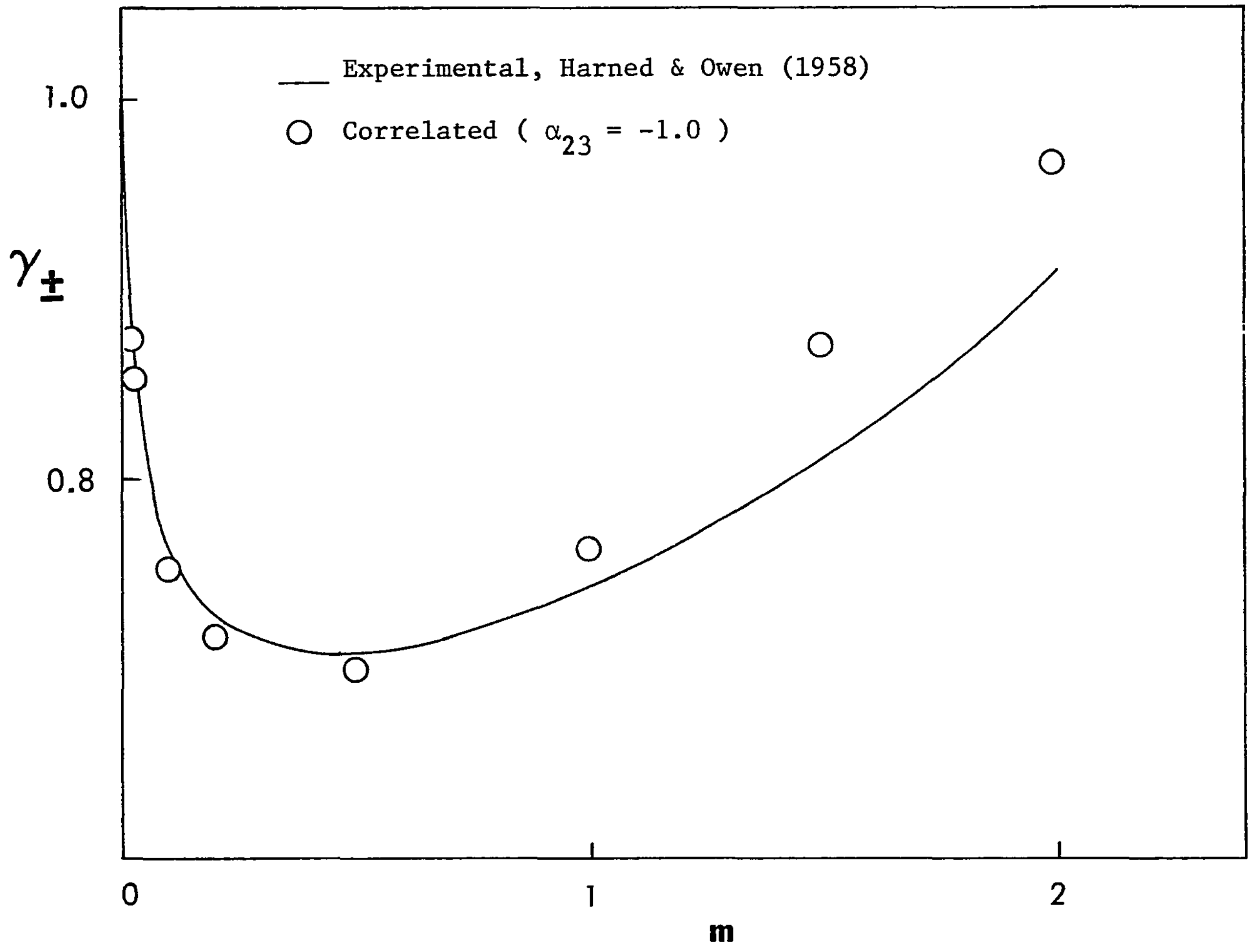


Figure H.14 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System HCl-$H_2O$-MeOH at 25°C and Constant $X'_{MeOH} = 0.1233$

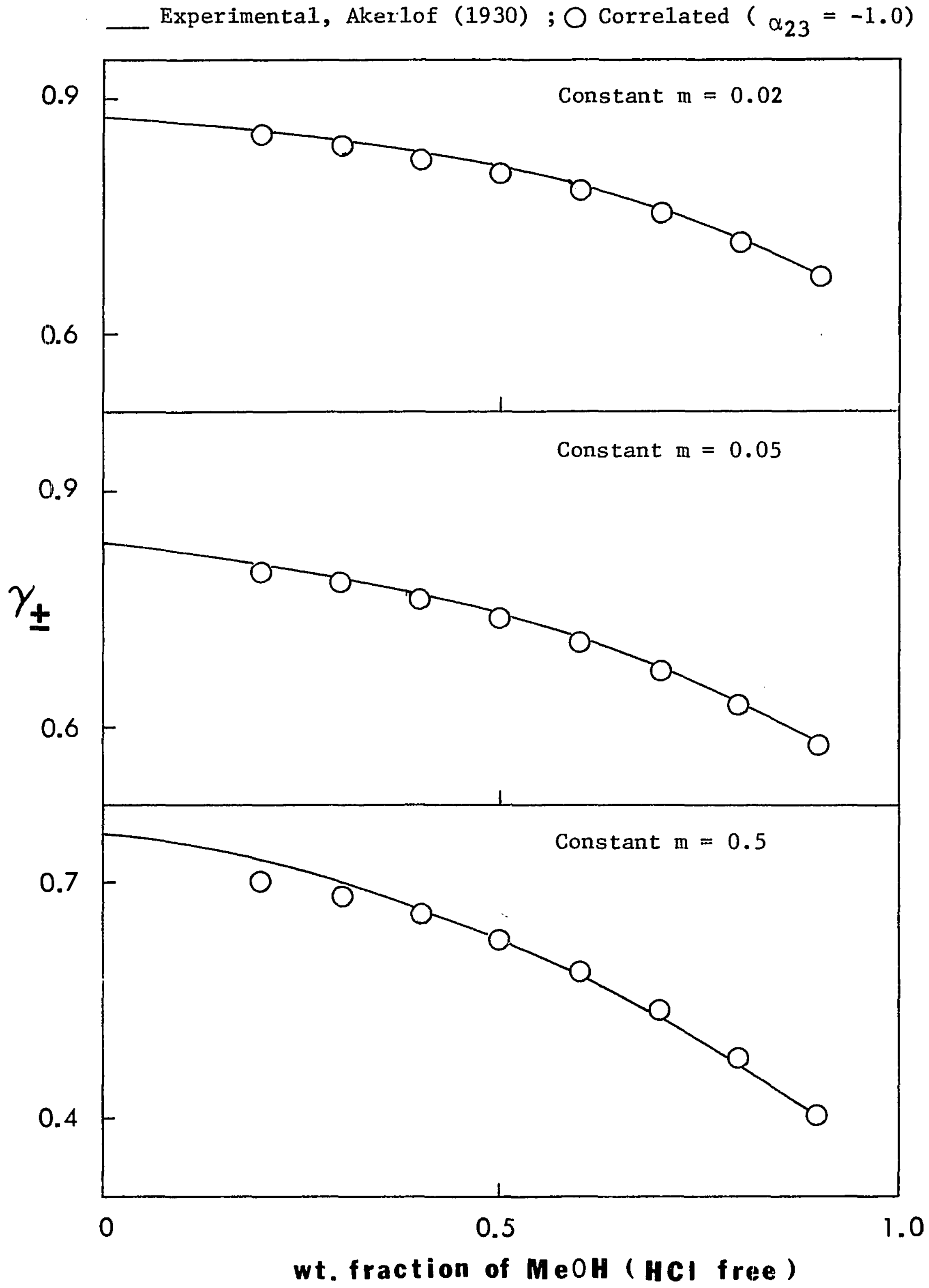


Figure H.15 Comparison of Experimental Mean Molal Activity Coefficients with Those Correlated by Model II for the System HCl-$H_2O$-MeOH at 25°C and Constant m = 0.02, 0.05, 0.5

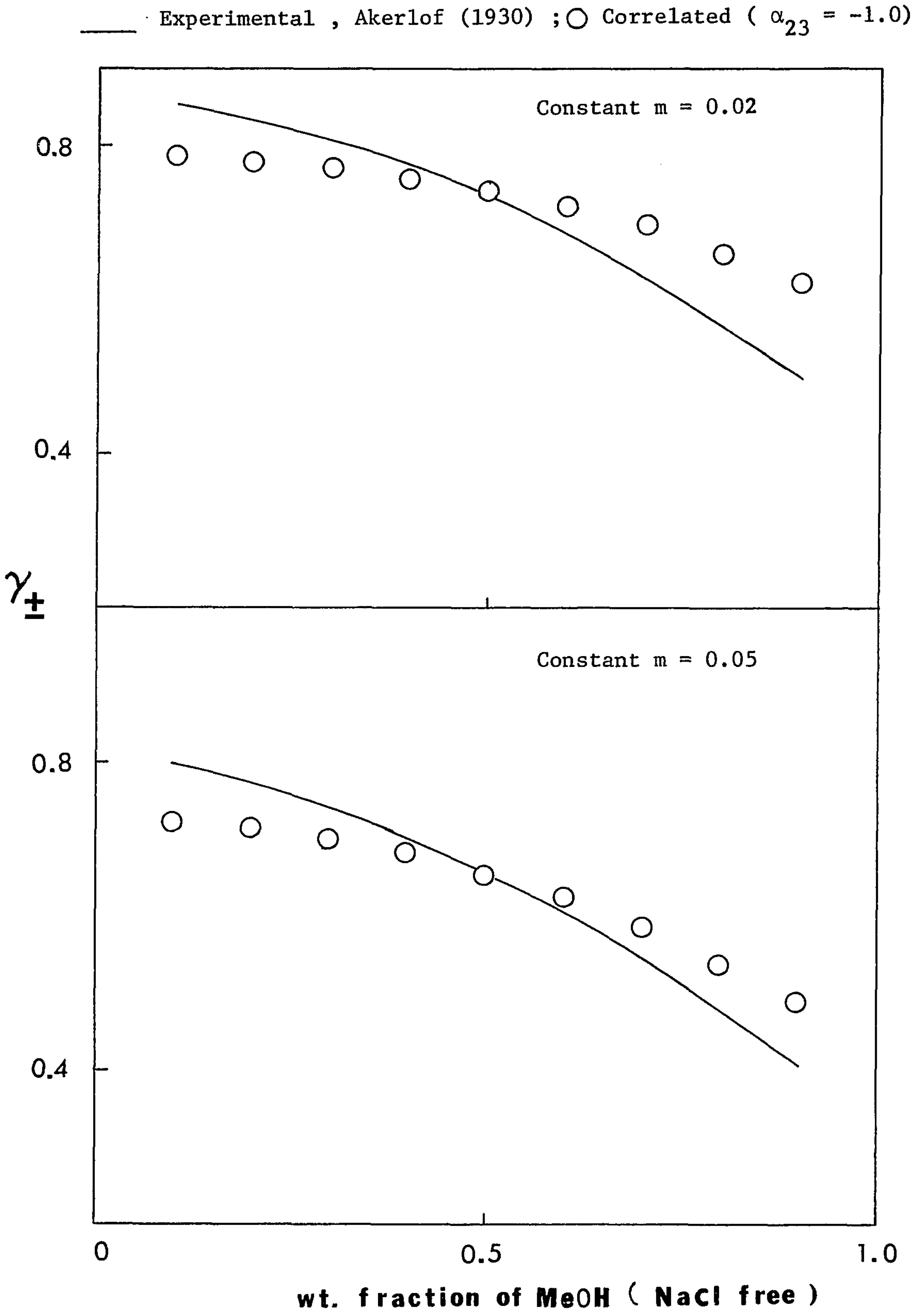


Figure H.16 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System NaCl-$H_2O$-MeOH at 25°C and Constant m = 0.02 and 0.05

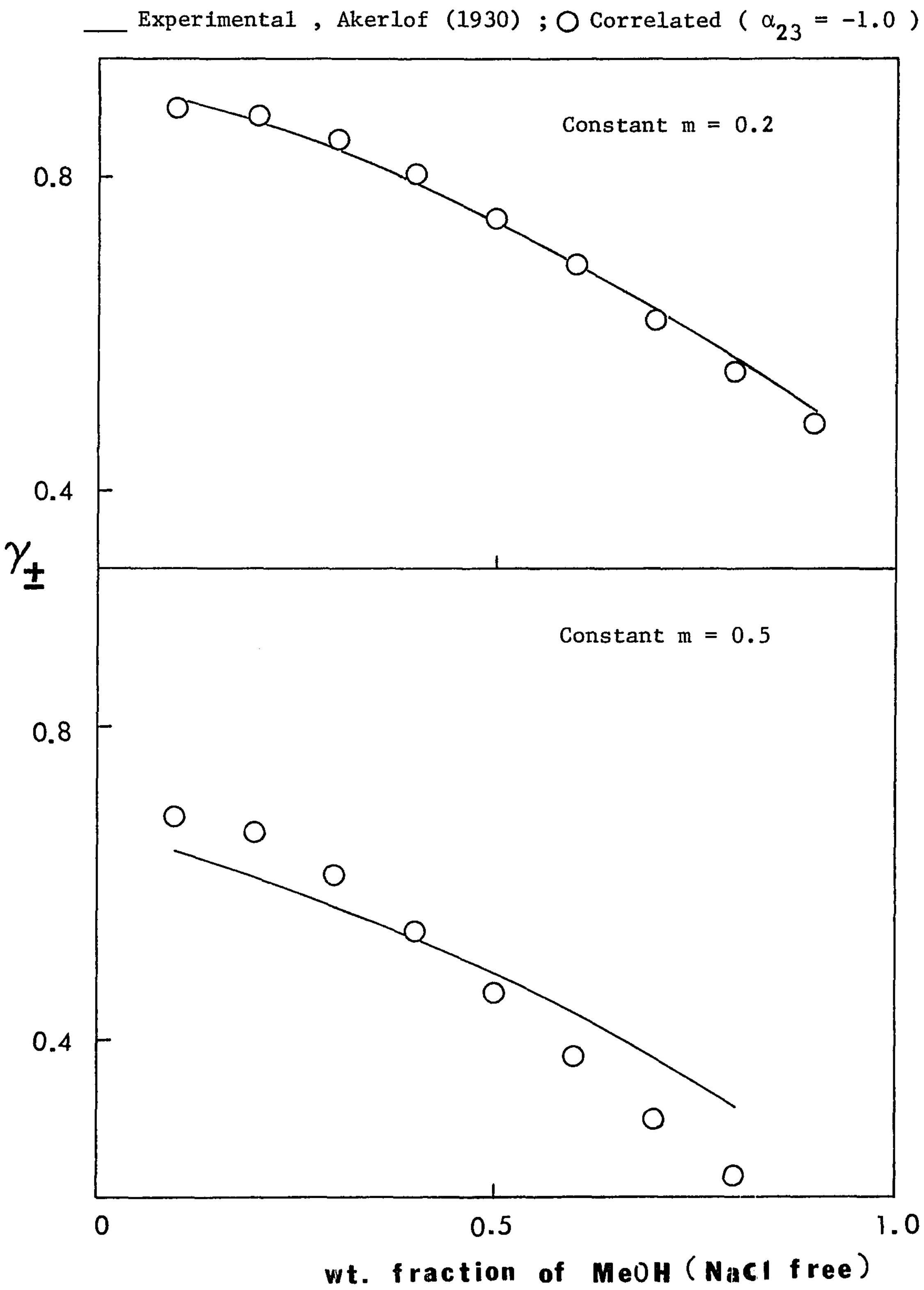


Figure H.17 Comparison of Experimental Mean Molal Activity Coefficients with those Correlated by Model II for the System NaCl-$H_2O$-MeOH at 25°C and Constant m = 0.2 , 0.5

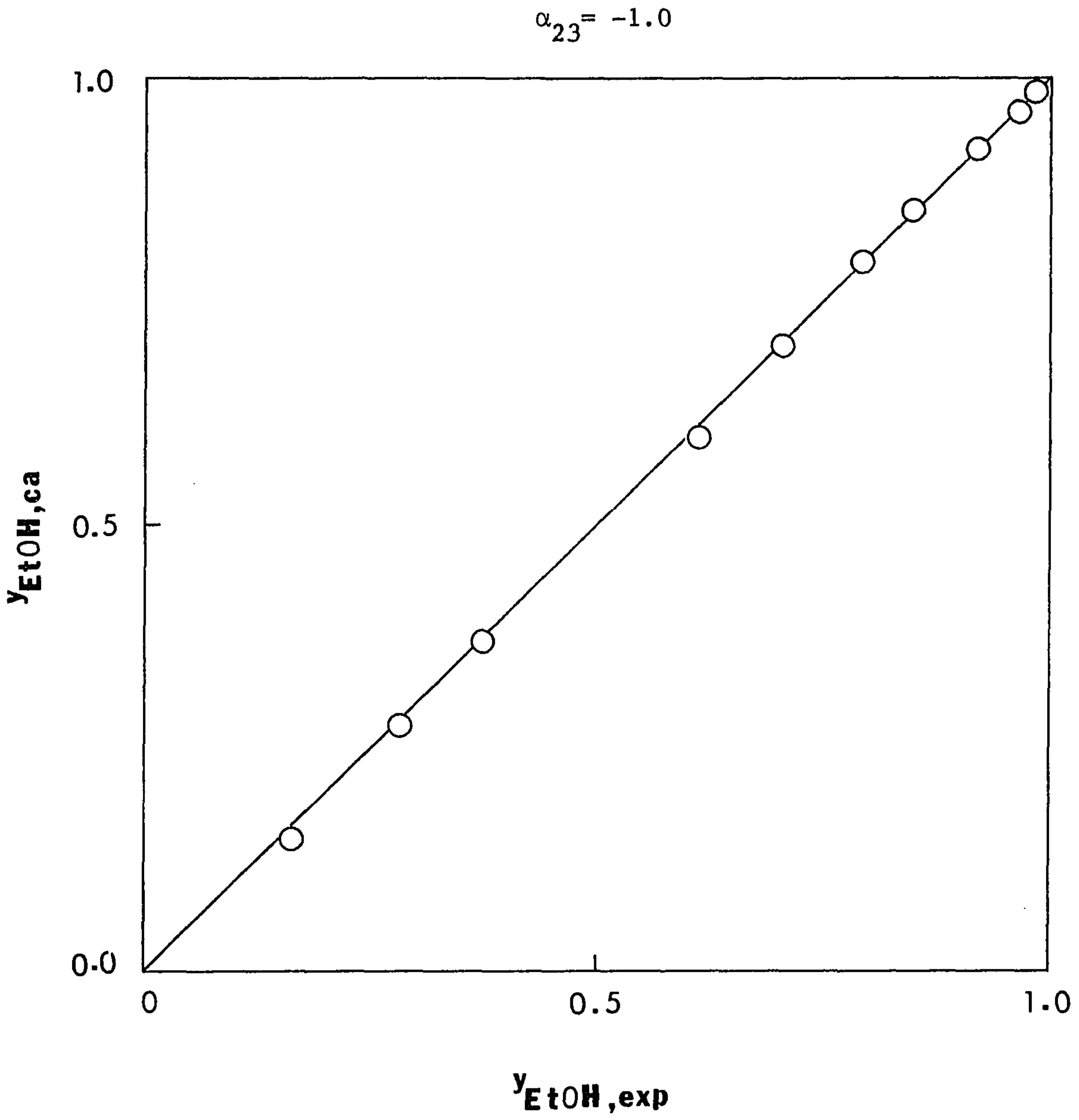


Figure H.18 Comparison of Experimental and Correlated Vapor-Phase Compositions Using Model II for the System LiCl-$H_2O$-EtOH at 25°C and Constant m = 0.5

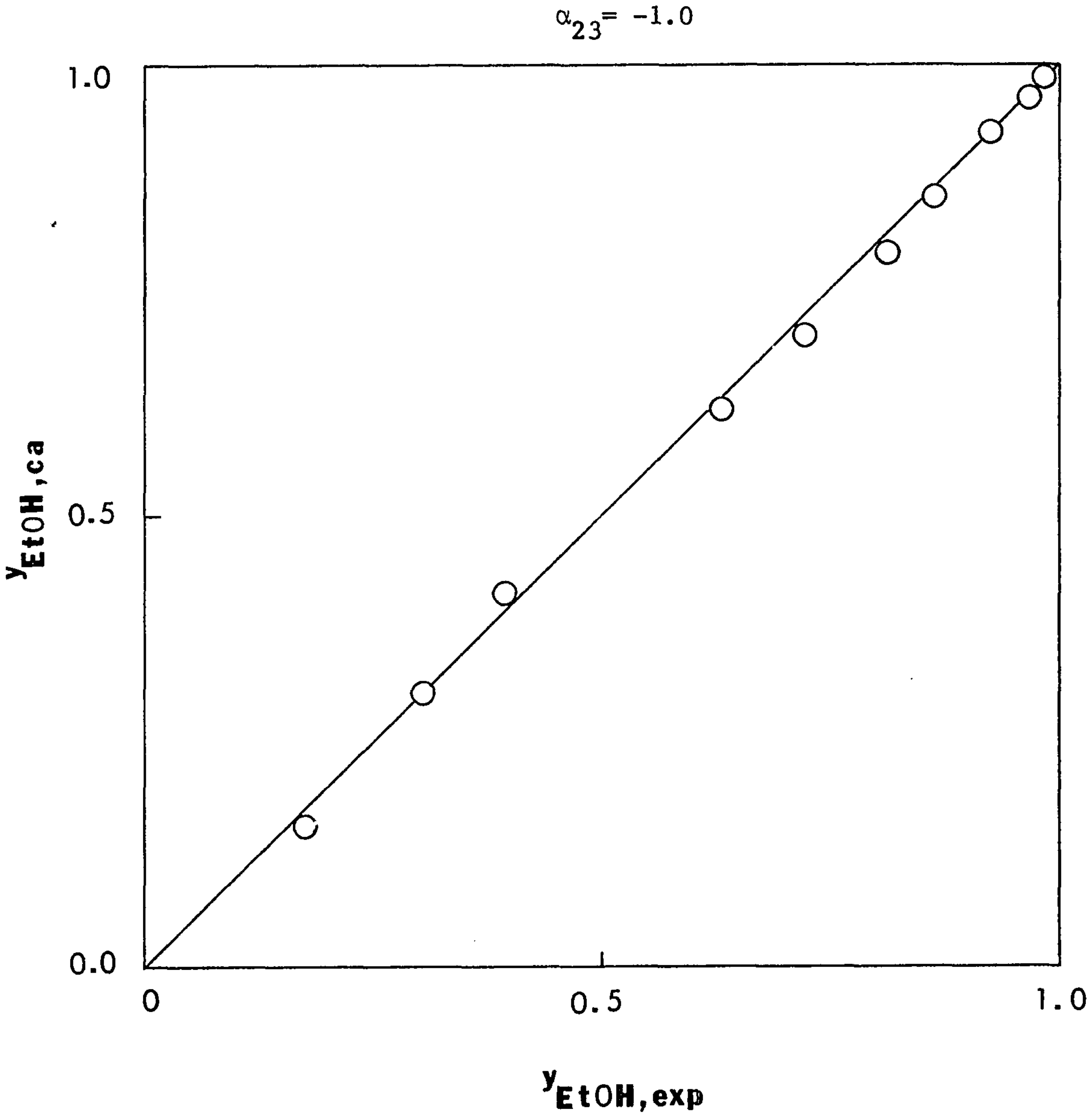


Figure H.19 Comparison of Experimental and Correlated Vapor-Phase Compositions Using Model II for the System LiCl-$H_2O$-EtOH at 25°C and Constant m = 1.0

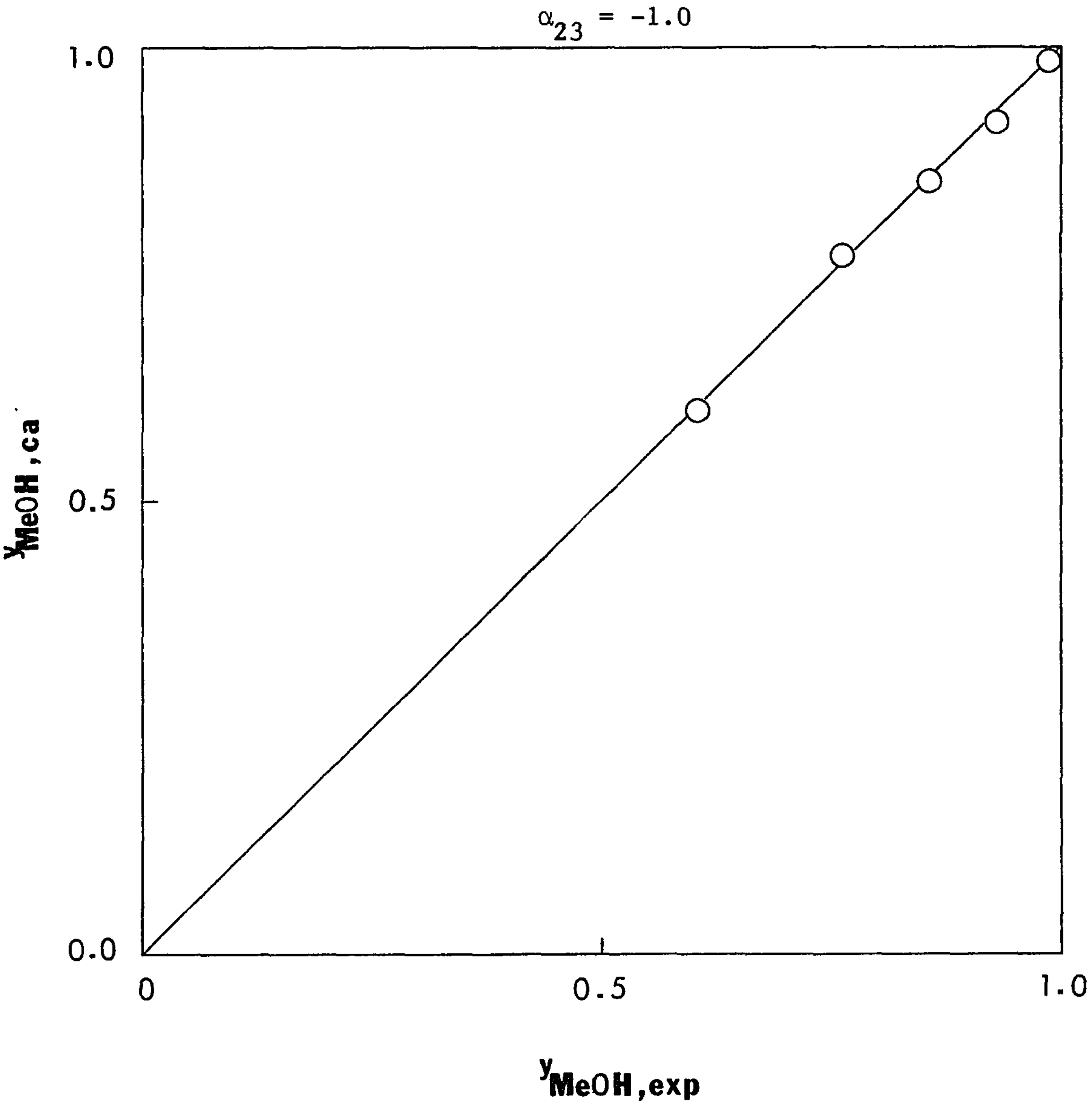


Figure H.20 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model II for the System LiCl-$H_2O$-MeOH at 25°C and Constant m = 1.0

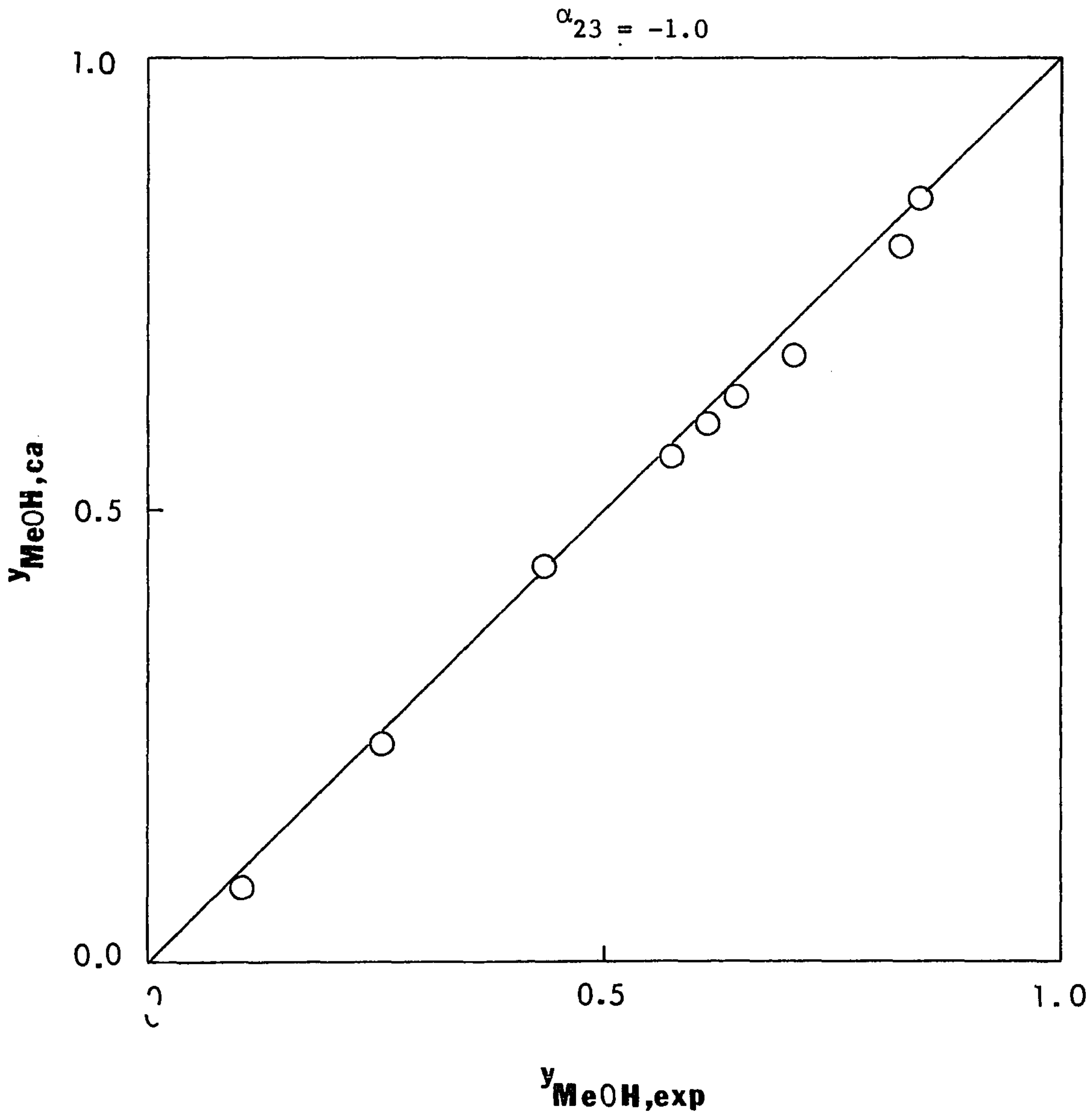


Figure H.21 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model II for the System LiCl-$H_2O$-MeOH at 60°C

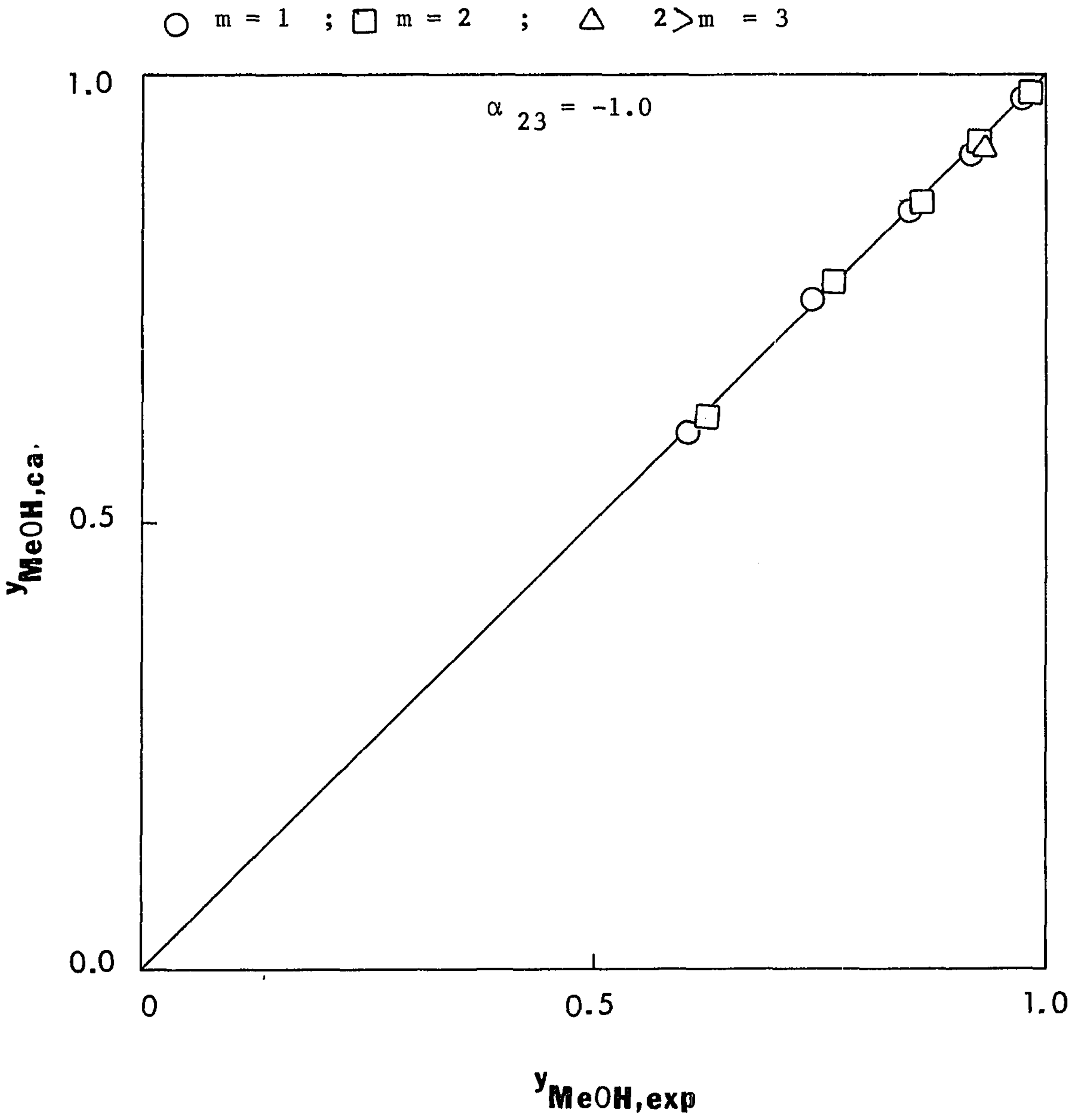


Figure H.22 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model II for the System NaBr-$H_2O$-MeOH at 25°C

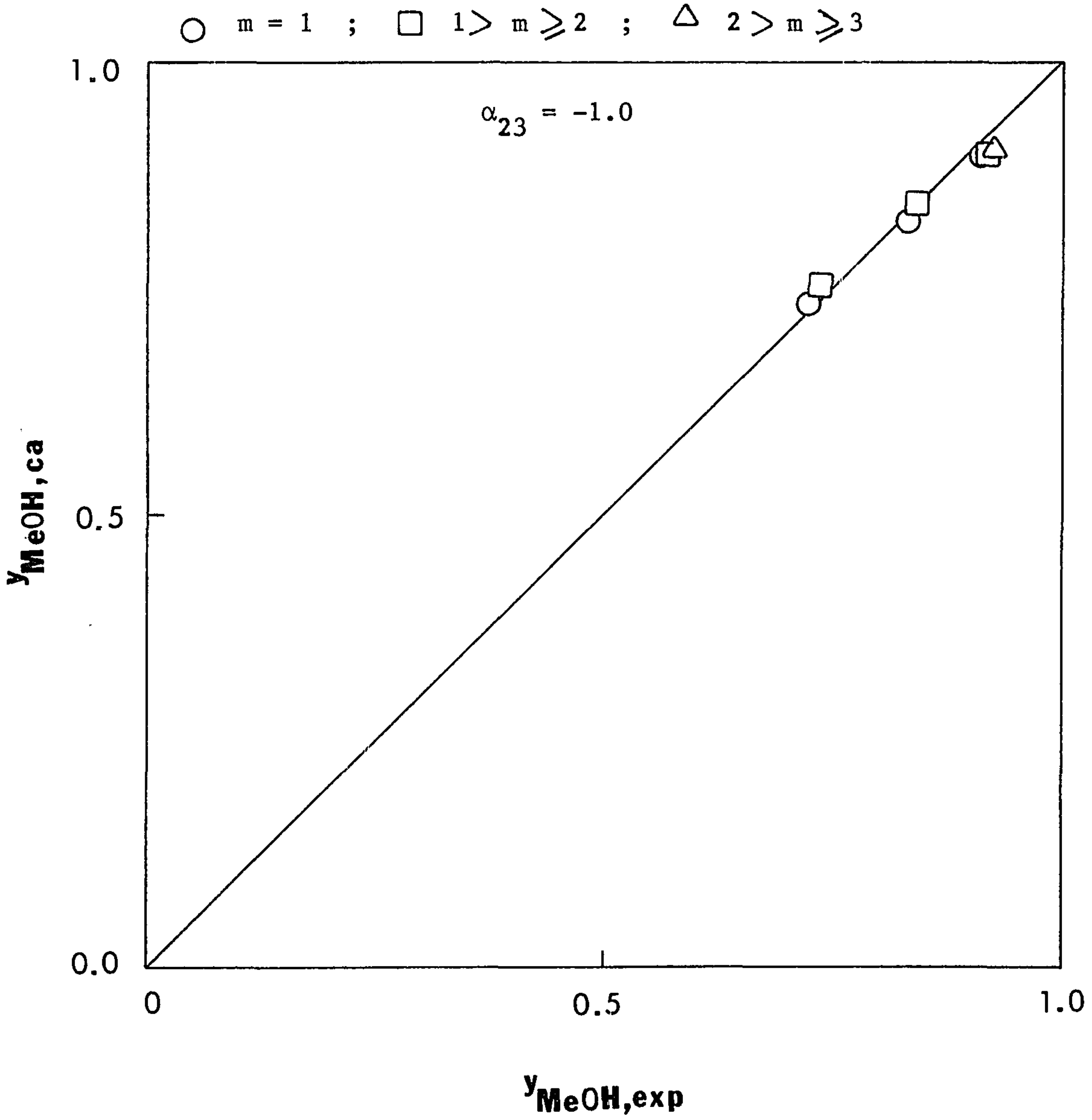


Figure H.23 Comparison of Experimental with Correlated Vapor-Phase Compositions Using Model II for the System NaBr-$H_2O$-MeOH at 40°C

# NOMENCLATURE

$\hat{a}_i$ - activity of solvent i

$A_\gamma$ - Debye-Hückel constant, $(\mathrm{Kg/g\ mole})^{1/2}$, Appendix-D

A - a constant used in equation (D-11)

$A_1, A_2, A_3, A_4, A_5, A_6$ - constants defined in equation (D-5)

$a_1, a_2, a_3, a_4, a_5, a_6$ - constants defined in equation (D-9)

$AD_1$ and $AD_2$ - constants defined in equation (D-10)

$a', b'$ and $c'$ - pure component liquid molar volume constants, equation (D-4)

$a_1^1$, $b_1^1$ and $c_1^1$ - constants used in equation (1-25)

$B_{1i}$ - binary 1-2 or 1-3 parameter in the Bromley Equation

$B_{ii}$ - second virial coefficient of component i, $\mathrm{cm^3/g\ mole}$

$B_{ij}$ - cross second virial coefficient, $\mathrm{cm^3/g\ mole}$

$B^*, B_1^1, B_2^1, B_3^1$ - constants defined in equation (3-18)

$B_{123}$ - ternary adjustable parameter in the Bromley Equation

c - molar concentration of the electrolyte, $\mathrm{g\ mole/cm^3}$ equation (A-4)

$c_1, c_2, c_3, c_4, c_5, c_6$ - pure component vapor pressure constants, equation (1-24)

$c^*, c_1^{11}, c_2^{11}, c_3^{11}$ - constants defined in equation (3-19)

d - density of the solvent/solvent mixture (electrolyte free), gm/cc

D - dielectric constant of the solvent/solvent mixture (electrolyte free)

$\hat{f}_i$ - fugacity of the component i, in the mixture

$F_i$ - a factor used in equation (1-10)

$g^E$ - molar excess Gibbs free energy, cal/g mole

$G^E$ - total excess Gibbs free energy, cal

$G_{ij}$ - binary 2-3 adjustable parameter, in equation (2-4)

$\Delta g_{ij}$ - temperature independent parameter in equation (2-4), cal/g mole

$G_{Ai}$ and $G_{Bi}$ - binary adjustable parameter, defined in equation (2-6)

$\Delta g_{Ai}$ and $\Delta g_{Bi}$ - binary adjustable temperature independent parameters, defined in equation (2-6), K joules/g mole

$G_{\pm i}$ - adjustable parameters for binary 1-2 or 1-3, in equation (2-5)

$H_1$ - Henry's constant, mmHg-Kg solvent/g mole

$I$ - ionic strength = $\frac{1}{2} \sum_k m_k z_k^2$, g mole/kg of solvent

$k$ - Boltzman constant, $1.38054 \times 10^{-23}$ J/K (molecules)

NP - total # of points in a system

$N_T$ - total # of moles of the solvent or solvent mixture (electrolyte free)

$m$ - molality of an electrolyte, g mole/Kg of solvent

$M_w$ - molecular weight of the solvent/solvent mixture, gm/g mole

$P$ - total pressure of the system, mmHg

$P_i^o$ - vapor pressure of the pure component i, mmHg

P.E. - poynting effect defined in equation (1-15)

$R$ - gas constant, 1.987 cal/g mole-°K

$R^1$ - gas constant, $8.314 \times 10^{-3}$ KJ/K-g mole

$T$ - temperature, °K

$V$ - molar volume, cc/g mole

$X_m$ - liquid-phase mole fraction of component m, defined in equations (1-22) and (1-23)

$X_i'$ - liquid-phase mole fraction of solvent i, electrolyte free

$Y_m$ - vapor-phase mole fraction of component m

$X, Y$ - defined in equation (3-15)

$Z_+ Z_-$ - valency of cation and anion, respectively

$Z_{ij}$ - binary 2-3 constant, defined in equation (2-4 )

$Z_{\pm i}, Z_{Ai}$ and $Z_{Bi}$ -binary parameters defined in equations (2-5) and (2-6), K Joules/g mole

## GREEK LETTERS

$\alpha_{23}$ - a constant used in equation (2-4) (= -1.0 or 0.2, 0.3, 0.47)

$\alpha_{Ai}$, $\alpha_{Bi}$ - constants defined in equation (2-6)

$\gamma_i$ - activity coefficient of solvent i

$\gamma_\pm$ - mean molal activity coefficient

$\gamma_\pm^*$ - mean molar activity coefficient

$\hat{\phi}_i$ - fugacity coefficient of the solvent i, in the mixture

$\phi_i^o$ - fugacity coefficient of the pure component i

$\phi$ - osmotic coefficient in a binary (1-2 or 1-3) mixture, as defined in equation (1-20)

$\sigma_1(\rho I^{1/2})$ - defined in equation (A-12)

$\psi_1(aI)$ - defined in equation (A-13)

$\sigma_1^1(\rho I^{1/2})$ - defined in equation (B-35)

$\psi_1^1(aI)$ - defined in equation (B-36)

$\sigma_2(\rho I^{1/2})$, $\psi_2(aI)$,
$\sigma_2^1(\rho I^{1/2})$ & $\psi_2^1(aI)$ - defined in equations (C-24) to (C-27), respectively

$\nu_A$, $\nu_B$ - number of cations and anions, respectively

$\nu$ - total number of ions (= $\nu_A + \nu_B$)

$\varepsilon$ - charge of an electron

$\delta_{123}$ - salting out ternary parameter, in equation (3-5)

$\delta_{23}$ - a constant in equation (E-7)

$\delta'$ - defined in equation (3-6)

$\omega$ - acentric factor

## SUPERSCRIPTS

o - pure component
L - liquid-phase
v - vapor-phase

## SUBSCRIPTS

1,2,3 - electrolyte, solvent 2 and solvent 3, respectively
A,B - cation and anion, respectively
C - critical property
Ca - calculated property
E - experimental
i,j - solvent 2 or 3
k - cation or anion
1i - binary 1-2 or 1-3
ij - solvent-solvent binary
123 - ternary 1-2-3
$\ell$,m,n - ions or electrolyte or solvent 2 or 3

# Selected Bibliography

Akerlöf, G., J. Am. Chem. Soc., 52, 2353 (1930).

Akerlöf, G., The Journal of the American Chemical Society, 54 (11), Nov. (1932).

Bakerman, E. and D. Tassios, American Chemical Society, National Meeting, Chicago, (1973).

Beutier, D. and H. Renon, Ind. Eng. Chem. Process Des. Dev., 17, 220, (1978).

Bixon, E. Raymond Gurrey, and Dimitrios Tassios, J. Chem. Eng. Data, 1, 24, (1979).

Bromley, L.A., J. Chem. Thermodynamics, 4, 669, (1972).

Bromley, L.A., AIChE Journal, vol. 19, No. 2, 313, March (1973).

Bromley, L.A., et al., AIChE Journal, vol. 20, No. 2, 326, March (1974).

Ciparis, J.N., Data of salt effects in vapor liquid equilibrium, Edition of Lithuanian Agricultural Academy, USSR, Kaunas, (1966).

Covington, A.K. and T. Dickinson, Physical Chemistry of Organic Solvent Systems, Plenum Press, London and New York (1973).

Cruz, L.L., and H. Renon; AIChE Journal, vol. 24, No. 5, Sept. (1978).

Davies, C.W., Ion Association, Butterworths, Washington (1962).

Debye, P. and E. Huckel; Physik. Z., 24, 185, 334 (1923); 25,97, (1924).

Edwards, T.J., J. Newman and J.M. Prausnitz, AIChE Journal, vol. 21, No. 2, 248, (1975).

Edwards, T.J., G. Maurer, and J. Newman, AIChE Journal, 24,966, (1978).

Evans, L.B., et al., Symposium on the Thermodynamics of Aqueous systems with Industrial Applications, Washington, D.C., Oct. 22, (1979); AIChE Journal (1979).

Gibbard, F.H., G. Scatchhard, Journal of Chemical and Engineering Data, vol. 19, No. 3, 281 (1974).

Gronwall, T.H., V.K. Lamer and K. Sandved, *Physic Z.*, 29, 358 (1928).

Gronwall, T.H., V.K. Lamer and L.J. Greiff, *J. Physical Chemistry*, 35, 2245 (1931).

Guggenheim, E.A. and J.C. Turgeon, *Phil. Mag.* 7, 11, 585, (1935).

Hala, E., Ind. Chem. E. Symposium Series, 32, 5, (1969).

Harned, H.S. and B.B. Owen, "The Physical Chemistry of Electrolytic Solutions," ACS Monograph Series No. 137, Third ed., Reinhold, New York (1958).

Janz, G.J., R.P.T. Tomkins, *"Non-Aqueous Electrolytes Handbook Vol. II*, Academic Press, N.Y. 1972.

Lewis, G.N., M. Randall, revised by Pitzer, K.S., L. Brewer, "*Thermodynamics*," 2nd edition, McGraw-Hill, N.Y. (1961).

Marina, J.M. and D.P. Tassios, *Ind. Eng. Chem.*, *Process Des. Dev.* 12, 67, (1973).

McGlashan, M.L. and A.G. Williamson, *Journal of Chemical and Engineering Data*, vol. 21, No. 2, (1976).

Mason, D.M. and R. Kao, Symposium on Thermodynamics of Aqueous Systems with Industrial Applications, Washington, D.C., Oct. 22, (1979).

Meissner, H.P. and C.L. Kusik, *AIChE Journal*, vol. 18, No. 2, 294, March (1972).

Meissner, H.P., C.L. Kusik and J.W. Tester, *AIChE Journal*, vol. 18, No. 3, 661, May (1972).

Ocon, J. and F. Rebolleda, *An. Real. Soc. Espan. defis. Y Quim*, 548 (7-8), 525 (1958).

Perry, R.H. and C.H. Chilton, "*Chemical Engineer's Handbook*," 5th ed., McGraw Hill Book Company, N.Y. (1973).

Pitzer, K.S., *The Journal of Physical Chemistry*, vol. 77, No. 2, 268 (1973).

Pitzer, K.S. and G. Mayorga, *The Journal of Physical Chemistry*, vol. 77, No. 19, 2300 (1973).

Pitzer, K.S. and G. Mayorga, *Journal of Solution Chemistry*, vol. 3, No. 7, 539 (1974).

Pitzer, K.S. and J.J. Kim, Journal of American Chemical Society, 96:18, 5701 Sept. (1974).

Pitzer, K.S., Accounts of Chemical Research, vol. 10, 371 (1977).

Pitzer, K.S., The conference on thermodynamics of Aqueous Systems with Industrial Applications, Washington, D.C., Oct. 22 (1979).

Prausnitz, et al., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," Monograph, Prentice-Hall, Inc., N.J. (1967).

Rastogi, A. and D. Tassios, Ind. Eng. Chem. Process Des. Dev., 19 (3), 477, July (1980).

Renon, H. and J.M. Prausnitz, AIChE Journal, 14, No. 1, 135, (1968).

Robinson, R.A. and R.H. Stokes, "Electrolyte Solutions," Butterworths, London, England (1955).

Rousseau, R.A., et al., AIChE Journal, vol. 18, No. 4, 825, July (1972).

Rousseau, R.A., et al., American Chemical Society, National Meeting, Chicago (1975).

Rousseau, R.A., et al., AIChE Journal, vol. 24, No. 4, 718, July (1978).

Skabichevskii, P.A., Russian Journal of Physical Chemistry, 43 (10), 1432, (1969).

Smith, J.M. and H.C. Vanness, "Introduction to Chemical Engineering Thermodynamics," Third ed., McGraw-Hill Book Company, N.Y., (1975).

Snipes, H.P., C. Manly, D.D. Ensor, Journal of Chemical and Engineering Data, vol. 20, No. 3, 287 (1975).

Taniguchi, H. and G.J. Janz, J. Phys. Chem., 61, 688, (1957).

Tomasula, P., "Osmotic and Mean Activity Coefficients of LiBr and LiCl in MeOH at 25, 35 and 45°C," M.S. Thesis, New Jersey Institute of Technology, New Jersey (1980).

Van Krevelen, D.W. and P.J. Hoftizer, Proc. of the 21st Cong., Inter. de chimie Industrielle, 21, 168, March (1948).

Van Krevelen, D.W., P.J. Hoftizer and F.J. Huntzens, Rec. Trav. Chim., Pays-Bas, 68, 191, (1949).

Waddington, T.C., "Non-Aqueous Solutions," Appleton-Century-Crafts, (1969).

Weast, R.C., Ed., "Handbook of Chemistry and Physics," The Chemical Rubber Co., Cleveland, Ohio (1969).