Density-Temperature Behavior of Pure And Defined Binary and Ternary Hydrocarbon Mixtures

by

Nasiru Mohammad Tukur

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

July, 1992

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Density-temperature behavior of pure and defined binary and ternary hydrocarbon mixtures

Tukur, Nasiru Mohammad, M.S.

King Fahd University of Petroleum and Minerals (Saudi Arabia), 1992

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

DENSITY-TEMPERATURE BEHAVIOR OF PURE AND DEFINED BINARY AND TERNARY HYDROCARBON MIXTURES

BY

NASIRU MOHAMMAD TUKUR

A Thesis Presented to the
FACULTY OF THE COLLEGE OF GRADUATE STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE
In

CHEMICAL ENGINEERING

JULY, 1992

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN 31261, SAUDI ARABIA

COLLEGE OF GRADUATE STUDIES

This thesis, written by

NASIRU MOHAMMAD TUKUR

under the direction of his Thesis Advisor, and approved by his Thesis Committee, has been presented to and accepted by the Dean, College of Graduate Studies, in partial fulfillment for the requirements for the degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Thesis Committee

Shafkat Ali Beg.

Chairman (Dr. Shafkat A. Beg)

Co-Chairman (Dr. Dulaihan K. Al-Harbi)

Esam Hamad

Member (Dr. Esam Hamad)

Mazen Shalabi

Dr. Mazen A. Shalabi
Department Chairman

Dr. Ala H. Al-Rabeh
Dean, College of Graduate Studies

Date : 6-7-92

ACKNOWLEDGEMENT

Acknowledgement is due to King Fahd University of Petroleum and Minerals for support of this research.

I wish to express my sincere gratitude and appreciation to my thesis supervisor Dr. Shafkat A. Beg for his invaluable support and guidance throughout the period of the research. I also wish to thank the other members of my Thesis Committee Dr. Dulaihan Al-Harbi and Dr. Esam Hamad for their constructive suggestions and analytical ideas which have contributed tremendously to the success of the thesis.

I also wish to acknowledge with deep appreciation, the cooperation and assistance extended to me by the Chairman of the Chemical Engineering department Dr. Mazen A. Shalabi during my stay in the department. I would also like to thank all the faculty in the Chemical Engineering Department for having learnt one thing or the other from them during the course of my studies at the King Fahd University of Petroleum and Minerals.

CONTENTS

CHAPTER Page

Acknowledgement iii
List of Tables vi
List of Figures viii
List of Symbols and Notations xi
Abstract xiii

1. INTRODUCTION 1

2. LITERATURE REVIEW 5

2.1 Experimental Studies 5

2.1.1 Pure Components 6
2.1.2 Defined Mixtures 7
2.1.3 Excess Volumes of Hydrocarbon Mixtures 11

2.2 Experimental Methods For Density Measurements 14

2.2.1 Hydrometers 14
2.2.2 Archimedean Bob Methods 16
2.2.3 Instruments Based on Direct Mass Volume Measurements 20
2.2.4 Other Methods 21

2.3 Theoretical Studies 23

2.3.1 Pure Liquids 23
2.3.2 Defined Mixtures 31

2.4 Effect of Pressure - Isothermal Compressibility 33

2.5 Statistical Mechanics And Computer Simulation 36

2.5.1 The N-Body System 41
2.5.2 The Lennard-Jones Potential 41

2.5.3 Macroscopic Properties From Computer Simulation 44

3. EXPERIMENTAL SET-UP AND PROCEDURE 46

3.1 Principle of The Density Measurements 46
3.2 Details of The Experimental Set-up 48
3.3 Procedure For Density Measurements 52
3.4 Calibration of Density Cells 54

4. RESULTS AND DISCUSSIONS 55

4.1 Calibration of Density Cells 55
4.2 Density-Temperature Behavior of The Pure Components And Their Mixtures 61

4.2.1 Density-Temperature Behavior of The Pure Components 61
4.2.2 Density-Temperature Behavior of The Binary Mixtures 66
4.2.3 Density-Temperature Behavior of The Ternary Mixtures 84

4.3 Excess Molar Volumes of The Binary Mixtures 92

4.3.1 Benzene - Cyclohexane Mixture 100
4.3.2 Benzene - n-Hexane Mixture 106
4.3.3 Cyclohexane - n-Hexane Mixture 108

4.4 Computer Simulation Results 113

5. SUMMARY AND CONCLUSIONS 134

6. RECOMMENDATIONS 137

REFERENCES 138

Appendix A 149

Appendix B 191

Appendix C 193

LIST OF TABLES

Table Page

2.1 Summary of Evaluation of Correlations With Low Temperature Hydrocarbon Data 29

4.1 Thermodynamic Properties of Benzene 56

4.2 Thermodynamic Properties of Cyclohexane 57

4.3 Thermodynamic Properties of n-Hexane 58

4.4 Comparison of Water Density Data Using The Proposed System And Literature Values 60

4.5 Comparison of The Experimental Density at 298.15K of Benzene, Cyclohexane and n-Hexane With Reported Experimental Data 67

4.6 Comparison of The Experimental Density of Benzene, Cyclohexane and n-Hexane With Predictions From Spencer-Danner Modified Rackett Equation (SDR) and The Hankinson-Brobst-Thompson (HBT) Correlation 68

4.7 Comparison of The Experimental Density Data of The Mixture of Benzene - Cyclohexane With Predictions From Spencer-Danner Modified Rackett Equation (SDR) and The Hankinson-Brobst-Thompson (HBT) Correlation 72

4.8 Comparison of The Experimental Density Data of The Mixture of Benzene - n-Hexane With Predictions From Spencer-Danner Modified Rackett Equation (SDR) and The Hankinson-Brobst-Thompson (HBT) Correlation 78

4.9 Comparison of The Experimental Density Data of The Mixture of Cyclohexane - n-Hexane With Predictions From Spencer-Danner Modified Rackett Equation (SDR) and The Hankinson-Brobst-Thompson (HBT) Correlation 83

4.10 Comparison of The Experimental Density Data of The Mixture of Benzene - Cyclohexane - n-Hexane With Predictions From Spencer-Danner Modified Rackett Equation (SDR) and The Hankinson-Brobst-Thompson (HBT) Correlation 93

4.11 Coefficients of The 3-constants Redlich-Kister Equation And The Deviation of The Excess Volume From The Correlation For A System of Benzene - Cyclohexane 104

4.12 Coefficients of Equations 4.3, 4.4 and 4.5 Evaluated From Linear Regression For The System of of Benzene - Cyclohexane 107

4.13 Coefficients of The 3-constants Redlich-Kister Equation And The Deviation of The Excess Volume From The Correlation For A System of Benzene - n-Hexane 109

4.14 Coefficients of Equations 4.3, 4.4 and 4.5 Evaluated From Linear Regression For The System of of Benzene - n-Hexane 111

4.15 Coefficients of The 3-constants Redlich-Kister Equation And The Deviation of The Excess Volume From The Correlation For A System of Cyclohexane - n-Hexane 114

4.16 Coefficients of Equations 4.3, 4.4 and 4.5 Evaluated From Linear Regression For The System of Cyclohexane - n-Hexane 116

4.17 Lennard-Jones Force Constants For Benzene, Cyclohexane And n-Hexane 117

4.18 Computer Simulation Results For The Density of Benzene As a Function of Temperature (298.15K to 473.15K) 121

4.19 Computer Simulation Results For The Density of Cyclohexane As a Function of Temperature (298.15K to 473.15K) 123

4.20 Computer Simulation Results For The Density of n-Hexane As a Function of Temperature (298.15K to 473.15K) 125

4.21 Comparison of The Experimental Density of of Benzene With The Results Obtained From Computer Simulation 127

4.22 Comparison of The Experimental Density of of Cyclohexane With The Results Obtained From Computer Simulation 128

4.23 Comparison of The Experimental Density of of n-Hexane With The Results Obtained From Computer Simulation 129

LIST OF FIGURES

Figure Page

2.1 Two Methods of Molecular Simulation 39

2.2 Lennard-Jones Potential 43

3.1 Schematic Diagram of Experimental Set-Up For Density Measurements 47

3.2 Schematic Diagram of Single Unit For Density Measurements 49

3.3 Schematic Diagram of Pycnometer Assembly 50

4.1 Calibration Data For The Volume of Density Cells As A Function of Temperature 59

4.2 Experimental Density - Temperature Data For Benzene 62

4.3 Experimental Density - Temperature Data For Cyclohexane 63

4.4 Experimental Density - Temperature Data For n-Hexane 64

4.5 Experimental Density - Temperature Data For Cyclohexane, n-Hexane And Benzene 65

4.6 Comparison Between Experimental Density Data of Benzene, Cyclohexane and n-Hexane, And Predictions By SDR And HBT 69

4.7 Experimental Density - Temperature Data For Defined Benzene - Cyclohexane Mixtures 71

4.8 Comparison Between Experimental Density Data And Predictions By SDR And HBT For The Mixtures of Benzene - Cyclohexane 73

4.9 Comparison Between Experimental Density Data And Predictions By SDR And HBT For The Mixtures of Benzene - Cyclohexane 74

4.10 Comparison Between Experimental Density Data And Predictions By SDR And HBT For The Mixtures of Benzene - Cyclohexane 75

4.11 Experimental Density - Temperature Data For Defined Benzene - n-Hexane Mixtures 76

4.12 Comparison Between Experimental Density Data And Predictions By SDR And HBT For The Mixtures of Benzene - n-Hexane 79

4.13 Comparison Between Experimental Density Data And Predictions By SDR And HBT For The Mixtures of Benzene - n-Hexane 80

4.14 Comparison Between Experimental Density Data And Predictions By SDR And HBT For The Mixtures of Benzene - n-Hexane 81

4.15 Experimental Density - Temperature Data For Defined Cyclohexane - n-Hexane Mixtures 82

4.16 Comparison Between Experimental Density Data And Predictions By SDR And HBT For The Mixtures of Cyclohexane - n-Hexane 85

4.17 Comparison Between Experimental Density Data And Predictions By SDR And HBT For The Mixtures of Cyclohexane - n-Hexane 86

4.18 Comparison Between Experimental Density Data And Predictions By SDR And HBT For The Mixtures of Cyclohexane - n-Hexane 87

4.19 Experimental Density - Temperature Data For The Ternary Mixtures of Benzene - Cyclohexane - n-Hexane 88

4.20 Experimental Density - Temperature Data For The Ternary Mixtures of Benzene - Cyclohexane - n-Hexane 89

4.21 Experimental Density - Temperature Data For The Ternary Mixtures of Benzene - Cyclohexane - n-Hexane 90

4.22 Comparison of Experimental Density Data With Predictions By SDR And HBT For Benzene - Cyclohexane - n-Hexane 95

4.23 Comparison of Experimental Density Data With Predictions By SDR And HBT For Benzene - Cyclohexane - n-Hexane 96

4.24 Comparison of Experimental Density Data With Predictions By SDR And HBT For Benzene - Cyclohexane - n-Hexane 97

4.25 Comparison of Experimental Density Data With Predictions By SDR And HBT For Benzene - Cyclohexane - n-Hexane 98

4.26 Comparison of Experimental Density Data With Predictions By SDR And HBT For Benzene - Cyclohexane - n-Hexane 99

4.27 Plot of Excess Volumes For Defined Binary Mixtures of Benzene - Cyclohexane 101

4.28 Plot of Excess Volumes For Defined Binary Mixtures of Benzene - n-Hexane 102

4.29 Plot of Excess Volumes For Defined Binary Mixtures of Cyclohexane - n-Hexane 103

4.30 Comparison of Experimental Density Data With Simulation Results For Benzene 130

4.31 Comparison of Experimental Density Data With Simulation Results For Cyclohexane 131

4.32 Comparison of Experimental Density Data With Simulation Results For n-Hexane 132

LIST OF SYMBOLS AND NOTATIONS

a	Constant in BWR equation of state
b	Constant in BWR equation of state
c	Constant in BWR equation of state
A_o	Constant in BWR equation of state
B_o	Constant in BWR equation of state
n	number of components in a mixture
N	number of components in simulation program
R	Universal gas constant
X	mole fraction of pure component
V	Liquid Specific Volume
P	Pressure
T	Temperature
HBT	Hankinson - Brobst - Thompson's Equation
SDR	Spencer - Danner Modified Rackett Equation
Z	Compressibility factor
Z_{RA}	Empirical parameter in modified Rackett equation
V_{sc}	Scaling volume defined by Gunn-Yamada
V_r^o	Parameter in Hankinson-Brobst-Thompson correlation
V^*	Parameter in Hankinson-Brobst-Thompson correlation
V_r^δ	Parameter in Hankinson-Brobst-Thompson correlation

Subscript

c	critical property
i	ith component in a mixture
m	mixture property
r	reduced property
s	saturated liquid property

Greek Symbol

α	constant in BWR equation of state
ψ	constant in BWR equation of state
ω	acentric facor
τ	Parameter in Gunn-Yamada correlation
ρ	Density

THESIS ABSTRACT

NAME OF STUDENT	: Nasiru Mohammad Tukur
TITLE OF STUDY	: Density - temperature Behavior of Pure and Defined Binary and Ternary Hydrocarbon Mixtures
MAJOR FIELD	: Chemical Engineering
DATE OF DEGREE	: June, 1992

Densities of the pure compounds of Benzene, Cyclohexane and n-Hexane as well as the densities of their binary and ternary mixtures have been measured using an experimental system whose accuracy and reliability have been previously established. The density measurements were carried out over a wide range of temperatures (ambient to 200°C) and concentrations. The experimental data were compared with predictions by two renowned correlations; the Hankinson-Brobst-Thompson correlation (HBT) and the Spencer-Danner modified Rackett (SDR) equation. The two correlations appear to be quite satisfactory in predicting the saturated liquid density of the pure and liquid mixtures considered. The SDR predicts the experimental results with an overall average absolute deviation (AAD%) of 0.29%, while the HBT has an AAD% of 0.61%.

The excess molar volumes, V^E for the binary liquid mixtures of benzene and cyclohexane, benzene and n-hexane, and cyclohexane and n-hexane from ambient to 200°C, were calculated from the density data. Values of the V^E, for the three systems have been correlated, first as function of concentration using a 3-constant Redlich-Kister expansion;

$$V^E = X(1-X)[A + B(1-2X) + C(1-2X)^2]$$

And secondly, as a function of temperature by expressing the coefficients in the Redlich-Kister expansion in terms of temperature. Values of V^E have been found to be positive for benzene and cyclohexane and benzene and n-hexane mixtures. For cyclohexane and n-hexane, the values of V^E have been found to change from positive to negative with increasing temperature.

The use of the Lennard-Jones potential to predict the density of benzene, cyclohexane and n-hexane through the use of molecular simulation was also investigated. The densities of benzene and n-hexane were predicted with a reasonable degree of accuracy, while the predictions made for cyclohexane involved considerable errors.

MASTER OF SCIENCE DEGREE

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS

Dhahran , Saudi Arabia

June 1992

خلاصة الرسالة

إسم الطالب الكامل : ناصر محمد تكر
عنوان الدراسة : تأثير الحرارة على كثافة بعض المركبات العضوية ومخاليطها الثنائية والثلاثية .
التخصص : الهندسة الكيميائية
تاريخ الشهادة : يونيو ١٩٩٢م

في هذا البحث تم قياس كثافة المركبات النقية لكل من البنزين - الهكسان الحلقي ، والهكسان بالإضافة إلى المركبات الثنائية والثلاثية المشتقة من المركبات النقية وقد أستعمل جهاز ذو دقة معلومة . أجريت قياسات الكثافة في مدى درجة حرارة من درجة حرارة الغرفة إلى ٢٠٠°م ودرجات تركيز مختلفة . أجريت مقارنة النتائج العملية مع تنبؤات علاقات ذات شهرة : علاقة هانكنسون - بروبست - تومسون (HBT) وعلاقة سبنسر - دانار المطورة من راكت (SDR) . وقد ظهر أن العلاقتين تبدوان في غاية الإرضاء في التنبؤ بكثافة السائل المشبع لكل المركبات النقية وخليطها الذي تم بحثه . علاقة (SDR) .

تتنبأ بالنتائج العملية بمتوسط إنحراف كلي (AAD) ٠ر٢٩٪ ، مع أن علاقة (HBT) لها (AAD) يساوي ٠ر٦١٪ .

تم حساب الحجم المولي الزائد (V^5) للخليط الثنائي لكل من البنزين والهكسان في مدى درجة الحرارة المذكورة أعلاه والهكسان الحلقي + الهكسان في مدى درجة الحرارة المذكورة أعلاه تم وضع علامة (V^5) للمركبات الثلاثة أعلاه كدالة في التركيز بإستعمال علاقة ريدلخ - كستر (Redlich - Kister) ذات الثوابت الثلاثة وهي :

$$V^E = x\,(1-x)\,[\,A + B\,(1-2x) + C\,(1-2x)^2]\,.$$

ومرة ثانية كدالة في درجة الحرارة وذلك بالتعبير عن الثوابت الثلاثة في العلاقة أعلاه بدلالة الحرارة . وجد أن قيمة (V^5) موجبة لكل من خليط البنزين والهكسان الحلقي وخليط البنزين والهكسان . كما وجد أن قيمة (V^5) لخليط الهكسان الحلقي والهكسان تتغير من الموجب إلى السالب بزيادة الحرارة .

تمت دراسة إستعمال المحاكاة الجزئية للتنبؤ بالكثافة وذلك بإستعمال جهد لينارد - جونز (Lennard - Jones) لكل من البنزين, الهكسان الحلقي والهكسان . تم التنبؤ بكثافة البنزين والهكسان بدرجة دقة معقولة . بينما وجد أن النتائج للهكسان الحلقي تضمنت بعض الأخطاء .

درجة الماجستير في العلوم
جامعة الملك فهد للبترول والمعادن
قسم الهندسة الكيميائية
الظهران ، المملكة العربية السعودية

CHAPTER 1

INTRODUCTION

Accurate and reliable data on the density of fluids and fluid mixtures play an important role in a variety of engineering problems. In modern industrial calculations, flow of heat and flow of mass are becoming extremely important in the design of almost every piece of process equipment in Chemical, Petrochemical and Petroleum refining and other related processes. If such calculations are to be reliable, it is essential to have accurate data on density of liquids at temperatures at which the calculations are to be made. In practice these temperatures are far above the range at which the density measurements are normally made.

Crude oils and crude oil products are complex mixtures of hydrocarbons plus organic compounds of sulfur, oxygen and nitrogen as well as compounds containing metallic constituents particularly vanadium, nickel, iron and copper. The hydrocarbon content may be as high as 97%, as; for example, in the lighter paraffinic petroleums, or as low as 50% or less as illustrated by heavier asphaltic crude oils. Nevertheless, crude oils with as little as 50% hydrocarbon compounds are still assumed to retain most of the essential characteristics of the hydrocarbons since the nonhydrocarbon portion of the crude may actually consist of molecules containing one or, perhaps, two atoms of elements other than carbon and hydrogen.

Further, it has been well established that hydrocarbon components of petroleum are composed of paraffinic, naphthenic and aromatic groups. Olefinic groups are not usually found in crude oils and acetylenic hydrocarbons are very rare indeed. It is convenient, therefore, to divide the hydrocarbon components of petroleum into paraffins, naphthenes and aromatics alone.

In order to obtain an insight into the overall density-temperature behavior of petroleum, it is therefore essential to study the role of each group of such compounds. However, studies on the density- -temperature behavior of mixtures of selected representive paraffinic, naphthenic and aromatic compounds with wide range of variation in their properties may be used to simulate petroleum. The effect of individual hydrocarbon group on the overall density - temperature behavior of petroleum can then be ascertained. Such studies may provide far more insight into the density-temperature behavior of the petroleum crude compared to studies on petroleum products alone.

Most of the data on liquid viscosity is available in terms of Kinematic viscosity. In order to obtain the absolute viscosity, density data is required at the desired temperature. Kinematic viscosity data have been obtained for various pure and defined hydrocarbons but there is an absence of reliable experimental density-temperature data. If such data are made available, it will not only be possible to obtain absolute viscosities for such systems but an attempt can also be made to obtain reliable generalized absolute viscosity - temperature correlations as well.

Liquid density can be studied by experiments, macroscopic correlations and molecular theory or computer simulation. Survey of literature reveals that liquid density determination can be classified into three; densities of pure liquids, densities of defined mixtures and densities of undefined mixtures. And a considerable amount of density data for these systems can be found scattered in the literature. However, the probability of finding an approximate value of density decreases as the molecular complexity of the material increases and/or as the condition shifts to extremes of temperatures or pressures.

Hale [1] prepared a bibliography of reported fluid densities for over 1000 pure substances. Experimental information on defined mixtures is also available. The data for multi-component systems involving more than three components is quite meager. However, in all these reported densities of fluid and fluid mixtures the range of temperature considered has been very limited. This is primarily as a result of the difficulty of keeping the test sample in liquid state at high temperatures. Saeed [2] discussed in details the limitations of the existing density measuring devices, both in terms of operations and accuracies.

The present study has been initiated with the following objectives :

a) To obtain reliable experimental data of the density of selected representatives of the three main groups of petroleum ; Benzene (aromatic), Cyclohexane(naphthene) and n-hexane(paraffin) over a wide range of temperature (ambient to 200°C).

b) To measure the experimental densities of the binary and ternary mixtures of above mentioned compounds from ambient to 200°C.

c) To investigate the effect of the individual hydrocarbon group on the overall density - temperature behavior of the simulated petroleum mixture.

d) To present a comprehensive survey of literature of the methods available for predicting the density of pure and defined liquid mixtures which may provide a basis for the development of a generalized correlation.

e) To develop a generalized correlations for estimating the density-temperature behavior of pure and defined hydrocarbon mixtures.

f) To investigate the use of Lennard-Jones potential to predict the density-temperature behavior of the selected pure and defined hydrocarbon mixtures through the use of computer molecular simulation (MD technique).

g) To compare the simulation and theoretical results with the experimentally obtained values.

CHAPTER 2

LITERATURE REVIEW

Densities of liquids can be studied by experiments, theoretical correlations and molecular theory or computer simulation. Survey of literature reveals that density determination can be classified into; densities of pure liquids, densities of defined mixtures and the densities of undefined mixtures.

2.1 EXPERIMENTAL STUDIES

A considerable amount of density experimental data have been reported for both pure and defined mixtures. However, the range of temperature considered has been very limited. This is primarily as a result of the difficulty of keeping the test sample in liquid state at high temperatures. The limitations of the existing density measuring devices, both in terms of operations and accuracies are discussed in details later in this chapter.

Saeed [2] developed a system for measuring the saturated liquid densities of undefined petroleum fractions over a wide range of temperatures from ambient to 230°C and pressures up to 1800psia. The investigators established the high accuracy and reliability of the system by comparing their representative measurements with measurements made with most accurate devices that can operate at low temperatures. Only a maximum difference of 0.17% between these two measurements was noticed.

In the literature, most investigators have only reported their experimental density measurements for pure and defined mixtures, Others attempted to generalize their experimental results by fitting an equation of state. Some of the available literature in this field is reviewed in this section.

2.1.1 Pure Components

Baghdoyan et al. [3] measured the densities of two olefinic hydrocarbons, 2,3-dimethyl-2-butene and 3,3-dimethyl-1-butene. Measurements were made over the temperature range of 20°C to 50°C at 5°C interval. Excellent agreement of data was given with that reported in the literature. Each set of data for the two compounds was fitted to a second degree polynomial to present the experimental data.

Dawson et al. [4] determined the density of 2,2-dimethylpropane over the temperature range of 70°C to 225°C at 5°C interval using the beattle method. High accuracy was reported in obtaining the the experimental data. An empirical polynomial equation was used to represent the experimental data.

Abraham et al. [5] measured the densities of isoamyl alcohol and benzyl alcohol at 25°C and between $30-70$°C at 10°C intervals with a modified Robertson pycnometer. The accuracy of the density measurements was reported to be ± 0.00005 g/m^3 or better. The authors fitted each set of their data to a second degree polynomial. Comparison of their data with that reported in the literature was satisfactory.

Mclure et al. [6] measured the density of purified samples of 2-butoxyethanol from 20 to 60°C by densimetry and pycnometry. The results were well described by a a second order polynomial equation with a standard deviation of ±0.00003 g/m^3.

Murieta-Guevara and Rodriguez [7] measured the liquid densities of pure samples of monoethanolamine, diethanolamine, sulfolane, N-methylpyrrolidone, and propylene carbonate at several temperatures ranging from 10 to 60°C. The experimental data as a function temperature were data fitted to a second order polynomial equation.

Tardajos et al. [8] measured the liquid densities of pure samples of n-hexane, 1-hexene, 1-hexyne, cyclohexane, cyclopentane, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, benzene, bicyclohexyl, cyclohexylbenzene and tetralin at 25°C. Comparison of their values with those reported in the literature was found to be satisfactory.

Serrano et al. [9] determined the densities, viscosities and refractive index of the pure chemicals of p-xylene, m-xylene, o-xylene and benzene at 25°C and their values agree within the experimental error with the literature values.

Banipal, Garg and Ahluwalia [10] measured the densities of liquid n-octane, n-nonane, n-decane, and n-hexadecane at temperatures from 45 to 100°C and at pressures up to 10MPa using a vibrating-tube densimeter. The results were compared with experimental literature values.

2.1.2 Defined Mixtures

Experimental density measurements for defined mixtures have been extensively reported in the literature.

Ahlert and Shimalla [11] measured the densities of the binary system of hydrazine-methylhydrazine from 30°C to 90°C The authors used an empirical equation to represent the experimental data for the binary mixture.

Sunni & Hutchinson [12] measured the densities of seven binary liquid systems at atmospheric pressure and at temperature ranging from 25°C to 60°C The systems studied included benzene-chloroform and cyclohexane-tetrachloromethane etc. . All reported data were claimed to be accurate within experimental error.

Kahre [13] obtained the liquid density data for the binary systems of ethane-propane. propane-isobutane, propane - n-butane and butane -isobutane at saturation pressure and temperature range between 15.6°C to 54.4°C

Sinka [14] measured the density of the binary mixture of monofluoro-monochloromethane & tetrafluoro-dichloroethane over the temperature range of -68°C to 32°C. Experimental density data was fitted to an empirical equation of Martin & Hou with standard deviation of 0.00025 and average percentage deviation of 0.015.

Mikhail & Kimel [15] measured the densities of methanol-water mixtures at 25°C ,30°C ,35°C ,40°C and 50°C and covered the entire range of composition. An empirical equation which has the form of a power series was used to represent the experimental data. Comparison of the experimental data in this study with that reported in the international critical tables was in good agreement.

Sivaramprasad [16] measured the densities of the binary mixtures of ethanol - 1, 2- dichloroethane, ethanol - 1, 1, 1- trichloroethane and ethanol - 1, 1, 2 ,2 -dichloroethane in the temperature range of 303 to 333K. The mixture density data agree with the values predicted from the law of additive volumes rearrange for convenience as :

$$\rho_m = \frac{\rho_1 \rho_2}{\rho_1 x_1 + \rho_2 x_2} \tag{2.1}$$

Serrano et al. [9] measured the density of binary & ternary liquid systems containing Xylenes for temperature range between 273.15 and 303.15K over the complete concentration ranges. Experimental densities were compared with those predicted by the Hankinson - Brobst - Thomson method, which showed an average deviation of about 0.3 percent.

Joshi, Aminabhavi and Balundgi [17] measured the densities and viscosities of binary liquid mixtures of nitrobenzene with cyclohexane and N,N,-dimethylformamide in the temperature range of 298K-313K. Excess volume, excess viscosity, excess free energy of activation of flow and contact parameter were computed for binary mixtures and the calculated quantities were discussed in terms of the nature of the molecular interactions between the components.

Popaloannou et al. [18] measured the densities of binary liquid mixtures of 2-propanane - 2, 2, 4 -trimethylpentane and n-heptane - ethanol. Excess volumes, isothermal compressibilities and thermal expansion coefficient were computed for the binary mixtures. The calculated properties were compared with the available data.

Yamamoto and Tokunaga [19] measured the densities of binary liquid mixtures of NH_4Br-NH_3 and NH_4I-NH_3 over a wide range of temperatures and concentrations. The observed densities were expressed as a function of temperature and concentration by means of polynomial equations. The temperature range considered was from 0 to 76.5°C and the accuracy of the measurements was ±0.1 percent.

Marchetti et al. [20] reported the densities of the binary mixture of 1,2-ethanediol and 2-methoxyethanol in the whole composition range at 19 temperatures between -10 and +80°C. The excess volumes calculated from the density data were found to be negative at all concentrations and become more negative with increasing temperature.

Jangkamolkulchal et al. [21] reported the densities of methyl tert -butyl ether (MTBE) and ethyl tert-butyl ether (ETBE) from -17.75 to 60.05°C, at pressures up to 8.3bar, and the densities and excess volumes of the binary mixture of 2,2,4-trimethylpentane - (MTBE or ETBE) at 15.55°C and atmospheric pressure.

Papanastasiou and Ziogas [22] determined the densities, viscosities, dielectric constants, and refractive indexes for ethanol-cyclohexane mixtures at 15°C, 20°C, 25°C, 30°C, 35°C and over the whole composition range. These properties were represented by means of empirical relations involving compositions and temperatures. The equations were found to fit the experimental data with an uncertainty of the same order of magnitude as involved in the experimental measurements.

Chevalier, Petrino and Gaston-Bonhomme [23] measured the densities and kinematic viscosities of 68 linear, branched, cyclic and aromatic hydrocarbons binary liquid systems at 25°C over the entire composition range. The data of the pure components were found to compare well with corresponding values reported in the literature.

Wel and Rowley [24] measured the liquid densities and viscosities of 24 binary systems as a function of composition at 25°C and ambient pressure. The data for the pure components have only a standard deviation of 0.0001 when compared with the literature values.

Krishnaiah and Viswanath [25] determined the density and viscosity of the binary mixtures of isopropyl acetate with cyclohexane at 25°C and 35°C over the entire range of composition. The derived excess volumes were found to be positive at both temperatures.

2.1.3 Excess Volumes of Hydrocarbon Mixtures

Whenever pure hydrocarbon components are mixed with one another, there exist a difference between the volume formed compared with the straight addition of the volume of the individual mixing components. This difference is what is referred to as excess volumes. It indicates the existence of nonidealities in the mixture, which results due to the unlike to unlike interactions between the mixing solvents.

Excess properties in general and excess volume in particular of binary systems are of considerable interest in understanding the existence of specific interactions such as dispersion , dipolar or or induction forces and hydrogen bonding interactions and others. Molar excess volumes can be measured using batch dilatometers or can be obtained from density measurements. A number of excess volumes measurements have been reported in the literature and below is a selective review of the available literature.

Kaur, Samra and Mahl [26] measured the excess volumes of the binary mixtures of n-propanol, n-butanol, n-pentanol, and n-hexanol with n-octane, n-decane, and n-dodecane at 25°C. The molar excess volumes of the mixtures were attributed to a balance between chemical, physical, and structural effects.

Bravo, Pintos and Amigo [27] determined the excess molar volumes of five liquid binary mixtures at 25°C from density measurements. The excess volumes obtained were fitted to a variable-degree polynomials expressing the results as a function of mole fraction. The possibilities of predicting excess molar volumes of the ternary mixtures using those of the binary mixtures were also analyzed.

Pickerell and Charles [28] reported the excess volumes measurements for the benzene - 1,1,2-trichloroethylene system at 10 and 40°C and atmospheric pressure. The excess volumes were positive, decreasing with temperature, and exhibited maxima at approximately 59.1 mol % benzene. The data were correlated by generalized equations.

Dernini, Anna and Pier [29] determined by means of a vibrating-tube densimeter the molar excess volumes of the binary liquid mixtures of cycloalkanones (cyclohexanone and cyclopentanone) individually with cyclohexane, benzene and tetrechloromethane. The data were reported over the complete mole fraction range at 15°C, 25°C and 35°C. An equation was used to express the dependence of the molar excess volume on composition.

Tanaka, Masami and Sachio [30] determined from density measurements the excess volumes of the binary mixtures of benzene individually with cyclopentane, methylcyclohexane and cyclooctane at 20°C, 25°C and 30°C. Each set of results was fitted to a polynomial equation and the values of the coefficients and the standard deviations were obtained.

Nath and Atma [31] measured the excess volumes of the binary liquid mixtures of acetone, toluene, p-xylene, and mesitylene at 25°C and 35°C using a dilatometer. The values of the excess volumes were found to be positive for some systems and negative for others.

Naidu and Ramachandra [32] measured the excess volumes of ternary mixtures containing methyl ethyl ketone, 1-alkanols, and an alkane using a dilatometer at 30°C. The experimental data for the ternary mixtures were found to give positive over the whole range of composition in all the systems.

Goates, Ott and Grigg [33] obtained the excess volumes of the binary mixtures of cyclohexane individually with n-hexane, n-heptane, n-octane, n-nonane, and n-decane at three temperatures 10°C, 25°C and 40°C using vibrating tube densimeter. The excess volume was found to increase regularly with increasing size of the alkyl group of the hydrocarbon.

Letcher, T. M. [34] carried out excess volume measurements of all the binary mixtures of benzene, cyclohexane, n-hexane, cyclohexene, and hex-1-ene over the whole composition range at 25°C using a glass-partition dilatometer.

Diaz Pena and Nunez [35] obtained the excess volumes of nine binary mixtures formed from benzene with n-hexane, n-octane, d-decane, n-dodecane, n-tetradecane, n-hexadecane, n-octadecane, n-eicosane, and n-docosane at 50°C, as a function of composition, by dilatometric method.

Weeks and Benson [36] determined the excess volume of cyclohexane - benzene mixture by means of a magnetic float densimeter at 25°C, and the results were compared with previous dilatometric measurements.

2.2 EXPERIMENTAL METHODS FOR DENSITY MEASUREMENTS

Density is defined as the mass per unit volume and is expressed in units as kg/m^3, lb/in^3, lb/ft^3, g/cm^3 and g/ml. The specific gravity on the other hand is the ratio of the mass of a given volume to the mass of an equal volume of water at 4°C or other specified temperature. Both density and specific gravity are temperature dependent. There are different methods available for laboratory or spot reading of density. These available methods can be divided into different groups as follows:

i) Hydrometers
ii) Archimedean Bob methods
iii) Instruments based on direct mass/volume measurements
iv) Other methods.

2.2.1 Hydrometers

The buoyancy of a body, totally immersed in a liquid suggests the basis for this method. A body immersed in liquid tends to be buoyed up or supported by a force equal to the weight of liquid it displaces. This weight is the product of the displaced volume (V) and the density (ρ) of the liquid. The buoyancy force is equal to this product and if the value of (V) remains substantially constant due to the body being totally immersed, the force will vary almost directly with the density of the liquid.

The hydrometer involves a weighed float to which a thin stem carrying a graduated scale is attached. The float sinks to a depth dependent on the buoyancy force and hence to the density or specific gravity of the liquid. The reading on the stem scale to which it is immersed then becomes a measure of the specific gravity [37].

2.2.1.1 Glass Hydrometer

This instrument is a weighted glass float carrying a scale and proportioned so that some part of the scale is submerged according to the specific gravity of the liquid in which it is floated. The reading is taken at the surface of the liquid and the accuracy is affected slightly by the meniscus. The ratio of weight to buoyancy is determined by the range required and the scale graduated in specific gravity units. Sometimes it is calibrated in arbitrary units considered more convenient for a particular application. An error is introduced by the surface tension which prevents the hydrometer sinking to the position it would occupy in the absence of surface tension. [37]

2.2.1.2 Bates Hydrometer

Bates hydrometers operate on same principle as glass hydrometer but modified to reduce the risk of breakage and arranged so that the weight can be varied and hence the range may be altered to avoid the necessity of having a large number of instruments. It is made of metal. The float is constructed from thin walled tube, while the weight is of solid metal and is threaded so that it can be removed when necessary. The scale is also of solid metal rod and marked arbitrarily. A factor is applied for readings according to the weight being used [37].

2.2.1.3 Sikes Hydrometers

This instrument is mainly used by brewers and distillers for the determination of alcoholic content. It consists of a gilded brass bulb, about 1.5 in. diameter, at the top of which is fixed a thin rectangular scale and the bottom accommodates fixed weight [37].

2.2.2 Archimedean Bob Methods

There are different types of density measuring equipment available which operate according to this principle. A solid object of known volume is completely immersed in the sample fluid through a suspension wire and the loss of weight (Δw) of the bob is related to the density of the liquid as:

$$\rho = \Delta w/V \qquad (2.2)$$

For measurement of density by Archimedes bob method, it is necessary that the volume (V) of the immersed body be accurately known. Usually the volumes of bob are determined from its buoyancy in several liquids of known density.

The various models developed on this principle only differ in the way the bob is suspended in the liquid and in the method used for weighing [38].

2.2.2.1 Westphal Gravity Balance

In this method, a glass plummet is suspended in air and the balance is brought in equilibrium to obtain the weight of the plummet and the suspension wire. Then the sample is taken in a cylinder and the plummet is suspended completely in the liquid and the weight recorded again. The loss of weight is related to the density of the liquid sample. This instrument is not capable of measurements at elevated temperature and pressure [37].

2.2.2.2 Archimedean Bob

This is a modified version of the method mentioned above and can be used for density determinations at temperatures above ambient. A set of samples in small tubes are placed in a constant temperature bath. After the thermal equilibrium is established one sample tube is transferred to the weighing position and elevated till the plummet is completely immersed in the liquid. Balance readings are recorded for plummet before and after immersion in the liquid. The balance is scaled in density unit g/ml and can obtain density within 0.00001 g/ml. The scale range is 0.65-0.95 g/ml for the version approved by API RP6-96 [39]. White and Soloman [40] modified the Archimedean bob method to enable measurements of densities at higher pressures.

Nissen and Macmillan [38] have described an oscillating plate method for viscosity determination at high temperatures where the damping of the plate motion is recorded through a "Linear Variable Differential Transformer"

(LVDT). Some modifications of this method have also been used for density measurements if the plate is replaced by a suitable Archimedean bob. The reading of LVDT are recorded and converted to weight for the bob, with and without the liquid sample. The apparatus can be used at temperature as high as 400°C and is suitable for molten salts. The experimental accuracy is about ±0.006 g/cm^3. If the density data is to be collected for different temperatures the bob volume should be corrected for the corresponding temperature. The whole apparatus described is micro-processor controlled for maintaining temperature and storage of the data.

2.2.2.3 Magnetically Levitated Bob

Beams and Clark [41] used a method where a float made of magnetically soft material was placed in a small cell containing the liquid sample. The cell was then placed in a set up where the bob was raised by an external solenoid (electromagnet). The height of the bob in the sample was fixed by observing through a microscope. The amount of current required to raise the bob was related to the buoyancy and hence to the density of the liquid. The main advantage of this and other similar magnetic suspension methods is that a very little amount of sample is required. Beams and Clark [41] have also described a modification of the system discussed above where all force measurements have been reduced to simple weighing operations.

Hales [42] has described a system for density measurement based on Beams and Clark [41] idea of using magnetic float. The float is levitated magnetically and the balance readings are taken before and after the suspension of the float.

The apparatus is designed for the temperature range 20 to 150°C and pressures up to 700 kN/m^2. Sample cell is heated by hot air circulating which has to be stopped when observations are made. It was observed that at temperatures above 100°C the bath did not maintain constant temperature when air was switched off. The distilled water was used for calibration purposes.

Hales and Townsend [43] measured liquid densities of nine aromatic hydrocarbons in the range 293°K to 490°K. The apparatus they used was a slight modification of the set-up described by Hales [42] The cell was placed in a copper well which was kept in an oil bath instead of air circulation system mentioned earlier. The float was made of silica instead of glass because leaching of glass was observed in water at high temperatures during calibration with water. Similar system was used to determine liquid densities of aliphatic alcohols in the same range of temperature [44] The accuracy of the results for aromatic and aliphatic compounds was considered to be ±0.15Kg/m^3. It was also noted that the densities at temperature above the upper limit 490°K. could not be estimated reliably.

Hales and Gundry [45] in a further modification of the magnetically levitated system extended the upper limit of temperature to nearly 700°K. Sample cell was heated in duralumin block electrically where the temperature could be kept within ±0.01°K for long periods. Since the bob was no more visible, its vertical position was sensed by means of searching coils. Different designs of magnetic float were used and the system was tested for benzene and propanol. Results obtained were consistent but did not match others reported in literature. The authors admitted that their technique suffered difficulties and failed. However, the experimental results were self-consistent and reproducible and it was suspected that the calibration of the float volume encountered unsuspected difficulties.

2.2.3 Instruments Based on Direct Mass/Volume Measurements

2.2.3.1 Pycnometer

This instrument is based on direct measurement of volume and mass of the samples under study. It consists of a calibrated bulb or cylinder connected to a capillary of uniform and preferably fine bore where the liquid sample could expand on heating. Both bulb and expansion tube require careful calibration. Provisions are also provided for high pressure and isothermal conditions. In theory the system is straight forward. The sample of liquid of known mass is introduced into the calibrated cylinder and the level in the capillary is recorded at different temperatures of interest to determine the volume at operating conditions.

Several types of pycnometer are in use depending upon the type of samples and the temperature and pressure of interest. The densities of phenols and chloro-nitrobenzenes were determined [46] with a Lipkin type pycnometer. The level of liquid in a tube was measured with travelling microscope. The tubes were calibrated using double distilled water with an overall accuracy of the density data of $\pm 0.0001 g/cm^3$.

Densities of carbon tetrafluoride were measured [47] from 90°K to 150°K.

using cylindrical copper vessel equipped with thermocouple. The copper cylinder was fitted with a borosilicate glass capillary tube of known internal diameter (approximately 0.1 cm^3 volume). Glass capillary was graduated which could be visually read outside the constant temperature bath. The liquid level in the tube gave the change in volume of the liquid in the pycnometer. The density data obtained for pure compounds and defined mixtures have been reported using pycnometers [48 & 49].

Some other systems have also been described in literature where sample is heated over a column of mercury called "mercury piston" [50]. The amount of mercury displaced is a measure of liquid expanded. In such methods corrections have to be applied for the mercury expansion with increasing temperature. Mercury piston densimeter have been used for high pressure application as well.

2.2.4 Other Methods

For pure liquids and defined mixtures, density at 20°C and 25°C at ambient pressure has been determined using specific gravity bottles. These bottles are normally made of glass and the calibrated volume is given at one temperature. The bottle is weighed with and without sample and density can be conveniently determined [12 & 40].

Isadale, Dymond and Brawn [51] have used acoustic technique to measure densities of n-hexane-cyclopropane mixtures. Digital density meters which are based on measuring the change of the natural frequency of hollow oscillator when filled with different liquid samples have also been used.

All the systems discussed above have been successfully used for liquid density determinations. However, methods based on magnetic float, hydrometers, pycnometers and dilatometer etc. require careful calibration with some liquids. The accuracy of these instruments depend upon how well and how long the temperature and pressures can be maintained and also on the uncertainties in density of calibrating liquids. The density measurements by almost any instrument is susceptible to errors, and the choice of the system is made according to specific application and accuracy requirement. However, it may be noted that hydrometers can be used only at ambient conditions and the density measurements are affected by changes in the surface tension of the liquid sample at different operating temperatures and the type of sample. In magnetic systems, the float is visually spotted and raised to a fixed height. Therefore, for opaque liquids it is difficult if not impossible to position the float up to the specified height. This leads to considerable more errors in measurements. The residual magnetism in the float necessitates the need for frequent calibrations of the system. Since in most cases of magnetically levitated bob systems hot air is circulated for heating the sample, the circulation has to be suspended when the observation is being made. This may lead to errors due to temperature variations.

Crude oil and it fractions from initial boiling point (IBP) to residue appear from clear water like material to opaque viscous liquid. Magnetically levitated bob method whose application is more suited to transparent liquids can not obviously be considered for accurate application to crude fractions, as some of them are opaque viscous liquids. Pycnometers made of glass are also not suitable for most crude oil fractions at high temperatures due to their high volatility. For high pressure applications both glass pycnometers and dilatometers are also unsuitable.

2.3 THEORETICAL STUDIES

Since it is virtually impossible to collect and tabulate density data for every hydrocarbon compound or pure defined mixtures and undefined mixtures that may be encountered in industry, the need for accurate prediction method is therefore inevitable. Through the development of science of thermodynamics, problems of estimating density and other thermodynamic properties have been simplified and only some experimental information is required to calculate these properties.

There are quite a number of techniques available for estimating pure liquid specific volumes or densities. Most of the methods involve equations based on some form of the law of corresponding states. This law states that the properties of fluids depend on intermolecular forces and are related to the critical properties in the same way for all compounds.

In this section, several well-established correlations for pure liquids and their mixtures will be reviewed as well as the respective mixing rules proposed.

2.3.1 Pure liquids

The Benedict-Webb-Rubin [52] equation of state has been found to be applicable to the data of some liquids.

$$P = RT\rho + (B_0RT - A_0 - \frac{C_0}{T^2})\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{C}{T^2}\rho^2(1 + \psi\rho^2)\exp(-\psi\rho^2)$$

(2.3)

Where A_o,B_o,C_o , a, b, c, α and ψ are constants and usually determined from pure-component volumetric data.

The liquid density at saturated pressure, ρ can be estimated from a reference density, ρ_{ref} , through the Watson relationship [53]:

$$\rho = \rho_r \left(\frac{\rho_{ref}}{\rho_{r,ref}}\right) \tag{2.4}$$

The reduced densities at system temperature, ρ_r and at the reference temperature of 60°F ($\rho_{r,ref}$) are calculated using a form of the Riedel equation [54]:

$$\rho_r = \frac{\rho}{\rho_c} = 1 + 0.85\,(1 - T_r) + (1.6916 + 0.9846\,\omega)(1 - T_r)^{\frac{1}{3}} \tag{2.5}$$

where ω is Pitzer's acentric factor defined as

$$\omega = -\log[P_r]_{T_r=0.7} - 1.0 \tag{2.6}$$

For pressures greater than saturation, Lyderson's [55] tabular correlation is used. The third parameter in Lyderson's correlation is the critical compressibility factor, Z_c which may be obtained from the acentric factor by the approximate relation :

$$Z_c = \frac{1}{3.41 + 1.28\,\omega} \tag{2.7}$$

Francis [56] proposed the following expressions for estimating the saturated densities of liquids :

$$\rho_s = A - BT - C/(E\text{-}T) \quad \text{(low temperature)} \tag{2.8}$$

$$(\rho_s - \rho_c)^H = C(T_c - T) \quad \text{(high temperature)} \tag{2.9}$$

where A, B, C, E, H are specified constants for each compound.

Holmes [57] also proposed a correlation for estimating the saturated densities of pure hydrocarbons. The correlation is as follows :

$$\rho_s / \rho_c = (1 - \omega)\rho_r^{(0)} + \omega \rho_r^{(1)} \tag{2.10}$$

where $\rho_r^{(0)}$ and $\rho_r^{(1)}$ are generalized functions of T_r and P_r.

Harmans [58] proposed the following equation for determining the densities of saturated liquids.

$$\rho_s / \rho_c = (0.43875 - 0.625 Z_c)\, f(T_r) \tag{2.11}$$

where $f(T_r)$ is a generalized density function plot.

Lyckman et al. [59] in their paper proposed a correlation for estimating the densities of saturated liquids. Their correlation is as follows :

$$\rho_s / \rho_c = V_r = V_r^{(0)} + \omega V_r^{(1)} + \omega^2 V_r^{(2)} \tag{2.12}$$

where $V_r^{(i)}$ s are generalized functions of T_r.

Yen and Woods [60] also reported a correlation for calculating the saturated densities of liquids. The correlation is as given below :

$$\rho_s / \rho_c = 1 + A(1 - T_r)^{1/3} + B(1 - T_r)^{2/3} + (0.93 - B)(1 - T_r)^{4/3} \quad (2.13)$$

where A and B are specified constants for each compound (constants have been generalized as functions of Z_c)

Ehrlich [61] proposed the following correlation for estimating the saturated liquid densities of hydrocarbon components :

$$\frac{[(\rho_s / \rho_c) - 1]^3}{[(\rho_s / \rho_c)(1 - T_r)]} = A + B(1 - T_r) + C(1 - T_r)^2 \quad (2.14)$$

where A and B are specified constants for each compound.

Narsimham [62] proposed the following correlation for estimating the saturated liquid densities of hydrocarbon components :

$$\rho_{s/rho_c} = 1 + [(0.422 \log P_c + 0.981)/(1 - T_b/T_c)^{0.40}](1 - T_r)^{0.40} \quad (2.15)$$

Harlacher [63] also proposed a correlation for estimating the saturated liquid densities of hydrocarbon components. The correlation is given as below :

$$\rho_s / \rho_c = 1 + K(1 - T_r)^{1/3} + L(1 - T_r)^{2/3} \quad (2.16)$$

where K and L are specified constants for each compound (constants have been generalized as function of ω).

Bradford and Thodos [64] also reported a correlation for estimating the densities of saturated liquids which is as follows :

$$\rho_s \; / \; \rho_c = 1 + (2.924 - 7.34 \, Z_c) (1 - T_r) - (1.139 - 3.796 \, Z_c)^*$$

$$(1 - T_r)^2 + (2.785 - 3.544 \, Z_c) (1 - T_r)^{(0.160 + 0.5357 Z_c)} \qquad (2.17)$$

Rackett [65] also proposed a correlation for estimating the densities of saturated liquids as follows :

$$\rho = \frac{P_c}{RT_c} (Z_c)^{-[1 + (1 - T_r)^{\frac{2}{7}}]} \qquad (2.18)$$

Gunn - Yamada [66] also proposed the following expression to estimate saturated liquid volumes :

$$\frac{V}{V_{sc}} = V_r^0 (1 - \omega \tau) \qquad (2.19)$$

Where

V = Liquid specific Volume

V_{sc} = Scaling Parameter

V_r^o and τ are functions of reduced temperature, (T_r)

ω = acentric factor

Spencer and Danner [67] surveyed all the relatively new correlation for predicting the effect of temperature on saturated liquid and after preliminary evaluation using the data for saturated liquid densities of hydrocarbon at low temperature (40°C below the critical and lower). Yen and Woods, Gunn and Yamada, Harlacher and Francis were found to be the most accurate. The summary of evaluation of the correlations is shown in Table 2.1.

Rackett equation being the simplest in form and requires no arbitrary constants for its evaluation except of course the critical constants T_c, P_c and Z_c. Spencer and Danner decided to modify the equation to :

$$\rho = \left(\frac{P_c}{R\,T_c}\right)(Z_{RA})^{-[1+(1-T_r)^{\frac{2}{7}}]} \tag{2.20}$$

Where Z_{RA} , which is closely related to the critical compressibility factor is obtained from :

$$\log Z_{RA} = \frac{\log\left(\frac{\rho R T_c}{P_c}\right)}{-[1+(1-T_{r,60^\circ F})^{2/7}]} \tag{2.21}$$

where,

ρ = molar density at 60°F

$T_{r,60^\circ F}$ = reduced temperature at 60°F

The Spencer and Danner modified Rackett equation was evaluated for the low temperature hydrocarbon data, and the average error of 0.38%

Table 2.1 : Summary of Evaluation of Correlations With Low Temperature Hydrocarbon Data

	No of compounds treated	No of data points	Deviation (%)
Riedel (1954)	9	641	1.16
Francis (1957)	36	1597	0.43
Holmes (1964)	6	353	1.80
Harmans (1965)	11	824	0.68
Lyckman (1965)	36	1597	4.22
Yen & Woods (1966)	24	1354	0.91
Ehrlich (1967)	5	248	1.30
Narsimham (1967)	32	1473	2.04
Harlacher (1968)	32	1473	0.81
Bradford and Thodos (1968)	36	1597	2.19
Rackett (1970)	36	1597	2.40
Gunn & Yamada (1971)	36	1597	0.59
SDR (1972)	36	1597	0.38

was obtained which is better than Francis with an average error of 0.43%.

Hankinson and Thomson [68] reviewed correlations developed earlier by Rackett and other authors and finally came up with the COSTALD (Corresponding States Liquid Density) correlation. The COSTALD correlation for saturated liquid densities is given by

$$\rho = \left(\frac{1}{V^*}\right)\left(\frac{1}{V_r^{(o)}}\right)\frac{1}{\left(1 - \omega_{srk} V_r^{(\delta)}\right)} \tag{2.22}$$

Where

$$V_r^{(o)} = 1 - 1.52816(1 - T_r)^{1/3} + 1.43907(1 - T_r)^{2/3} - 0.81446(1 - T_r) + 0.190454(1 - T_r)^{4/3} \tag{2.23}$$

$$V_r^{(\delta)} = (-0.296123 + 0.386914\,T_r - 0.0427258\,T_r^2 - 0.0480645\,T_r^3)/(T_r - 1.00001) \tag{2.24}$$

and ω_{srk} is an acentric factor value derived from the Soave-Redlich-Kwong equation of state. V^* is a pure component characteristics volume generally within 1 to 4 percent of the critical volume. Values of V^* and ω_{srk} for over 400 compounds are given in reference [69]. If the value of V^* is not available, it may be estimated by :

$$V^{*} = \frac{R\,T_c}{V_c}\,(\,a + b\,\omega_{srk} + c\,\omega^2_{srk}\,) \tag{2.25}$$

Values of the constants a, b & c are given in reference [69]. However, if no data are available for a compound, ω^2_{srk} should be replaced by the true acentric factor, and likewise V^{*} may be replaced by the true critical volume. The resulting error will often be less than 1 percent but can be as high as 4 percent.

2.3.2 Defined Mixtures

In order to calculate the liquid density of liquid containing mixtures, mixing rules are needed for the calculation of the appropriate pseudocritical constants. Recent investigators, Hankinson and Thomson [68], Spencer and Danner [70], Veeranna and Rihani [71] have examined several potential combination rules for calculating T_{cm},P_{cm},Z_{cm}, and ω_m for use in predicting liquid densities. The results of these investigations are summarized in this section for each of the saturated liquid density correlations under consideration.

For both the Riedel and Rackett correlations, Eqs. 2.5 and 2.20, the mixture pseudocritical temperature is predicted by the correlation proposed by Chueh and Prausnitz [72].

$$T_{cm} = \sum_i \sum_j \varphi_i\, \varphi_j\, T_{cij} \tag{2.26}$$

$$\varphi = \frac{x_i\, V_{ci}}{\sum_j x_j\, V_{cj}} \tag{2.27}$$

$$T_{cij} = (\,1 - k_{ij}\,)(\,T_{ci}\, T_{cj}\,)^{1/2} \tag{2.28}$$

$$1 - k_{ij} = 8\,(\,V_{ci}\, V_{cj})^{1/2}/(\,V_{ci}^{\;1/3} + V_{cj}^{\;1/3}\,)^3 \tag{2.29}$$

The modified Rackett equation for mixtures thus becomes,

$$V_m = R\left(\sum_i \frac{x_i T_{ci}}{P_{ci}}\right) Z_{RA_m}^{\,[1+(1-T_r)^{2/7}]} \tag{2.30}$$

$$Z_{RA_m} = \sum_i x_i Z_{RA_i} \tag{2.31}$$

$$T_r = T/T_c \tag{2.32}$$

The COSTALD correlation uses the following mixing rules :

$$T_{cm} = [\sum_i \sum_j x_i x_j V^*_{ij} T_{cij}] / V^*_m \tag{2.33}$$

$$V^*_m = \frac{1}{4}\{\sum_i x_i V^*_i + 3(\sum_i x_i V_i^{*2/3})(\sum_i x_i V_i^{*1/3})\} \tag{2.34}$$

$$V^*_{ij} T_{cij} = (V^*_i T_{ci} V^*_j T_{cj})^{1/3} \tag{2.35}$$

$$\omega_m = \sum x_i \omega_{srki} \tag{2.36}$$

$$Z_{cm} = 0.291 - 0.080\,\omega_m \tag{2.37}$$

$$P_{cm} = Z_{cm} R T_{cm} / V^*_m \tag{2.38}$$

Yen and Wood [60] utilized the following mixing rules developed by Prausnitz and Gunn [73]

$$T_{cm} = \sum_{i=0}^{n} x_i T_{ci} \tag{2.39}$$

$$V_{cm} = \sum_{i=0}^{n} x_i V_{ci} \tag{2.40}$$

$$Z_{cm} = \sum_{i=0}^{n} x_i Z_{ci} \tag{2.41}$$

$$P_{cm} = Z_{cm} R T_{cm} / V_{cm} \tag{2.42}$$

The mixing rules for the Riedel correlation critical density are given by the following relationships [74].

$$\frac{1}{\rho_{om}} = \sum_i \frac{x_i}{\rho_{ci} (1.85 + 1.6916 + 0.9846 \omega_i)} \qquad (2.43)$$

$$\rho_{cm} = \frac{\rho_{om}}{1.85 + 1.6916 + 0.9846 \omega_m} \qquad (2.44)$$

Where ρ_{om} is the hypothetical liquid mixture density at 0°R as given by the Riedel equation and assuming ideal volumetric mixing. For both the Riedel and Rackett correlations, P_{cm} is obtained from :

$$\frac{1}{P_{cm}} = \frac{1}{T_{cm}} \sum_i x_i \frac{T_{ci}}{P_{ci}} \qquad (2.45)$$

When the HBT correlation (COSTALD) and the mixing rules were tested for 2,969 points of liquid mixtures, the correlation gave an average absolute error of 1.4 percent compared to 3.59 percent for Yen-Wood's and 2.97 percent for Rackett's equation as modified by Spencer and Danner [68].

2.4 EFFECT OF PRESSURE : ISOTHERMAL COMPRESSIBILITY

At pressures greater than saturation, the densities of liquids increase with increasing pressure at constant temperature. The isothermal compressibility, β, is defined as

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \qquad (2.46)$$

where ρ is the molar density. Equation (2.46) is typically the basis for correlations of the effect of pressure on liquid density. Alternatively, the Watson relationship. Eq. (2.4) can be restated as

$$\rho = \left(\frac{K}{K_{ref}}\right)\rho_{ref} \tag{2.47}$$

Where ρ and ρ_{ref} are the desired density and the density at some reference condition, respectively, and K and K_{ref} are values of the corresponding correlation parameters and are generally functions of T_r and P_r. Both approaches have been used to correlate the effect of pressure on liquid density.

In their analysis, Hwang et al. [75] made use of Lydersen's tabular correlation for predicting the liquid density at pressures greater than saturation. The Lydersen tabulation provides the reduced density, ρ_r, as a function of T_r and P_r, and the critical compressibility factor, Z_c, which may be obtained from Eq. (2.7).

Thus from the Riedel correlation, Eq. (2.5), the Lydersen correlation, and the Watson relationship, Eq. (2.4), the liquid density at reduced temperatures from 0.30 to 1.00 and reduced pressures up to 30 could be predicted.

Two alternatives to the Lyderson correlation for predicting the effect of pressure on liquid density are the correlations of Chueh and Prausnitz [72] which incorporates the isothermal compressibility β, and the correlation presented by Rea et al. [76].

The Chueh-Prausnitz correlation is given by

$$\left(\frac{\rho}{\rho^s}\right) = [1 + 9\beta(P - P^s]^{1/9} \tag{2.48}$$

$$\beta = \frac{V_c}{R\,T_c}\,(\,1 - 0.89\,\sqrt{\omega}\,)\,\exp\,(\,6.9547 - 76.2853\,T_r$$

$$+\ 191.306\,T_r^{\,2} - 203.5472\,T_r^{\,3} + 82.7631\,T_r^{\,4}) \qquad (2.49)$$

where ρ^s and P^s are the saturation density and pressure, respectively, and V_c is the critical volume. Equations 2.48 and 2.49 are valid for reduced temperatures ranging from 0.40 to 0.98.

The correlation reported by Rea et al. [76] is of the form

$$K = A_o + A_1\,T_r + A_2\,T_r^2 + A_3\,T_r^3 \qquad (2.50)$$

$$A_i = B_{oi} + B_{1i}\,P_r + B_{2i}\,P_r^2 + B_{3i}\,P_r^3 + B_{4i}P_r^4 \qquad (2.51)$$

where K is the correlation parameter for the Watson relationship , Eq. (2.47). The values of the coefficients B_{ji} are given below.

i	B_{oi}	B_{1i}	$B_{2i}(10^3)$	$B_{3i}(10^5)$	$B_{4i}(10^6)$
0	1.6368	-0.04615	2.1138	-0.7845	-0.6923
1	-1.9693	0.21874	-8.0028	8.2823	-5.2604
2	2.4638	-0.36461	12.8763	14.8059	-8.6895
3	-1.5841	0.25136	-11.3805	9.5672	-2.1812

Finally, the COSTALD correlation includes the effect of pressure given by a modified form of the Tait equation [68].

$$\rho = \rho_s\,[\,1 - C\ln\,(\,\frac{B+P}{B+P^s}\,)\,]^{-1} \qquad (2.52)$$

where

$$\frac{B}{P_c} + 1 = -9.070217(1 - T_r)^{1/3} + 62.4532(1 - T_r)^{2/3}$$

$$-135.1102(1 - T_r) + e(1 - T_r)^{4/3} \qquad (2.53)$$

$$e = \exp(4.79594 + 0.250047\,\omega + 1.14188\,\omega^2) \qquad (2.54)$$

$$C = 0.0861488 + 0.0344483\,\omega \qquad (2.55)$$

All of the correlations described above for predicting the effect of pressure on liquid density have generally been developed from data on light hydrocarbons and compounds typically found in petroleum-derived fluids. Their applicability to other classes of mixtures needs to be demonstrated.

2.5 STATISTICAL MECHANICS AND COMPUTER SIMULATION

The theoretical study of the physical properties of fluids from the perspective of statiscal mechanics has made significant advances in recent years. The progress has been due chiefly to developments in molecular theories based on the methods of statistical mechanics and numerical simulations of molecular movements on fast electronic computers.

Earlier models of liquids involved physical manipulation and analysis of the packaging of a large number of gelatine balls, representing the molecules; this resulted in a good 3-dimensional picture of the structure of a liquid. This was the case in the 1950's, 1960's and 1970's. However, the use of large number of physical objects to represent molecules can be very time consuming and there are also limitations on the types of interactions between them and the effects of gravity can never be eliminated [77].

The new methods of investigation which were made possible as a result of the development of the probability distribution function theories in statistical mechanics & refinements of computer simulation methods (Monte Carlo simulation and molecular dynamics solution of equations of motions) utilize mathematical rather than physical model and in addition perform the analysis by computer.

Fluids with polar forces (water, ammonia & alcohols) and nonspherical shapes (polyatomic and hydrocarbon) are now studied. In addition charged particles (ionic solutions), long chain molecules (polymer solutions) and liquid metals are also being investigated. This new approach is expanding rapidly into fluid materials such as colloidal solutions, polyelectrolytes and biological fluids. Diverse phenomena found in the fluid state are being examined such as phase transition, chemical reactions, adsorption at interfaces and transport phenomena. [77]

Statistical mechanics is a method of accounting, whereby collective microscopic states are averaged, resulting in macroscopically measurable quantities. As the name applies, mechanics deals with forces, and statistics is a procedure of averaging. Thus, statistical mechanics offers a prescription for averaging the molecular forces in order to obtain values for the gross properties [77].

Computer Simulations have a valuable role to play in providing essentially exact results for problems in statistical mechanics which would otherwise only be solvable by approximate methods. Computer Simulation in this sense is a test of theories and historically, simulations have indeed discriminated between well founded approaches and ideas that are plausible. The results of computer simulation may also be compared with those of real experiments. Thus, simulation acts a a connecting link between models and theoretical predictions on one hand and between models and experimental results on the other [78].

Sometimes, it may be difficult or impossible to carry out experiments under extremes of temperature and pressure, while a computer simulation of the material in extremes of temperature and pressure (eg in nuclear reactors) would be perfectly feasible. While the speed of molecular events is itself an experimental difficulty, it presents no hindrance to the simulation.

Two methods are commonly used, the Monte Carlo (MC) and molecular dynamics (MD) techniques, Figure 2.1. The Monte Carlo method makes use of a random number generator to "move" the molecules in a random fashion. Statistical mechanics suggests that for a fixed temperature and density, the probability of a particular arrangement of the molecules is proportional to exp(-U/kT), where U is the total energy of the collection of molecules, k is the Boltzmann constant, and T is the temperature. In MC, the random moves are accepted or rejected according to a recipe ensuring that the various generated molecular arrangements appear with the probabilities given by this law. After generating a long series of such arrangements, they can be averaged to obtain the various equilibrium properties of the system of molecules.

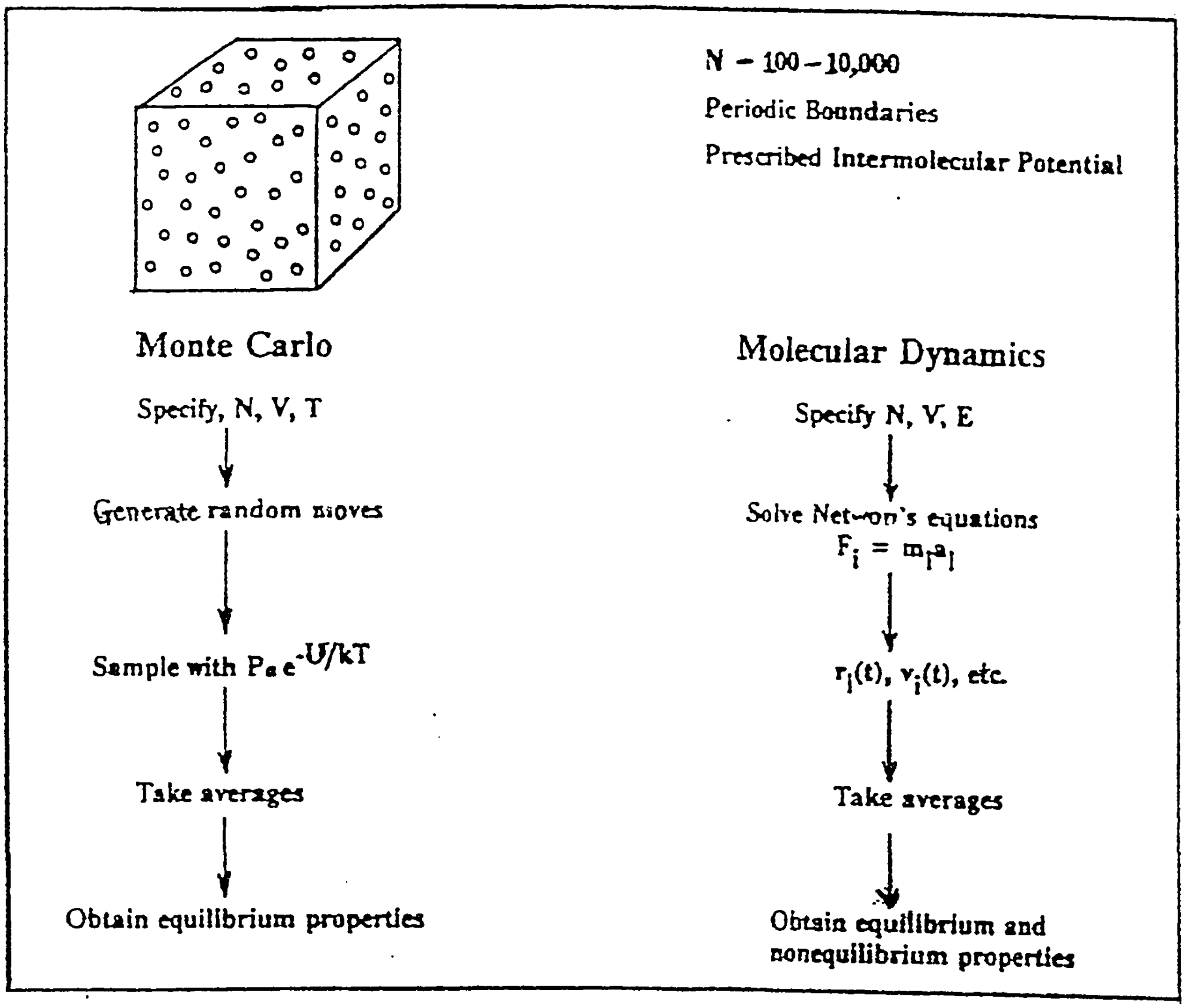

Figure 2.1 : Two Methods of Molecular Simulation

In molecular dynamics method, the molecules are allowed to move naturally under the influence of their own intermolecular forces. The positions and velocities of each molecule are followed in time by solving Newton's equation of motion (force equals mass times acceleration, a second order differential equation) using standard numerical methods. The macroscopic properties are calculated by averaging the appropriate functions of molecular positions and velocities over time.

In both techniques, accurate results can be expected provided the simulation runs are carried on long enough and that the number of molecules is large enough. In order to minimize boundary effects in such small samples, it is customary to use periodic boundary conditions; that is, the sample is surrounded on all sides by replicas of itself so that when a molecule moves through a boundary and out of the sample it is automatically replaced by a molecule moving into the sample through the opposite face of the box [79].

Molecular dynamics (MD) was first accomplished for a system of hard spheres by Alder and Wright [80]. In this case, the particles move at constant velocity between perfectly elastic collisions, and it is possible to solve the dynamic problem without making any approximations, within the limits imposed by machine accuracy. Rahman [81] solved the equations of motions for a set of Lennard-Jones particles for the first time. An approximate step-by-step procedure was used since the forces change continuously as the particles move. Since then, the properties of the Lennard-Jones model have been a subject of investigation [82 and 83].

Berne and Harp [84] modelled a diatomic molecular liquid using molecular dynamics. Barker and Watts [85] made an attempt to model liquid water by the technique of Monte Carlo, Rahman and Stillwater [86] also made an attempt to model liquid water but by the technique of molecular dynamics. Ryckaert and Bellemans [87] undertook a study of flexible hydrocarbon, while McCammon, Gelin and karplus [88] studied large molecules such as proteins. Computer simulation has also been used to improve the understanding of phase transitions and behavior at interfaces [89].

2.5.1 The N-Body System

An N-body syatem is a collection of N material particles. These particles could be molecules, charged ions, or colloidal particles. In statistical mechanics, material is considered as composed of spatially discrete units. This is in contrast to the continuum view where matter is continous and homogeneous. This later view is known as as the macroscopic view and it is very useful in the field of fluid mechanics and heat transfer. However, the microscopic view is used for the study of properties because it is necessary to understand the specific forces of interaction among the particles that compose the material. [77]

2.5.2 The Lennard-Jones Potential

Real molecules possess repulsive forces as well as attractive forces. A simple pair potential that possesses both the repulsive and the inverse sixth power London forces is the Lennard-Jones (LJ) potential given as :

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2.56}$$

where r is the intermolecular separation and σ and ε are force constants characteristics of the molecular species. The LJ potential is plotted in Figure 2.2.

1. The energy parameter ε has the unit of energy and is the well depth of the LJ u(r) :

$$\min u(r) = -\varepsilon$$

2. the size parameter σ has the unit of length and is the location where $u(r)=0$ that is

$$u(\sigma) = 0$$

3. The distance r^* for the minimum of u(r) can be obtained by setting $du/dr=0$, and is related to σ by

$$r^* = (2)^{1/6}\sigma = 1.1224\,\sigma$$

Ordinarily, σ is expressed in angstroms (A) and ε/k (k being the Boltzman constant) in Kelvin. It is worthwhile to note that all LJ fluids have the same properties at same reduced T^* and ρ^*. This is the basis of the corresponding states theory. Temperature is expressed in reduced units as

$$T^* = \frac{kT}{\varepsilon}$$

and pressure as

$$P^* = \frac{P\sigma^3}{\varepsilon}$$

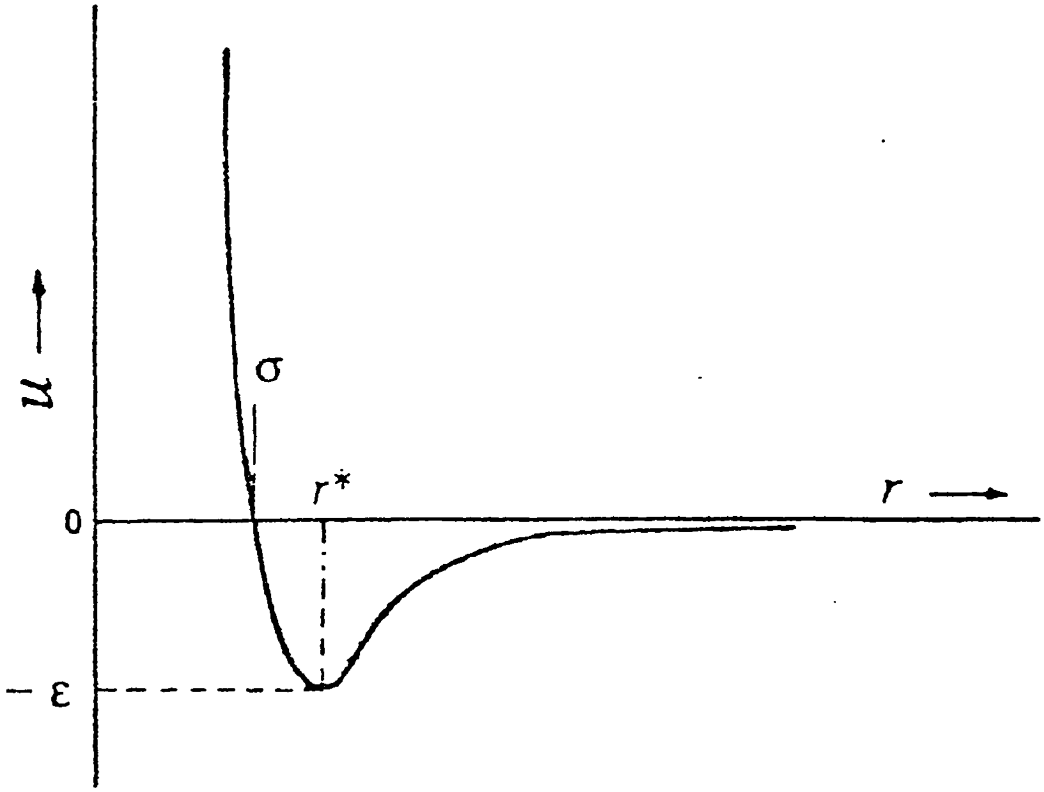

Figure 2.2 : Lennard - Jones Potential

and density as

$$\rho^{*} = \rho \sigma^{3}$$

2.5.3 Macroscopic Properties From Computer Simulation

Some macroscopic properties that can be obtained from computer simulation by averaging the appropriate functions of molecular positions and velocities over time include among others; The Hamiltonian, kinetic energy, potential energy, enthalpy & density.

2.5.3.1 The Hamiltonian

The partcles in an N-body system are in constant motion undertaking movements in all directions. The total energy of the system, TE, is calculated as the sum of the kinetic contribution, KE, and the potential contribution, PE. The Hamiltonian, H_N, of the system is defined to be its total energy, TE, and is a function of the kinetic variables (i.e., the linear momenta p_i) and spatial variables (e.g., the center-of-mass positions r_i of the particles).

2.5.3.2 Kinetic Energy

Kinetic energy is associated with the motion of particles. It is separated into translational, rotational, and vibrational modes.

Translational Energy

$$KE_t = \frac{1}{2} \sum_{i=1}^{N} \frac{p_i^2}{m_i} \qquad (2.57)$$

Rotational Energy

$$KE_r = \frac{1}{2}\sum_{i=1}^{N}\alpha_i \cdot I_i \cdot \alpha_i \tag{2.58}$$

Vibrational Energy

$$KE_v = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{n'} m_i\,\omega_{ij}^2\,a_{ij}^2 \tag{2.59}$$

where p_i is the momentum, m_i is the mass of particle i, I_i is the moment of inertia, α_i the angular velocity, ω_{ij} the frequency of vibration of mode j in molecule i, a_{ij} the amplitude of vibration, and $n' = 3n - 5$ for linear molecules and 3n-6 for nonlinear molecules. [75]

2.5.3.2 Potential Energy

Potential energy arises due to interactions among particles and between particles and surroundings. The strength of interaction is dependent on the distances that separate these particles and their relative orientations. The total potential energy is a function of spatial configuration of the particles. For a conservative system, the force acting on the system is given by the negative gradient of the potential energy.

CHAPTER 3

EXPERIMENTAL SET-UP AND PROCEDURE

As Discussed in the review of literature, Saeed [2] designed and constructed a system that enabled accurate measurements of saturated densities of crude oils and their fractions from ambient temperature to 230°C and pressures of up to 1800psia. Comparing representative measurements from this system with measurements made with most accurate devices, it was observed that only a maximum difference of 0.17% was noticed. This system will be used for all the density measurements.

3.1 PRINCIPLE OF THE DENSITY MEASUREMENTS

The schematic diagram of the system is shown in Figure 3.1. The principle of density measurement involve complete evacuation of a stainless steel cylinder (density cell) of known volume by connecting it to a vacuum line. When the air in the density cell has been displaced, the cell is disconnected and weighed. It is later filled by connecting it to a filling line which not only maintain any desired pressure but also used to displaced the liquid from the sample reservoir to fill the evacuated density cell.

The density cell is then placed in a constant temperature bath set at the desired temperature. After the thermal equilibrium is achieved, the density cell is disconnected from the filling line, properly cleaned, dried and weighed. The difference in weights give the weight of sample in density cell. As the volume of the cell is already known from the calibration data, density can easily be

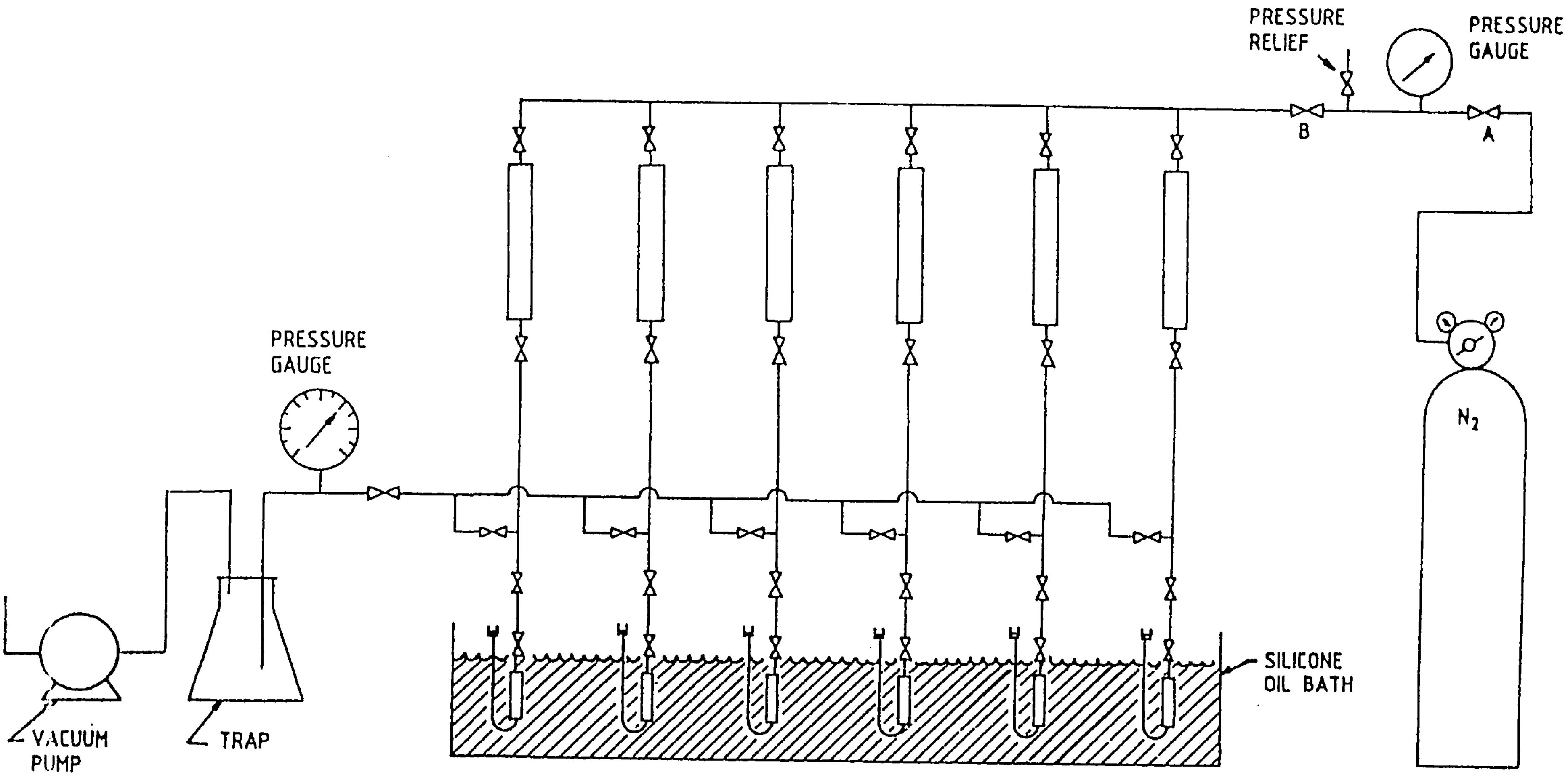

Figure 3.1 · Schematic Diagram of Experimental Set-Up For Density Measurements

calculated by following expression :

$$\rho = \text{Weight of liquid sample} / \text{Cell Volume}$$

3.2 DETAILS OF EXPERIMENTAL SET-UP

The experimental setup consisted of six units which could be operated independent of each other. Figure 3.2 shows the schematic diagram of one assembly used for density measurement. It consists of about 40 cm^3 double ended 316-stainless steel cylinder as shown Figure 3.3 with 1/8 inch female threads on both ends. On the bottom end of density cell Cromel-Alumel thermocouple (type K) manufactured by Omega Engineering were fixed. It was made sure that the stainless tube covering the thermocouple would extend sufficiently within the cylinder cavity to enable temperature measurement of liquid within the central core of the cell. A needle valve was attached to the upper end of the density cell through 1/8 inch stainless steel tube of about 10 cm length. The male connectors on the two sides of the cell provided connections for ferrule type compression fittings for holding thermocouple tube at the bottom end and needle valve on the top end as shown in Figure 3.3.

A 150 cm^3 double ended stainless steel cylinder with 1/4 inch female threads on both ends has been used as the sample reservoir. The male connector on the upper end of the cylinder provided connection to the high pressure line via a globe valve. On the bottom end a 1/8 inch tube served as the filling line, at the end of which a needle valve is also connected for flow control.

A vacuum line was drawn for evacuating air from the density cell. This line

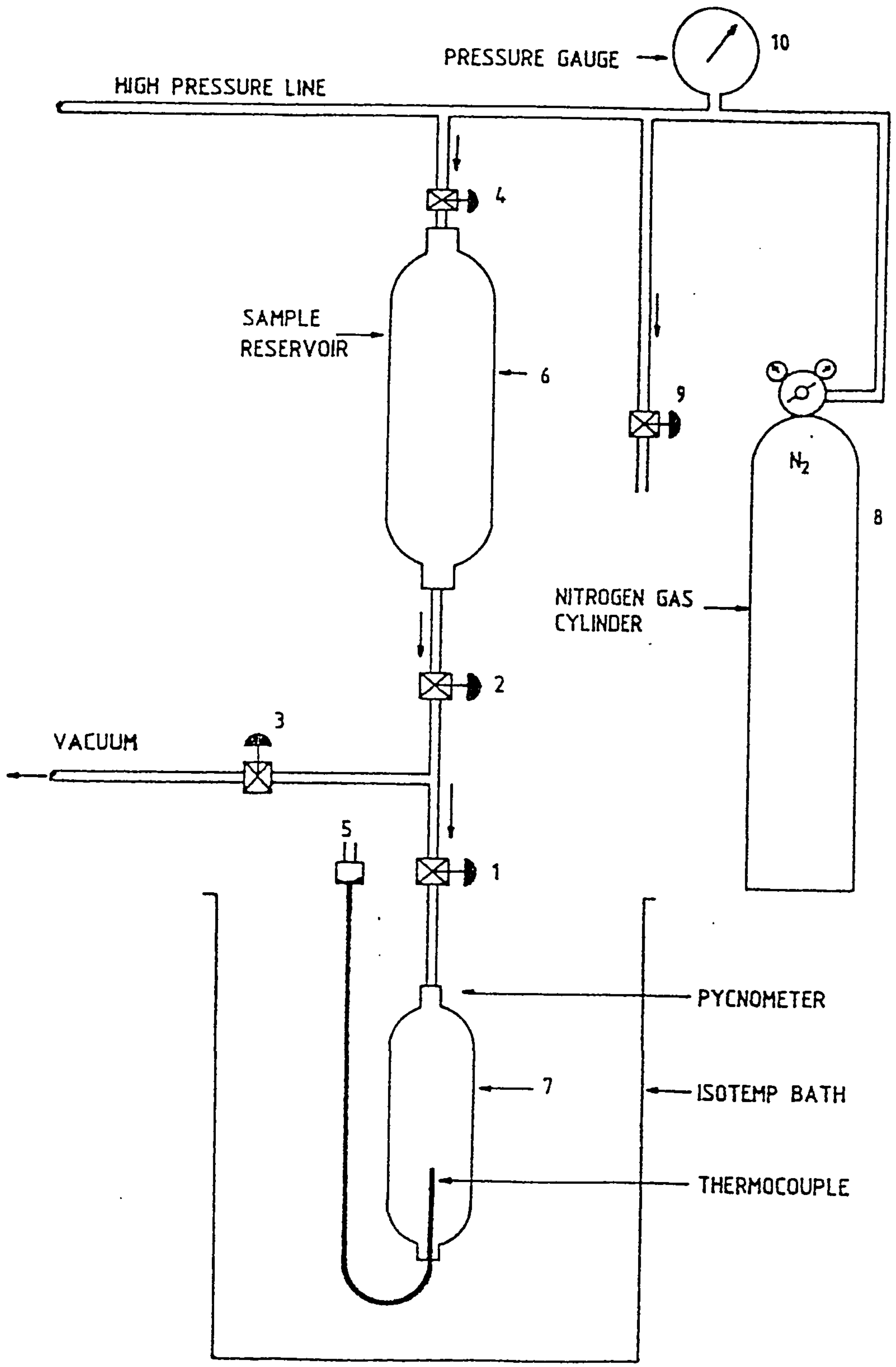

Figure 3.2 : Schematic Diagram of Single Unit For Density Measurements

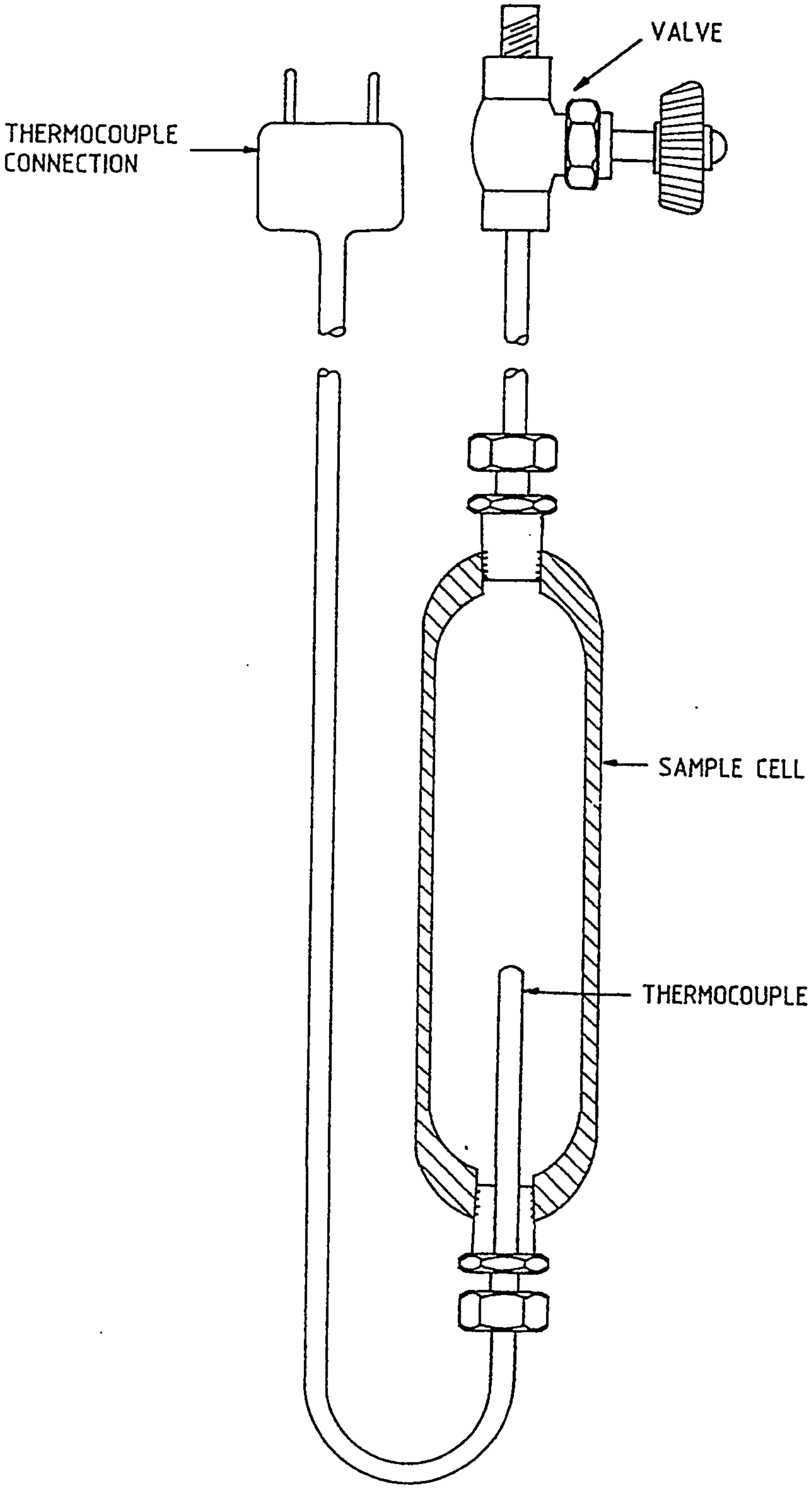

Figure 3.3 : Schematic Diagram of Pycnometer Assembly

was 1/4 inch stainless steel tube with six ports for making connections to the density cells. A vacuum pump was connected to a flexible rubber tube via a liquid trap to safe guard against liquid going into the vacuum pump. A digital pressure gauge was also connected to the vacuum line which gives absolute pressure in millibar.

A 1/8 inch TEE joined the sample reservoir, the density cell and the vacuum line as shown in Figure 3.2, so that air from the cell may be evacuated or the sample may be filled in by turning one valve open and keeping the other closed. The pressure was applied to the system by the nitrogen gas available in standard gas cylinder.

The gas cylinder was fitted with special Matheson pressure regulator suitable for cylinder pressure of upto 10,000 psig and delivery pressure of 5000 psig to control pressure in the system. All six sample reservoirs were connected to the high pressure line via a globe valve on their upper ends. A Budenberg pressure gauge of 10 inches diameter (0-1600 psi) was provided for easy pressure read out in the high pressure line. A 1/8 inch stainless steel tube extending from the pressure regulator connected the gas cylinder and high pressure line via an on/off globe valve for emergency pressure release of the system.

Tamson TCV-70 constant temperature bath supplied by Neslab was used for operation temperatures from ambient to 230°C. The bath had volume of 70 liters and was supplied with a digital temperature set point and read out upto 0.1°C. The offset between the set point and the actual temperature of the bath was also displayed on the digital read out. The bath was provided with a 800 watt control heater and 1750 watt booster heater for quick heating. The bath used a specially designed baffled stirring system that eliminated laminar flow and provided true turbulent agitation resulting in excellent stability and uniformity. The temperature in bath could be maintained with in constancy and uniformity of ±0.02°C.

Neslab DR-2 digital read out compact thermometer with independent system that could monitor temperature in a bath in the range from -100°C to 200°C was obtained for measuring the operating bath temperatures. This system was supplemented with Fluke model 2180A RTD digital thermometer which had temperature range from -200°C to 204°C and a resolution of 0.01°C as a double check on the bath temperature measurements.

Mettler PC-2000 balance was employed for the measurement of weight of the density cells. The balance had a weighing range up to 2100 g and a readability of 0.01 g.

3.3 PROCEDURE FOR DENSITY MEASUREMENT

When density was to be determined for any component, it was made certain that every valve in the set-up shown in Figure 3.2 was closed. The sample reservoir 6 was disconnected from nitrogen line from valve 4 and filled with the sample. After the filling process had been completed the sample reservoir was reconnected to the nitrogen line.

The valves 1 and 3 were opened and the air inside the pycnometer was evacuated by starting the vacuum pump and the pressure in the vacuum line was monitored on the digital pressure indicator. The vacuum was applied for about 15 minutes using vacuum pump capable of reducing pressure to 10 mbar absolute after which both valves 1 and 3 were closed. The pycnometer assembly (density cell along with the thermocouple well) was removed by disconnecting at valve 1 and weighed carefully on Mettler PC-2000 balance. This reading was recorded as the initial weight of the evacuated pycnometer. The pycnometer was reconnected to the system and immersed into the constant temperature bath which had already attained a steady state predetermined operating temperature. As valves 2 and 1 were closed, valve 3 was opened so that the interconnecting tube among valves 1,2 and 3 was once again evacuated to pycnometer pressure. The valve 3 was then closed and vacuum pump was disconnected. The nitrogen pressure in the system was adjusted through the regulator of compressed nitrogen gas to any desired magnitude for filling purposes. This pressure could directly be read on the Budenberg pressure gauge with a range of 0-1600 psig. The valves 4,2 and 1 were successively opened to allow the liquid sample to be forced into the pycnometer under the nitrogen pressure.

After the filling process was complete, for which at least 10 minutes are given, the operating pressure was adjusted to any desired operating condition. It may be noted that the operating pressure may be different from the pressure applied to achieve the proper filling of the pycnometer.

The temperature of the bath was observed at various locations in the bath using platinum resistance thermometer with a resolution of 0.01°C to check the steady state temperature of the bath. After the steady state was reached at the central core of the cell the cell was kept for additional 15 minutes to make sure that no temperature gradient exist within the liquid sample in the pycnometer. This process takes between 30-45 minutes. After the system was kept at constant temperature for 15 minutes, then valves 1, 2 and 4 were successively closed. The pressure in the system was released through relief valve 9 and pycnometer was removed from the constant temperature bath. It was left to cool and then washed carefully with methanol to remove any bath oil left from the surface of the density cell. The cell was now dried by blowing warm air. The density cell assembly was weighed and the difference between this weight and initial weight of the evacuated cell provided the weight of sample in the cell. If the volume of the cell at the operating temperature is known , the density could be calculated easily. It was, therefore, essential to calibrate the volume of the density cells as a function of temperature.

3.4 CALIBRATION OF DENSITY CELL

The density cells shown in the experimental set-up in Figure 3.1 were calibrated for their volume at various temperatures using mercury as a density standard. Similar procedure as described earlier for the density measurement of liquid hydrocarbon sample was used. It may be noted that it was found necessary to tap the cell gently to allow smooth flow of mercury from the sample reservoir into the density cell. The filling could then be conveniently accomplished at ambient pressure. The weight of mercury in the cell was determined from the weights of empty cell and when it was filled with mercury. Since the weight (W) of mercury in the cell and its density, ρ [90] at the temperature of calibration is known, the volume could be calculated at any desired temperature.

CHAPTER 4

RESULTS AND DISCUSSION

Tables 4.1, 4.2 and 4.3 give some of the thermodynamic properties of the hydrocarbon samples used in the experimental work, i.e benzene, cyclohexane and n-hexane. The properties tabulated are the critical temperature, pressure and volume, acentric factor, SRK acentric factor, modified critical compressibility factor which is used in the Spencer-Danner modified Rackett equation and the characteristics volume for pure components.

4.1 CALIBRATION OF DENSITY CELLS

Before initiating work on the density measurement for the pure hydrocarbon samples and their mixtures, the density measuring cells were calibrated. The calibration procedure is described in details in the experimental section of the thesis. The calibration data for the density cells are reported in Appendix A. The data for each cell is plotted in Figure 4.1, and it may be observed that the expansion of the cells is almost linear with temperature.

The reliability and accuracy of the experimental system for measuring the density of hydrocarbon components has been established previously [2]. The available accurate data of the density of water which has been most extensively reported in the literature was used for comparison. The density of doubled distilled water was measured from 40°C to 100°C and each observation was repeated three times. The data obtained were compared to that reported in the literature in Table 4.4. The comparison shows a maximum difference of 0.21% and thus establishes the reliability of the system both in terms of accuracy and

Table 4.1 : Thermodynamic Properties of Benzene

Properties	Value
Molecular Weight	78.114
T_c	562.54 K
P_c	48.9 bar
Z_{RA}	0.2698
V^*	256.40 cm^3/mol
V_c	259.0 cm^3/mol
T_b	353.2 K
ω	0.2120
ω_{SRK}	0.2137

Table 4.2 : Thermodynamic Properties of Cyclohexane

Properties	Value
Molecular Weight	84.162
T_c	553.54 K
P_c	40.7 bar
Z_{RA}	0.2729
V^*	309.00 cm^3/mol
V_c	308.0 cm^3/mol
T_b	353.8 K
ω	0.2120
ω_{SRK}	0.2128

Table 4.3 : Thermodynamic Properties of n-Hexane

Properties	Value
Molecular Weight	86.178
T_c	507.43 K
P_c	30.1 bar
Z_{RA}	0.2635
V^*	367.70cm^3/mol
V_c	370.0cm^3/mol
T_b	341.9 K
ω	0.2990
ω_{SRK}	0.3007

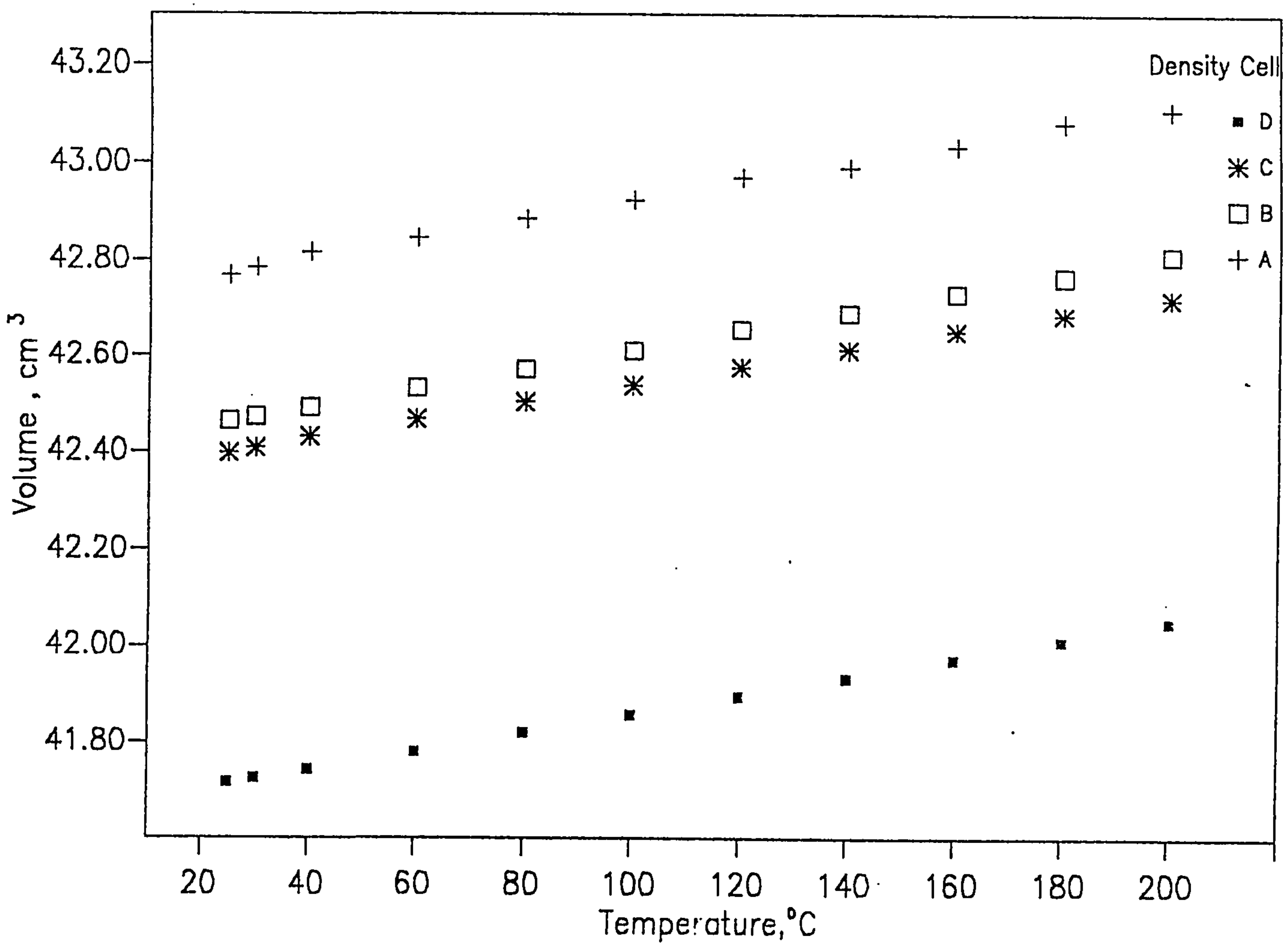

FIGURE 4.1 : CALIBRATION DATA FOR THE VOLUME OF DENSITY CELLS AS A FUNCTION OF TEMPERATURE

Table 4.4 : **Comparison of Water Density Data Using The Proposed System And Literature Value**

Temp.	Vol. of cell	Wt of water in cell	Measured Density (A)	Reported Density (B)	Deviation (%)
(C)	cm^3	g	g/cm^3	g/cm^3	
40.0	41.221	40.94	0.99318	0.99225	+0.09
		40.85	0.99099		-0.13
		40.88	0.99173		-0.05
60.0	41.255	40.52	0.98218	0.98324	-0.11
		40.48	0.98121		-0.21
		40.55	0.98291		-0.03
80.0	41.379	40.19	0.97126	0.97183	-0.06
		40.20	0.97126		-0.03
		40.24	0.97151		+0.06
100.0	41.301	39.57	0.95808	0.95838	-0.03
		39.61	0.95905		+0.07
		39.63	0.95954		+0.12

* Deviation(%) = (A-B)/A * 100

reproducibility.

4.2 DENSITY-TEMPERATURE BEHAVIOR OF THE PURE COMPONENTS AND THEIR MIXTURES

Densities of benzene, cyclohexane and n-hexane and their binary and ternary mixtures were measured from ambient temperature 25°C to 200°C using the experimental system described in chapter 3.

4.2.1 Density-Temperature Behavior of The Pure Components

Since the objective of the project is to measure the density of the pure components as saturated liquids upto the operating temperature of 200°C, it was essential to apply a back pressure on the samples to keep them in the liquid state. The pressure to be exerted on the system was kept slightly above the the vapor pressure estimate from correlations. For the present study, a pressure of about 150psia was applied at 25°C to about 600psia at 200°C for the components. Thus for the operating conditions above 25°C, the pressure was increased by about 30psia for every 10°C rise in temperature.

The density data for benzene, cyclohexane and n-hexane are given in Appendix A. The data have also been plotted in Figures 4.2 to 4.5. It may be observed that the density of each component decreases with increase in temperature. There is no erratic variations in density with temperature which could be due to a phase change in the sample.

Figure 4.5 shows a comparison between the density data of the three components. Benzene, an aromatic has the highest density in the whole range of

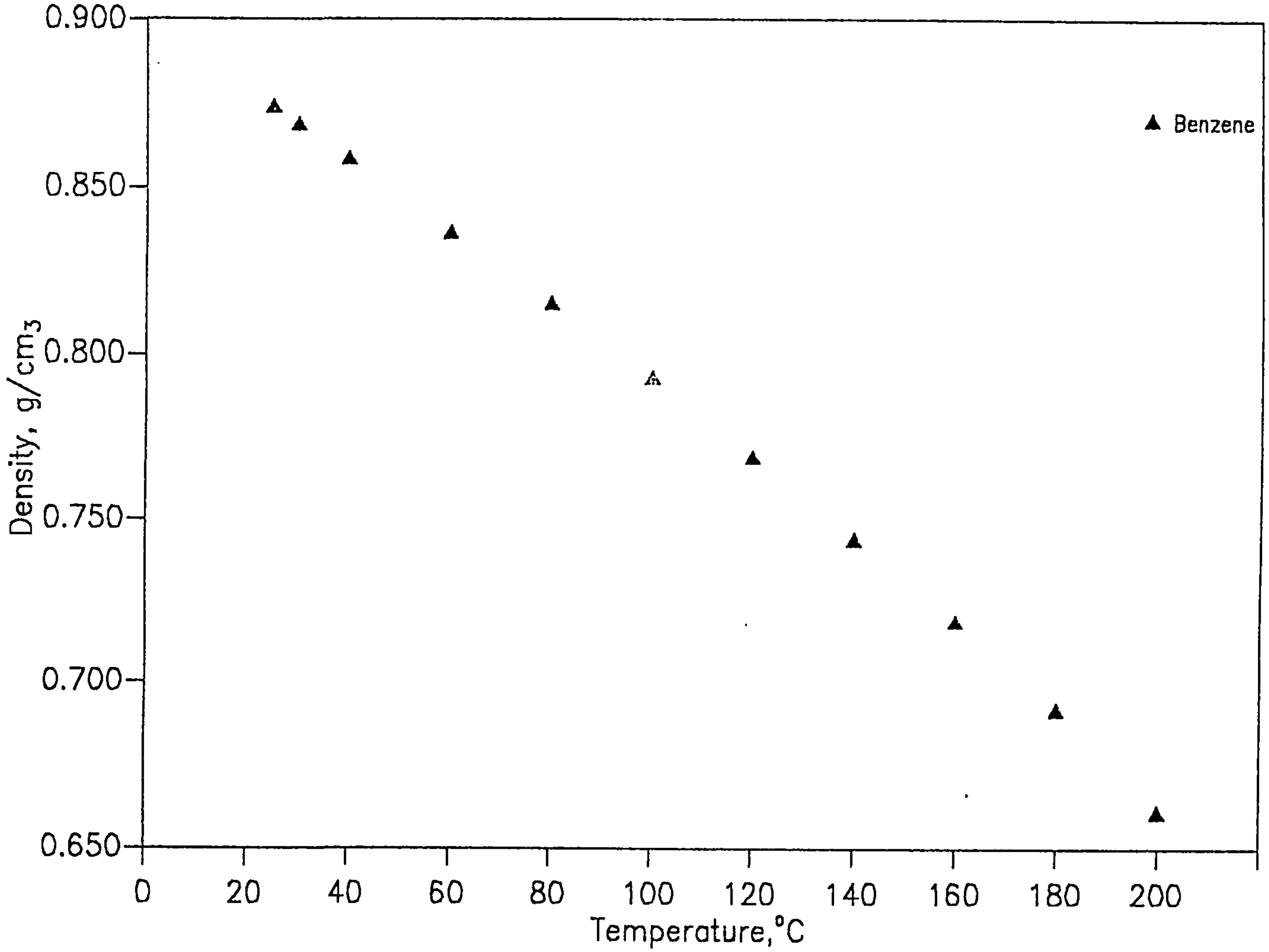

FIGURE 4.2 : EXPERIMENTAL DENSITY – TEMPERATURE DATA FOR BENZENE

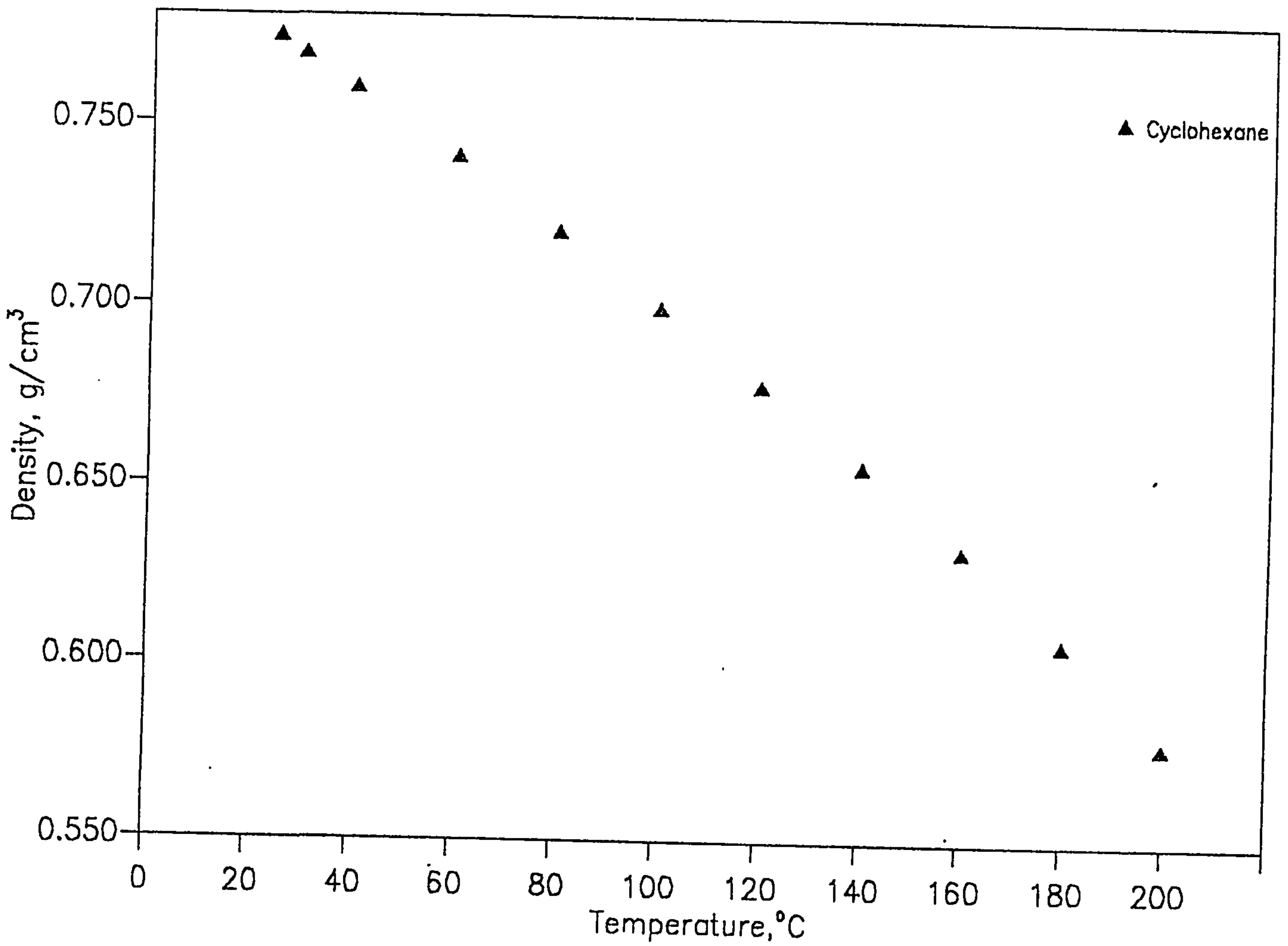

FIGURE 4.3 : EXPERIMENTAL DENSITY – TEMPERATURE DATA FOR CYCLOHEXANE

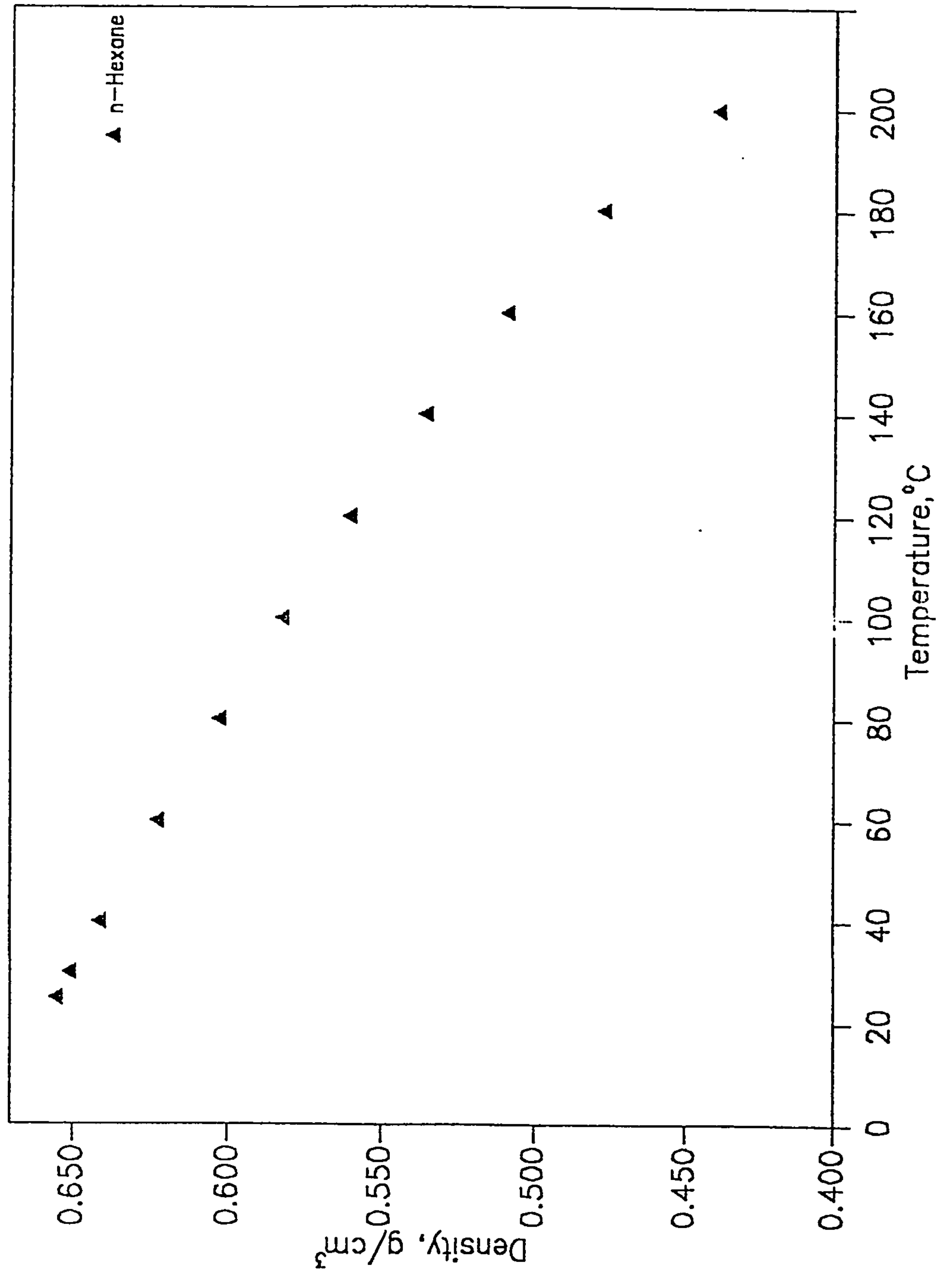

FIGURE 4.4 : EXPERIMENTAL DENSITY – TEMPERATURE DATA FOR n–HEXANE

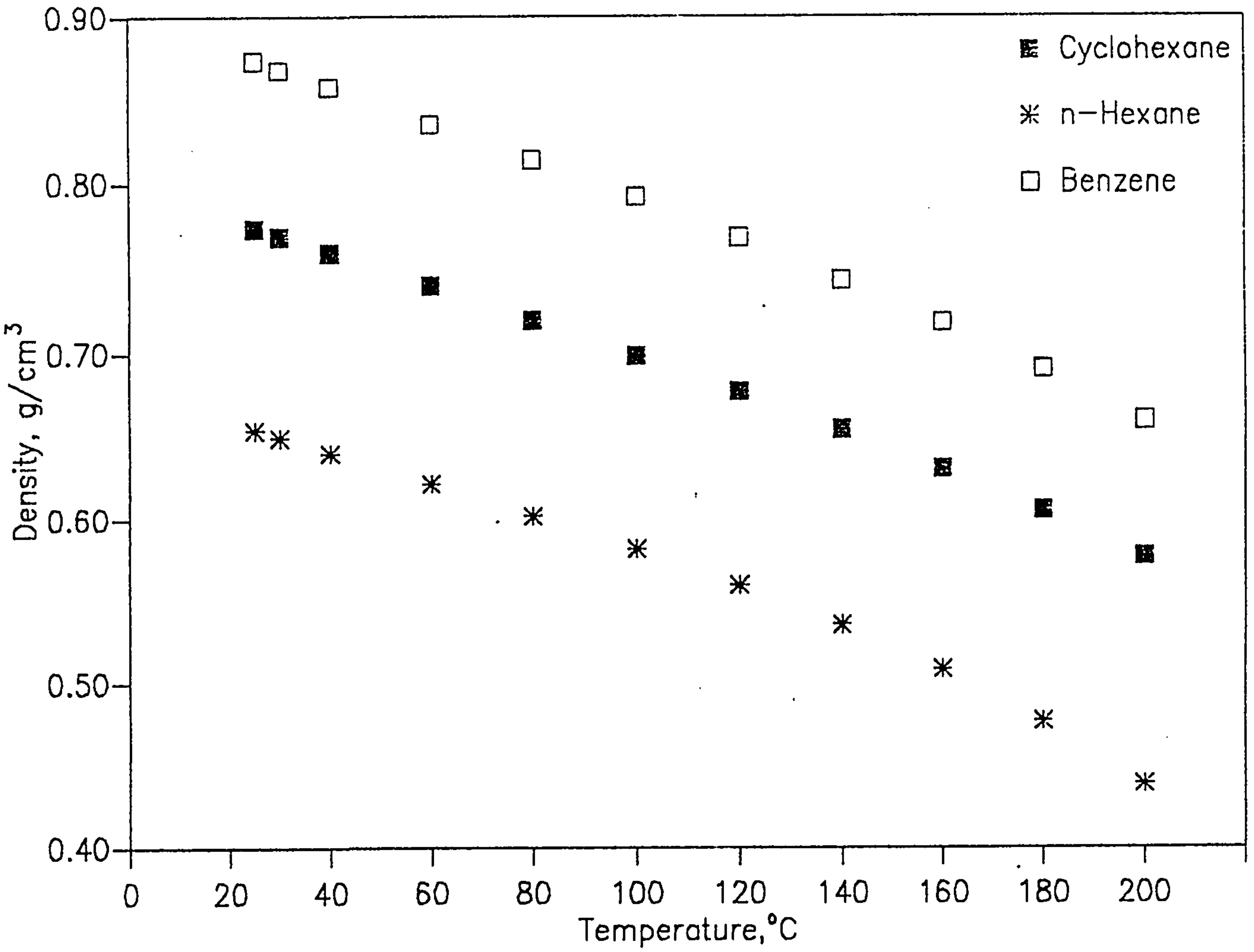

FIGURE 4.5: EXPERIMENTAL DENSITY – TEMPERATURE DATA FOR CYCLOHEXANE, n–HEXANE AND BENZENE

temperatures considered, while n-hexane, a paraffin, has the lowest density.

Table 4.5 gives a comparison between the density data for the three components obtained in the present investigation at 25°C with some of the experimental values reported in the literature. It may be noted from this table that there exist an excellent agreement between the experimental density data obtained in comparison with those reported in the literature. Comparison at other temperatures was not possible because very little experimental data has been reported at higher temperatures.

Table 4.6 gives the errors in the prediction of the density using the Spencer-Danner modified Rackett equation (SDR) and the HankinsonBrobst-Thompson correlation. For example, the SDR correlation gave a percentage average absolute deviation (AAD%) of 0.29 for benzene while the HBT correlation predicted the density of benzene with an (AAD%) of 0.25 when compared with the experimentally obtained values. The predicted density values are plotted in Figure 4.6 versus temperature. The corresponding experimental data are also shown in this Figure for easy comparison. The two correlations seem to predict the experimental values pretty well. The point by point errors obtained in the prediction of the density by the two correlations are given in Appendix C.

4.2.2 Density-Temperature Behavior of The Binary Mixtures

The experimental data for the binary mixtures of benzene, cyclohexan and n-hexane are also given in Appendix A. The data have been plotted in Figure 4.7 for benzene - cyclohexane mixtures, Figure 4.11 for benzene - n-hexane mixtures and Figure 4.15 for cyclohexane - n-hexane mixtures.

Table 4.5 : **Comparison of The Experimetal Density at 298.15 K of Benzene, Cyclohexane And n-Hexane With Reported Experimetal Data**

Component	Experimental Value	Reported Expt. Value
Benzene	0.8737	0.87365 {9}
		0.87344 {23}
		0.8735 {18}
		0.87369 {8}
Cyclohexane	0.7739	0.77389 {17}
		0.77376 {23}
		0.77388 {25}
		0.7738 {18}
		0.78284 {22}
		0.77387 {8}
		0.7736 {24}
n-Hexane	0.6548	0.65508 {23}
		0.65504 {8}
		0.6562 {24}

Table 4.6 : **Comparison of The Experimental Density Data of Benzene, Cyclohexane and n-Hexane With Predictions From Spencer-Danner Modified Rackett Equation (SDR) and The Hankinson-Brobst-Thompson (HBT) correlation**

Component	Correlation	Minimun Absolute Deviation (MAD%)	Maximum Absolute Deviation (MAD%)	Average Absolute Deviation (AAD%)
Benzene	SDR	0.13	0.61	0.29
	HBT	0.10	0.43	0.25
Cyclohexane	SDR	0.04	0.18	0.08
	HBT	0.02	0.23	0.12
n-Hexane	SDR	0.08	1.25	0.48
	HBT	0.08	0.54	0.30

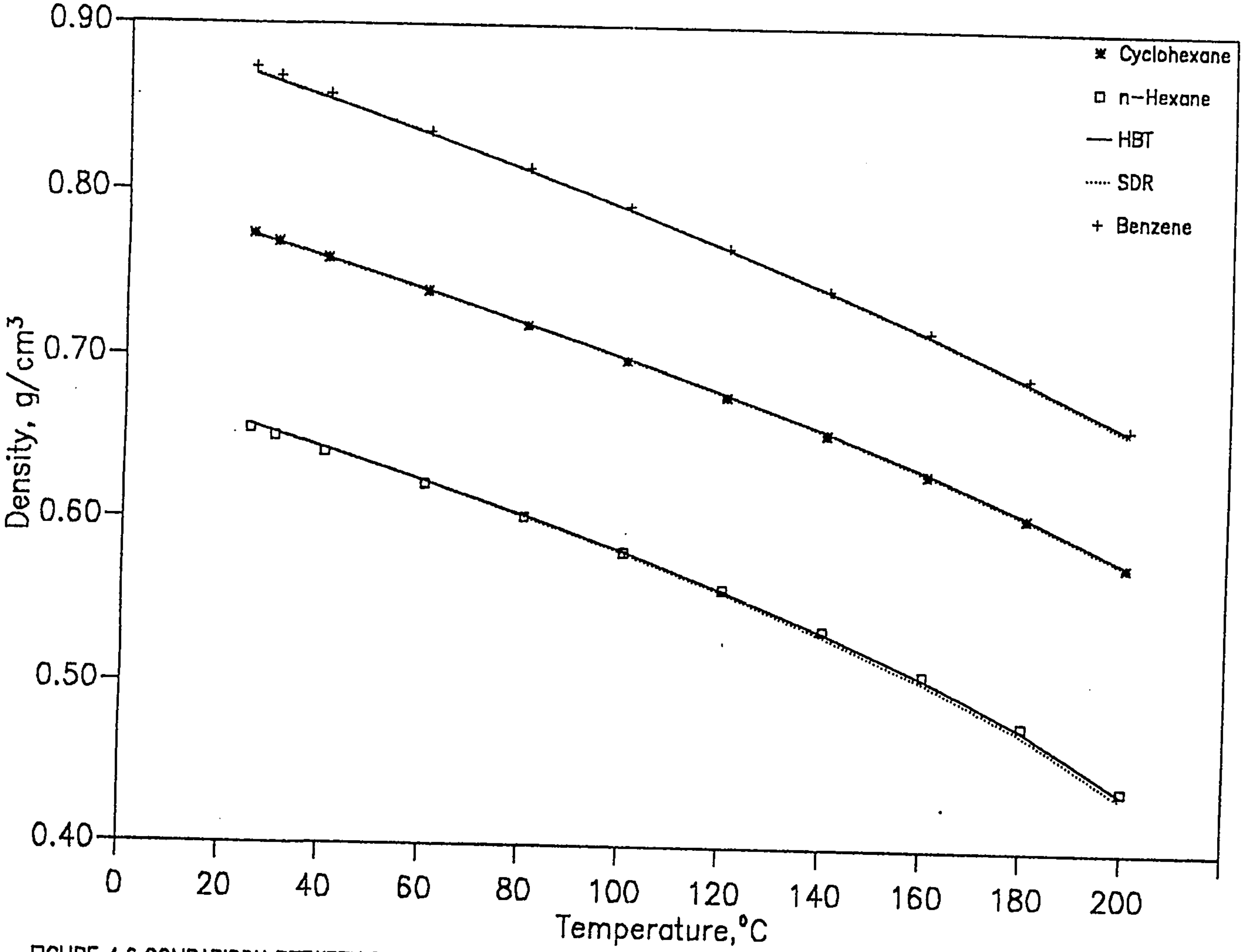

FIGURE 4.6:COMPARISON BETWEEN EXPERIMENTAL DENSITY DATA OF BENZENE,CYCLOHEXANE & N-HEXANE AND PREDICTIONS BY SDR AND HBTCORRELATIONS

4.2.2.1 Benzene - Cyclohexane Mixtures

It may be observed in Figure 4.7 that the density of each mixture decreases with increasing temperature. There is no sudden change in density with temperature which could have been attributed to a phase change in the mixture. It is also observed that as the amount of the aromatic component, benzene, is increased, there arise an increase in the density of the mixture. This is reflected in the data as the mass fraction of benzene is increased from 0.2 to 0.8 at any given temperature.

Table 4.7 gives the errors in the prediction of the density using the Spencer-Danner modified Rackett equation (SDR) and the HankinsonBrobst-Thompson correlation. The SDR correlation predicted the density of the benzene - cyclohexane mixtures with an overall percentage average absolute deviation (AAD%) of 0.58. The HBT correlation on the otherhand also predicted the density with an overall (AAD%) of 0.58 compared to the experimentally obtained values. The predicted density values are plotted in Figures 4.8 to 4.10 versus temperature. The corresponding experimental data are also shown in the Figures for easy comparison. The two correlations predict the experimental values with a reasonable degree of accuracy. The point by point errors obtained in the prediction of the density by the two correlations are given in Appendix C.

4.2.2.2 Benzene - n-Hexane Mixtures

From the plots in Figure 4.11, it is observed also that the density of the mixture of benzene - n-hexane decreases with increasing temperature. It is also observed that as the amount of benzene increases, the density of the mixture

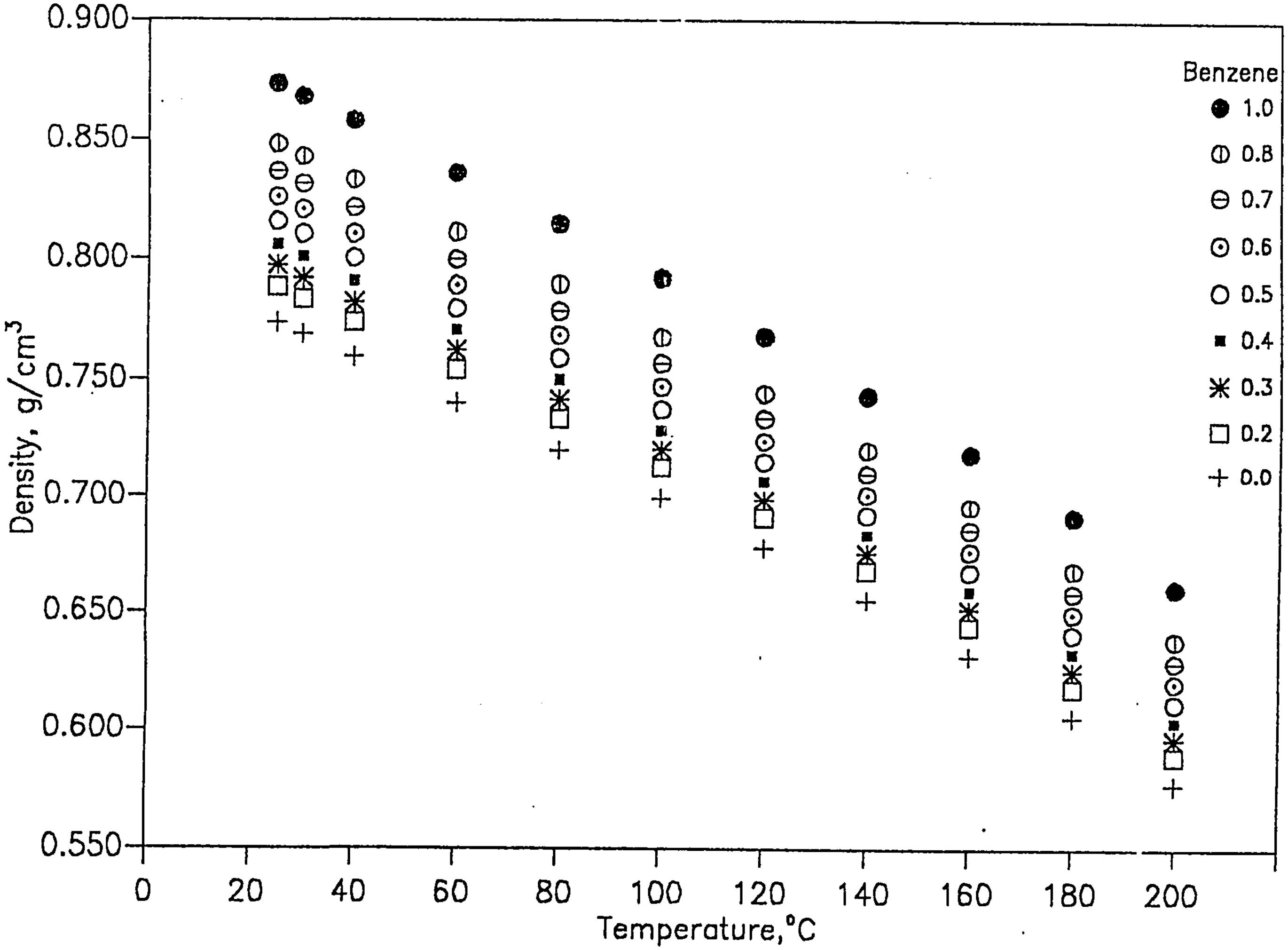

FIGURE 4.7 : EXPERIMENTAL DENSITY – TEMPERATURE DATA FOR DEFINED BENZENE – CYCLOHEXANE MIXTURES

Table 4.7 : **Comparison of The Experimental Density Data of The Mixture of Benzene - Cyclohexane With Predictions From Spencer-Danner Modified Rackett Equation (SDR) and The Hankinson-Brobst-Thompson (HBT) correlation**

Mass Fract. of Benzene	Correlation	Minimun Absolute Deviation (MAD%)	Maximum Absolute Deviation (MAD%)	Average Absolute Deviation (AAD%)
0.2	SDR	0.29	0.68	0.48
	HBT	0.36	0.72	0.53
0.3	SDR	0.41	0.82	0.61
	HBT	0.46	0.83	0.63
0.4	SDR	0.51	0.89	0.68
	HBT	0.55	0.88	0.68
0.5	SDR	0.55	0.91	0.70
	HBT	0.56	0.89	0.68
0.6	SDR	0.52	0.87	0.66
	HBT	0.51	0.85	0.64
0.7	SDR	0.40	0.77	0.55
	HBT	0.38	0.75	0.54
0.8	SDR	0.21	0.57	0.37
	HBT	0.17	0.57	0.36

Overall Percentage Average Absolute Deviation (SDR) = 0.58

Overall Percentage Average Absolute Deviation (HBT) = 0.58

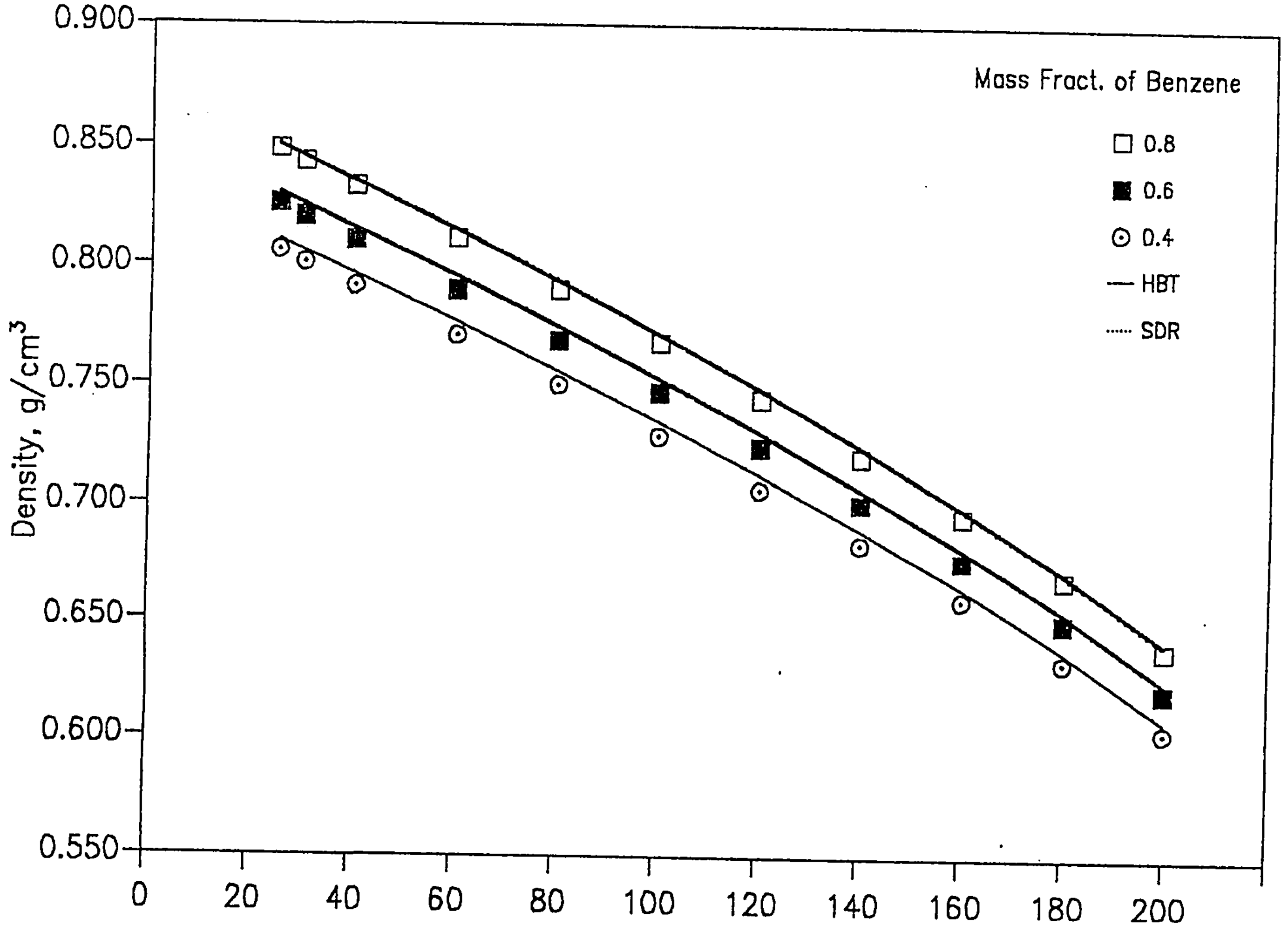

FIGURE 4.8 :COMPARISON BETWEEN EXPERIMENTAL DENSITY DATA AND PREDICTIONS BY SDR AND HBT FOR THE MIXTURES OF BENZENE – CYCLOHEXANE

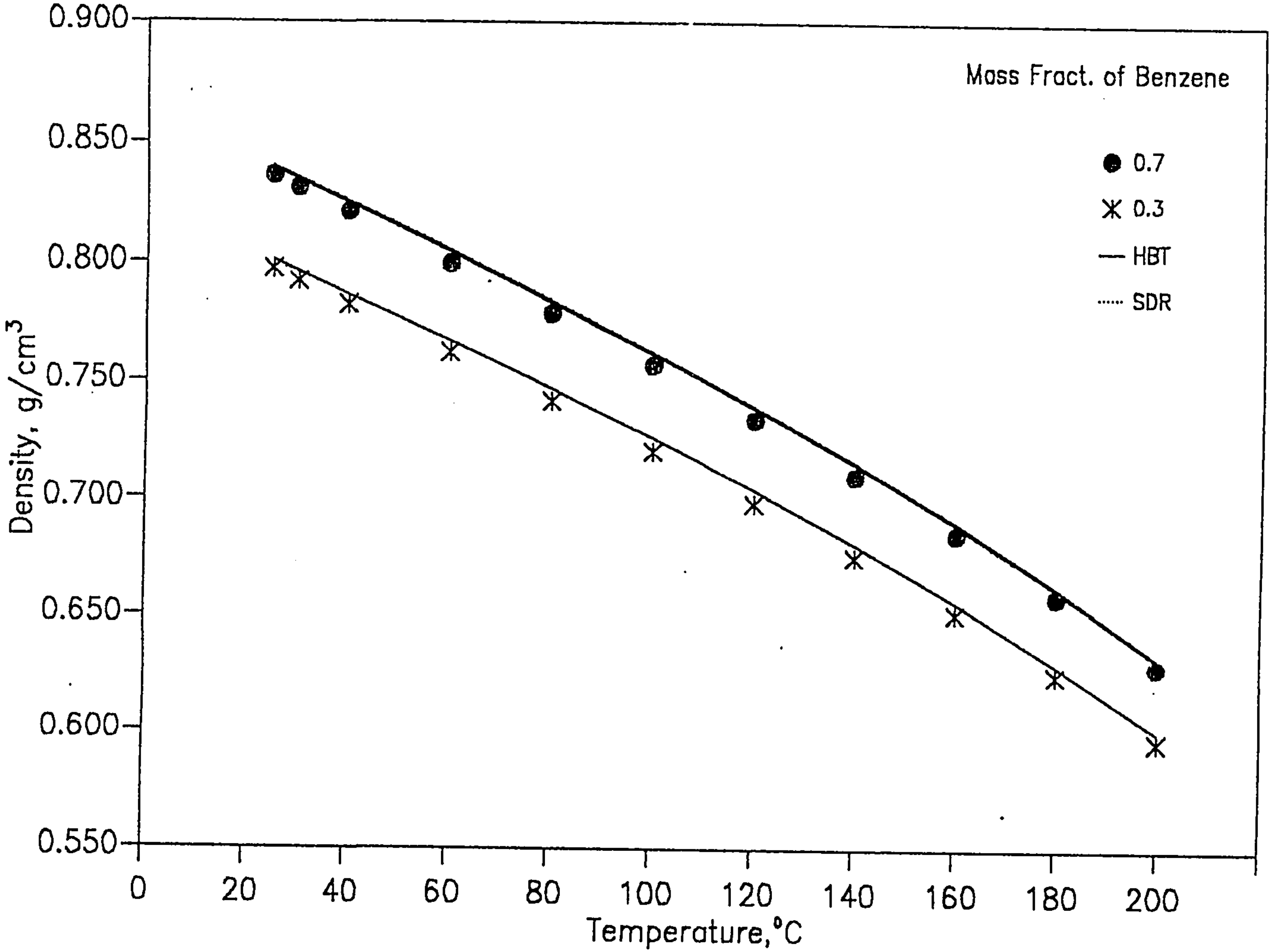

FIGURE 4.9 :COMPARISON BETWEEN EXPERIMENTAL DENSITY DATA AND PREDICTIONS BY SDR AND HBT FOR BENZENE – CYCLOHEXANE MIXTURES

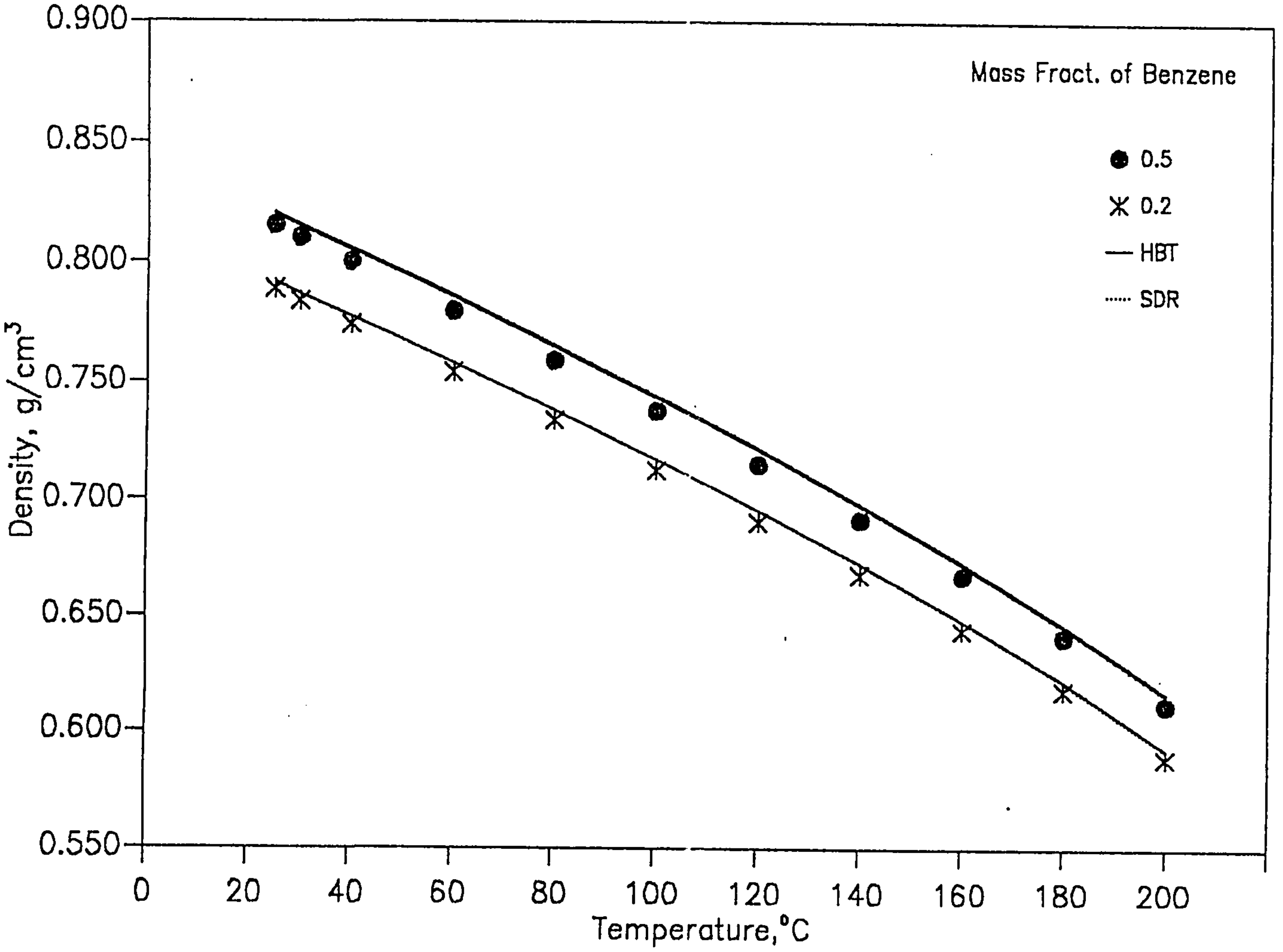

FIGURE 4.10:COMPARISON OF EXPERIMENTAL DENSITY DATA WITH PREDICTIONS BY SDR AND HBT FOR BENZENE – CYCLOHEXANE MIXTURES

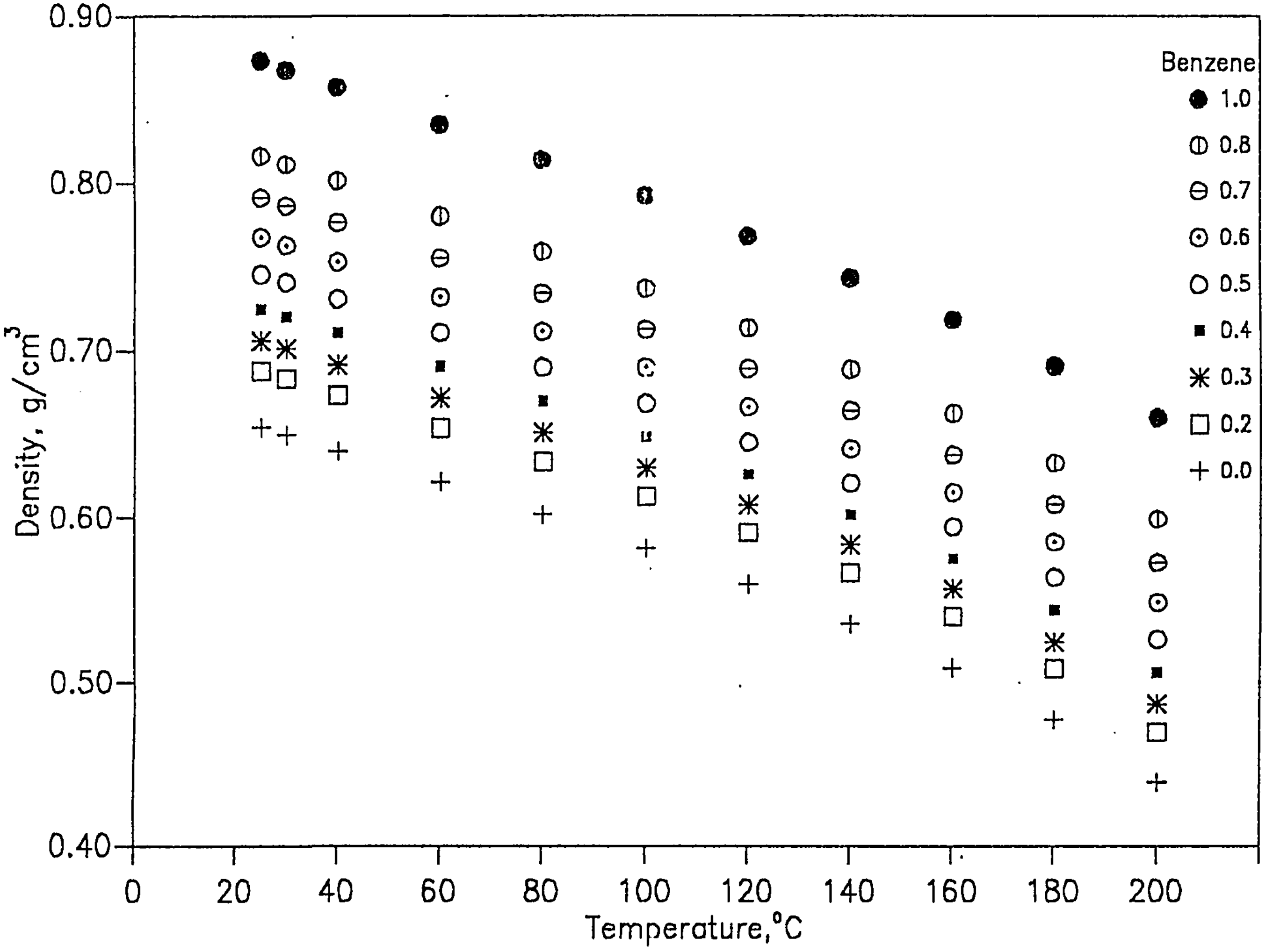

FIGURE 4.11: EXPERIMENTAL DENSITY – TEMPERATURE DATA FOR DEFINED BENZENE – n–HEXANE MIXTURES

also increases. This is reflected in the whole range of composition considered.

Table 4.8 gives the errors in the prediction of the density using the Spencer-Danner modified Rackett equation (SDR) and the HankinsonBrobst-Thompson correlation. The SDR correlation predicted the density of the benzene - n-hexane mixtures with an overall percentage average absolute deviation (AAD%) of 0.15 , while the HBT correlation predicted the density of the same mixtures with an overall (AAD%) of 0.85 compared with the experimentally obtained values. The predicted density values are plotted in Figures 4.12 to 4.14 versus temperature. The corresponding experimental data are also shown in the Figures for easy comparison. The two correlations predict the experimental values with a reasonable degree of accuracy. The point by point errors obtained in the prediction of the density by the two correlations are given in Appendix C.

4.2.2.3 Cyclohexane - n-Hexane Mixtures

The plots in Figure 4.15 show how the cyclohexane - n-hexane mixtures vary with temperature. It is evident from this plot that that there is a decrease in the density of all the mixtures as the temperature increases. It is also observed that for any mixture, as the amount of the paraffin component n-hexane increases, the density of the mixture decreases for the whole range of composition considered. This may be attributed to the fact that n-hexane has a lower density than cyclohexane.

Table 4.9 gives the errors in the prediction of the density using the Spencer-Danner modified Rackett equation (SDR) and the HankinsonBrobst-Thompson correlation. The SDR correlation predicted the density of the cyclohexane -

Table 4.8 : Comparison of The Experimental Density Data of The Mixture of Benzene - n-Hexane With Predictions From Spencer-Danner Modified Rackett Equation (SDR) and The Hankinson-Brobst-Thompson (HBT) correlation

Mass Fract. of Benzene	Correlation	Minimun Absolute Deviation (MAD%)	Maximum Absolute Deviation (MAD%)	Average Absolute Deviation (AAD%)
0.2	SDR	0.016	0.45	0.22
	HBT	0.82	1.12	0.53
0.3	SDR	0.013	0.37	0.19
	HBT	0.93	1.03	0.88
0.4	SDR	0.026	0.65	0.17
	HBT	0.92	0.21	1.01
0.5	SDR	0.00	0.79	0.15
	HBT	0.96	2.25	1.06
0.6	SDR	0.01	0.79	0.13
	HBT	0.87	2.17	1.01
0.7	SDR	0.01	0.67	0.10
	HBT	0.69	1.90	0.87
0.8	SDR	0.00	0.39	0.07
	HBT	0.43	1.39	0.62

Overall Percentage Average Absolute Deviation (SDR) = 0.15

Overall Percentage Average Absolute Deviation (HBT) = 0.85

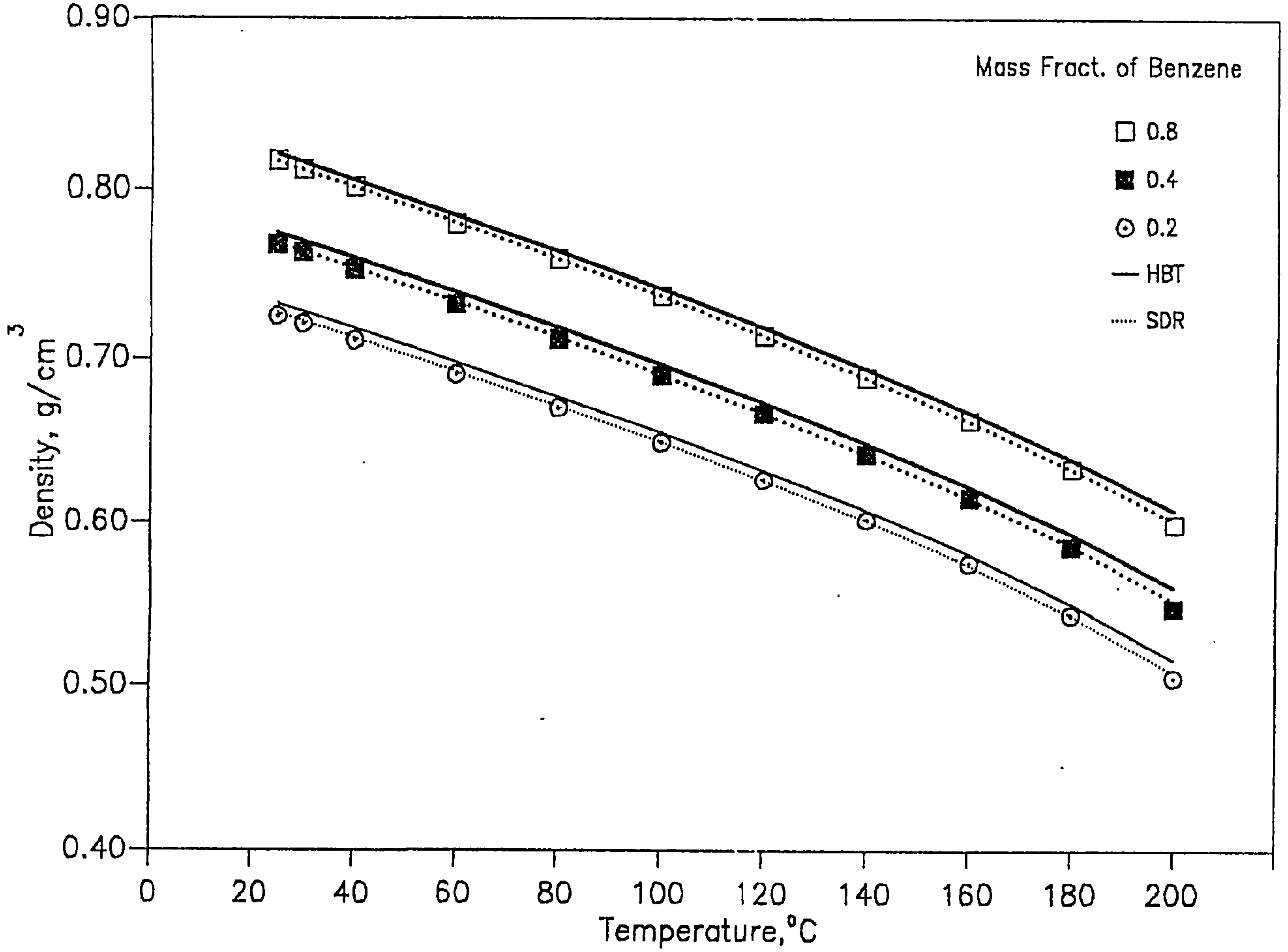

FIGURE 4.12 :COMPARISON BETWEEN EXPERIMENTAL DENSITY DATA WITH PREDICTIONS BY SDR AND HBT FOR BENZENE – n-HEXANE MIXTURES

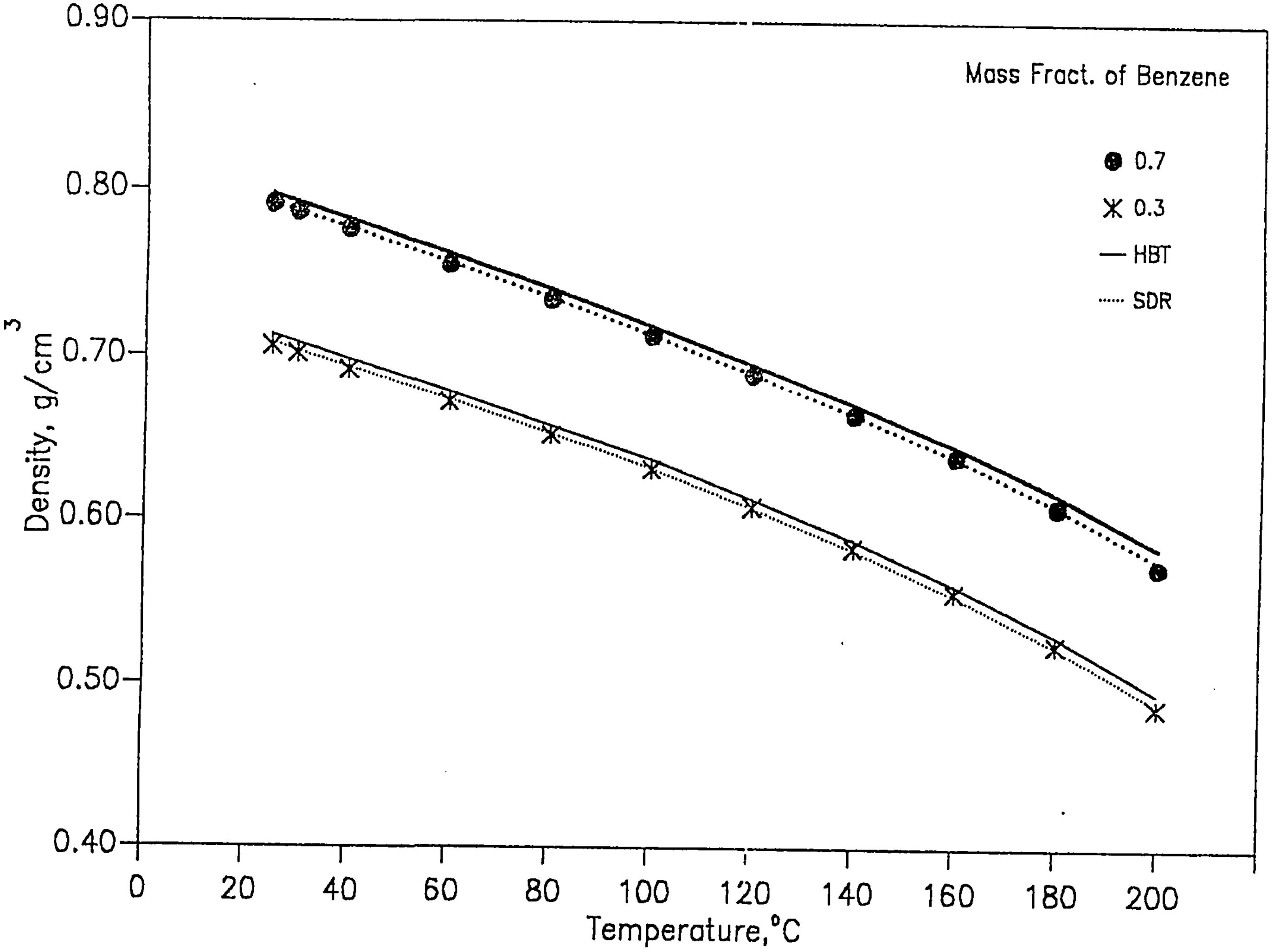

FIGURE 4.13 :COMPARISON OF EXPERIMENTAL DENSITY DATA WITH PREDICTIONS BY SDR AND HBT FOR BENZENE – n–HEXANE MIXTURES

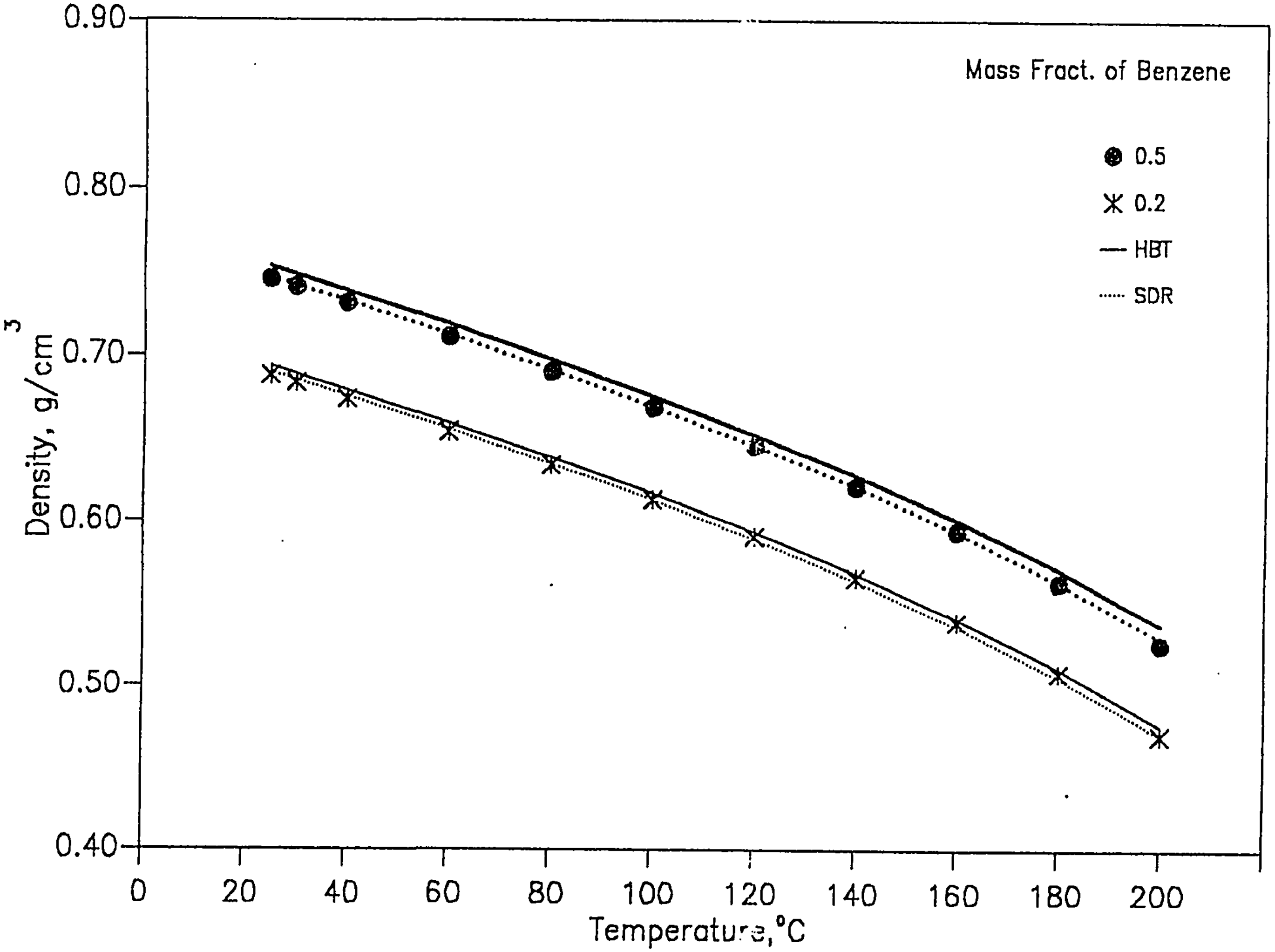

FIGURE 4.14 :COMPARISON OF EXPERIMENTAL DENSITY DATA WITH PREDICTIONS BY SDR AND HBT FOR BENZENE – n–HEXANE MIXTURES

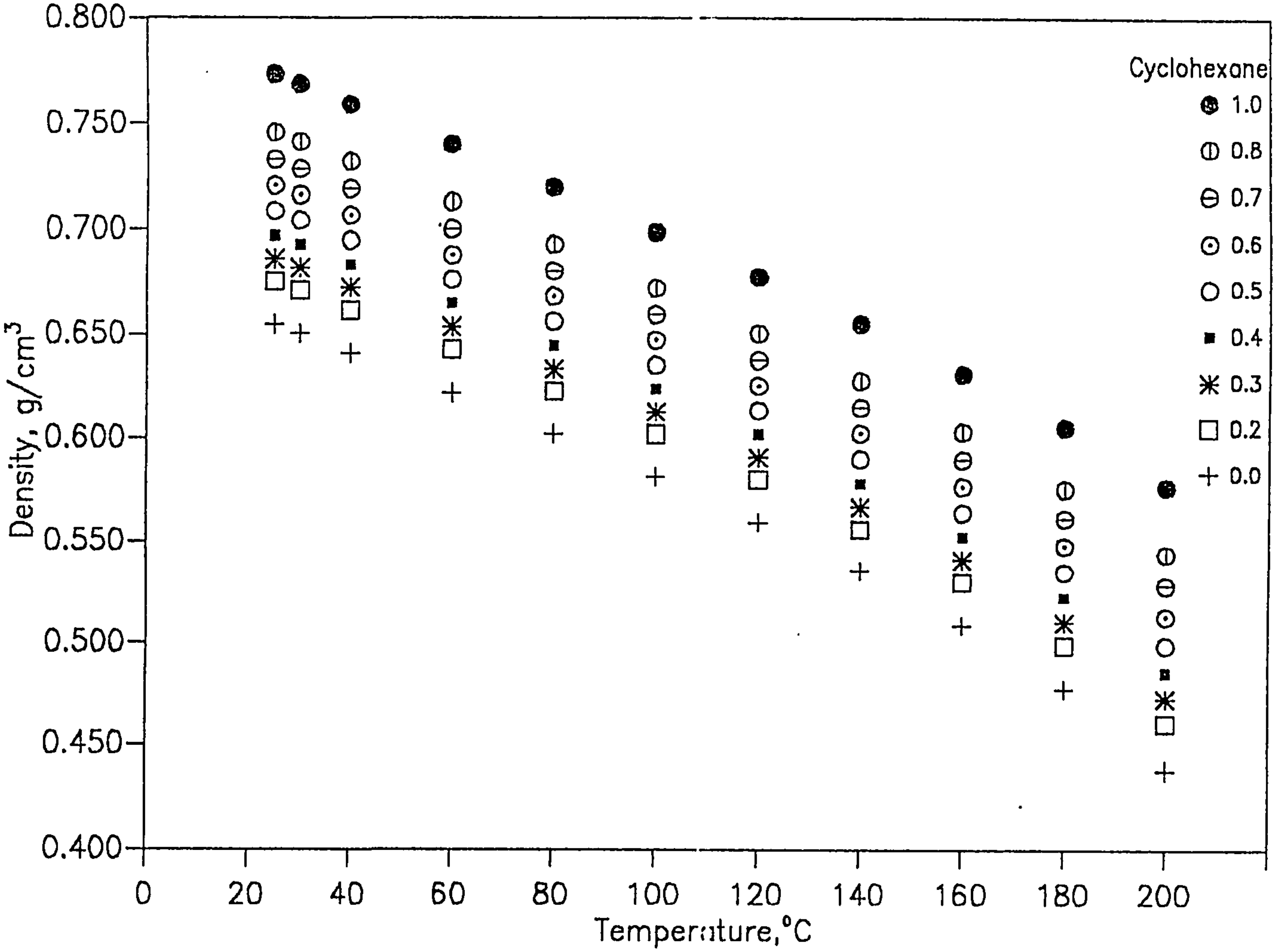

FIGURE 4.15 : EXPERIMENTAL DENSITY – TEMPERATURE DATA FOR DEFINED CYCLOHEXANE – n–HEXANE MIXTURES

Table 4.9 : Comparison of The Experimental Density Data of The Mixture of Cyclohexane - n-Hexane With Predictions From Spencer-Danner Modified Rackett Equation (SDR) and The Hankinson-Brobst-Thompson (HBT) correlation

Mass Fract. of Cyclohexane	Correlation	Minimun Absolute Deviation (MAD%)	Maximum Absolute Deviation (MAD%)	Average Absolute Deviation (AAD%)
0.2	SDR	0.0146	0.45	0.20
	HBT	0.053	0.71	0.30
0.3	SDR	0.023	0.34	0.16
	HBT	0.21	1.04	0.39
0.4	SDR	0.00	0.21	0.13
	HBT	0.30	0.57	0.45
0.5	SDR	0.01	0.71	0.12
	HBT	0.65	0.13	0.47
0.6	SDR	0.01	0.70	0.10
	HBT	0.33	1.29	0.45
0.7	SDR	0.00	0.60	0.08
	HBT	0.33	1.13	0.41
0.8	SDR	0.09	0.53	0.33
	HBT	0.63	1.20	0.89

Overall Percentage Average Absolute Deviation (SDR) = 0.16

Overall Percentage Average Absolute Deviation (HBT) = 0.48

n-hexane with an overall percentage average absolute deviation (AAD%) of 0.16. The HBT correlation on the otherhand predicted the density of the same mixtures with an overall (AAD%) of 0.48 when compared with the experimentally obtained values. The predicted density values are plotted in Figures 4.16 to 4.18 versus temperature. The corresponding experimental data are also shown in the Figures for easy comparison. The two correlations can be said to predict the experimental values with a reasonable degree of accuracy. The point by point errors obtained in the prediction of the density by the two correlations are given in Appendix C.

It may be noted that the Spencer and Danner modified Rackett equation (SDR) which predicts better results is based on the law of corresponding state involving more reliable experimentally estimated values of parameter Z_{RA} used in the correlation compared to the relatively less reliable theoretically estimated parameters involved in the HBT equation.

4.2.3 Density-Temperature Behavior of The Ternary Mixtures

The experimental density data for the ternary mixtures of benzene, cyclohexane and n-hexane are given in Appendix A. The data have been plotted in Figures 4.19, 4.20 & 4.21.

The plots in Figure 4.19 show how the density of the ternary mixtures change with increasing temperature. The density generally decreases as the temperature increases. In the four mixtures considered, the mass fraction of benzene was increased from 0.333 to 0.8 while keeping the mass fraction of the

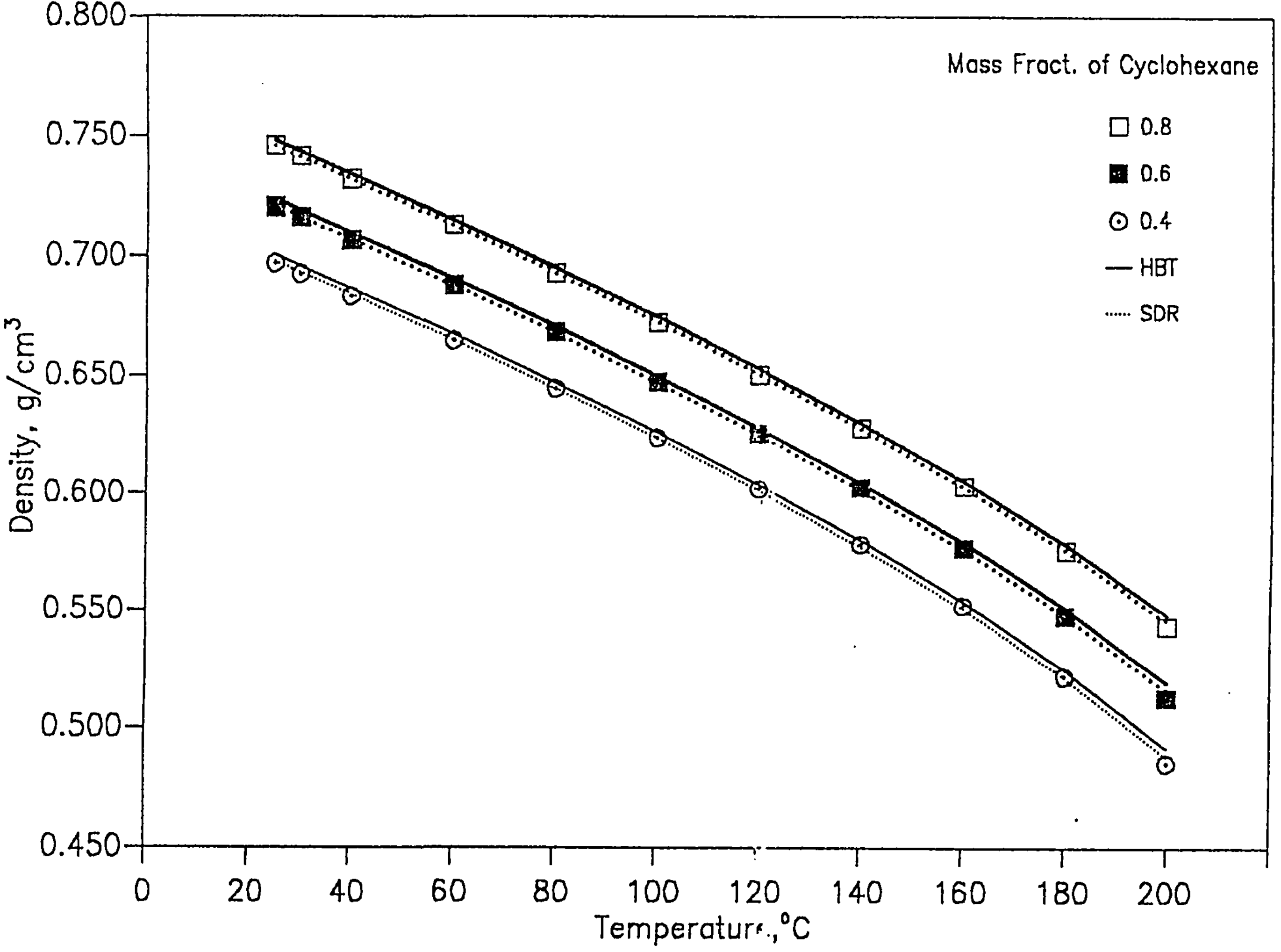

FIGURE 4.16 :COMPARISON OF EXPERIMENTAL DENSITY DATA WITH PREDICTIONS BY SDR AND HBT FOR CYCLOHEXANE — n-HEXANE MIXTURES

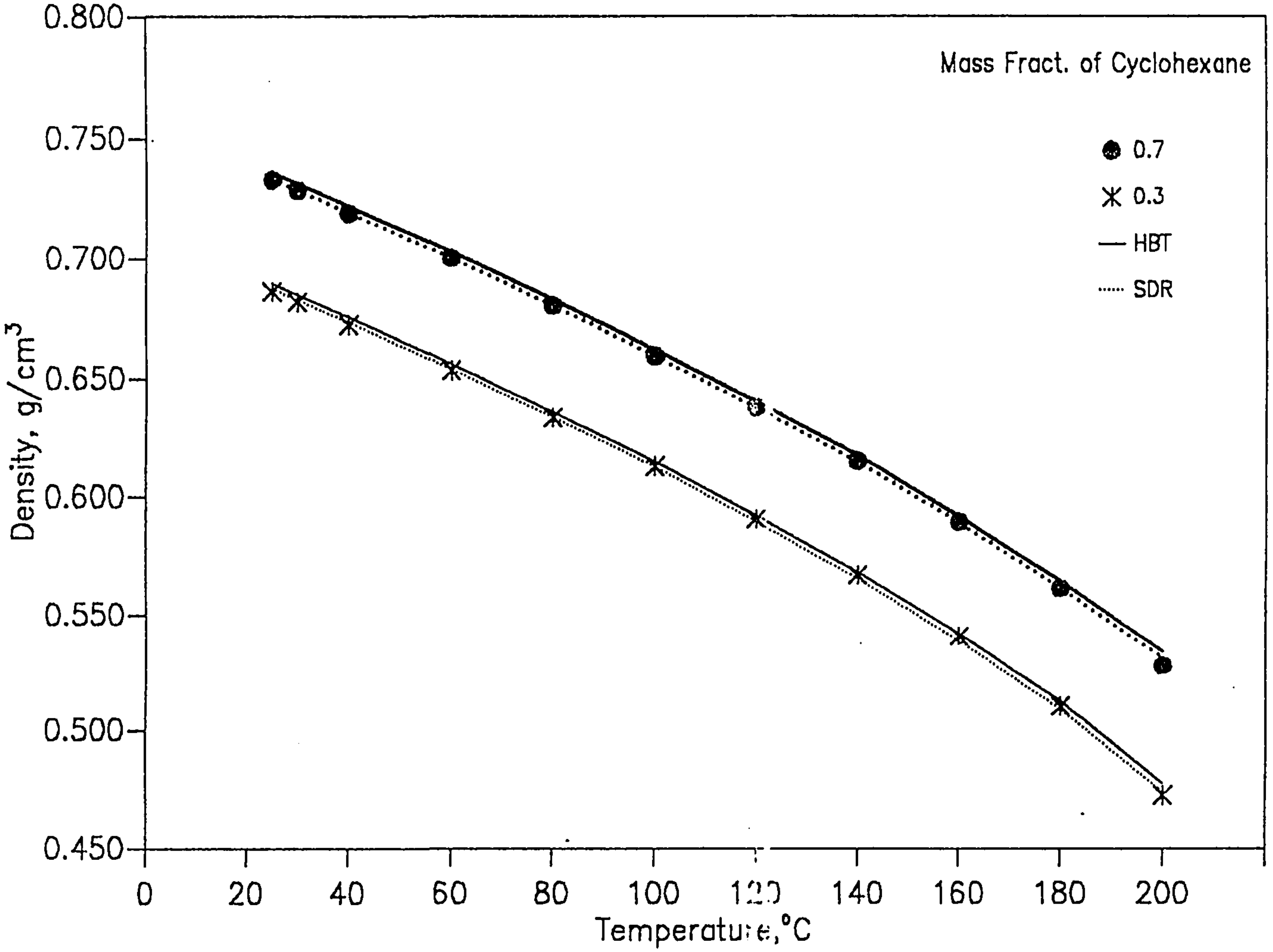

FIGURE 4.17 :COMPARISON OF EXPERIMENTAL DENSITY DATA WITH PREDICTIONS BY SDR AND HBT FOR CYCLOHEXANE – n-HEXANE MIXTURES

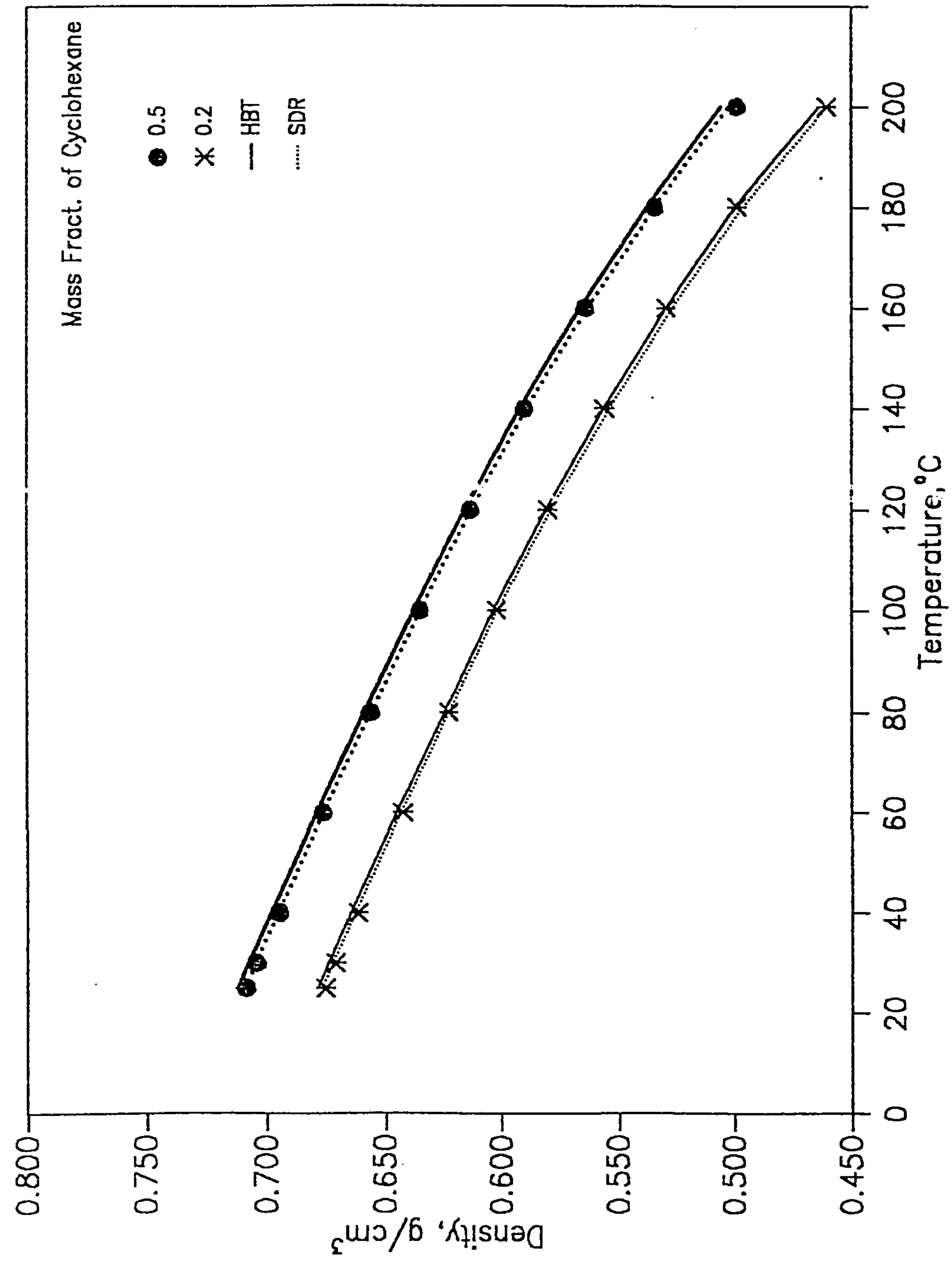

FIGURE 4.18 : COMPARISON OF EXPERIMENTAL DENSITY DATA WITH PREDICTIONS BY SDR AND HBT FOR CYCLOHEXANE – n-HEXANE

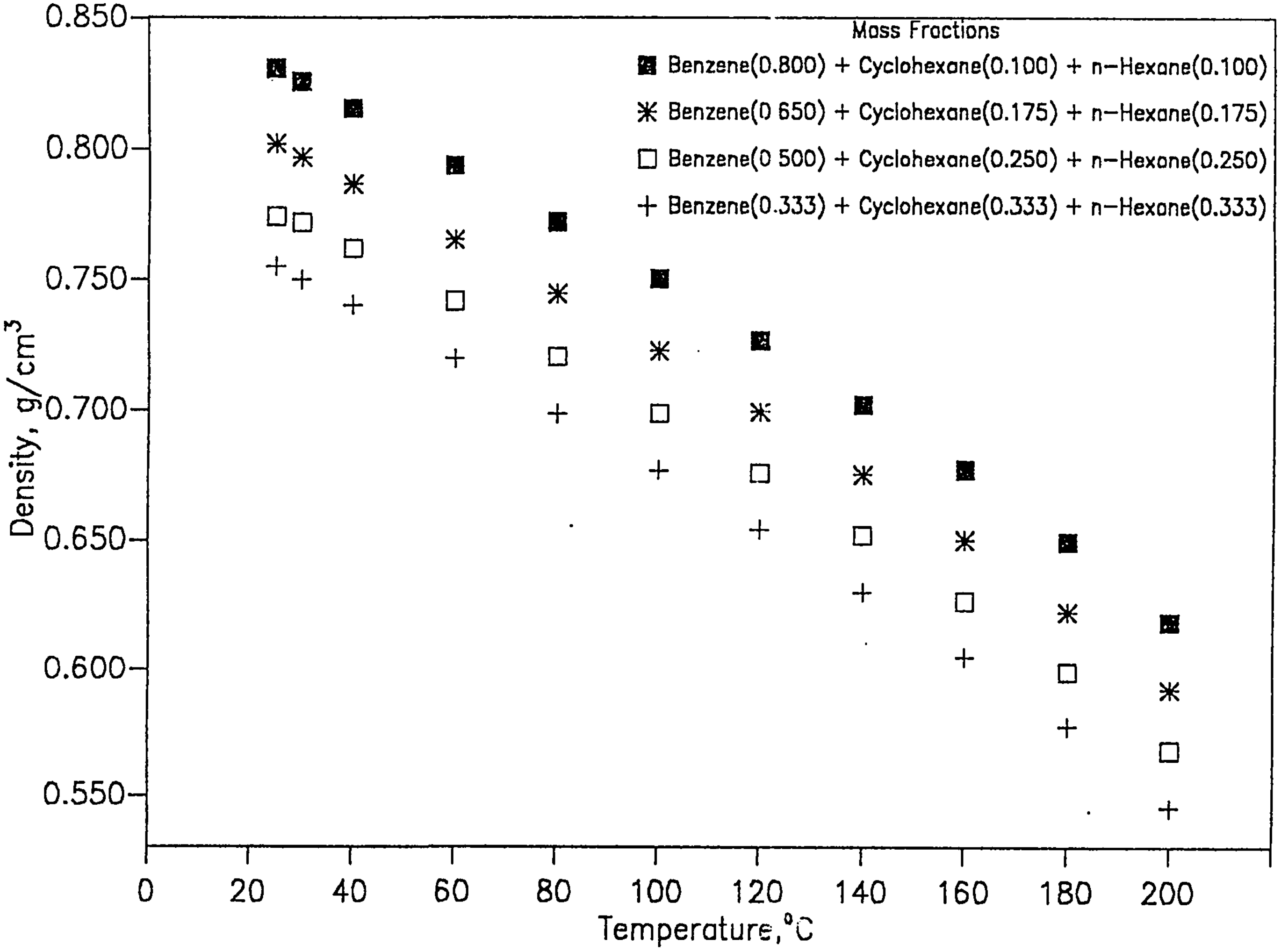

FIGURE 4.19 : EXPERIMENTAL DENSITY − TEMPERATURE DATA FOR THE TERNARY MIXTURES OF BENZENE − CYCLOHEXANE − n−HEXANE

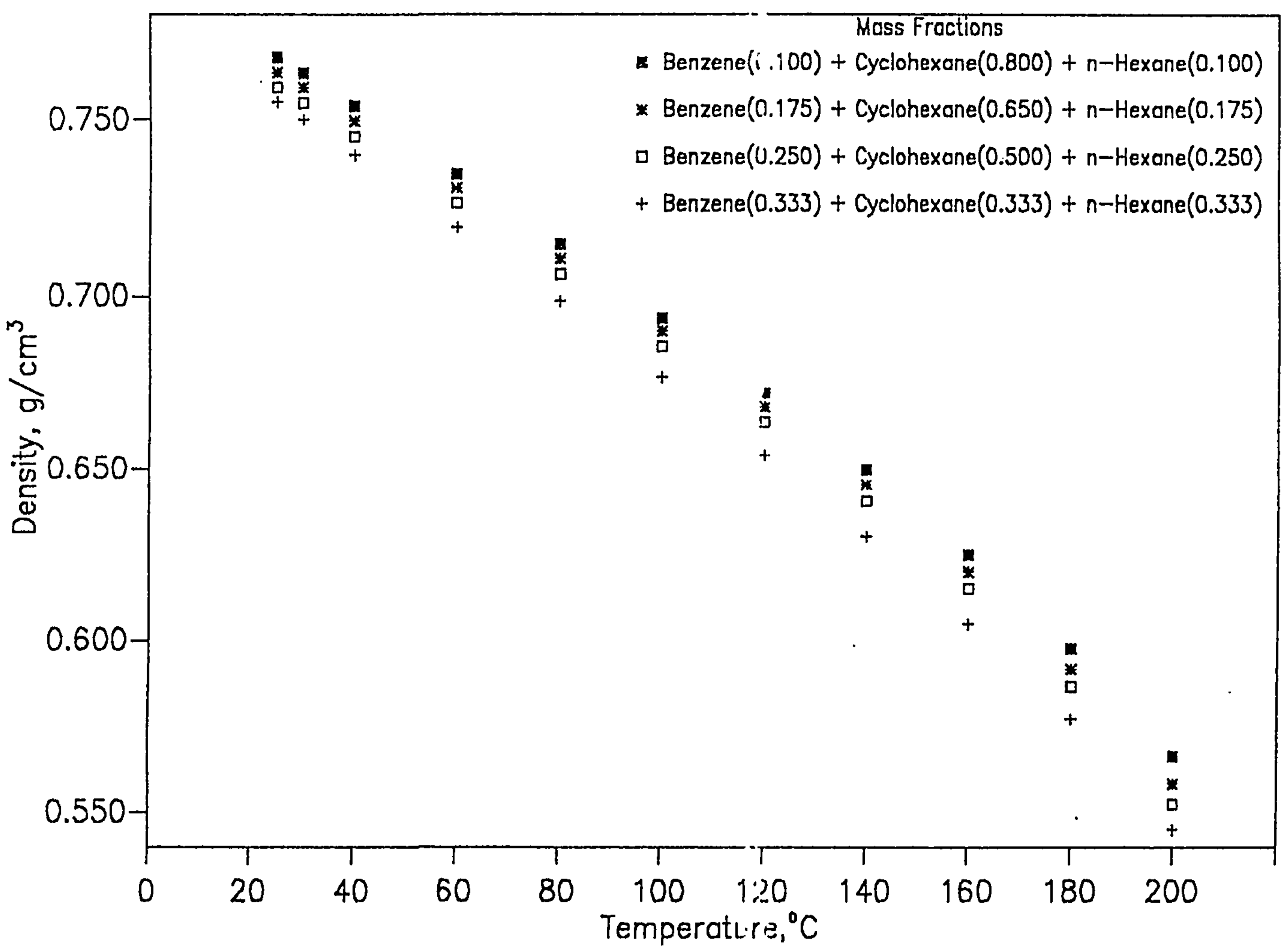

FIGURE 4.20 : EXPERIMENTAL DENSITY – TEMPERATURE DATA FORTHE TERNARY MIXTURES OF BENZENE – CYCLOHEXANE – n–HEXANE

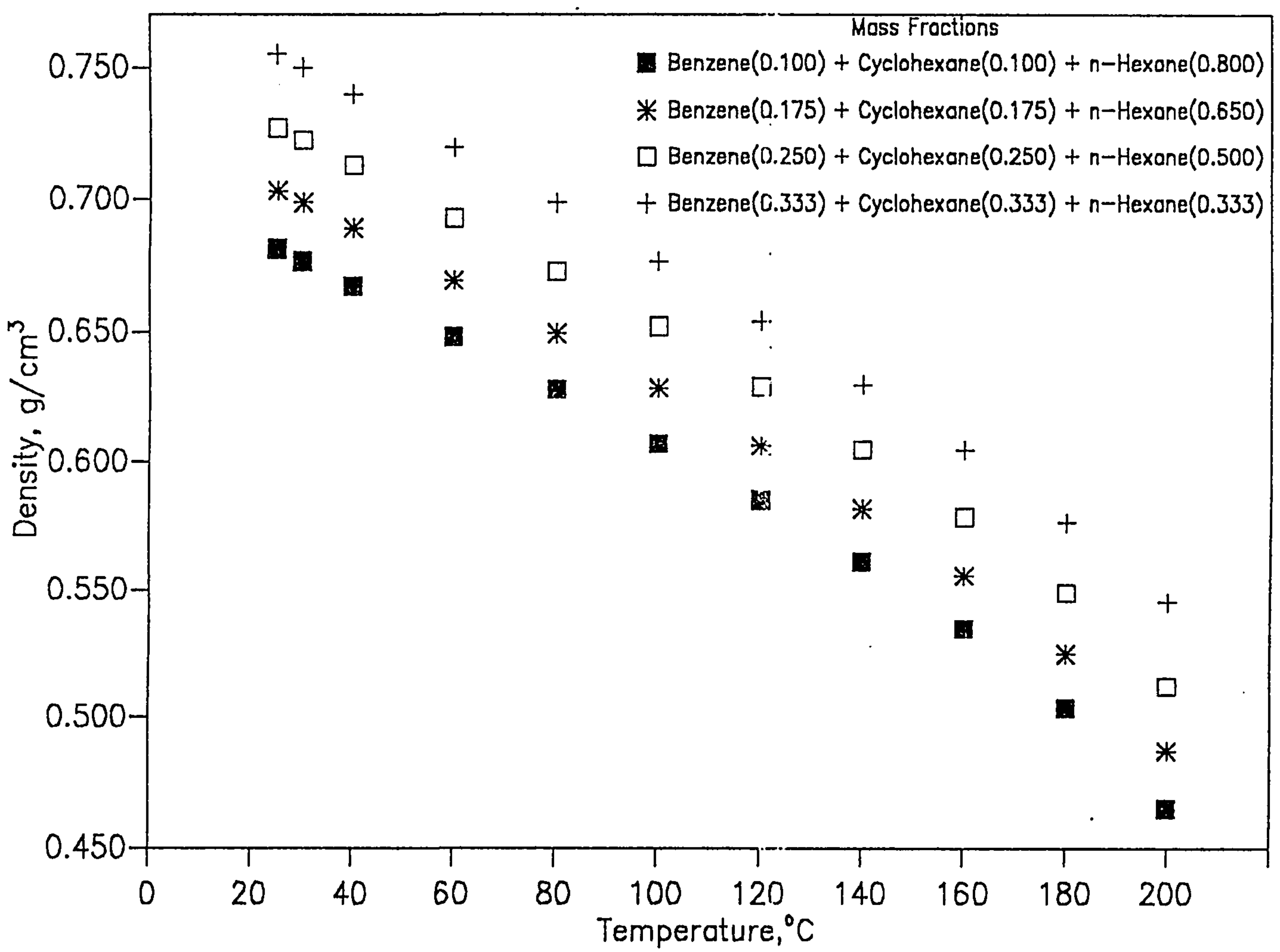

FIGURE 4.21 : EXPERIMENTAL DENSITY – TEMPERATURE DATA FOR THE TERNARY MIXTURES OF BENZENE – CYCLOHEXANE – n–HEXANE

other two components equal. It was observed that as the concentration of benzene increases from 0.333 to 0.80 at any particular temperature, the density increased by about 18%. This trend is seen in the whole range of composition considered. It may therefore be concluded that an increase in the concentration of an aromatic component in petroleum leads to an increase in the overall density.

Figure 4.20 shows the variations of the density of another ternary mixtures of benzene, cyclohexane and n-hexane in which the mass fraction of cyclohexane was increased from 0.333 to 0.80 while the mass fractions of the remaining constituents were kept equal. The densities of the mixtures were found to decrease with increasing temperature . It was also observed from the plots, as the concentration of cyclohexane increases from 0.333 to 0.80 at any particular temperature, the density increases by about 4.4% for the whole range of variation of the concentration of cyclohexane. It may therefore be concluded that an increase in the concentration of a naphthenic component in petroleum leads to a slight increase in the overall density.

Figure 4.21 shows the variations of density for another ternary mixtures of benzene, cyclohexane and n-hexane. For the four mixtures considered, the mass fraction of n-hexane was increased from 0.333 to 0.80 while the mass fractions of the remaining components were kept equal. The density of each of the mixture was found to decrease with increasing temperature. It was observed from the data obtained that as the concentration of n-hexane increases from 0.333 to 0.80 at any given temperature, the density decreases by about 16.0% for the whole range of variation of the n-hexane. It may be concluded therefore, that an increase in the concentration of a paraffinic component in petroleum leads to a decrease in its overall density.

Table 4.10 gives the errors in the prediction of the density using the Spencer-Danner modified Rackett equation (SDR) and the HankinsonBrobst-Thompson correlation. The SDR correlation gave an overall percentage average absolute deviation (AAD%) of 0.29 for the ten ternary mixtures of benzene - cyclohexane - n-hexane considered. The HBT correlation predicted the density of the mixtures with an overall (AAD%) of 0.70 when compared with the experimentally obtained values. The predicted density values are plotted in Figures 4.22 to 4.26 as a function of temperature for the representative compositions. The corresponding experimental data are also shown in the Figures for easy comparison. The point by point errors obtained in the prediction of the density by the two correlations are given in Appendix C.

4.3 EXCESS MOLAR VOLUMES OF THE BINARY MIXTURES

Excess volumes of each of the three binary mixtures were computed from the density and composition using the equation below :

$$V^E = [X_1M_1 + X_2M_2]/\rho_m - X_1M_1/\rho_1 - X_2M_2/\rho_2] \qquad (4.1)$$

Where X_1 and X_2 represent the mole fraction of component 1 and component 2 respectively, M_1, M_2 are the molecular masses of the mixing components and ρ_m, ρ_1, ρ_2 are the densities of the mixture, component 1 and component 2 respectively. The excess volumes data ($V^E/\mathrm{cm}^3\,\mathrm{mol}^{-1}$) for the three binary mixtures are given in Appendix A. The data have been plotted

Table 4.10 : **Comparison of The Experimental Density Data of The Mixture of Benzene - Cyclohexane - n-Hexane With Predictions From Spencer-Danner Modified Rackett Equation (SDR) and The Hankinson-Brobst-Thompson (HBT) correlation**

Mass Fract. of the Components	Correlation	Minimun Absolute Deviation (MAD%)	Maximum Absolute Deviation (MAD%)	Average Absolute Deviation (AAD%)
Benzene (0.33) Cyclohexane(0.33) n-Hexane (0.33)	SDR HBT	0.09 0.63	0.53 1.20	0.33 0.89
Benzene (0.50) Cyclohexane(0.25) n-Hexane (0.25)	SDR HBT	0.54 1.04	0.92 1.57	0.71 1.24
Benzene (0.65) Cyclohexane(0.18) n-Hexane (0.18)	SDR HBT	0.54 0.94	0.90 1.41	0.68 1.12
Benzene (0.80) Cyclohexane(0.10) n-Hexane (0.10)	SDR HBT	0.22 0.47	0.58 0.95	0.38 0.69
Benzene (0.25) Cyclohexane(0.50) n-Hexane (0.25)	SDR HBT	0.01 0.28	0.52 1.08	0.12 0.43
Benzene (0.18) Cyclohexane(0.65) n-Hexane (0.18)	SDR HBT	0.00 0.14	0.65 1.06	0.11 0.33
Benzene (0.10) Cyclohexane(0.80) n-Hexane (0.10)	SDR HBT	0.00 0.17	0.33 0.34	0.06 0.24
Benzene (0.25) Cyclohexane(0.25) n-Hexane (0.50)	SDR HBT	0.019 0.68	0.84 1.81	0.14 0.79

Benzene (0.18)	SDR	0.014	0.67	0.17
Cyclohexane(0.18)	HBT	0.62	1.69	0.75
n-Hexane (0.65)				
Benzene (0.10)	SDR	0.01	0.50	0.22
Cyclohexane(0.10)	HBT	0.24	0.94	0.50
n-Hexane (0.80)				

Overall Percentage Average Absolute Deviation (SDR) = 0.29 Overall Percentage Average Absolute Deviation (HBT) = 0.70

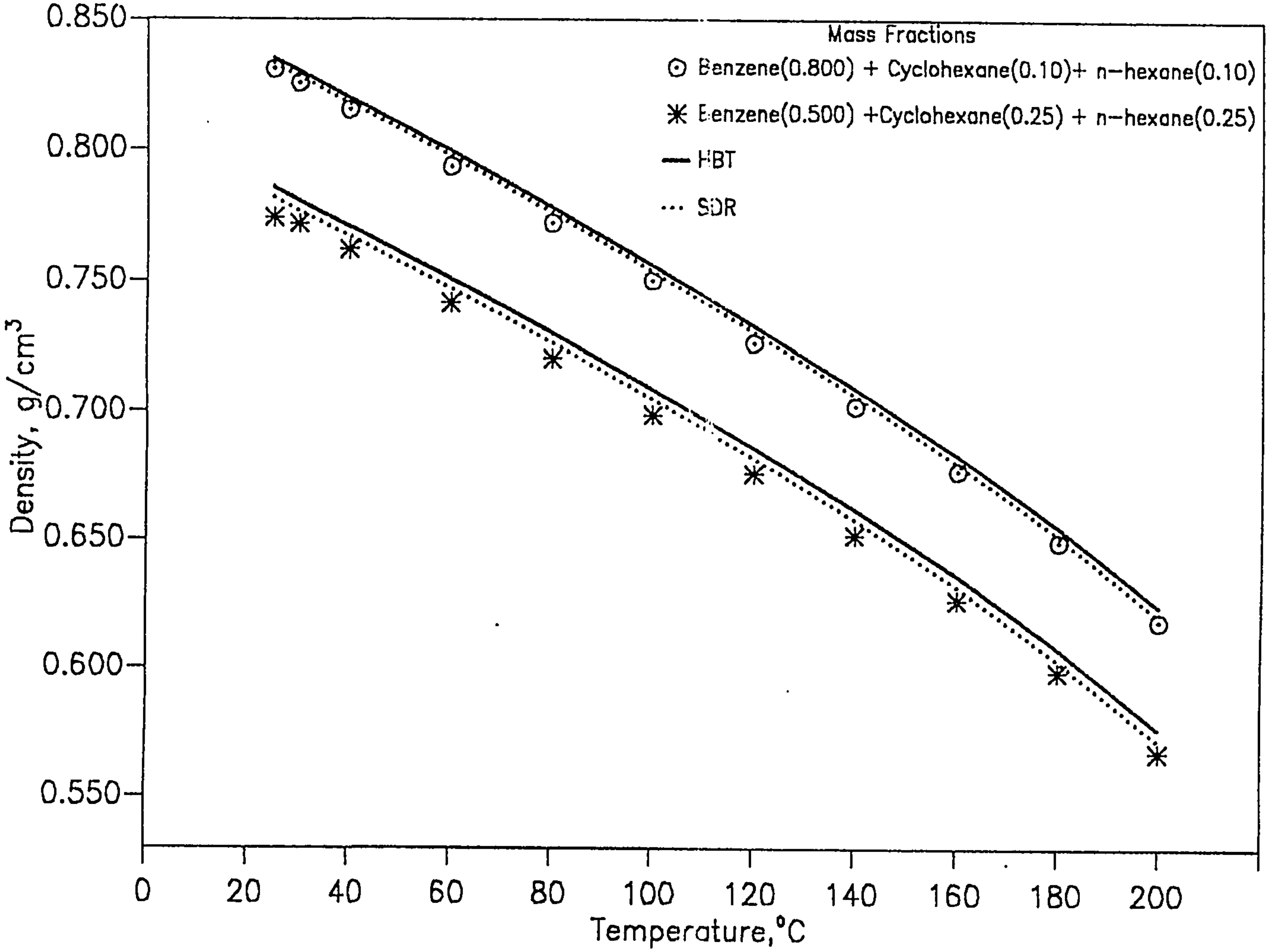

FIGURE 4.22 :COMPARISON OF EXPERIMENTAL DENSITY DATA WITH PREDICTIONS BY SDR AND HBT FOR BENZENE – CYCLOHEXANE – n–HEXANE

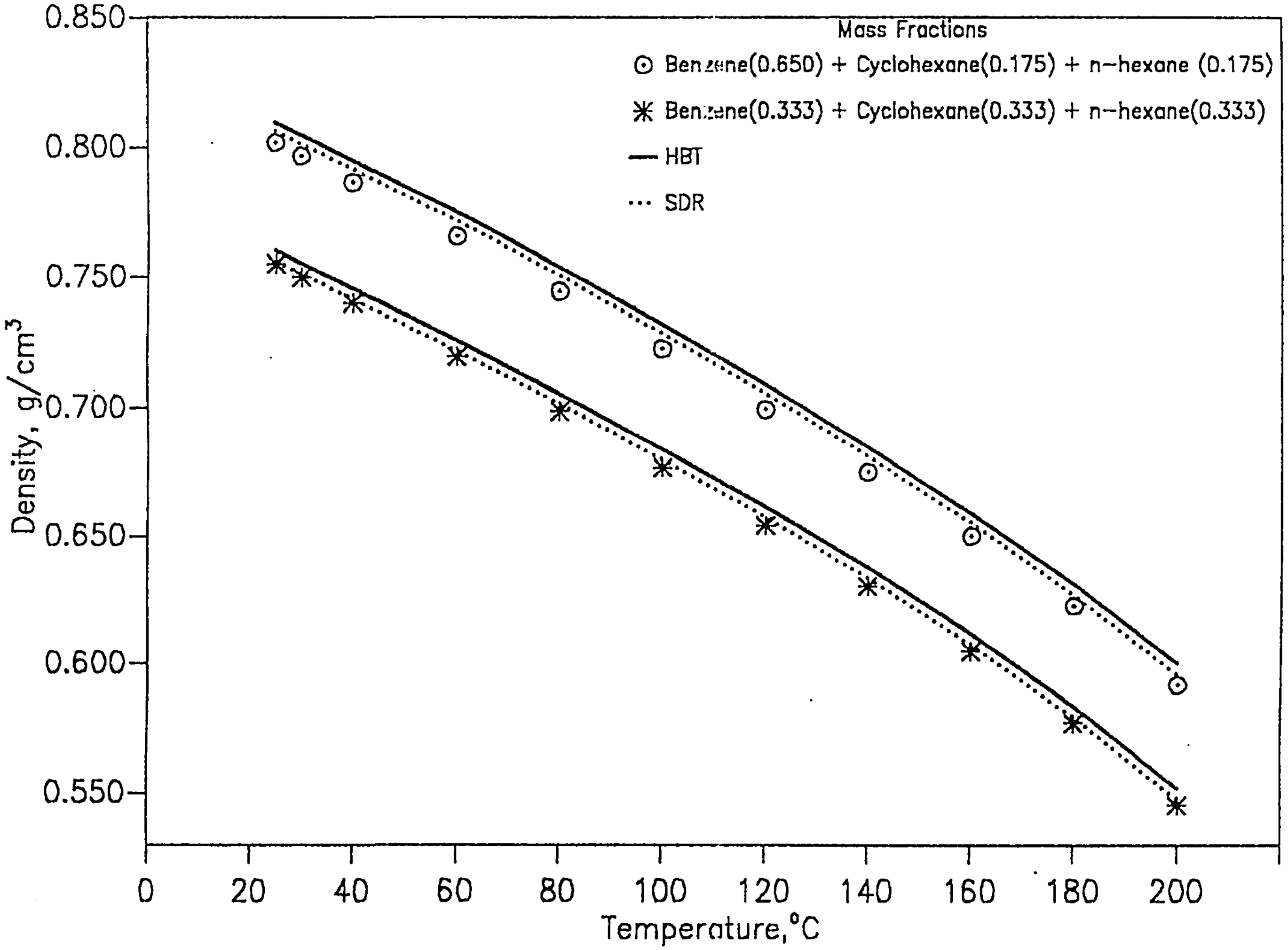

FIGURE 4.23 :COMPARISON OF EXPERIMENTAL DENSITY DATA WITH PREDICTIONS BY SDR AND HBT FOR BENZENE – CYCLOHEXANE – n−HEXANE

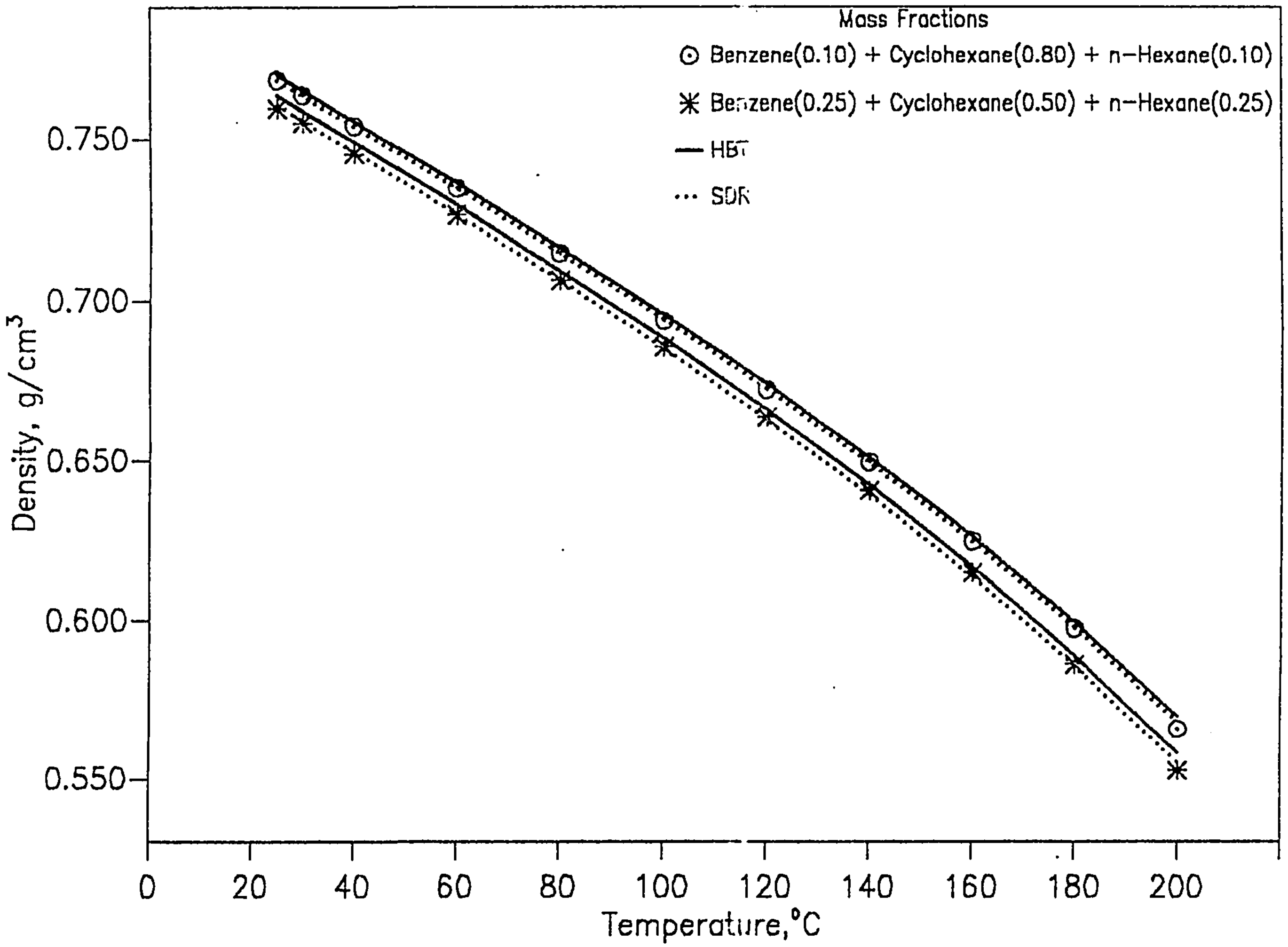

FIGURE 4.24 :COMPARISON OF EXPERIMENTAL DENSITY DATA WITH PREDICTIONS BY SDR AND HBT FOR BENZENE − CYCLOHEXANE − n- HEXANE

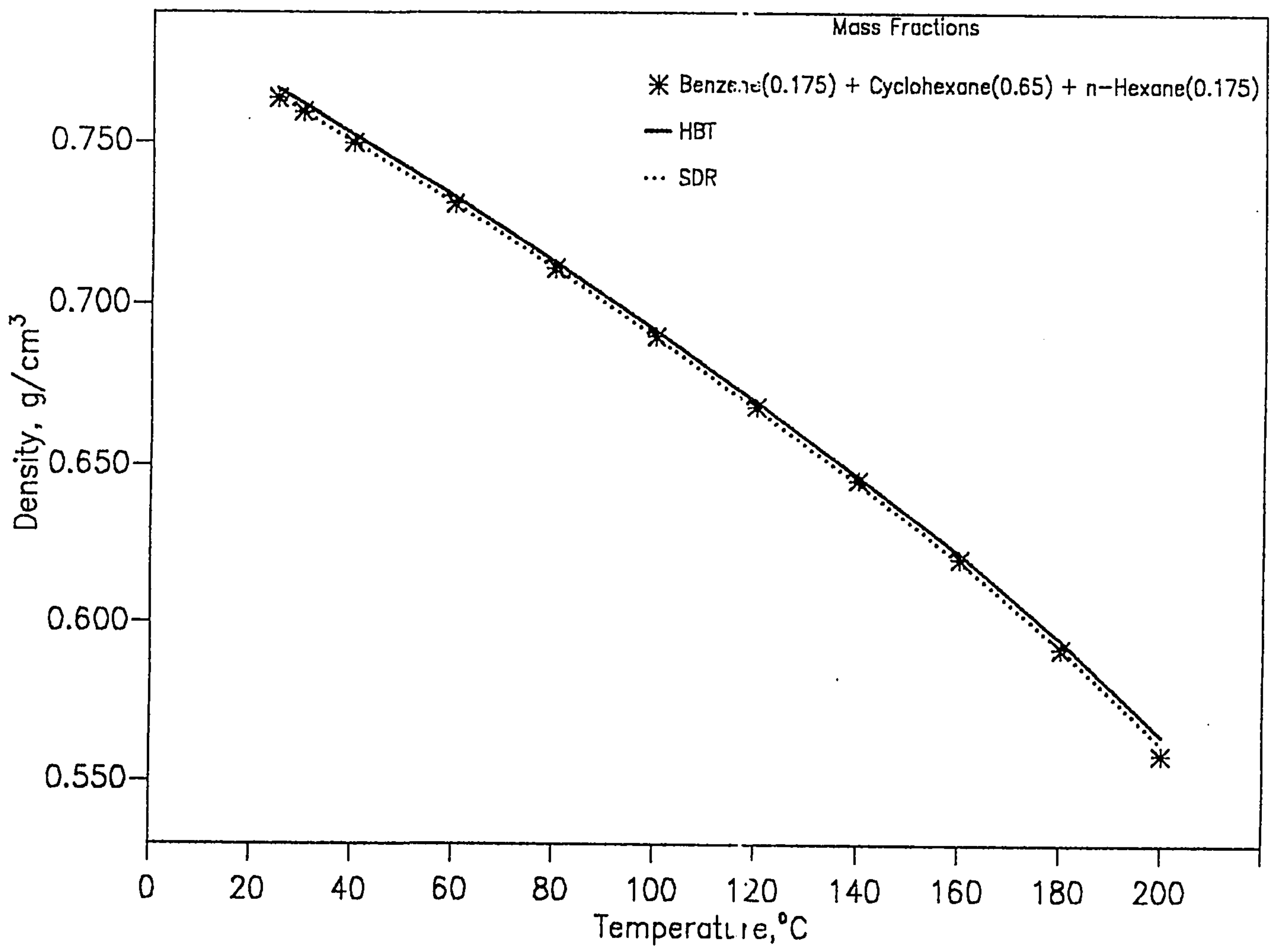

FIGURE 4.25 :COMPARISON OF EXPERIMENTAL DENSITY DATA WITH PREDICTIONS BY SDR AND HBT FOR BENZENE – CYCLOHEXANE – n-HEXANE

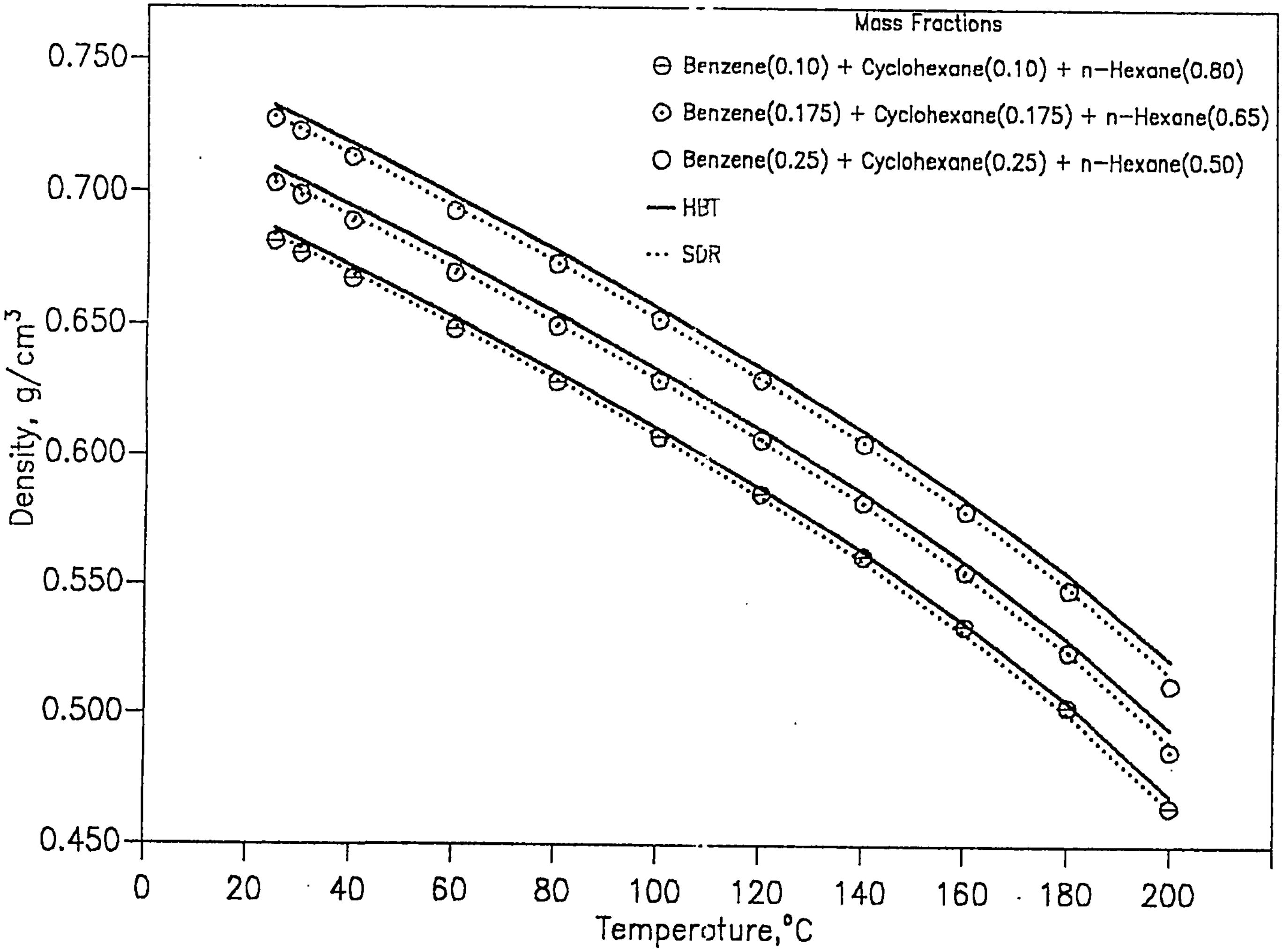

FIGURE 4.26:COMPARISON OF EXPERIMENTAL DENSITY DATA WITH PREDICTIONS BY SDR AND HBT FOR BENZENE – CYCLOHEXANE – n–HEXANE

against composition in Figures 4.27, 4.28 and 4.29.

4.3.1 Benzene - Cyclohexane Mixture

The mixture of benzene and cyclohexane exhibit positive deviations from ideality for the whole range of temperature considered in the present studies. The deviations or the excess volumes increase with increasing temperature.

Positive deviations from ideality were obtained when benzene is mixed with cyclohexane because of the existence of voids when these two components are mixed. Voids develop because of the incompatible structures of the mixing components. Benzene is rigid with more or less spherical shape while cyclohexane molecules are acknowledged to be in the form of an arm-chair or boat shaped. Furthermore, with increasing temperatures, the molecules vibrate due to increasing kinetic energy leaving more voids. This makes the volume of the mixture to get bigger compared to the total volume of the individual mixing component as the temperature increases. The positive values V^E also point to the fact that the dispersion forces are predominant between the components. For the data obtained, the excess molar volumes for the binary mixture were correlated as a function of composition using 3-constant Redlich - Kister expansion :

$$V^E(\mathrm{cm^3\,mol^{-1}}) = x(1-x)[A + B(1-2x) + C(1-2x)^2] \qquad (4.2)$$

The coefficients A, B and C were determined by carrying out non-linear regression using statistical analysis system. The coefficients and the average deviations of the excess volumes from the correlation are shown in Table 4.11.

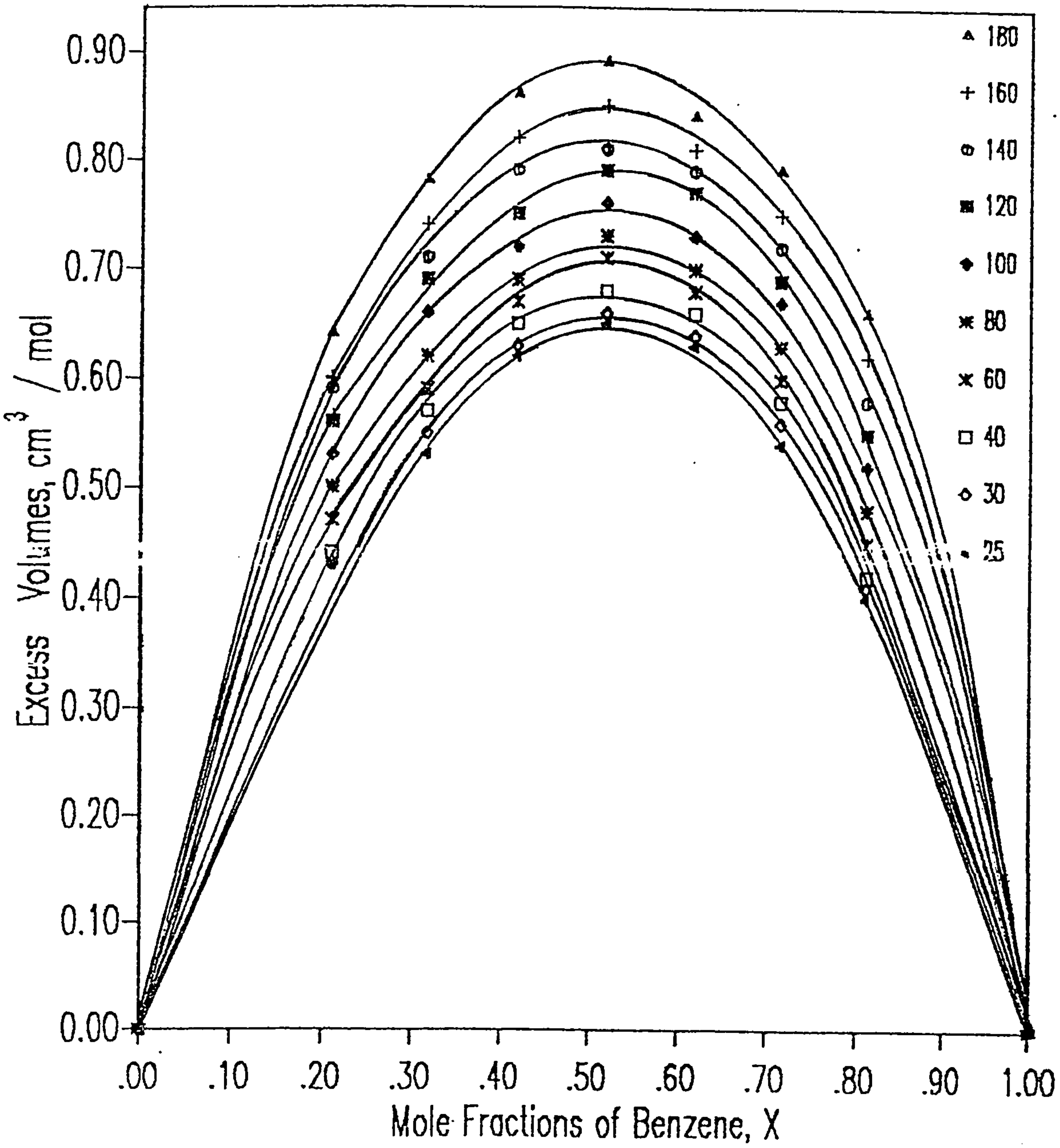

Figure 4.27 : Plot of Excess Volumes For Defined Binary Mixture of Benzene - Cyclohexane

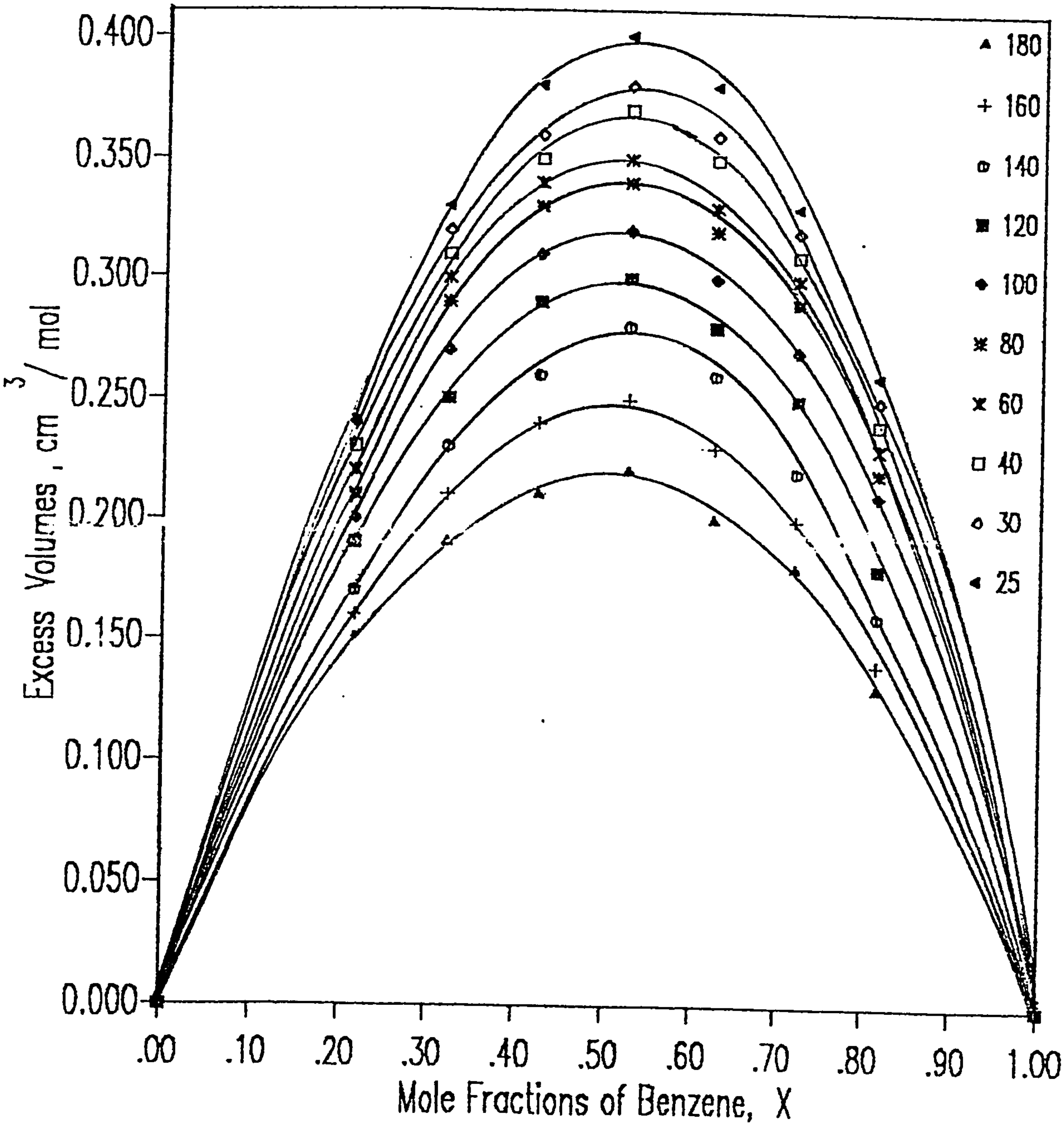

Figure 4.28 : Plot of Excess Volumes For Defined Binary Mixture of Benzene - n-Hexane

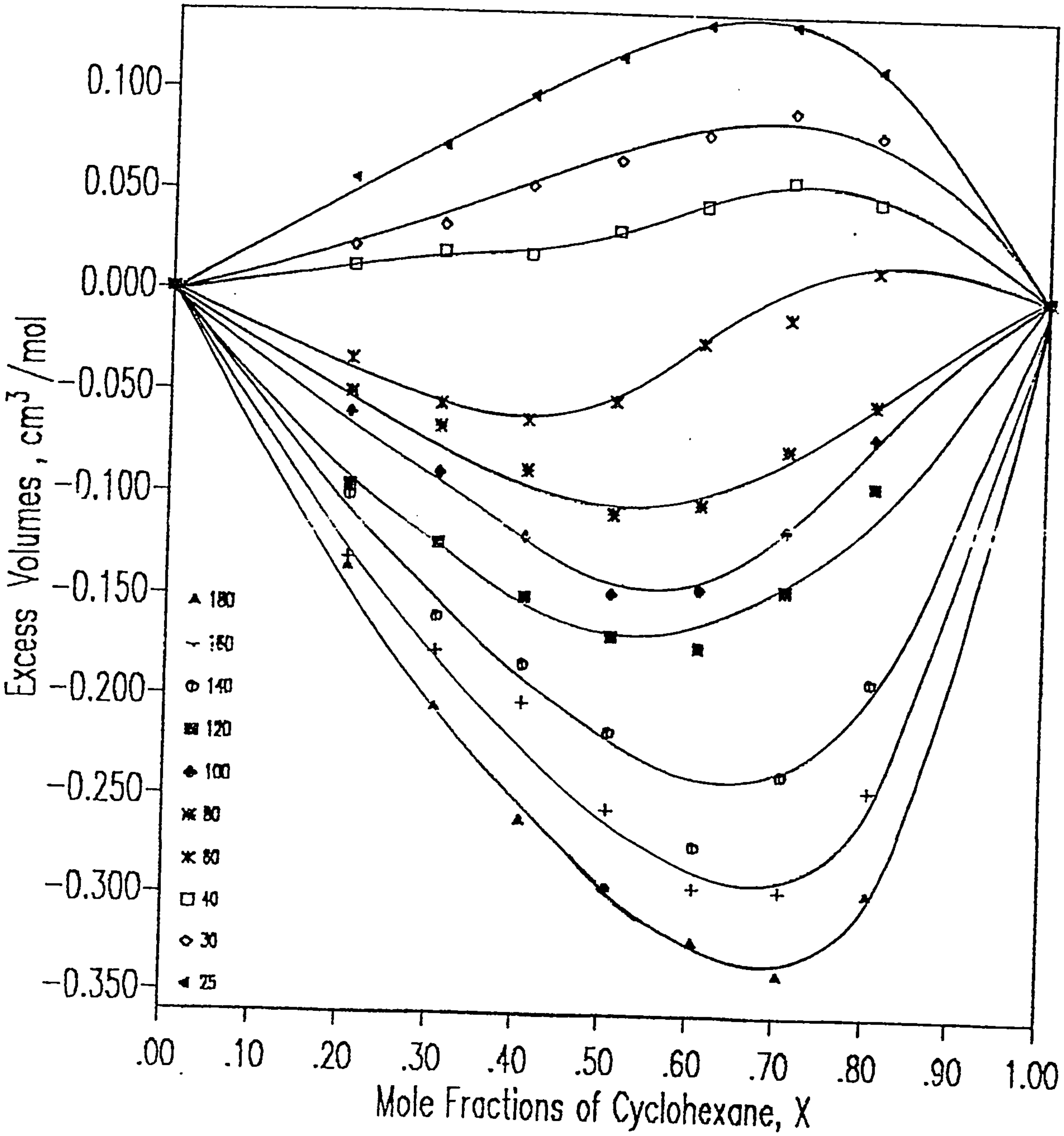

Figure 4.29 : Plot of Excess Volumes For Defined Binary Mixture of Cyclohexane - n-Hexane

Table 4.11 : **Coefficients of The 3-constants Redlich-Kister Equation And The Deviation of The Excess Volume From The Correlation For A System Benzene - Cyclohexane Mixture**

Temp. (C)	Coefficients		Percentage Average Absolute Deviation
25	A	2.5765	1.72
	B	-0.1427	
	C	-0.0461	
30	A	2.6511	1.23
	B	-0.1473	
	C	-0.0981	
40	A	2.7504	1.02
	B	-0.1538	
	C	-0.1552	
60	A	2.8016	0.89
	B	-0.1209	
	C	0.3400	
80	A	2.8807	1.29
	B	-0.1157	
	C	0.5696	
100	A	3.0154	0.68
	B	-0.1536	
	C	0.8225	
120	A	3.1422	0.45
	B	-0.1085	
	C	1.0068	
140	A	3.2559	0.64
	B	-0.1255	
	C	1.1839	

160	A	3.3530	0.71
	B	-0.2505	
	C	1.3928	
180	A	3.5117	1.03
	B	-0.2233	
	C	1.6849	
200	A	3.6386	1.37
	B	-0.2777	
	C	1.8550	

Further attempt were made to express the excess volumes of the benzene - cyclohexane mixture as a function of both composition and temperature by correlating the coefficients of the Redlich-Kister expansion (Eq. 4.2) as a function of temperature.

$$A = A_0 + A_1 T + A_2 T_2 \tag{4.3}$$

$$B = B_0 + B_1 T + B_2 T_2 \tag{4.4}$$

$$C = C_0 + C_1 T + C_2 T_2 \tag{4.5}$$

Values for the coefficients A_i, $B_i$and C_i are listed in Table 4.12. These coefficients reproduce the excess volumes enable the prediction of the excess volumes of the benzene - cyclohexane mixtures with an overall percentage average absolute deviation of 1.38%.

4.3.2 Benzene - n-Hexane Mixture

The mixture of benzene and n-hexane also exhibit positive deviations from ideality for all the temperatures considered as shown in Figure 4.28. However, the excess volumes decrease with increasing temperature. This is in contrast to the benzene - cyclohexane mixture, in which the excess volumes increase with increasing temperature.

Positive deviations from ideality were obtained as well when benzene gets mixed with n-hexane. This is primarily as a results of the voids that exist when the two components are mixed. Voids develop because of the incompatible structures of the mixing components. Benzene is rigid with more or less spherical shape while n-hexane molecules are acknowledged to have a chain structure.

Table 4.12 : Coefficients of Equations 4.3, 4.4 and 4.5 Evaluated From Non-Linear Regression For The system of Benzene - Cyclohexane

A		B		C	
A_0	2.4965	B_0	0.4743E-02	C_0	0.4687E-05
A_1	-0.2018	B_1	0.2097E-02	C_1	-0.1226E-04
A_2	-0.0993	B_2	-0.1852E-03	C_2	0.6391E-04

Overall Average Absolute Deviation is 1.38%

However, as the temperature increases, the flexible chain structure of n-hexane gets accommodated more easily into the spaces between the benzene molecules leading to a drop in the volume of the mixture as observed in the case of the benzene - n-hexane mixture.

The excess molar volumes of the benzene - n-hexane systems were correlated as a function of composition using 3-constant Redlich - Kister expansion (Equation 4.2) for each temperature considered. The coefficients A, B and C were determined by carrying out nonlinear regression using statistical analysis system. The coefficients and the average deviations of the excess volumes from the correlation are given in Table 4.13.

Further attempt was made to express the excess volumes of the benzene - n-hexane mixture as a function of both composition and temperature by correlating the coefficients of the Redlich-Kister expansion (Eq. 4.2) as a function of temperature (see Equations 4.3, 4.4 and 4.5).

The estimated values for the coefficients $A_{i,}$ $B_i$and C_i are listed in Table 4.14. These coefficients predict the excess volumes data of the benzene + n-hexane mixture with a percentage average absolute deviation of 2.03%.

4.3.3 Cyclohexane - n-Hexane Mixture

It is interesting to note that while the excess volumes of benzene - cyclohexane and benzene - n-hexane showed positive deviations at all the temperatures considered, the cyclohexane - n-hexane mixtures exhibit changes in excess volumes from positive to negative as the temperature increases as shown

Table 4.13 : **Coefficients of The 3-constants Redlich-Kister Equation And The Deviation of The Excess Volume From The Correlation For A System of Benzene - n-Hexane Mixture**

Temp. (C)	Coefficients		Percentage Average Absolute Deviation
25	A	1.5617	1.02
	B	-0.2235	
	C	-0.0535	
30	A	1.4942	1.04
	B	-0.2355	
	C	0.02947	
40	A	1.4628	1.97
	B	-0.2138	
	C	-0.0849	
60	A	1.3764	1.16
	B	-0.1684	
	C	0.1267	
80	A	1.3519	1.11
	B	-0.1198	
	C	0.0104	
100	A	1.2368	0.76
	B	-0.1161	
	C	0.1192	
120	A	1.1547	1.45
	B	-0.1480	
	C	0.0817	
140	A	1.0612	1.39
	B	-0.0587	
	C	-0.0558	

160	A	0.9876	1.44
	B	-0.0310	
	C	-0.2554	
180	A	0.8153	1.26
	B	0.08373	
	C	0.2751	
200	A	0.7214	3.59
	B	0.0751	
	C	0.0639	

Table 4.14 : Coefficients of Equations 4.3, 4.4 and 4.5 Evaluated From Non-Linear Regression For The system of Benzene - n-Hexane

A		B		C	
A_0	1.5886	B_0	-024508E-02	C_0	-0.9521E-05
A_1	-0.2045	B_1	-0.3591E-04	C_1	0.7360E-05
A_2	0.0245	B_2	-0.7930E-03	C_2	0.4609E-05

Overall Average Absolute Deviation is 2.03%

in Figure 4.29. The data showed that above 40°C the excess volumes are all positive, while below 40°C the excess volumes start exhibiting negative deviations. This implies that the excess volumes decrease as the temperature increases. it is also interesting to note that the excess volume curves are skewed towards n-hexane.

Deviations from ideality were obtained in the mixture of cyclohexane with n-hexane because of the existence of voids when these two components are mixed. Voids develop because of the incompatible structures of the mixing components. Cyclohexane has an arm-chair structure while n-hexane molecules have a chain structure. However, as the temperature increases, the flexible chain structure of the n-hexane molecules get accommodated more easily into the spaces between the cyclohexane molecules. This as temperature increases, the molecules vibrate leaving more voids due to the increasing kinetic energy.

It should be noted that the higher the excess volume the less efficient is the packing arrangement. The efficiency of packing arrangement in the three mixtures considered will increase in the following order.

Benzene-Cyclohexane < Benzene-n-Hexane < Cyclohexane-n-hexane

Excess volume data from the three mixtures confirm the above assertion. The excess volume at 25°C for the equimolar mixture of benzene - cyclohexane is 0.6506 $cm^3 mol^{-1}$, that of the equimolar mixture of benzene - n-hexane at the same temperature is 0.3914 $cm^3 mol^{-1}$, and the value for the equimolar mixture of cyclohexane - n-hexane is 0.1158 $cm^3 mol^{-1}$.

The excess molar volumes for the cyclohexane - n-hexane mixture like the excess volumes of the other two mixtures were fitted to a a 3-constant Redlich - Kister expansion (Equation 4.2). The coefficients A, B and C were determined by carrying out a nonlinear regression using statistical analysis system available at the Data Processing Center of K.F.U.P.M. The coefficients and the average deviations of the excess volumes from the correlation are given in Table 4.15.

Further attempt was made to express the excess volumes of the cyclohexane - n-hexane mixture as a function of both composition and temperature by correlating the coefficients of the Redlich-Kister expansion (Eq. 4.2) as a function of temperature (see Equations 4.3, 4.4 and 4.5). Values for the coefficients $A_{i,}$ $B_i$and C_i are listed in Table 4.16. These coefficients predict the excess volumes data of the cyclohexane - n-hexane mixture with a percentage average absolute deviation of 22.3%.

4.4 COMPUTER SIMULATION RESULTS

The molecular dynamics (MD) technique was used in the computer simulation. Furthermore, the Lennard-Jones potential was used as an approximate potential to represent the intermolecular forces in the hydrocarbon samples. Table 4.17 shows the values of Lennard-Jones constants, σ in Angstrom and ε/k in kelvin for benzene, cyclohexane and n-hexane determined from viscosity data of the solvents.

Table 4.15 : **Coefficients of The 3-constants Redlich-Kister Equation And The Deviation of The Excess Volume From The Correlation For A System of Cyclohexane - n-Hexane Mixture**

Temp. (C)	Coefficients		Percentage Average Absolute Deviation
25	A	0.4582	2.61
	B	-0.3390	
	C	0.2012	
30	A	0.2611	2.92
	B	-0.3222	
	C	0.1733	
40	A	0.1188	10.00
	B	-0.2070	
	C	0.2256	
60	A	-0.1999	13.64
	B	-0.2411	
	C	0.3439	
80	A	-0.3996	5.96
	B	0.0446	
	C	0.2304	
100	A	-0.5645	5.91
	B	0.0983	
	C	0.4398	
120	A	-0.6755	4.93
	B	0.0541	
	C	0.2311	
140	A	-0.9058	4.74
	B	0.5156	
	C	-0.0752	

160	A	-1.000	2.89
	B	0.6573	
	C	-0.5483	
180	A	-1.2011	2.21
	B	0.8258	
	C	-0.4209	
200	A	-1.325	4.02
	B	0.9926	
	C	-0.6403	

Table 4.16 : Coefficients of Equations 4.3, 4.4 and 4.5 Evaluated From Non-Linear Regression For The system of Cyclohexane - n-Hexane

A		B		C	
A_0	0.7862	B_0	-0.1846E-01	C_0	0.4361E-04
A_1	-0.3677	B_1	0.6355E-02	C_1	-0.2011E-04
A_2	0.9069E-02	B_2	0.8267E-02	C_2	-0.6249E-04

Overall Average Absolute Deviation is 22.3%

Table 4.17 : **Lennard-Jones Force Constants For Benzene, Cyclohexane And n-Hexane.**

Component	σ (A^3)	ε / k (K)
Benzene	5.27	440
Cyclohexane	6.093	324
n-Hexane	5.909	413

A computer program was modified to calculate the density and other thermodynamics properties of the pure components of the hydrocarbon mixtures. The simulation was performed at constant N (no of molecules), constant P (pressure) and constant T (temperature). The basic simulation parameters are first inputted, these are the desired temperature, pressure and the number of molecules (N). Other program entities that need to be specified are the box size, potential cut-off, time-step, number of steps, interval between prints and the interval box and momentum scales. Typically, molecular dynamics treat a sample of N-molecules in a box of volume V (shown in Figure 2.1 as being cubic in shape).

A subroutine FCC sets up the initial configuration on an α -FCC lattice for the N-molecules. The simulation box is made a unit cube centered at the origin, and N is of the form {4*(NC**3)} where NC is the number of FCC unit cells in each direction.

Another subroutine COMVELL is called to set up the centre of mass velocities for the configuration of the linear molecules at the given temperature. Unit molecular mass was assumed in the program. A gaussian distribution is assumed for the velocity. It is also assumed that it has zero mean and unit variance. The initial velocities, their first, second and third derivatives are all assumed zero initially.

A subroutine PREDICT using the given time step predicts the positions of each molecule, subsequently another subroutine FORCE is called to compute the intermolecular forces from the potential function. And the positions and velocities are followed in time by solving Newton's equation of motion (force equals mass times acceleration, a second order differential equation) using a standard numerical technique, Gear Predictor - Corrector Method. The values are corrected by a subroutine known as CORRECT. Subroutine SCALE scales the momenta and the box size to give the desired temperature and pressure. Properties of interest such as kinetic energy, potential energy and others are calculated by averaging the appropriate functions of the molecular positions and velocities over time.

Since the box size changes as the simulation goes on upto the desired temperature, the density in any run is calculated as :

$$\text{Vol} = \text{Box} ** 3 \tag{4.6}$$

$$\text{Density} = \text{Real(N)} / \text{Vol} \tag{4.7}$$

The density obtained is in reduced units, therefore it has to be converted to g/cm^3 using the relation :

$$\rho = \frac{\rho^*}{\sigma^3} \tag{4.8}$$

For benzene ($\sigma = 5.27A$),

$$\rho = \rho^* \frac{1}{\sigma^3 A^3} \frac{1 A^3}{10^{-24} cm^3} \frac{78.114 g}{1 gmole} \frac{1 gmole}{6.02*10^{23}}$$

This implies,

$$\rho = 0.8865\, \rho^*$$

Similarly for cyclohexane ($\sigma = 6.093A$),

$$\rho = \rho^{*} \frac{1}{\sigma^{3}\,A^{3}} \frac{1A^{3}}{10^{-24}cm^{3}} \frac{84.162g}{1gmole} \frac{1gmole}{6.02*10^{23}}$$

This implies,

$$\rho = 0.6181\ \rho^{*}$$

Also for n-hexane ($\sigma = 5.909A$),

$$\rho = \rho^{*} \frac{1}{\sigma^{3}\,A^{3}} \frac{1\ A^{3}}{10^{-24}cm^{3}} \frac{86.178g}{1gmole} \frac{1gmole}{6.02*10^{23}}$$

This implies,

$$\rho = 0.6938\ \rho^{*}$$

Tables 4.18, 4.19 & 4.20 show the results obtained from the computer simulation for benzene, cyclohexane and n-hexane respectively. Tables 4.21, 4.22 & 4.23 show the comparison between the simulation results and the experimentally obtained values. These results have also been plotted in Figures 4.30, 4.31 & 4.32.

The prediction by simulation is not very accurate due to high errors most especially for cyclohexane. However, errors are expected because of the fundamental assumption that the hydrocarbon samples are Lennard-Jones fluid (i.e spherical nonpolar molecules) which of course they are not. The results obtained for n-hexane are closer to the experimental values may be because of the fact that the chain structure of n-hexane assumes a more or less spherical shape at its lowest energy level. However, the problem may be solved if the site

Table 4.18 : **Computer Simulation Results For The Density of Benzene As A Function of Temperature (298.15K to 473.15K)**

Temp. (C)	Reduced Temp. & Pressure	Reduced Density ρ^*	Density g/cm^3
25	T^* 0.6776 P^* 0.0332	0.9667	0.8570
30	T^* 0.6890 P^* 0.0399	0.9625	0.8533
40	T^* 0.7117 P^* 0.0465	0.8435	0.7478
60	T^* 0.7572 P^* 0.0532	0.8328	0.7383
80	T^* 0.8026 P^* 0.0598	0.7925	0.7026
100	T^* 0.8481 P^* 0.0665	0.7806	0.6920
120	T^* 0.8935 P^* 0.0798	0.7683	0.6811
140	T^* 0.9390 P^* 0.0930	0.7441	0.6597
160	T^* 0.9844 P^* 0.1063	0.7302	0.6474
180	T^* 1.0299	0.7031	0.6233

	P^* 0.1196		
200	T^* 1.0753 P^* 0.1329	0.6908	0.6124

Table 4.19 : **Computer Simulation Results For The Density of Cyclohexane As A Function of Temperature (298.15K to 473.15K)**

Temp. (C)	Reduced Temp. & Pressure	Reduced Density ρ^*	Density g/cm^3
25	T^* 0.9202 P^* 0.0697	0.7538	0.4659
30	T^* 0.9357 P^* 0.0837	0.7398	0.4572
40	T^* 0.9665 P^* 0.0976	0.7377	0.4559
60	T^* 1.0282 P^* 0.1116	0.7001	0.4327
80	T^* 1.090 P^* 0.1255	0.6775	0.4187
100	T^* 1.1517 P^* 0.1395	0.6197	0.3830
120	T^* 1.2134 P^* 0.1534	0.5812	0.3592
140	T^* 1.2752 P^* 0.1674	0.5600	0.3461
160	T^* 1.3369 P^* 0.1813	0.4841	0.2992
180	T^* 1.3986	0.4591	0.2837

	P^* 0.1953		
200	T^* 1.4603 P^* 0.2092	0.3796	0.2346

Table 4.20 : **Computer Simulation Results For The Density of n-Hexane As A Function of Temperature (298.15K to 473.15K)**

Temp. (C)	Reduced Temp. & Pressure	Reduced Density ρ^*	Density g/cm^3
25	T^* 0.7219 P^* 0.0499	0.8393	0.5823
30	T^* 0.7340 P^* 0.0599	0.8390	0.5821
40	T^* 0.7582 P^* 0.0699	0.8206	0.5694
60	T^* 0.8067 P^* 0.0798	0.8049	0.5585
80	T^* 0.8551 P^* 0.0898	0.7936	0.5506
100	T^* 0.9035 P^* 0.0998	0.7631	0.5295
120	T^* 0.9519 P^* 0.1098	0.7351	0.5101
140	T^* 1.0004 P^* 0.1198	0.7192	0.4990
160	T^* 1.0488 P^* 0.1297	0.7051	0.4892
180	T^* 1.0972	0.6474	0.4492

	P^* 0.1397		
200	T^* 1.1456 P^* 0.1497	0.6297	0.4369

Table 4.21 : **Comparison of The Experimetal Density of Benzene With The Results Obtained From Computer Simulation**

Temp. (C)	Experimental Value	Simulation Value	Deviation (%)
25	0.8737	0.8570	1.95
30	0.8683	0.8533	1.76
40	0.8581	0.7478	14.75
60	0.8358	0.7383	13.21
80	0.8146	0.7026	15.94
100	0.7926	0.6920	14.54
120	0.7685	0.6811	12.83
140	0.7437	0.6597	12.73
160	0.7188	0.6474	11.03
180	0.6912	0.6233	10.89
200	0.6607	0.6124	7.89

Percentage Average Absolute Deviation = 9.79%

Table 4.22 : **Comparison of The Experimetal Density of Cyclohexane With The Results Obtained From Computer Simulation**

Temp. (C)	Experimental Value	Simulation Value	Deviation (%)
25	0.7739	0.4659	66.11
30	0.7691	0.4572	68.22
40	0.7595	0.4559	66.59
60	0.7404	0.4327	71.11
80	0.7201	0.4187	71.99
100	0.6992	0.3830	82.56
120	0.6778	0.3592	88.70
140	0.6554	0.3461	89.37
160	0.6314	0.2992	111.03
180	0.6055	0.2837	113.43
200	0.5768	0.2346	145.87

Percentage Average Absolute Deviation = 81.25%

Table 4.23 : Comparison of The Experimctal Density of n-Hexane With The Results Obtained From Computer Simulation

Temp. (C)	Experimental Value	Simulation Value	Deviation (%)
25	0.6548	0.5823	12.45
30	0.6504	0.5821	11.73
40	0.6409	0.5694	12.56
60	0.6221	0.5585	11.39
80	0.6023	0.5506	9.39
100	0.5816	0.5295	9.84
120	0.5596	0.5101	9.70
140	0.5355	0.4990	7.31
160	0.5087	0.4892	3.99
180	0.4773	0.4492	6.26
200	0.4381	0.4369	0.27

Percentage Average Absolute Deviation = 7.91

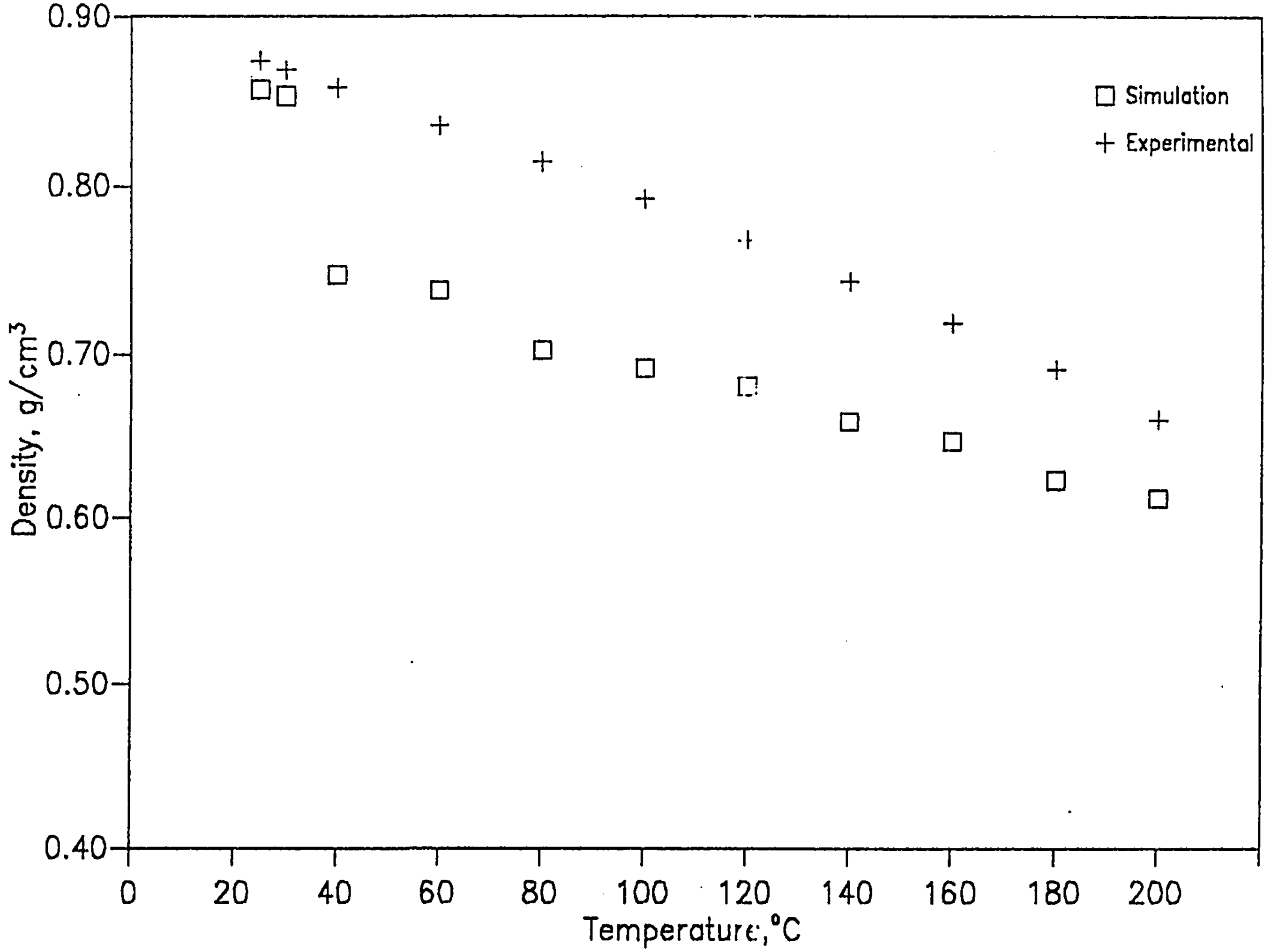

FIGURE 4.30 :COMPARISON OF EXPERIMENTAL DENSITY DATA WITH SIMULATION RESULTS OBTAINED FOR BENZENE

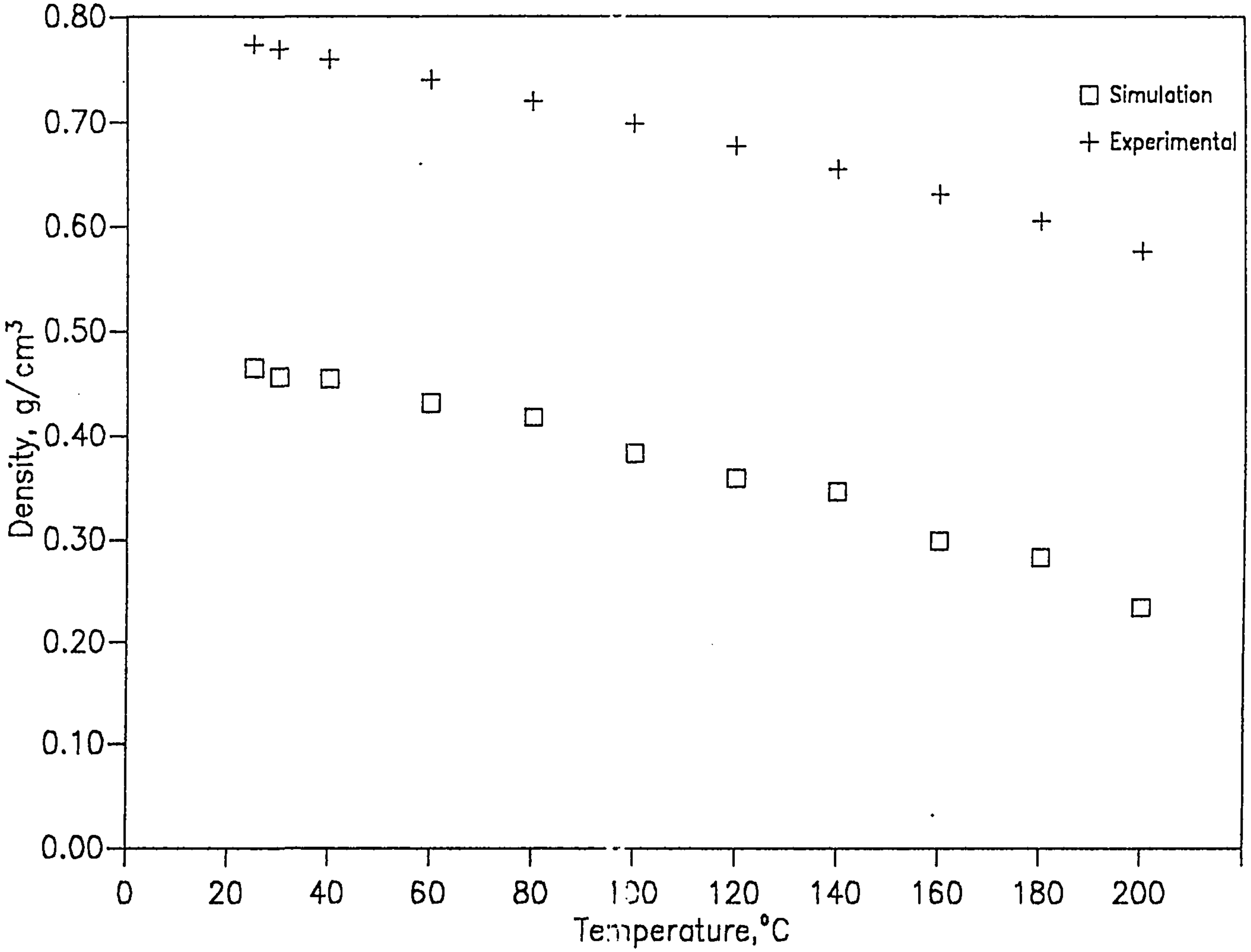

FIGURE 4.31 :COMPARISON OF EXPERIMENTAL DENSITY DATA WITH SIMULATION RESULTS OBTAINED FOR CYCLOHEXANE

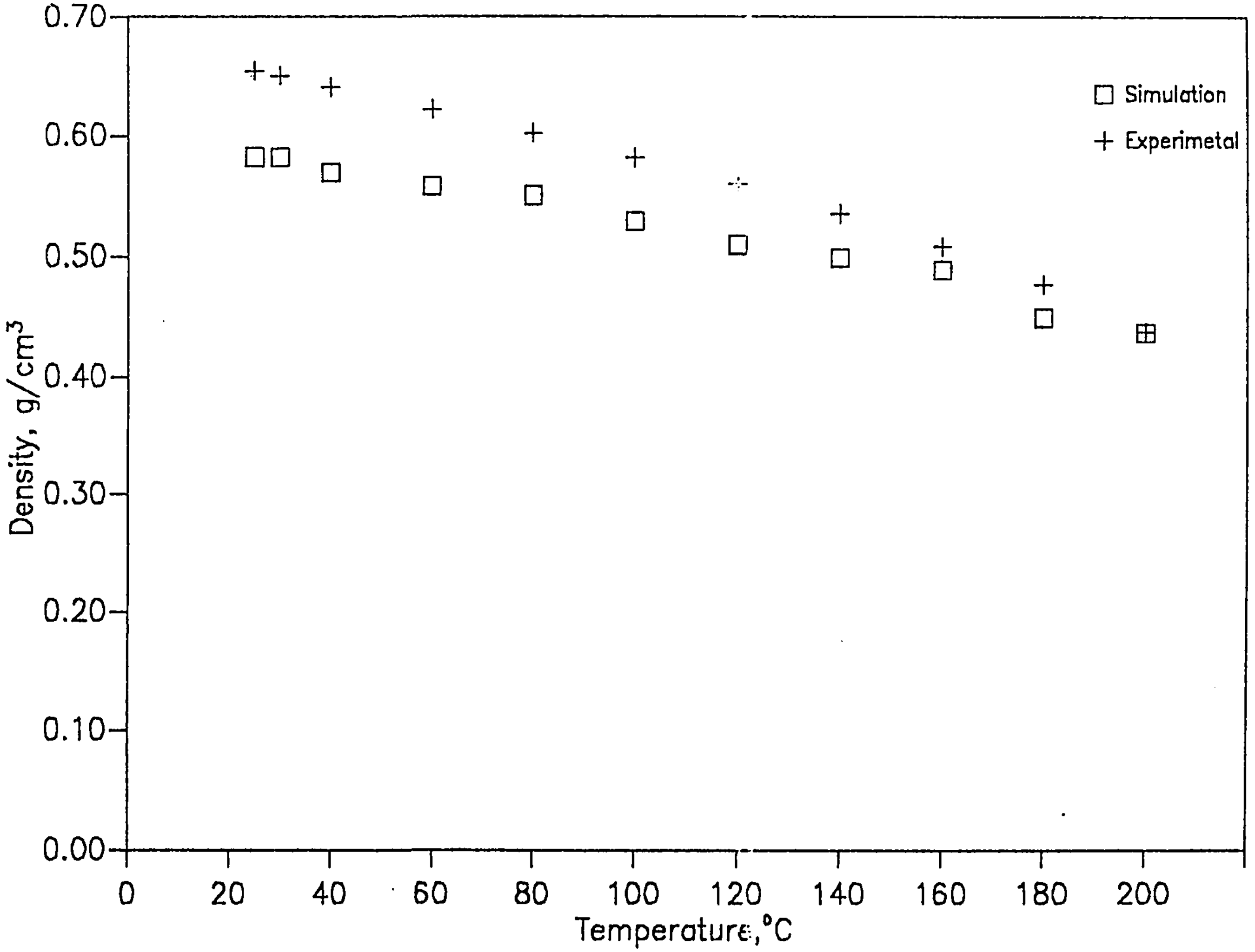

FIGURE 4.32 :COMPARISON OF EXPERIMENTAL DENSITY DATA WITH SIMULATION RESULTS OBTAINED FOR n–HEXANE

- interaction model is used to express the intermolecular forces between the molecules. Some effort was put into the later model but not much success was achieved due to the time constraint.

Effort was also put into the simulation of the binary mixtures of the hydrocarbon compounds, but the problem of not having an appropriate intermolecular function that takes structure into consideration hindered obtaining good results.

CHAPTER 5

SUMMARY AND CONCLUSIONS

The following conclusions may be drawn from the present studies of the density behavior of the pure compounds of benzene, cyclohexane and n-hexane, their binary and ternary mixtures.

1.) An experimental system that allows for the measurements of density from ambient to 230°C and pressure upto 1800psia was used in the experimetal density determination. The system could accomodate six independent units.

2.) Calibration of volume as a function of temperature for six density cells (pycnometers) was carried out for the whole range of temperature considered in the studies.

3.) The accuracy and reproducibility of the experimental technique was checked by comparing the measured density of double distilled water with the values reported in the literature. A maximum difference of 0.21% was obtained between the two measurements.

4.) The density of benzene, cyclohexane and n-hexane has been measured from 25°C to 200°C.

5.) The density measurements of three binary mixtures; benzene - cyclohexane, benzene - n-hexane, and cyclohexane - n-hexane have also been carried out over a wide range of temperatures from 25°C to 200°C.

6.) The density of ten ternary mixtures of benzene - cyclohexane - n-hexane has also been measured from 25°C to 200°C.

7.) From the results of the density data of the ternary mixtures, it was concluded that increasing the aromatic content of the mixture leads to a significant increase in its density, whereas, increasing the naphthenic content of the mixture leads to only a slight increase in the density of the overall mixture. On the contrary, an increase in the paraffinic content gives rise to a significant decrease in the density of the mixture.

8.) All the experimental data obtained for the pure, binary and ternary mixtures were compared with predictions made by the Spencer - Danner modified Rackett equation (SDR) and the Hankinson-Brobst-Thompson (COSTALD) correlation. The SDR has been found to predict the experimental data with an average deviation (AAD%) of 0.29% while the COSTALD or the HBT has an AAD% of 0.61%.

9.) Excess molar volumes expressing the degree of nonidealities in a mixture were calculated for the binary mixtures of benzene - cyclohexane, benzene - n-hexane and cyclohexane - n-hexane. The values were calculated from the density data. Benzene - cyclohexane mixtures and Benzene - n-hexane mixtures have positive deviations in the whole range of concentration considered. However, the mixtures of cyclohexane - n-hexane show both positive and negative deviations.

10.) The excess molar volumes have been correlated both as a fuction concentration and temperature using the 3-constants Redlich-Kister expansion :

$$V^E = [\, x(1-x)(A + B(1-2x) + C(1-2x)^2 \,] \, .$$

The constants in the above expression were correlated as a function of temperature as follows :

$$A = A_0 + A_1 T + A_2 T^2$$

$$B = B_0 + B_1 T + B_2 T^2$$

$$C = C_0 + C_1 T + C_2 T^2$$

12.) An attempt was made to predict the density of the pure component of benzene, cyclohexane and n-hexane using the Lennard-Jones potential through the use computer molecular simultaion (MD technique). The predicted results were found not to be very accurate due the non-availability of an appropriate expression for the intermolecular potential.

CHAPTER 6

RECOMMENDATIONS

1. Reliable vapor pressure data for pure, defined and undefined hydrocarbon mixtures should be determined to cover wide range of temperature.

2. Also, reliable thermal conductivity data for pure, defined and undefined hydrocarbon mixtures should be obtained at high temperatures and high pressures.

3. Reliable heat capacity data for pure, defined and undefined hydrocarbon mixtures should be determined at high temperature ranges.

4. Studies on other excess properties such as excess viscosity, excess free energy should be conducted.

5. Efforts should be directed at obtaining expressions for intermolecular potentials that take structures of molecules into consideration.

REFERENCES

1. Hales, J.L., "Biliography of Fluid Density: Experimental Range Exceeding 40K." NPL Report Chem., National Physical Lab., Div., Chem. Strand, U.K (1980).

2. Saeed, M. R., M.S Thesis, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia, May 1986.

3. Baghdoyan, A., Malik, J., and Fried, V.,"Vapour Pressures and Densities of 2, 3-Dimethyl- 2- butene and 3, 3-Dimethyl -1 -Butene." J. Chem. Eng. Data 16 (1971) : 96.

4. Dawson, P.P.Jr., Silberburg, I.H. and McKetta, J.J.,"Volumetric Behaviour, Vapour pressures and critical Properties of Neopentane." J. Chem. Eng. Data 18 (1973) : 7.

5. Abraham, T., Berry, V., and Kudchodker, A. P.,"Densities of Some Organic Subtances." J. Chem. Eng. Data 16 (1971) : 355.

6. Mclure, I. A., Francisco, G. F., and Pegg, I. L., "Density of 2-Butoxyethanol from 20 to 60°C." J. Chem. Eng. Data 27 (1982) : 398-399.

7. Murrieta-Guevara, F., and Rodrigez, A. T., "Liquid Density As a Function of Temperature of Five Organic Solvents." J. Chem. Eng. Data 29 (1984) : 204-206.

8. Tarjados, G., Diaz Pena, G. M., Lainez, A., and Aicart, E."Speed of Sound , Isothermal Compressibility And Isobaric Expansitivty of Pure Liquids At 298.15K." J. Chem. Eng. Data 31 (1986) : 492-493.

9. Serrano, L., Alves Silva, J., and Farelo, F., "Densities and Viscosities of Binary and Ternary liquid Systems containing Xylenes." J. Chem. Eng. Data 35 (1990) : 288-291.

10 Banipal, T. S., Garg, S. K., and Ahluwalia, J. C., "Heat Capacities And Densities of Liquid n-octane, n-nonane, n-decane, and n-hexadecane At Temperature From 318.15K to 373.15K and At Pressures Upto 10MPa." J. Chem. Thermodynamics 23 (1991) : 923-931.

11. Ahlert R. C., "Densities of Hydrazine - Methylhydrazine System." J. Chem. Eng. Data 13 (1968) : 108-109.

12 Sunni, S. A., and Hutchinson, P., "Densities and Diffusivities for Binary Mixtures." J. Chem. Eng. Data 18 (1973) : 317.

13. Kahre, L. C., "Liquid Densities of light hydrocarbon Mixtures." J. Chem. Eng. Data 18 (1973) : 287.

14. Sinka, J. V., "Physical properties of a refrigerant mixture of Monofluoro-Monochloro-methane and Tetrafluoro-dichloro-ethane." J. Chem. Eng. Data 15 (1970) : 17-19.

15. Mikhail, S. Z., and Kimel, W. R., "Densities and Viscosities of Methanol-Water mixtures." J. Chem. Eng. Data 8 (1963) : 323.

16. Sivaramprasad, G., and Venkateshwara, R. M.,"Density and Viscosity of Ethanol + 1, 2- Dichloroethane, Ethanol + 1, 1, 1- Trichloroethane, and ethanol + 1, 1, 2, 2,- Tetrachloroethane binary mixtures." J. Chem. Eng. Data 35 (1990) : 122-124.

17. Joshi, S. S., Aminabhavi, T. M., Balundgi, R. H., "Densities and Viscosities of Binary liquid mixtures of Nitrobenzene with cyclohexane and N, N- Dimethlformamide." J. Chem. Eng. Data 35 (1990) : 185.

18. Papaloannou, D., Ziakas, D., and Panaylotou, C., "Volumetric properties of Binary Mixtures of 1, 2- propanone + 2, 2, 4- Trimethylpentane and n-Heptane + Ethanol Mixtures." J. Chem. Eng. Data 36 (1991) : 35.

19. Yamamoto, H and Tokunaga, J., "Densities And Viscosities of NH_4Br-NH_3 and NH_4I-NH_3 Systems." J. Chem. Eng. Data 36 (1991) : 277-280.

20. Marchetti, A., Tagaliazucchi, M., Tassi, L., and Tossi, G., "Densities And Excess Molar Volumes of The 1,2-Ethanediol + 2-Methoxyethanol Solvent-System At Various Temperatures." J. Chem. Eng. Data 36 (1991) : 368-371.

21. Jangkamolkulchal, A., Alired, G. C., and Parrish, W. R., "Densities And Excess Molar Volumes of Methyl Tert - Butyl Ether With Hydrocarbons From 255.4 to 333.2K." J. Chem. Eng. Data 36 (1991) : 481-484.

22. Papanastaslou, G. E., and Ziogas, I. I., "Physical Behavior of Some Reaction Media. Density, Viscosity, Dielectric Constant, and Refractive

Index Changes of Ethanol-Cyclhexane Mixtures At Several Temperatures." J. Chem. Eng. Data 36 (1991) : 46-51.

23. Chevalier, J. L. E., Petrino, P. J., and Gaston-Bonhomme, Y. H., "Viscosity And Density of Some Aliphatic, Cyclic, And Aromatic Hydrocarbons Binary Liquid Mixtures." J. Chem. Eng. Data 35 (1990) : 206-212.

24. Wei, I-Chien and Rowley, R. L., "Binary Liquid Viscosities And Densities." J. Chem. Eng. Data 29 (1984) : 332-335.

25. Krishnaiah, A. and Viswanath, D. S., "Densities, Viscosities and Excess Volumes of Isopropyl Acetate + Cyclohexane Mixtures At 298.15 And 308.15K." J. Chem. Eng. Data 36 (1991) : 317-318.

26. Kaur, H., Samra, S., and Mahl, B. S.,"Excess Volumes of Binary Liquid Mixtures of n-Alkanols And Cycloalkanols With n-Alkanes And The Theoretical Treatment Using The ERAS-Model." Fluid Phase Equilibra 67 (1991) : 241-257.

27. Bravo, R., Pintos, M., and Amigo, A.,"Excess Molar Volumes of (o-xylene + nheptane + toluene or n-hex-1-ene) At the Temperature 298.15K." J. Chem. Thermodynamics 23 (1991) : 905-910.

28. Pickerell, D. S., and Plank, C. A.,"Excess Volumes of The System Benzene + 1,1,2- Trichloroethylene At 283.15K And 313,15K." J. Chem. Eng. Data 34 (1989) : 278-280.

29. Denini, S., Poicaro, A. M., and Ricci, P. F., and Maronglu, B.,

"Thermodynamic Properties of Binary Mixtures Containing Cycloalkanones. 3 Excess Volumes of Cycloalkanones + Cyclohexane, + Benzene, And + Tetrachloromethane." J. Chem. Eng. Data 34 (1989) : 165-167.

30. Tanaka, R., Takenaka, M., Murakami, S.,"Excess Volumes For Mixtures of Benzene With Some Cycloalkanes At 293.15,298.15 And 303.15K." J. Chem. Eng. Data 29 (1984) : 69-72.

31. Nath, J., and Dixit, A. P.,"Excess Volumes For Binary Liquid Mixtures of Acetone With Benzene, Toluene, p-xylene, Mesitylene, And Cyclohexane." J. Chem. Eng. Data 28 (1983) : 190-191.

32. Naidu, G. R. and Ramachandra N. P., "Excess Volumes of Ternary Mixtures Containing Methyl Ethyl Ketone, 1-Alkanols, and an Alkane." J. Chem. Eng. Data 26 (1981) : 197-200.

33. Goates, J. R., Bevan Ott J., and Grigg, R. B.,"Excess Volumes of Cyclohexane + n-hexane, + n-heptane, + n-octane, + n-nonane, and + n-decane." J. Chem. Thermodynamics 11 (1979) : 497-506.

34. Letcher, T. M. "The Excess Volumes of Some Mixtures of Saturated And Unsaturated C_6 Hydrocarbons." J. Chem. Thermodynamics 7 (1975) : 205-209.

35. Diaz Pena, M., and Nunez Delgado, J.,"Excess Volumes At 323.15K of Binary Mixtures of Benzene With n-Alkanes." J. Chem. Eng. Data 7 (1975) : 201-204.

36. Weeks, I. A. and Benson, G. C.,"Determination of The Excess Volumes of Cyclohexane + Benzene By Means of A Magnetic Float Densimeter." J. Chem. Thermodynamics 5 (1973) : 107-115.

37. The Instrument Manual, 5th Edition, United Press Ltd., 1975

38. Nissen, D. A. and Macmillan, D. C., "Apparatus For Precise Measurement of The Physical Properties of Liquids At Elevated Temperature And Pressure." Rev. Sci. Instrum., 54.7 (1983) : 861.

39. Rossini, F. D., Mair, B. J., Sfreiff, J., Hydrocarbons From Petroleum, Reinhold Publishing Corp., New York, pp. 209.

40. White, M. S. and Solomans, C."Linear Oscillation Viscometer." Rev. Sci. Instrum., 40.2 (1969) : 339.

41. Beams, J. W., and Clark, A. M.,"Magnetic Suspension Balance Method For Determining Densities And Partial Specific Volumes." Rev. Sci. Instrum., 33.7 (1962) : 750.

42. Hales, J. L.," An Apparatus For Accurate Measurement of Liquid Densities Over An Extended Temperature Range."J. Physics E; Sci. Instrum., 3 (1970) : 855.

43. Hales, J. L., and Townsend, R., "Liquid Densities From 293 To 490K of Nine Aromatic Hydrocarbons." J. Chem. Thermodynamics 4(1972) : 763.

44. Hales, J. L., and Ellender, J. H.,"Liquid Densities From 293 To 490K of

Nine Aliphatic Alcohols." J. Chem. Thermodynamics 8 (1976) : 1177.

45. Hales, J. L., and Gundry, H. A., " An Apparatus For Accurate Measurement of Liquid And Vapor Densities on The Saturation Upto The Critical Temperature." J. Physics E; Sci. Instrum., 16 (1983) : 91.

46. Badachappe, R. B., Garpurey, M. K., and Biswas, A. B., "Density and surface tension of Phenols (mono-, di-, and tri- chlorophenols), Salol and (o- and m-) chloronitrobenzene." J. Chem. Eng. Data 10 (1965) : 143.

47. Knobler, C. M. and Pings, C. J."Saturated Liquid Densities of carbon Tetrafluoride From 90 to 150K." J. Chem. Eng. Data 10 (1963) : 129.

48. Connolly, J. F. "Volume Changes in Mixing Hydrocarbons." Ind. Eng. Chem. 48 (1956) : 813.

49. Jasper, J. J. and Wadlick, H. L., "Effect of Temperature on The Surface Tension And Density of Trifluoro-Acetic Acid." J. Chem. Eng. Data. 18 (1973) : 267.

50. Malbrunot, P. E., Meanier, P. A., Scatena, G. M., Mears, W. H., Murphy, K. P., and Sinka, J. V., "Pressure - Volume - Temperature Behavior of Difuoro-methane." J. Chem. Eng. Data 13 (1968) : 16.

51. Isadale, J, D., Dymond, H. J., and Brown, T. A., "Viscosity and Density of n-Hexane-Cylopropane Mixtures between 25 & 100 C." High Temperature and High Pressures 11 (1979) : 571.

52. Benedict, M., Webb, G. E., and Rubin, L. C., Chem. Eng. Prog., 47, 419

(1951).

53. Watson, K.M., "Thermodynamics of liquid state", Ind. Eng. Chem., 35, 398 (1943).

54. Riedel, L., "Liquid Density in the Saturated State", Chem. - Ing. - Tech., 26, 259 (1954).

55. Lyderson, A. L., Greenkorn, R. A., Hougen, O. A.,"Generalized Thermodynamic properties of pure Fluids", Univ. Wisconsin Eng. Exp. Sta. Report , 4, Madison, October 1955.

56. Francis, A. W., Chem. Eng. Sci. 10 (1959) : 37.

57. Holmes, A. S., MS Thesis, The Pennsylvania State University, University Park, Pa., 1964.

58. Harmans, A. Chem. Eng. Sci., 20 (1965) : 813.

59. Lyckman, E. W., Eckert, C. A., Prausnitz, J. M., Chem. Eng. Sci., 20 (1965) : 703.

60. Yen, L. C., and Woods, S. S. AIChE J., 12 (1966) :95.

61. Ehrlich, P., "Advances in Thermophysical Properties At Extreme Temperature And Pressure." ASME, 1967.

62. Narsimham, G., Brit. Chem. Eng. 12 (1967) :1239.

63. Harlacher, E. A., PhD Thesis, The Pennsylvania State University, University Park, Pa., 1968.

64. Bradford, N.L., Thodos, G., Can. J. Chem. Eng., 46 (1968) : 277.

65. Rackett, H. G., "Equation of State of Saturated Liquids", J. Chem. Eng. Data 15 (1970) : 514.

66. Gunn, R.D., and Yamada, T., "A Corresponding States Correlation of Saturated Liquid Volumes." AIChE J., 17 (1971) : 1341.

67. Spencer, F. and Danner, R. P., "Improved Equation For Prediction of Saturated Liquid Densities." J. Chem. Eng. Data 17 (1972) : 236-241.

68. Hankinson, R.W., and Thomson, G. H., "Calculate Liquid Densities Accurately." Hydrocarbon Processing, 58.9 (1979) : 277.

69. Reid, C.R., Prausnitz, J. M., and Poling, B. E.,"The Properties of Gases and Liquids", McGraw-Hill Book Co., New York (1987).

70. Spencer, C.F., and Danner, R. P., "Prediction of Bubble-Point Density of Mixtures." J. Chem. Eng. Data 18 (1973) : 230.

71. Veeranna, D., and Rihani, D.N., "Review of density estimation of Saturated Liquid Mixtures." J. Chem. Eng. Data 25 (1980) : 267.

72. Chueh, P.L., and Prausnitz, J. M.,"Vapor-Liquid Equilibra at High Pressures: Calculation of Critical Temperatures, Volumes, and Pressures of Nonpolar Mixtures." AIChE J., 13 (1967) : 1107.

73. Prausnitz, J.M., and Gunn, R. D.,"Volumetric Properties of non- Polar Gaseous Mixtures." AIChE J., 4.430 (1958) : 495.

74. Tsonopoulos, C., Heidman, J.L., Hwang, S. C.,"Thermodynamic and Transport Properties of Coal Liquids." John Wiley & Sons, New York, 134 (1986).

75. Hwang, S.C., and Tsonopoulos, C., Cunningham, J. R.,and Wilson, G. M.,"Density, Viscosity and Surface Tension of Coal Liquids At High Temperatures And Pressures." Ind. Eng. Chem. Process Des. Dev., 21 (1982) : 127.

76. Rea, H.E., and Spencer, C. F., and Danner, R. P.,"Effect of Pressure on The Liquid Densities of Pure Hydrocarbons." J. Chem. Eng. Data, 18 (1973) : 227.

77. Leed, L.L., "Molecular Thermodynamics of Non Ideal Fluids," Butterworths, Boston (1987).

78. Allen, M.P., and Tildesley, D. J., "Computer Simulation of Liquids," Clarendon Press, Oxford (1987).

79. Gubbins, K.E., "The Future of Thermodynamics," Chem. Eng. Prog. 85.2(1989).

80. Alder, B. J. and Wainwright, T. E. 'Phase Transition For a hard Sphere System." J. Chem. Phys. 27, 1208-9.

81. Rahman, A. "Correlations in The Motions of Atom in Liquid Argon." Phys. Rev. 136A, 405-11.

82. Verlet, L. "Computer Experiments On Classical Fluids. II. Equilibrium

Correlation Functions." Phys. Rev. 165, 201-14.

83. Nicolas, J. J., Gubbins, K. E., Streett, W. B., and Tildesley, D. J. "Equation of State For The Lennard-Jones Fluid." Mol. Phys. 37, 1429-54.

84. Berne, B. J. and Harp, G. D. "On The Calculation of Time Correlation Functions" Adv. Chem. Phys. 17, 63-227.

85. Barker, J. A. and Watts, R. O. "Structure of Water:A Monte Carlo Calculation." Chem. Phys. Lett. 3, 144-145.

86. Rahman, A. and Stillinger, F. H. "Molecular Dynamics Study of Liquid Water." J. Chem. Phys. 55, 3336-59.

87. Ryckaert, J .P. and Bellemans, A. "Molecular Dynamics of Liquid n-butane near its boiling point. Chem. Phys. Lett. 30, 123-5.

88. McCammon, J. A., Gelin, B. R., and Karplus, N. "Dynamics of folded proteins." Nature 267, 585-90.

89. Lee, J. K., Barker J. A., and Pound, G. M. "Surface Structure And Surface Tension: Perturbation Theory And Monte Carlo Calculation." J. Chem. Phys. 60, 1976-80.

90. Perry, R. H. and Chilton, C. H. Chemical Engineers' Handbook. McGraw-Hill International Book Co., London (1974).

APPENDIX A

Table A.1 : Calibration Data For Volume of Density Cell {A} As a Function of Temperature

Wt. of Evacuated Cell = 271.06g

Run	Temp.	Wt. of Cell Filled with Hg	Wt. of Hg in Cell	Density of Hg	Vol. of Cell	Av. Vol
	(C)	g	g	g/cm^3	cm^3	cm^3
1	25	849.92	578.86	13.5336	42.772	
2		849.84	578.78		42.766	42.769
3	30	849.50	578.44	13.5213	42.780	
4		849.64	578.58		42.790	42.785
5	40	848.94	577.88	13.4969	42.816	
6	60	847.26	576.20	13.4482	42.846	
7	80	845.64	574.58	13.3998	42.880	
8		845.78	574.72		42.890	42.885
9	100	844.16	573.10	13.3515	42.924	
10	120	842.75	571.69	13.3040	42.971	
11	140	841.00	569.94	13.2563	42.994	
12		840.95	569.89		42.990	42.992
13	160	839.50	568.44	13.2090	43.034	
14	180	845.78	567.03	13.1617	43.082	
15	200	836.41	565.35	13.1145	43.109	

Table A.2 : **Calibration Data For Volume of Density Cell {B} As a Function of Temperature**

Wt. of Evacuated Cell = 233.71g

Run	Temp.	Wt. of Cell Filled with Hg	Wt. of Hg in Cell	Density of Hg	Vol. of Cell	Av. Vol
	(C)	g	g	g/cm^3	cm^3	cm^3
1	25	808.45	574.74	13.5336	42.468	
2	30	807.97	574.26	13.5213	42.471	
3		808.01	574.30		42.474	42.473
4	40	807.22	573.51	13.4969	42.492	
5	60	805.70	571.99	13.4482	42.533	
6	80	804.14	570.43	13.3998	42.570	
7		804.19	570.48		42.574	42.572
8	100	802.63	568.92	13.3515	42.611	
9	120	801.22	567.51	13.3040	42.657	
10	140	799.62	565.91	13.2563	42.690	
11		799.65	565.94		42.692	42.691
12	160	798.16	564.45	13.2090	42.732	
13	180	796.58	562.87	13.1617	42.766	
14	200	795.15	561.44	13.1145	42.811	

Table A.3 : **Calibration Data For Volume of Density Cell (C) As a Function of Temperature**

Wt. of Evacuated Cell = 268.27g

Run	Temp.	Wt. of Cell Filled with Hg	Wt. of Hg in Cell	Density of Hg	Vol. of Cell	Av. Vol
	(C)	g	g	g/cm^3	cm^3	cm^3
1	25	842.07	573.80	13.5336	42.398	
2	30	841.68	573.41	13.5213	42.408	
3		841.69	573.42		42.409	42.409
4	40	840.97	572.70	13.4969	42.432	
5	60	839.39	571.12	13.4482	42.468	
6	80	837.82	569.55	13.3998	42.504	
7	100	836.22	567.95	13.3515	42.538	
8	120	834.70	566.43	13.3040	42.576	
9	140	833.15	564.88	13.2563	42.612	
10		833.20	564.93		42.616	42.613
11	160	831.66	563.39	13.2090	42.652	
12	180	830.10	561.83	13.1617	42.687	
13	200	828.55	560.28	13.1145	42.722	
14		828.52	560.25		42.720	42.721

Table A.4 : Calibration Data For Volume of Density Cell (D) As a Function of Temperature

Wt. of Evacuated Cell = 237.52g

Run	Temp.	Wt. of Cell Filled with Hg	Wt. of Hg in Cell	Density of Hg	Vol. of Cell	Av. Vol
	(C)	g	g	g/cm^3	cm^3	cm^3
1	25	802.10	564.58	13.5336	41.717	
2	30	801.70	564.18	13.5213	41.725	
3		801.72	564.20		41.727	41.726
4	40	800.93	563.41	13.4969	41.744	
5	60	799.40	561.88	13.4482	41.781	
6	80	797.91	560.39	13.3998	41.821	
7	100	796.37	558.85	13.3515	41.857	
8	120	794.89	557.37	13.3040	41.895	
9	140	794.41	555.89	13.2563	41.934	
10		793.38	555.86		41.932	41.933
11	160	791.93	554.41	13.2090	41.972	
12	180	790.46	552.94	13.1617	42.011	
13	200	788.98	551.46	13.1145	42.050	

Table A.5 : Density Data For Benzene

Wt. of Evacuated Density Cell (A) = 271.05g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	308.42	37.37	42.769	0.8737	
30	308.20	37.15	42.785	0.8683	
40	307.79	36.74	42.816	0.8581	
60	306.86	35.81	42.846	0.8358	
80	305.98	34.93	42.885	0.8146	
100	305.05 305.09	34.00 34.04	42.924	0.7922 0.7930	0.7926
120	304.07	33.02	42.971	0.7685	
140	303.02	31.97	42.992	0.7437	
160	301.98	30.93	43.034	0.7188	
180	300.83	29.78	43.082	0.6912	
200	299.53	28.48	43.109	0.6607	

Table A.6 : Density Data For Cyclohexane

Wt. of Evacuated Density Cell {B} = 233.71g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	266.58	32.87	42.468	0.7739	
30	266.38	32.67	42.473	0.7691	
40	265.98	32.27	42.492	0.7595	
60	265.20	31.49	42.533	0.7404	
80	264.39 264.34	30.68 30.63	42.572	0.7206 0.7195	0.7201
100	263.50	29.79	42.611	0.6992	
120	262.62	28.91	42.657	0.6778	
140	261.69	27.98	42.691	0.6554	
160	260.69	26.98	42.732	0.6314	
180	259.60	25.89	42.766	0.6055	
200	258.40	24.69	42.811	0.5768	

Table A.7 : **Density Data For n-Hexane**

Wt. of Evacuated Density Cell {C} = 268.27g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	296.03	27.76	42.398	0.6548	
30	295.85	27.58	42.409	0.6504	
40	295.46	27.19	42.432	0.6409	
60	294.69	26.42	42.468	0.6221	
80	293.87	25.60	42.504	0.6023	
100	293.01	24.74	42.538	0.5816	
120	292.10	23.83	42.576	0.5596	
140	291.11 291.07	22.84 22.80	42.613	0.5359 0.5351	0.5355
160	289.97	21.70	42.652	0.5087	
180	288.64	20.37	42.687	0.4773	
200	286.99	18.72	42.721	0.4381	

Table A.8 : **Density Data For The Binary Mixture of Benzene {0.2} And Cyclohexane {0.8}**

Mass Fraction of Benzene = 0.2
Mole Fraction of Benzene = 0.2111
Mass Fract. of Cyclohexane = 0.8
Mole Fract. of Cyclohexane = 0.7889

Wt. of Evacuated Density Cell {A} Used = 271.05g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	304.78	33.73	42.769	0.7887	
30	304.59	33.54	42.785	0.7838	
40	304.19	33.14	42.816	0.7741	
60	303.37	32.32	42.846	0.7543	
80	302.52	31.47	42.885	0.7338	
100	301.64	30.59	42.924	0.7127	
120	300.73 300.74	29.68 29.69	42.971	0.6907 0.6909	0.6908
140	299.77	28.72	42.992	0.6680	
160	298.76	27.71	43.034	0.6440	
180	297.67	26.62	43.082	0.6178	
200	296.44	25.39	43.109	0.5889	

Table A.9 : **Density Data For The Binary Mixture of Benzene {0.3} And Cyclohexane {0.7}**

Mass Fraction of Benzene = 0.3
Mole Fraction of Benzene = 0.3159
Mass Fract. of Cyclohexane = 0.7
Mole Fract. of Cyclohexane = 0.6841

Wt. of Evacuated Density Cell {A} Used = 271.05g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	305.15	34.10	42.769	0.7973	
30	304.94	33.89	42.785	0.7922	
40	304.55	33.50	42.816	0.7823	
60	303.72	32.67	42.846	0.7624	
80	302.87	31.82	42.885	0.7419	
100	301.98	30.93	42.924	0.7206	
120	301.07	30.02	42.971	0.6985	
140	300.10	29.05	42.992	0.6756	
160	299.08	28.03	43.034	0.6514	
180	297.98	26.93	43.082	0.6251	
200	296.76 296.74	25.71 25.69	43.109 43.109	0.5963 0.5959	0.5961

Table A.10 : Density Data For The Binary Mixture of Benzene (0.4) And Cyclohexane (0.6)

Mass Fraction of Benzene = 0.4
Mole Fraction of Benzene = 0.4180
Mass Fract. of Cyclohexane = 0.6
Mole Fract. of Cyclohexane = 0.5820

Wt. of Evacuated Density Cell {B} Used = 233.71g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	267.94	34.23	42.468	0.8060	
30	267.73	34.02	42.473	0.8009	
40	267.32	33.61	42.492	0.7910	
60	266.50	32.79	42.533	0.7709	
80	265.65	31.94	42.572	0.7503	
100	264.74	31.06	42.611	0.7290	
120	263.86	30.15	42.657	0.7067	
140	262.89	29.18	42.691	0.6835	
160	261.88	28.17	42.732	0.6593	
180	260.79	27.08	42.766	0.6332	
	260.76	27.05	42.766	0.6324	0.6328
200	259.55	25.84	42.811	0.6036	

Table A.11 : **Density Data For The Binary Mixture of Benzene {0.5} And Cyclohexane {0.5}**

Mass Fraction of Benzene = 0.5
Mole Fraction of Benzene = 0.5186
Mass Fract. of Cyclohexane = 0.5
Mole Fract. of Cyclohexane = 0.4814

Wt. of Evacuated Density Cell {B} Used = 233.71g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	268.34	34.63	42.468	0.8154	
30	268.13	34.42	42.473	0.8103	
40	267.72	34.01	42.492	0.8004	
60	266.88	33.17	42.533	0.7799	
80	266.04	32.33	42.572	0.7593	
100	265.15	31.44	42.611	0.7379	
120	264.22	30.51	42.657	0.7153	
140	263.25	29.54	42.691	0.6919	
160	262.23	28.52	42.732	0.6676	
180	261.13 261.11	27.42 27.40	42.766 42.766	0.6412 0.6408	0.6410
200	259.89	26.18	42.811	0.6116	

Table A.12 : **Density Data For The Binary Mixture of Benzene {0.6} And Cyclohexane (0.4)**

Mass Fraction of Benzene = 0.6
Mole Fraction of Benzene = 0.6178
Mass Fract. of Cyclohexane = 0.4
Mole Fract. of Cyclohexane = 0.3822

Wt. of Evacuated Density Cell {C} Used = 268.26g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm³	g/cm³	g/cm³
25	303.26	35.00	42.398	0.8255	
30	302.62	34.36	42.409	0.8201	
	302.63	34.37	42.409	0.8205	0.8203
40	302.64	34.38	42.432	0.8103	
60	301.79	33.53	42.468	0.7895	
80	300.94	32.68	42.504	0.7688	
100	300.05	31.79	42.538	0.7473	
120	299.10	30.84	42.576	0.7244	
140	298.12	29.86	42.613	0.7008	
160	297.11	28.85	42.652	0.6764	
180	296.00	27.74	42.687	0.6497	
200	294.76	26.50	42.721	0.6202	

Table A.13 : Density Data For The Binary Mixture of Benzene {0.7} And Cyclohexane {0.3}

Mass Fraction of Benzene = 0.7
Mole Fraction of Benzene = 0.7154
Mass Fract. of Cyclohexane = 0.3
Mole Fract. of Cyclohexane = 0.2846

Wt. of Evacuated Density Cell {C} Used = 268.26g

Temp. (C)	Wt. of Cell Filled with Sample g	Wt. of Sample g	Vol. of the Density Cell cm^3	Density of the Sample g/cm^3	Average Density of the Sample g/cm^3
25	303.72	345.46	42.398	0.8364	
30	303.51	35.25	42.409	0.8311	
40	303.10	34.84	42.432	0.8210	
60	302.23	33.97	42.468	0.7999	
80	301.37	33.11	42.504	0.7789	
100	300.45	32.19	42.538	0.7568	
	300.49	32.23		0.7576	0.7572
120	299.52	31.26	42.576	0.7342	
140	298.52	30.26	42.613	0.7102	
160	297.51	29.25	42.652	0.6857	
180	296.38	28.12	42.687	0.6587	
200	295.13	26.87	42.721	0.6289	

Table A.14 : Density Data For The Binary Mixture of Benzene {0.8} And Cyclohexane {0.2}

Mass Fraction of Benzene = 0.8
Mole Fraction of Benzene = 0.8117
Mass Fract. of Cyclohexane = 0.2
Mole Fract. of Cyclohexane = 0.1883

Wt. of Evacuated Density Cell {D} Used = 237.52g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	272.90	35.38	41.717	0.8481	
30	272.69	35.17	41.726	0.8428	
40	272.28	34.76	41.744	0.8327	
60	271.40	33.88	41.781	0.8110	
80	270.55 270.57	33.03 33.05	41.821	0.7898 0.7902	0.7900
100	269.67	32.15	41.857	0.7681	
120	268.72	31.20	41.895	0.7446	
140	267.73	30.21	41.933	0.7204	
160	266.72	29.20	41.972	0.6956	
180	265.60	28.08	42.011	0.6684	
200	264.36	26.84	42.050	0.6384	

Table A.15 : **Density Data For The Binary Mixture of Benzene {0.2} And n-Hexane {0.8}**

Mass Fraction of Benzene = 0.2
Mole Fraction of Benzene = 0.2162
Mass Fraction of n-Hexane = 0.8
Mole Fraction of n-Hexane = 0.7838

Wt. of Evacuated Density Cell {A} Used = 271.06g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	300.49	29.43	42.769	0.6880	
30	300.30	29.24	42.785	0.6835	
40	299.91	28.85	42.816	0.6739	
60	299.10	28.04	42.846	0.6545	
80	298.27	27.21	42.885	0.6344	
100	297.39	26.33	42.924	0.6134	
120	296.45 296.46	25.39 25.40	42.971	0.5908 0.5912	0.5910
140	295.42	24.36	42.992	0.5666	
160	294.29	23.23	43.034	0.5399	
180	292.96	21.90	43.082	0.5083	
200	291.30	20.24	43.109	0.4694	

Table A.16 : Density Data For The Binary Mixture of Benzene {0.3} And n-Hexane {0.7}

Mass Fraction of Benzene = 0.3
Mole Fraction of Benzene = 0.3210
Mass Fraction of n-Hexane = 0.7
Mole Fraction of n-Hexane = 0.6790

Wt. of Evacuated Density Cell {A} Used = 271.06g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	301.26	30.20	42.769	0.7061	
30	301.07	30.01	42.785	0.7015	
40	300.68	29.62	42.816	0.6918	
60	299.86	28.80	42.846	0.6722	
80	299.02	27.96	42.885	0.6519	
100	298.14	27.08	42.924	0.6308	
120	297.21 297.18	26.15 26.12	42.971	0.6086 0.6078	0.6082
140	296.15	25.09	42.992	0.5837	
160	295.02	23.96	43.034	0.5568	
180	293.70	22.64	43.082	0.5255	
200	292.05	20.99	43.109	0.4869	

Table A.17 : Density Data For The Binary Mixture of Benzene {0.4} And n-Hexane {0.6}

Mass Fraction of Benzene = 0.4
Mole Fraction of Benzene = 0.4238
Mass Fraction of n-Hexane = 0.6
Mole Fraction of n-Hexane = 0.5762

Wt. of Evacuated Density Cell {B} Used = 233.71g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	264.51	30.80	42.468	0.7253	
30	264.32	30.61	42.473	0.7207	
40	263.92	30.21	42.492	0.7109	
60	263.10	29.39	42.533	0.6910	
80	262.26	28.55	42.572	0.6706	
100	261.38	27.67	42.611	0.6494	
120	260.43	26.72	42.657	0.6266	
140	259.41	25.70	42.691	0.6019	
160	258.29	24.58	42.732	0.5751	
180	256.97	23.26	42.766	0.5440	
200	255.36 255.37	21.65 21.66	42.811	0.5056 0.5060	0.5058

Table A.18 : **Density Data For The Binary Mixture of Benzene {0.5} And n-Hexane {0.5}**

Mass Fraction of Benzene = 0.5
Mole Fraction of Benzene = 0.5245
Mass Fraction of n-Hexane = 0.5
Mole Fraction of n-Hexane = 0.4755

Wt. of Evacuated Density Cell {B} Used = 233.71g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	265.39	31.68	42.468	0.7459	
30	265.19	31.48	42.473	0.7412	
40	264.79	31.08	42.492	0.7314	
60	263.96	30.25	42.533	0.7112	
80	263.11	29.40	42.572	0.6906	
100	262.23	28.52	42.611	0.6692	
120	261.27	27.56	42.657	0.6461	
140	260.23	26.52	42.691	0.6214	
160	259.13 259.11	25.42 25.40	42.732	0.5949 0.5945	0.5947
180	257.82	24.11	42.766	0.5639	
200	256.24	22.53	42.811	0.5262	

Table A.19 : Density Data For The Binary Mixture of Benzene {0.6} And n-Hexane {0.4}

Mass Fraction of Benzene = 0.6 Mole Fraction of Benzene = 0.6233 Mass Fraction of n-Hexane = 0.4 Mole Fraction of n-Hexane = 0.3767

Wt. of Evacuated Density Cell {C} Used = 268.27g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	300.83	32.56	42.398	0.7679	
30	300.63	32.36	42.409	0.7631	
40	300.23	31.96	42.432	0.7532	
60	299.38	31.11	42.468	0.7326	
80	298.53	30.26	42.504	0.7119	
100	297.64	29.37	42.538	0.6904	
120	296.67	28.40	42.576	0.6671	
140	295.64	27.37	42.613	0.6423	
160	294.54	26.27	42.652	0.6158	
180	293.27 293.24	25.00 24.97	42.687	0.5857 0.5849	0.5853
200	291.70	23.43	42.721	0.5485	

Table A.20 : Density Data For The Binary Mixture of Benzene {0.7} And n-Hexane {0.3}

Mass Fraction of Benzene = 0.7
Mole Fraction of Benzene = 0.7202
Mass Fraction of n-Hexane = 0.3
Mole Fraction of n-Hexane = 0.2798

Wt. of Evacuated Density Cell {C} Used = 268.27g

Temp. (C)	Wt. of Cell Filled with Sample g	Wt. of Sample g	Vol. of the Density Cell cm^3	Density of the Sample g/cm^3	Average Density of the Sample g/cm^3
25	301.83	33.56	42.398	0.7915	
30	301.64 301.61	33.37 33.34	42.409 42.409	0.7868 0.7862	0.7865
40	301.22	32.95	42.432	0.7766	
60	300.36	32.09	42.468	0.7556	
80	299.50	31.23	42.504	0.7348	
100	298.60	30.33	42.538	0.7131	
120	297.63	29.36	42.576	0.6896	
140	296.60	28.33	42.613	0.6648	
160	295.51	27.24	42.652	0.6386	
180	294.25	25.98	42.687	0.6085	
200	292.74	24.47	42.721	0.5727	

Table A.21 : Density Data For The Binary Mixture of Benzene {0.8} And n-Hexane {0.2}

Mass Fraction of Benzene = 0.8 Mole Fraction of Benzene = 0.8153 Mass Fraction of n-Hexane = 0.2 Mole Fraction of n-Hexane = 0.1847

Wt. of Evacuated Density Cell {D} Used = 237.52g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3 -	g/cm^3 -	g/cm^3
25	271.59	34.07	41.717	0.8168	
30	271.38	33.86	41.726	0.8115	
	271.40	33.88		0.8119	0.8117
40	270.99	33.47	41.744	0.8017	
60	270.12	32.60	41.781	0.7803	
80	269.28	31.76	41.821	0.7594	
100	268.39	30.87	41.857	0.7376	
120	267.43	29.91	41.895	0.7139	
140	266.42	28.90	41.933	0.6891	
160	265.36	27.84	41.972	0.6632	
180	264.14	26.62	42.011	0.6337	
200	262.72	25.20	42.050	0.5993	

Table A.22 : **Density Data For The Binary Mixture of Cyclohexane {0.2} And n-Hexane {0.8}**

Mass Fract. of Cyclohexane = 0.2
Mole Fract. of Cyclohexane = 0.2039
Mass Fraction of n-Hexane = 0.8
Mole Fraction of n-Hexane = 0.7962

Wt. of Evacuated Density Cell {A} Used = 271.06g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	299.94	28.88	42.769	0.6753	
30	299.77	28.71	42.785	0.6710	
40	299.38	28.32	42.816	0.6615	
60	298.60	27.54	42.846	0.6428	
80	297.79 297.76	26.73 26.70	42.885	0.6232 0.6226	0.6229
100	296.90	25.84	42.924	0.6021	
120	295.99	24.93	42.971	0.5802	
140	294.97	23.91	42.992	0.5562	
160	293.86	22.80	43.034	0.5297	
180	292.55	21.49	43.082	0.4988	
200	290.92	19.86	43.109	0.4606	

Table A.23 : Density Data For The Binary Mixture of Cyclohexane {0.3} And n-Hexane {0.7}

Mass Fract. of Cyclohexane = 0.3
Mole Fract. of Cyclohexane = 0.3050
Mass Fraction of n-Hexane = 0.7
Mole Fraction of n-Hexane = 0.6950

Wt. of Evacuated Density Cell {A} Used = 271.06g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	300.40	29.34	42.769	0.6861	
30	300.23	29.17	42.785	0.6818	
40	299.85	28.79	42.816	0.6723	
60	299.07	28.01	42.846	0.6537	
80	298.25 298.22	27.19 27.16	42.885	0.6340 0.6334	0.6337
100	297.37	26.31	42.924	0.6129	
120	296.46	25.40	42.971	0.5910	
140	295.45	24.39	42.992	0.5672	
160	294.33	23.27	43.034	0.5408	
180	293.04	21.98	43.082	0.5103	
200	291.44	20.38	43.109	0.4728	

Table A.24 : Density Data For The Binary Mixture of Cyclohexane {0.4} And n-Hexane {0.6}

Mass Fract. of Cyclohexane = 0.4
Mole Fract. of Cyclohexane = 0.4057
Mass Fraction of n-Hexane = 0.6
Mole Fraction of n-Hexane = 0.5943

Wt. of Evacuated Density Cell {B} Used = 233.71g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	263.32	29.61	42.468	0.6972	
30	263.14	29.43	42.473	0.6929	
40	262.75	29.04	42.492	0.6835	
60	261.99	28.28	42.533	0.6649	
80	261.16	27.45	42.572	0.6449	
100	260.30	26.59	42.611	0.6241	
120	259.40	25.69	42.657	0.6022	
140	258.41	24.70	42.691	0.5785	
160	257.32 257.30	23.61 23.59	42.732	0.5526 0.5520	0.5523
180	256.05	22.34	42.766	0.5223	
200	254.49	20.78	42.811	0.4855	

Table A.25 : **Density Data For The Binary Mixture of Cyclohexane (0.5) And n-Hexane (0.5)**

Mass Fract. of Cyclohexane = 0.5
Mole Fract. of Cyclohexane = 0.5059
Mass Fraction of n-Hexane = 0.5
Mole Fraction of n-Hexane = 0.4941

Wt. of Evacuated Density Cell (B) Used = 233.71g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	263.81	30.10	42.468	0.7087	
30	263.63	29.92	42.473	0.7044	
40	263.24	29.53	42.492	0.6950	
60	262.48	28.77	42.533	0.6764	
80	261.66	27.95	42.572	0.6565	
100	260.80	27.09	42.611	0.6357	
120	259.89	26.18	42.657	0.6138	
140	258.91	25.20	42.691	0.5903	
160	257.83	24.12	42.732	0.5644	
180	256.60	22.89	42.766	0.5352	
180	256.56	22.85		0.5344	0.5348
200	255.07	21.36	42.811	0.4989	

Table A.26 : Density Data For The Binary Mixture of Cyclohexane {0.6} And n-Hexane {0.4}

Mass Fract. of Cyclohexane = 0.6
Mole Fract. of Cyclohexane = 0.6057
Mass Fraction of n-Hexane = 0.4
Mole Fraction of n-Hexane = 0.3943

Wt. of Evacuated Density Cell {C} Used = 268.27g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	298.82	30.55	42.398	0.7206	
30	298.65	30.38	42.409	0.7163	
40	298.25 298.28	29.98 30.01	42.432	0.7066 0.7072	0.7069
60	297.50	29.23	42.468	0.6882	
80	296.68	28.41	42.504	0.6684	
100	295.82	27.55	42.538	0.6476	
120	294.91	26.64	42.576	0.6258	
140	293.95	25.68	42.613	0.6027	
160	292.88	24.61	42.652	0.5770	
180	291.66	23.39	42.687	0.5479	
200	290.19	21.92	42.721	0.5131	

Table A.27 : Density Data For The Binary Mixture of Cyclohexane {0.7} And n-Hexane {0.3}

Mass Fract. of Cyclohexane = 0.7
Mole Fract. of Cyclohexane = 0.7049
Mass Fraction of n-Hexane = 0.3
Mole Fraction of n-Hexane = 0.2951

Wt. of Evacuated Density Cell {C} Used = 268.27g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	299.35	31.08	42.398	0.7330	
30	299.17	30.90	42.409	0.7286	
40	298.80 298.78	29.53 30.51	42.432	0.7194 0.7190	0.7192
60	298.02	29.75	42.468	0.7005	
80	297.20	28.93	42.504	0.6806	
100	296.34	28.07	42.538	0.6598	
120	295.44	27.17	42.576	0.6381	
140	294.49	26.22	42.613	0.6152	
160	293.43	25.16	42.652	0.5900	
180	292.24	23.97	42.687	0.5616	
200	290.83	22.56	42.721	0.5280	

Table A.28 : Density Data For The Binary Mixture of Cyclohexane {0.8} And n-Hexane {0.2}

Mass Fract. of Cyclohexane = 0.8 Mole Fract. of Cyclohexane = 0.8038

Mass Fraction of n-Hexane = 0.2 Mole Fraction of n-Hexane = 0.1962

Wt. of Evacuated Density Cell {D} Used = 237.52g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	268.64	31.12	41.717	0.7460	
30	268.46	30.94	41.726	0.7415	
40	268.08	30.56	41.744	0.7321	
60	267.32	29.80	41.781	0.7132	
80	266.51	28.99	41.821	0.6933	
100	265.66	28.14	41.857	0.6724	
120	264.79	27.27	41.895	0.6508	
140	263.86	26.34	41.933	0.6282	
160	262.85	25.33	41.972	0.6034	
180	261.71	24.19	42.011	0.5758	
200	260.40 260.37	22.88 22.85	42.050	0.5440 0.5434	0.5437

Table A.29 : Density Data For The Ternary Mixture of Benzene {0.333} , Cyclohexane {0.333} And n-Hexane {0.333}

Mass Fraction of Benzene = 0.333
Mole Fraction of Benzene = 0.3528
Mass Fract. of Cyclohexane = 0.333
Mole Fract. of Cyclohexane = 0.3274
Mass Fraction of n-Hexane = 0.333
Mole Fraction of n-Hexane = 0.3198

Wt. of Evacuated Density Cell {A} Used = 271.06g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	303.36	32.30	42.769	0.7552	
30	303.15	32.09	42.785	0.7501	
40	302.75	31.69	42.816	0.7402	
60	301.90	30.84	42.846	0.7198	
80	301.03	29.97	42.885	0.6988	
100	300.12	29.06	42.924	0.6770	
120	299.17	28.11	42.971	0.6542	
140	298.14 298.18	27.08 27.12	42.992	0.6298 0.6308	0.6303
160	297.09	26.03	43.034	0.6049	
180	295.91	24.85	43.082	0.5769	
200	294.57	23.51	43.109	0.5453	

Table A.30 : Density Data For The Ternary Mixture of Benzene {0.5} , Cyclohexane {0.25} And n-Hexane {0.25}

Mass Fraction of Benzene = 0.50
Mole Fraction of Benzene = 0.5216
Mass Fract. of Cyclohexane = 0.25
Mole Fract. of Cyclohexane = 0.2420
Mass Fraction of n-Hexane = 0.25
Mole Fraction of n-Hexane = 0.2364

Wt. of Evacuated Density Cell (B) Used = 233.71g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	266.60	32.89	42.468	0.7744	
30	266.50	32.79	42.473	0.7721	
40	266.10	32.39	42.492	0.7622	
60	265.26	31.55	42.533	0.7418	
80	264.38 264.40	30.67 30.69	42.572	0.7204 0.7210	0.7207
100	263.49	29.78	42.611	0.6989	
120	262.55	28.84	42.657	0.6760	
140	261.54	27.83	42.691	0.6520	
160	260.49	26.78	42.732	0.6268	
180	259.32	25.61	42.766	0.5989	
200	258.01	24.30	42.811	0.5676	

Table A.31 : **Density Data For The Ternary Mixture of Benzene {0.65} , Cyclohexane {0.175} And n-Hexane {0.175}**

Mass Fraction of Benzene = 0.65
Mole Fraction of Benzene = 0.6694
Mass Fract. of Cyclohexane = 0.175
Mole Fract. of Cyclohexane = 0.1673
Mass Fraction of n-Hexane = 0.175
Mole Fraction of n-Hexane = 0.1633

Wt. of Evacuated Density Cell {C} Used = 268.27g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	302.26	33.99	42.398	0.8018	
	302.28	34.01		0.8022	0.8020
30	302.06	33.79	42.409	0.7968	
40	301.65	33.38	42.432	0.7867	
60	300.78	32.51	42.468	0.7656	
80	299.92	31.65	42.504	0.7447	
100	299.02	30.75	42.538	0.7229	
120	298.06	29.79	42.576	0.6996	
140	297.05	28.78	42.613	0.6754	
160	296.00	27.73	42.652	0.6502	
180	294.85	26.58	42.687	0.6226	
200	293.55	25.28	42.721	0.5918	

Table A.32 : **Density Data For The Ternary Mixture of Benzene {0.8} , Cyclohexane {0.1} And n-Hexane {0.1}**

Mass Fraction of Benzene = 0.8
Mole Fract. of Benzene = 0.8038
Mass Fract. of Cyclohexane = 0.1
Mole Fract. of Cyclohexane = 0.0944
Mass Fraction of n-Hexane = 0.1
Mole Fraction of n-Hexane = 0.0921

Wt. of Evacuated Density Cell {D} Used = 237.52g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	272.18	34.66	41.717	0.8308	
30	271.97	34.45	41.726	0.8256	
40	271.56	34.04	41.744	0.8154	
60	270.68	33.16	41.781	0.7937	
80	269.81 269.84	32.29 32.32	41.821	0.7721 0.7729	0.7725
100	268.93	31.41	41.857	0.7505	
120	267.97	30.45	41.895	0.7268	
140	266.97	29.45	41.933	0.7024	
160	265.94	28.42	41.972	0.6772	
180	264.81	27.29	42.011	0.6495	
200	263.54	26.02	42.050	0.6188	

Table A.33 : **Density Data For The Ternary Mixture of Benzene (0.25) , Cyclohexane (0.50) And n-Hexane (0.25)**

Mass Fraction of Benzene = 0.25
Mole Fraction of Benzene = 0.2658
Mass Fract. of Cyclohexane = 0.50
Mole Fract. of Cyclohexane = 0.4933
Mass Fraction of n-Hexane = 0.25
Mole Fraction of n-Hexane = 0.2409

Wt. of Evacuated Density Cell {A} Used = 271.06g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	303.54	32.48	42.769	0.7594	
30	303.36	32.30	42.785	0.7549	
40	302.96	31.92	42.816	0.7454	
60	302.19	31.13	42.846	0.7266	
80	301.34 301.38	30.28 30.32	42.885	0.7061 0.7069	0.7065
100	300.49	29.43	42.924	0.6857	
120	299.59	28.53	42.971	0.6639	
140	298.61	27.55	42.992	0.6407	
160	297.54	26.48	43.034	0.6153	
180	296.33	25.27	43.082	0.5866	
200	294.88	23.82	43.109	0.5526	

Table A.34 : **Density Data For The Ternary Mixture of Benzene {0.175} , Cyclohexane {0.65} And n-Hexane {0.175}**

Mass Fraction of Benzene = 0.175
Mole Fraction of Benzene = 0.1868
Mass Fract. of Cyclohexane = 0.650
Mole Fract. of Cyclohexane = 0.6439
Mass Fraction of n-Hexane = 0.175
Mole Fraction of n-Hexane = 0.1693

Wt. of Evacuated Density Cell (B) Used = 233.71g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	266.14	32.43	42.468	0.7636	
30	265.96	32.25	42.473	0.7593	
40	265.57	31.86	42.492	0.7498	
60	264.80	31.09	42.533	0.7309	
80	263.98	30.27	42.572	0.7110	
100	263.12	29.41	42.611	0.6902	
120	262.22	28.51	42.657	0.6684	
140	261.27	27.56	42.691	0.6455	
160	260.21	26.50	42.732	0.6202	
180	259.02	25.31	42.766	0.5918	
200	257.64 257.59	23.93 23.88	42.811	0.5584 0.5579	0.5584

Table A.35 : Density Data For The Ternary Mixture of Benzene {0.10} , Cyclohexane {0.80} And n-Hexane {0.10}

Mass Fraction of Benzene = 0.10
Mole Fraction of Benzene = 0.1072
Mass Fract. of Cyclohexane = 0.80
Mole Fract. of Cyclohexane = 0.7957
Mass Fraction of n-Hexane = 0.10
Mole Fraction of n-Hexane = 0.0971

Wt. of Evacuated Density Cell {C} Used = 268.27g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	300.83	32.56	42.398	0.7680	
30	300.65	32.38	42.409	0.7635	
40	300.27	32.00	42.432	0.7541	
60	299.48	31.21	42.468	0.7349	
80	298.69	30.42	42.504	0.7157	
	298.63	30.36	42.504	0.7143	0.7150
100	297.79	29.52	42.538	0.6939	
120	296.90	28.63	42.576	0.6724	
140	295.96	27.69	42.613	0.6498	
160	294.93	26.66	42.652	0.6251	
180	293.79	25.52	42.687	0.5978	
200	292.46	24.19	42.721	0.5662	

Table A.36 : **Density Data For The Ternary Mixture of Benzene {0.25} , Cyclohexane {0.25} And n-Hexane {0.50}**

Mass Fraction of Benzene = 0.25
Mole Fraction of Benzene = 0.2673
Mass Fract. of Cyclohexane = 0.25
Mole Fract. of Cyclohexane = 0.2481
Mass Fraction of n-Hexane = 0.50
Mole Fraction of n-Hexane = 0.4846

Wt. of Evacuated Density Cell {A} Used = 271.06g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	302.17	31.11	42.769	0.7273	
30	301.98	30.92	42.785	0.7226	
40	301.58	30.52	42.816	0.7129	
60	300.75	29.69	42.846	0.6930	
80	299.93	28.87	42.885	0.6731	
100	299.05	27.99	42.924	0.6521	
120	298.10 298.11	27.04 27.05	42.971	0.6292 0.6296	0.6294
140	297.07	26.01	42.992	0.6051	
160	295.98	24.92	43.034	0.5790	
180	294.71	23.65	43.082	0.5489	
200	293.14	22.08	43.109	0.5122	

Table A.37 : Density Data For The Ternary Mixture of Benzene {0.175} , Cyclohexane {0.175} And n-Hexane {0.65}

Mass Fraction of Benzene = 0.175
Mole Fraction of Benzene = 0.1889
Mass Fract. of Cyclohexane = 0.175
Mole Fract. of Cyclohexane = 0.1753
Mass Fraction of n-Hexane = 0.65
Mole Fraction of n-Hexane = 0.6358

Wt. of Evacuated Density Cell (B) Used = 233.71g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	263.57	29.86	42.468	0.7032	
30	262.37 263.41	29.66 29.70	42.473	0.6984 0.6992	0.6988
40	263.00	29.29	42.492	0.6892	
60	262.19	28.48	42.533	0.6696	
80	261.36	27.65	42.572	0.6496	
100	260.51	26.80	42.611	0.6289	
120	259.58	25.87	42.657	0.6065	
140	258.56	24.85	42.691	0.5822	
160	257.46	23.75	42.732	0.5557	
180	256.16	22.45	42.766	0.5249	
200	254.55	20.84	42.811	0.4869	

Table A.38 : **Density Data For The Ternary Mixture of Benzene {0.10} , Cyclohexane {0.10} And n-Hexane {0.80}**

Mass Fraction of Benzene = 0.10
Mole Fraction of Benzene = 0.1089
Mass Fract. of Cyclohexane = 0.10
Mole Fract. of Cyclohexane = 0.1011
Mass Fraction of n-Hexane = 0.80
Mole Fraction of n-Hexane = 0.7900

Wt. of Evacuated Density Cell {C} Used = 268.27g

Temp.	Wt. of Cell Filled with Sample	Wt. of Sample	Vol. of the Density Cell	Density of the Sample	Average Density of the Sample
(C)	g	g	cm^3	g/cm^3	g/cm^3
25	297.16	28.89	42.398	0.6815	
30	296.98	28.71	42.409	0.6769	
40	296.59	28.32	42.432	0.6674	
60	295.79	27.52	42.468	0.6481	
	295.81	27.54		0.6485	0.6483
80	294.98	26.71	42.504	0.6283	
100	294.11	25.84	42.538	0.6074	
120	293.20	24.93	42.576	0.5855	
140	292.19	23.92	42.613	0.5613	
160	291.08	22.81	42.652	0.5348	
180	289.77	21.50	42.687	0.5036	
200	288.14	19.87	42.721	0.4651	

Table A.39 : **Excess Volumes For The Binary Mixture of Benzene And Cyclohexane**

Temp.	Mole Fraction of Benzene						
(C)	0.2111	0.3159	0.4180	0.5186	0.6178	0.7154	0.8117
25	0.4241	0.5229	0.6183	0.6506	0.6270	0.5396	0.3990
30	0.4283	0.5471	0.6358	0.6609	0.6417	0.5574	0.4075
40	0.4365	0.5770	0.6596	0.6773	0.6624	0.5805	0.4196
60	0.4792	0.5985	0.6715	0.7025	0.6842	0.5944	0.4565
80	0.5076	0.6190	0.6972	0.7171	0.6996	0.6332	0.4765
100	0.5337	0.6653	0.7303	0.7497	0.7297	0.6722	0.5185
120	0.5700	0.7005	0.7602	0.7868	0.7700	0.6825	0.5506
140	0.6018	0.7180	0.7944	0.8169	0.7928	0.7245	0.5757
160	0.6072	0.7523	0.8166	0.8428	0.8192	0.7488	0.6255
180	0.6513	0.7936	0.8696	0.8841	0.8456	0.7941	0.6661
200	0.6778	0.8157	0.9046	0.9256	0.8673	0.8366	0.7011

Table A.40 : **Excess Volumes For The Binary Mixture of Benzene And n-Hexane**

Temp.	Mole Fraction of Benzene						
(C)	0.2162	0.3210	0.4238	0.5245	0.6233	0.7202	0.8153
25	0.2394	0.3196	0.3814	0.3914	0.3759	0.3272	0.2567
30	0.2294	0.3129	0.3611	0.3730	0.3587	0.3232	0.2512
40	0.2185	0.3068	0.3592	0.3597	0.3501	0.3062	0.2399
60	0.2222	0.2912	0.3412	0.3359	0.3352	0.2962	0.2323
80	0.2143	0.2905	0.3298	0.3318	0.3246	0.2812	0.2158
100	0.2039	0.2674	0.2964	0.3089	0.2971	0.2678	0.2033
120	0.1870	0.2440	0.2672	0.2962	0.2818	0.2527	0.1903
140	0.1744	0.2187	0.2573	0.2644	0.2553	0.2201	0.1597
160	0.1479	0.2126	0.2377	0.2454	0.2307	0.1873	0.1386
180	0.1609	0.1941	0.2040	0.1965	0.1949	0.1693	0.1299
200	0.1364	0.1602	0.1740	0.1902	0.1598	0.1481	0.1030

Table A.41 : **Excess Volumes For The Binary Mixture of Cyclohexane And n-Hexane**

Temp.	Mole Fraction of Cyclohexane						
(C)	0.2038	0.3050	0.4057	0.5059	0.6057	0.7049	0.8038
25	0.0550	0.0718	0.0971	0.1158	0.1336	0.1340	0.1125
30	0.0217	0.0325	0.0524	0.0661	0.0792	0.0911	0.0801
40	0.0117	0.0190	0.0182	0.0310	0.0441	0.0569	0.0472
60	-0.0344	-0.0558	-0.0629	-0.0536	-0.0239	-0.0113	0.0129
80	-0.0507	-0.0672	-0.0879	-0.1085	-0.1036	-0.0762	-0.0532
100	-0.0607	-0.0898	-0.1204	-0.1479	-0.1452	-0.1158	-0.0695
120	-0.0965	-0.1243	-0.1502	-0.1691	-0.1740	-0.1452	-0.0934
140	-0.1011	-0.1606	-0.1837	-0.2173	-0.2740	-0.2375	-0.1901
160	-0.1318	-0.1777	-0.2029	-0.2557	-0.2950	-0.2957	-0.2447
180	-0.1368	-0.2059	-0.2621	-0.2957	-0.3227	-0.3390	-0.2971
200	-0.1488	-0.2445	-0.2814	-0.3188	-0.3652	-0.3775	-0.3558

APPENDIX B

DEFINITION OF ERRORS

Absolute Standard Percentage Error

$$= \frac{\rho_{Exp.} - \rho_{Pred.}}{\rho_{Exp.}} * 100$$

Absolute Average Percentage Error

$$= \frac{\sum (\text{Percetage Error})}{N}$$

Where

$\rho_{Pred.}$ = Predicted Value of Sample Density

$\rho_{Exp.}$ = Experimental Value of Density

N = Number of data points

APPENDIX C

```
------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE

------------------------------------------------------------

1.0000      0.0000      0.0000


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)     H-B-T    ERROR(%)

 298.15      0.8737      0.8705   0.36947E+00   0.8700  0.42755E+00
 303.15      0.8683      0.8655   0.32454E+00   0.8650  0.38437E+00
 313.15      0.8581      0.8554   0.31724E+00   0.8549  0.37888E+00
 333.15      0.8358      0.8347   0.13766E+00   0.8342  0.19470E+00
 353.15      0.8146      0.8131   0.18070E+00   0.8128  0.22232E+00
 373.15      0.7926      0.7907   0.24033E+00   0.7906  0.25524E+00
 393.15      0.7685      0.7672   0.17003E+00   0.7674  0.14716E+00
 413.15      0.7437      0.7424   0.17438E+00   0.7429  0.10257E+00
 433.15      0.7188      0.7160   0.38612E+00   0.7170  0.25496E+00
 453.15      0.6912      0.6877   0.51379E+00   0.6890  0.31458E+00
 473.15      0.6607      0.6567   0.61467E+00   0.6585  0.34152E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.28574E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.25199E+00
------------------------------------------------------------
ANALYSIS OF DATA FOR  CYCLOHEXANE

------------------------------------------------------------

0.0000      1.0000      0.0000


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)     H-B-T    ERROR(%)

 298.15      0.7739      0.7725   0.18396E+00   0.7735  0.57844E-01
 303.15      0.7691      0.7680   0.14816E+00   0.7689  0.28318E-01
 313.15      0.7595      0.7588   0.90615E-01   0.7596 -0.18439E-01
 333.15      0.7404      0.7400   0.51927E-01   0.7407 -0.42898E-01
 353.15      0.7201      0.7205  -0.51351E-01   0.7211 -0.14189E+00
 373.15      0.6992      0.7001  -0.12174E+00   0.7007 -0.21751E+00
 393.15      0.6778      0.6786  -0.11773E+00   0.6794 -0.22843E+00
 413.15      0.6554      0.6559  -0.74818E-01   0.6568 -0.20913E+00
 433.15      0.6314      0.6316  -0.35605E-01   0.6327 -0.20031E+00
 453.15      0.6055      0.6054   0.24025E-01   0.6066 -0.17519E+00
 473.15      0.5768      0.5764   0.72191E-01   0.5777 -0.16000E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.81009E-01

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.12333E+00
------------------------------------------------------------
ANALYSIS OF DATA FOR  HEXANE

------------------------------------------------------------
```

```
0.0000      0.0000      1.0000

TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)     H-B-T    ERROR(%)

 298.15     0.6548      0.6572  -0.36504E+00    0.6576 -0.42801E+00
 303.15     0.6504      0.6525  -0.32640E+00    0.6529 -0.39043E+00
 313.15     0.6409      0.6430  -0.33366E+00    0.6435 -0.40278E+00
 333.15     0.6221      0.6234  -0.21296E+00    0.6240 -0.30479E+00
 353.15     0.6023      0.6028  -0.83859E-01    0.6036 -0.21564E+00
 373.15     0.5816      0.5810   0.11028E+00    0.5821 -0.79515E-01
 393.15     0.5596      0.5576   0.36285E+00    0.5591  0.95879E-01
 413.15     0.5355      0.5322   0.62099E+00    0.5341  0.25777E+00
 433.15     0.5087      0.5041   0.91899E+00    0.5065  0.44051E+00
 453.15     0.4773      0.4719   0.11531E+01    0.4747  0.54302E+00
 473.15     0.4381      0.4327   0.12503E+01    0.4359  0.49767E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.47820E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.30467E+00
------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.2) + CYCLOHEXANE (0.8)

------------------------------------------------------------

0.2111      0.7889      0.0000

TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)     H-B-T    ERROR(%)

 298.15     0.7887      0.7910  -0.29095E+00    0.7916 -0.36491E+00
 303.15     0.7838      0.7864  -0.33098E+00    0.7869 -0.39792E+00
 313.15     0.7741      0.7771  -0.38466E+00    0.7775 -0.43923E+00
 333.15     0.7543      0.7580  -0.48321E+00    0.7582 -0.51974E+00
 353.15     0.7338      0.7381  -0.58058E+00    0.7383 -0.60816E+00
 373.15     0.7127      0.7173  -0.64567E+00    0.7175 -0.67271E+00
 393.15     0.6908      0.6955  -0.68193E+00    0.6958 -0.71610E+00
 413.15     0.6680      0.6725  -0.66939E+00    0.6728 -0.71719E+00
 433.15     0.6440      0.6479  -0.60365E+00    0.6483 -0.66862E+00
 453.15     0.6178      0.6213  -0.56927E+00    0.6218 -0.65029E+00
 473.15     0.5889      0.5921  -0.54145E+00    0.5926 -0.62888E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.48181E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.53198E+00
------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.3) + CYCLOHEXANE (0.7)

------------------------------------------------------------

0.3159      0.6841      0.0000

TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)     H-B-T    ERROR(%)
```

```
 298.15     0.7973      0.8006   -0.41107E+00    0.8010  -0.46075E+00
 303.15     0.7922      0.7959   -0.47091E+00    0.7963  -0.51372E+00
 313.15     0.7823      0.7865   -0.54015E+00    0.7868  -0.57012E+00
 333.15     0.7624      0.7672   -0.63149E+00    0.7673  -0.64314E+00
 353.15     0.7419      0.7472   -0.70774E+00    0.7472  -0.70953E+00
 373.15     0.7206      0.7263   -0.77859E+00    0.7263  -0.77854E+00
 393.15     0.6985      0.7043   -0.82104E+00    0.7043  -0.82657E+00
 413.15     0.6756      0.6811   -0.80169E+00    0.6812  -0.81837E+00
 433.15     0.6514      0.6563   -0.74492E+00    0.6565  -0.77553E+00
 453.15     0.6251      0.6295   -0.70543E+00    0.6298  -0.74756E+00
 473.15     0.5961      0.6002   -0.67533E+00    0.6004  -0.71703E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.60736E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.63007E+00
--------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.4) + CYCLOHEXANE (0.6)

--------------------------------------------------------------

0.4180      0.5820      0.0000


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.8060      0.8102   -0.51823E+00    0.8104  -0.54591E+00
 303.15     0.8009      0.8055   -0.57258E+00    0.8057  -0.59325E+00
 313.15     0.7910      0.7960   -0.63092E+00    0.7961  -0.63917E+00
 333.15     0.7709      0.7765   -0.72597E+00    0.7765  -0.71605E+00
 353.15     0.7503      0.7563   -0.79295E+00    0.7561  -0.77337E+00
 373.15     0.7290      0.7352   -0.84018E+00    0.7350  -0.81879E+00
 393.15     0.7067      0.7130   -0.88591E+00    0.7129  -0.86993E+00
 413.15     0.6835      0.6896   -0.88499E+00    0.6896  -0.87989E+00
 433.15     0.6593      0.6646   -0.80388E+00    0.6647  -0.81168E+00
 453.15     0.6328      0.6377   -0.77005E+00    0.6378  -0.78778E+00
 473.15     0.6036      0.6082   -0.74823E+00    0.6082  -0.76308E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.68116E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.68324E+00
--------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.5) + CYCLOHEXANE (0.5)

--------------------------------------------------------------

0.5186      0.4814      0.0000


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.8154      0.8199   -0.55274E+00    0.8200  -0.56014E+00
 303.15     0.8103      0.8152   -0.60103E+00    0.8152  -0.60158E+00
 313.15     0.8004      0.8056   -0.64744E+00    0.8055  -0.63647E+00
 333.15     0.7799      0.7859   -0.76889E+00    0.7857  -0.74114E+00
 353.15     0.7593      0.7655   -0.81133E+00    0.7652  -0.77512E+00
```

```
 373.15     0.7379     0.7442  -0.84600E+00   0.7439 -0.80920E+00
 393.15     0.7153     0.7218  -0.90577E+00   0.7216 -0.87571E+00
 413.15     0.6919     0.6982  -0.90578E+00   0.6981 -0.88786E+00
 433.15     0.6676     0.6731  -0.81177E+00   0.6730 -0.80815E+00
 453.15     0.6410     0.6459  -0.76356E+00   0.6460 -0.77149E+00
 473.15     0.6116     0.6162  -0.74360E+00   0.6162 -0.75039E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.69649E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.68477E+00
-------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.6) + CYCLOHEXANE (0.4)

-------------------------------------------------------------

0.6178     0.3822     0.0000


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.8255     0.8298  -0.51768E+00   0.8297 -0.50728E+00
 303.15     0.8203     0.8250  -0.57154E+00   0.8249 -0.55490E+00
 313.15     0.8103     0.8153  -0.61765E+00   0.8151 -0.59017E+00
 333.15     0.7895     0.7955  -0.75020E+00   0.7951 -0.70814E+00
 353.15     0.7688     0.7748  -0.77899E+00   0.7745 -0.73079E+00
 373.15     0.7473     0.7533  -0.79869E+00   0.7530 -0.75266E+00
 393.15     0.7244     0.7308  -0.86915E+00   0.7305 -0.83268E+00
 413.15     0.7008     0.7069  -0.86665E+00   0.7068 -0.84571E+00
 433.15     0.6764     0.6816  -0.75590E+00   0.6815 -0.75318E+00
 453.15     0.6497     0.6542  -0.68885E+00   0.6543 -0.70231E+00
 473.15     0.6202     0.6242  -0.64826E+00   0.6244 -0.66682E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.65530E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.63705E+00
-------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.7) + CYCLOHEXANE (0.3)

-------------------------------------------------------------

0.7154     0.2846     0.0000


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.8364     0.8398  -0.40161E+00   0.8396 -0.37525E+00
 303.15     0.8311     0.8349  -0.46015E+00   0.8347 -0.42831E+00
 313.15     0.8210     0.8252  -0.50438E+00   0.8248 -0.46338E+00
 333.15     0.7999     0.8051  -0.64473E+00   0.8047 -0.59215E+00
 353.15     0.7789     0.7843  -0.68225E+00   0.7838 -0.62716E+00
 373.15     0.7572     0.7625  -0.69756E+00   0.7621 -0.64876E+00
 393.15     0.7342     0.7397  -0.74849E+00   0.7395 -0.71355E+00
 413.15     0.7102     0.7157  -0.76709E+00   0.7156 -0.75278E+00
 433.15     0.6857     0.6901  -0.63593E+00   0.6902 -0.64615E+00
 453.15     0.6587     0.6625  -0.57556E+00   0.6627 -0.60992E+00
```

```
 473.15     0.6289      0.6323  -0.54182E+00    0.6326 -0.59153E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.55496E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.53741E+00
------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.8) + CYCLOHEXANE (0.2)

------------------------------------------------------------

0.8117      0.1883      0.0000


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)     H-B-T    ERROR(%)

 298.15     0.8481      0.8499  -0.21040E+00    0.8495 -0.17055E+00
 303.15     0.8428      0.8450  -0.26104E+00    0.8446 -0.21661E+00
 313.15     0.8327      0.8351  -0.28997E+00    0.8347 -0.23852E+00
 333.15     0.8110      0.8148  -0.47096E+00    0.8144 -0.41214E+00
 353.15     0.7900      0.7938  -0.47629E+00    0.7933 -0.41962E+00
 373.15     0.7681      0.7718  -0.48284E+00    0.7715 -0.43783E+00
 393.15     0.7446      0.7488  -0.56296E+00    0.7486 -0.53801E+00
 413.15     0.7204      0.7245  -0.57066E+00    0.7246 -0.57358E+00
 433.15     0.6956      0.6987  -0.44254E+00    0.6989 -0.47888E+00
 453.15     0.6684      0.6709  -0.36822E+00    0.6714 -0.43979E+00
 473.15     0.6384      0.6404  -0.31753E+00    0.6411 -0.41930E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.37112E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.36207E+00
------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.2) + HEXANE (0.8)

------------------------------------------------------------

0.2162      0.0000      0.7838


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)     H-B-T    ERROR(%)

 298.15     0.6880      0.6900  -0.28855E+00    0.6937 -0.81712E+00
 303.15     0.6835      0.6853  -0.25867E+00    0.6889 -0.78897E+00
 313.15     0.6739      0.6757  -0.26549E+00    0.6793 -0.80184E+00
 333.15     0.6545      0.6559  -0.21540E+00    0.6596 -0.77608E+00
 353.15     0.6344      0.6352  -0.12162E+00    0.6390 -0.72342E+00
 373.15     0.6134      0.6133   0.20536E-01    0.6174 -0.64068E+00
 393.15     0.5910      0.5899   0.17934E+00    0.5943 -0.55998E+00
 413.15     0.5666      0.5648   0.32297E+00    0.5695 -0.51415E+00
 433.15     0.5399      0.5372   0.51084E+00    0.5423 -0.44542E+00
 453.15     0.5083      0.5060   0.44878E+00    0.5116 -0.64635E+00
 473.15     0.4694      0.4693   0.15532E-01    0.4753 -0.12408E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.22064E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.66290E+00
```

```
-------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.3) + HEXANE (0.7)

-------------------------------------------------------------

0.3210      0.0000      0.6790


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.7061      0.7079  -0.25142E+00  0.7127 -0.93091E+00
 303.15     0.7015      0.7031  -0.23241E+00  0.7080 -0.91388E+00
 313.15     0.6918      0.6935  -0.24561E+00  0.6983 -0.93316E+00
 333.15     0.6722      0.6736  -0.21227E+00  0.6785 -0.92395E+00
 353.15     0.6519      0.6528  -0.14093E+00  0.6578 -0.89330E+00
 373.15     0.6308      0.6309  -0.13340E-01  0.6360 -0.82393E+00
 393.15     0.6082      0.6076   0.10473E+00  0.6130 -0.78270E+00
 413.15     0.5837      0.5825   0.20813E+00  0.5883 -0.77530E+00
 433.15     0.5568      0.5551   0.30810E+00  0.5612 -0.79228E+00
 453.15     0.5255      0.5244   0.20335E+00  0.5310 -0.10343E+01
 473.15     0.4869      0.4888  -0.37932E+00  0.4957 -0.17756E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.19163E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.88161E+00
-------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.4) + HEXANE (0.6)

-------------------------------------------------------------

0.4238      0.0000      0.5762


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.7253      0.7269  -0.21967E+00  0.7326 -0.99231E+00
 303.15     0.7207      0.7221  -0.19690E+00  0.7278 -0.97158E+00
 313.15     0.7109      0.7124  -0.21542E+00  0.7181 -0.99601E+00
 333.15     0.6910      0.6925  -0.21121E+00  0.6981 -0.10150E+01
 353.15     0.6706      0.6716  -0.14516E+00  0.6773 -0.98848E+00
 373.15     0.6494      0.6496  -0.29858E-01  0.6555 -0.92968E+00
 393.15     0.6266      0.6263   0.51755E-01  0.6324 -0.92224E+00
 413.15     0.6019      0.6013   0.10356E+00  0.6078 -0.96310E+00
 433.15     0.5751      0.5741   0.17729E+00  0.5809 -0.10025E+01
 453.15     0.5440      0.5439   0.26369E-01  0.5511 -0.12859E+01
 473.15     0.5058      0.5091  -0.64559E+00  0.5167 -0.21097E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.16856E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.10147E+01
-------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.5) + HEXANE (0.5)

-------------------------------------------------------------
```

```
0.5245      0.0000      0.4755


TEMP.   DENSITY EXPT.   RACKETT    ERROR(%)      H-B-T     ERROR(%)

 298.15      0.7459      0.7471   -0.16096E+00    0.7532  -0.96698E+00
 303.15      0.7412      0.7423   -0.14782E+00    0.7484  -0.95555E+00
 313.15      0.7314      0.7326   -0.15706E+00    0.7386  -0.97021E+00
 333.15      0.7112      0.7125   -0.17842E+00    0.7185  -0.10134E+01
 353.15      0.6906      0.6915   -0.13003E+00    0.6976  -0.10024E+01
 373.15      0.6692      0.6695   -0.39468E-01    0.6757  -0.96576E+00
 393.15      0.6461      0.6461   -0.61990E-02    0.6526  -0.10027E+01
 413.15      0.6214      0.6212    0.31049E-01    0.6280  -0.10537E+01
 433.15      0.5947      0.5942    0.85064E-01    0.6014  -0.11074E+01
 453.15      0.5639      0.5644   -0.81587E-01    0.5719  -0.13998E+01
 473.15      0.5262      0.5304   -0.79220E+00    0.5383  -0.22529E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.15082E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.10576E+01
--------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.6) + HEXANE (0.4)

--------------------------------------------------------------

0.6233      0.0000      0.3767.


TEMP.   DENSITY EXPT.   RACKETT    ERROR(%)      H-B-T     ERROR(%)

 298.15      0.7679      0.7686   -0.95405E-01    0.7747  -0.87154E+00
 303.15      0.7631      0.7638   -0.90906E-01    0.7698  -0.86823E+00
 313.15      0.7532      0.7540   -0.10404E+00    0.7599  -0.88619E+00
 333.15      0.7326      0.7338   -0.16222E+00    0.7397  -0.96361E+00
 353.15      0.7119      0.7127   -0.11583E+00    0.7187  -0.95199E+00
 373.15      0.6904      0.6906   -0.33227E-01    0.6968  -0.91949E+00
 393.15      0.6671      0.6673   -0.28244E-01    0.6737  -0.98039E+00
 413.15      0.6423      0.6424   -0.16970E-01    0.6491  -0.10516E+01
 433.15      0.6158      0.6156    0.38858E-01    0.6226  -0.10967E+01
 453.15      0.5853      0.5861   -0.13359E+00    0.5935  -0.13863E+01
 473.15      0.5485      0.5529   -0.78706E+00    0.5607  -0.21716E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.13386E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.10123E+01
--------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.7) + HEXANE (0.3)

--------------------------------------------------------------

0.7202      0.0000      0.2798


TEMP.   DENSITY EXPT.   RACKETT    ERROR(%)      H-B-T     ERROR(%)
```

```
 298.15     0.7915     0.7916  -0.11920E-01   0.7970 -0.69124E+00
 303.15     0.7865     0.7867  -0.27964E-01   0.7921 -0.70784E+00
 313.15     0.7766     0.7768  -0.31305E-01   0.7822 -0.71484E+00
 333.15     0.7556     0.7565  -0.12252E+00   0.7619 -0.82264E+00
 353.15     0.7348     0.7354  -0.76338E-01   0.7408 -0.80756E+00
 373.15     0.7131     0.7132  -0.13305E-01   0.7188 -0.79020E+00
 393.15     0.6896     0.6898  -0.33110E-01   0.6957 -0.87008E+00
 413.15     0.6648     0.6650  -0.28414E-01   0.6711 -0.94131E+00
 433.15     0.6386     0.6383   0.48942E-01   0.6448 -0.95663E+00
 453.15     0.6085     0.6091  -0.10381E+00   0.6160 -0.12165E+01
 473.15     0.5727     0.5766  -0.66820E+00   0.5838 -0.19005E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.97153E-01

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.86828E+00
---------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.8) + HEXANE (0.2)

---------------------------------------------------------------

0.8153      0.0000      0.1847


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.8168     0.8161   0.81709E-01   0.8203 -0.42972E+00
 303.15     0.8117     0.8112   0.58883E-01   0.8154 -0.45226E+00
 313.15     0.8017     0.8013   0.53217E-01   0.8054 -0.46024E+00
 333.15     0.7803     0.7808  -0.67404E-01   0.7850 -0.59399E+00
 353.15     0.7594     0.7596  -0.19940E-01   0.7638 -0.57336E+00
 373.15     0.7376     0.7373   0.39952E-01   0.7417 -0.55383E+00
 393.15     0.7139     0.7139  -0.55939E-03   0.7186 -0.64784E+00
 413.15     0.6891     0.6891   0.94282E-03   0.6941 -0.71439E+00
 433.15     0.6632     0.6625   0.10254E+00   0.6678 -0.69585E+00
 453.15     0.6337     0.6337   0.66880E-02   0.6394 -0.88739E+00
 473.15     0.5993     0.6017  -0.39250E+00   0.6078 -0.13931E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.68695E-01

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.61683E+00
---------------------------------------------------------------
ANALYSIS OF DATA FOR  CYCLOHEXANE (0.2) + HEXANE (0.8)

---------------------------------------------------------------

0.0000      0.2038      0.7962


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.6753     0.6769  -0.23138E+00   0.6787 -0.49700E+00
 303.15     0.6710     0.6722  -0.18491E+00   0.6740 -0.44924E+00
 313.15     0.6615     0.6629  -0.20470E+00   0.6646 -0.46923E+00
 333.15     0.6428     0.6435  -0.10476E+00   0.6453 -0.38025E+00
 353.15     0.6229     0.6231  -0.40020E-01   0.6250 -0.34119E+00
```

```
 373.15     0.6021      0.6017    0.68492E-01    0.6038  -0.27384E+00
 393.15     0.5802      0.5788    0.23866E+00    0.5811  -0.15997E+00
 413.15     0.5562      0.5541    0.37009E+00    0.5568  -0.99061E-01
 433.15     0.5297      0.5271    0.49912E+00    0.5300  -0.52780E-01
 453.15     0.4988      0.4965    0.45454E+00    0.4997  -0.18592E+00
 473.15     0.4606      0.4605    0.14043E-01    0.4639  -0.70620E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.20089E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.30122E+00
---------------------------------------------------------------
ANALYSIS OF DATA FOR  CYCLOHEXANE (0.3) + HEXANE (0.7)

---------------------------------------------------------------

0.0000     0.3050     0.6950


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.6861      0.6873  -0.16833E+00    0.6896  -0.50285E+00
 303.15     0.6818      0.6827  -0.12505E+00    0.6849  -0.45749E+00
 313.15     0.6723      0.6733  -0.15027E+00    0.6755  -0.48066E+00
 333.15     0.6537      0.6540  -0.51053E-01    0.6562  -0.38738E+00
 353.15     0.6337      0.6338  -0.22541E-01    0.6361  -0.37853E+00
 373.15     0.6129      0.6126   0.56408E-01    0.6150  -0.33325E+00
 393.15     0.5910      0.5899   0.18357E+00    0.5925  -0.25402E+00
 413.15     0.5672      0.5656   0.28868E+00    0.5684  -0.20913E+00
 433.15     0.5408      0.5390   0.34315E+00    0.5420  -0.22480E+00
 453.15     0.5103      0.5091   0.22605E+00    0.5124  -0.41512E+00
 473.15     0.4728      0.4744  -0.34232E+00    0.4778  -0.10446E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.16312E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.39066E+00
---------------------------------------------------------------
ANALYSIS OF DATA FOR  CYCLOHEXANE (0.4) + HEXANE (0.6)

---------------------------------------------------------------

0.0000     0.4057     0.5943


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.6972      0.6980  -0.12102E+00    0.7007  -0.50177E+00
 303.15     0.6929      0.6935  -0.80770E-01    0.6961  -0.45839E+00
 313.15     0.6835      0.6842  -0.96225E-01    0.6867  -0.46994E+00
 333.15     0.6649      0.6650  -0.11330E-01    0.6675  -0.38661E+00
 353.15     0.6449      0.6449  -0.12015E-02    0.6474  -0.39096E+00
 373.15     0.6241      0.6238   0.51093E-01    0.6264  -0.36584E+00
 393.15     0.6022      0.6014   0.13983E+00    0.6041  -0.31742E+00
 413.15     0.5785      0.5773   0.20684E+00    0.5803  -0.30174E+00
 433.15     0.5523      0.5511   0.21475E+00    0.5543  -0.35354E+00
 453.15     0.5223      0.5220   0.62714E-01    0.5253  -0.56689E+00
```

```
 473.15     0.4855      0.4884   -0.58946E+00    0.4917  -0.12666E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.13127E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.44831E+00
------------------------------------------------------------
ANALYSIS OF DATA FOR  CYCLOHEXANE (0.5) + HEXANE (0.5)

------------------------------------------------------------

0.0000      0.5059      0.4941


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.7087      0.7092   -0.77324E-01    0.7121  -0.48061E+00
 303.15     0.7044      0.7047   -0.39712E-01    0.7075  -0.43938E+00
 313.15     0.6950      0.6954   -0.59509E-01    0.6982  -0.45347E+00
 333.15     0.6764      0.6763    0.12021E-01    0.6790  -0.37952E+00
 353.15     0.6565      0.6564    0.20678E-01    0.6590  -0.38052E+00
 373.15     0.6357      0.6354    0.49306E-01    0.6381  -0.37379E+00
 393.15     0.6138      0.6132    0.10375E+00    0.6160  -0.35302E+00
 413.15     0.5903      0.5894    0.15520E+00    0.5923  -0.34544E+00
 433.15     0.5644      0.5636    0.14360E+00    0.5667  -0.40809E+00
 453.15     0.5348      0.5350   -0.45752E-01    0.5383  -0.64953E+00
 473.15     0.4989      0.5025   -0.70703E+00    0.5057  -0.13495E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.11782E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.46774E+00
------------------------------------------------------------
ANALYSIS OF DATA FOR  CYCLOHEXANE (0.6) + HEXANE (0.4)

------------------------------------------------------------

0.0000      0.6057      0.3943


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.7206      0.7209   -0.42241E-01    0.7238  -0.44364E+00
 303.15     0.7163      0.7164   -0.70642E-02    0.7192  -0.40408E+00
 313.15     0.7069      0.7071   -0.30623E-01    0.7099  -0.42036E+00
 333.15     0.6882      0.6881    0.14648E-01    0.6908  -0.36935E+00
 353.15     0.6684      0.6682    0.22700E-01    0.6709  -0.36698E+00
 373.15     0.6476      0.6474    0.29830E-01    0.6501  -0.37708E+00
 393.15     0.6258      0.6254    0.68996E-01    0.6281  -0.36595E+00
 413.15     0.6027      0.6018    0.14225E+00    0.6047  -0.33056E+00
 433.15     0.5770      0.5764    0.10211E+00    0.5794  -0.41487E+00
 453.15     0.5479      0.5484   -0.93231E-01    0.5515  -0.65526E+00
 473.15     0.5131      0.5167   -0.69900E+00    0.5198  -0.12944E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.10439E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.45354E+00
```

```
-------------------------------------------------------------
ANALYSIS OF DATA FOR  CYCLOHEXANE (0.7) + HEXANE (0.3)

-------------------------------------------------------------

0.0000     0.7049     0.2951


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T   ERROR(%)

 298.15     0.7330     0.7330  -0.18702E-02   0.7358 -0.37595E+00
 303.15     0.7286     0.7285   0.17551E-01   0.7312 -0.35134E+00
 313.15     0.7192     0.7193  -0.91736E-02   0.7219 -0.36960E+00
 333.15     0.7005     0.7003   0.26027E-01   0.7028 -0.32590E+00
 353.15     0.6806     0.6806   0.60432E-02   0.6830 -0.34797E+00
 373.15     0.6598     0.6598  -0.63955E-02   0.6623 -0.37359E+00
 393.15     0.6381     0.6380   0.19900E-01   0.6405 -0.37075E+00
 413.15     0.6152     0.6147   0.84285E-01   0.6173 -0.33910E+00
 433.15     0.5900     0.5896   0.70990E-01   0.5923 -0.39144E+00
 453.15     0.5616     0.5621  -0.84856E-01   0.5649 -0.58755E+00
 473.15     0.5280     0.5312  -0.59761E+00   0.5340 -0.11309E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.77059E-01

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.41367E+00
-------------------------------------------------------------
ANALYSIS OF DATA FOR  CYCLOHEXANE (0.8) + HEXANE (0.2)

-------------------------------------------------------------

0.0000     0.8038     0.1962


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T   ERROR(%)

 298.15     0.7460     0.7456   0.48202E-01   0.7480 -0.27152E+00
 303.15     0.7415     0.7411   0.52695E-01   0.7434 -0.26137E+00
 313.15     0.7321     0.7319   0.23706E-01   0.7342 -0.28068E+00
 333.15     0.7132     0.7130   0.22595E-01   0.7151 -0.27088E+00
 353.15     0.6933     0.6934  -0.89833E-02   0.6954 -0.30181E+00
 373.15     0.6724     0.6728  -0.53123E-01   0.6748 -0.35579E+00
 393.15     0.6508     0.6510  -0.37152E-01   0.6531 -0.35964E+00
 413.15     0.6282     0.6280   0.37435E-01   0.6302 -0.31374E+00
 433.15     0.6034     0.6032   0.38302E-01   0.6055 -0.34795E+00
 453.15     0.5758     0.5761  -0.55040E-01   0.5786 -0.47826E+00
 473.15     0.5437     0.5459  -0.40853E+00   0.5484 -0.86171E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.65480E-01

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.34194E+00
-------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.333) + CYCLOHEXANE (0.333) + HEXANE (0.333)

-------------------------------------------------------------
```

```
0.3528      0.3274      0.3198

TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)     H-B-T    ERROR(%)

 298.15     0.7552      0.7559  -0.90911E-01  0.7600 -0.62621E+00
 303.15     0.7501      0.7512  -0.14549E+00  0.7552 -0.67722E+00
 313.15     0.7402      0.7417  -0.19932E+00  0.7456 -0.72614E+00
 333.15     0.7198      0.7221  -0.31796E+00  0.7259 -0.84336E+00
 353.15     0.6988      0.7017  -0.41056E+00  0.7055 -0.94626E+00
 373.15     0.6770      0.6803  -0.48220E+00  0.6841 -0.10398E+01
 393.15     0.6542      0.6577  -0.53138E+00  0.6616 -0.11223E+01
 413.15     0.6303      0.6336  -0.52856E+00  0.6377 -0.11630E+01
 433.15     0.6049      0.6077  -0.46828E+00  0.6120 -0.11547E+01
 453.15     0.5769      0.5794  -0.42770E+00  0.5837 -0.11697E+01
 473.15     0.5453      0.5475  -0.40737E+00  0.5519 -0.12002E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.33414E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.88907E+00
-------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.500) + CYCLOHEXANE (0.250) + HEXANE (0.250)

-------------------------------------------------------------

0.5216      0.2420      0.2364

TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)     H-B-T    ERROR(%)

 298.15     0.7774      0.7816  -0.53937E+00  0.7856 -0.10377E+01
 303.15     0.7721      0.7769  -0.61181E+00  0.7807 -0.11069E+01
 313.15     0.7622      0.7672  -0.65204E+00  0.7710 -0.11430E+01
 333.15     0.7418      0.7474  -0.74357E+00  0.7511 -0.12345E+01
 353.15     0.7207      0.7267  -0.82421E+00  0.7304 -0.13265E+01
 373.15     0.6989      0.7051  -0.87326E+00  0.7088 -0.13982E+01
 393.15     0.6760      0.6823  -0.91858E+00  0.6861 -0.14775E+01
 413.15     0.6520      0.6581  -0.92135E+00  0.6621 -0.15245E+01
 433.15     0.6268      0.6321  -0.83488E+00  0.6363 -0.14911E+01
 453.15     0.5989      0.6038  -0.80401E+00  0.6081 -0.15182E+01
 473.15     0.5676      0.5722  -0.80282E+00  0.5767 -0.15729E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.71049E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.12359E+01
-------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.650) + CYCLOHEXANE (0.175) + HEXANE (0.175)

-------------------------------------------------------------

0.6694      0.1673      0.1633


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)     H-B-T    ERROR(%)
```

```
 298.15     0.8020      0.8063  -0.53696E+00   0.8096 -0.94265E+00
 303.15     0.7968      0.8015  -0.58657E+00   0.8048 -0.98947E+00
 313.15     0.7867      0.7917  -0.63440E+00   0.7949 -0.10338E+01
 333.15     0.7656      0.7716  -0.78104E+00   0.7748 -0.11815E+01
 353.15     0.7447      0.7507  -0.80194E+00   0.7539 -0.12148E+01
 373.15     0.7229      0.7289  -0.81831E+00   0.7321 -0.12553E+01
 393.15     0.6996      0.7059  -0.88939E+00   0.7093 -0.13609E+01
 413.15     0.6754      0.6815  -0.89747E+00   0.6851 -0.14145E+01
 433.15     0.6502      0.6554  -0.79899E+00   0.6592 -0.13707E+01
 453.15     0.6226      0.6271  -0.72219E+00   0.6312 -0.13548E+01
 473.15     0.5918      0.5958  -0.66849E+00   0.6000 -0.13627E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.67798E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.11234E+01
--------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.800) + CYCLOHEXANE (0.200) + HEXANE (0.200)

--------------------------------------------------------------

0.8135      0.0944      0.0921


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0 8308      0.8326  -0.22174E+00   0.8348 -0.47381E+00
 303.15     0.8256      0.8278  -0.25983E+00   0.8298 -0.50932E+00
 313.15     0.8154      0.8178  -0.29796E+00   0.8199 -0.54485E+00
 333.15     0.7937      0.7975  -0.47358E+00   0.7995 -0.72285E+00
 353.15     0.7725      0.7763  -0.49161E+00   0.7784 -0.75465E+00
 373.15     0.7505      0.7542  -0.49366E+00   0.7564 -0.78198E+00
 393.15     0.7268      0.7310  -0.57802E+00   0.7334 -0.90201E+00
 413.15     0.7024      0.7065  -0.57912E+00   0.7091 -0.94994E+00
 433.15     0.6772      0.6803  -0.45569E+00   0.6832 -0.88317E+00
 453.15     0.6495      0.6520  -0.38076E+00   0.6552 -0.87215E+00
 473.15     0.6188      0.6208  -0.32369E+00   0.6243 -0.88199E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.37964E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.68973E+00
--------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.250) + CYCLOHEXANE (0.500) + HEXANE (0.250)

--------------------------------------------------------------

0.2658      0.4933      0.2409


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.7594      0.7602  -0.99347E-01   0.7633 -0.51667E+00
 303.15     0.7549      0.7555  -0.80913E-01   0.7586 -0.49340E+00
 313.15     0.7454      0.7461  -0.93613E-01   0.7491 -0.49812E+00
 333.15     0.7266      0.7267  -0.19151E-01   0.7296 -0.41625E+00
 353.15     0.7065      0.7066  -0.99205E-02   0.7094 -0.40964E+00
```

```
 373.15     0.6857     0.6854   0.36565E-01   0.6883 -0.37646E+00
 393.15     0.6639     0.6632   0.10752E+00   0.6661 -0.32870E+00
 413.15     0.6407     0.6395   0.18348E+00   0.6425 -0.28416E+00
 433.15     0.6153     0.6141   0.19549E+00   0.6172 -0.30886E+00
 453.15     0.5866     0.5863   0.42817E-01   0.5895 -0.49801E+00
 473.15     0.5525     0.5554  -0.51582E+00   0.5585 -0.10812E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.11539E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.43428E+00
------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.175) + CYCLOHEXANE (0.650) + HEXANE (0.175)

------------------------------------------------------------

0.1868      0.6439     0.1693


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.7636     0.7639  -0.42414E-01   0.7664 -0.36272E+00
 303.15     0.7593     0.7593  -0.28102E-02   0.7617 -0.31751E+00
 313.15     0.7498     0.7500  -0.25972E-01   0.7523 -0.33089E+00
 333.15     0.7309     0.7308   0.10986E-01   0.7330 -0.28207E+00
 353.15     0.7119     0.7109   0.14689E+00   0.7129 -0.14460E+00
 373.15     0.6902     0.6900   0.33821E-01   0.6920 -0.26494E+00
 393.15     0.6684     0.6680   0.64024E-01   0.6701 -0.25164E+00
 413.15     0.6455     0.6446   0.13517E+00   0.6468 -0.20491E+00
 433.15     0.6202     0.6196   0.98538E-01   0.6219 -0.27046E+00
 453.15     0.5918     0.5923  -0.90694E-01   0.5947 -0.48795E+00
 473.15     0.5584     0.5620  -0.64762E+00   0.5644 -0.10614E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.10824E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.33159E+00
------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.100) + CYCLOHEXANE (0.800) + HEXANE (0.100)

------------------------------------------------------------

0.1072      0.7957     0.0971


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.7680     0.7676   0.47427E-01   0.7694 -0.18454E+00
 303.15     0.7635     0.7631   0.56045E-01   0.7648 -0.16949E+00
 313.15     0.7541     0.7538   0.36396E-01   0.7554 -0.17841E+00
 333.15     0.7349     0.7348   0.10740E-01   0.7363 -0.18995E+00
 353.15     0.7150     0.7150  -0.66519E-02   0.7165 -0.20263E+00
 373.15     0.6939     0.6944  -0.67856E-01   0.6958 -0.26887E+00
 393.15     0.6724     0.6726  -0.33142E-01   0.6741 -0.24801E+00
 413.15     0.6498     0.6496   0.35722E-01   0.6511 -0.20099E+00
 433.15     0.6251     0.6249   0.34863E-01   0.6265 -0.22833E+00
 453.15     0.5978     0.5981  -0.46890E-01   0.5998 -0.33719E+00
```

```
 473.15     0.5662      0.5684  -0.38620E+00   0.5702 -0.69512E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.63494E-01

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.24196E+00
------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.250) + CYCLOHEXANE (0.250) + HEXANE (0.500)

------------------------------------------------------------

0.2673      0.2481      0.4846


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.7273      0.7280  -0.91720E-01   0.7323 -0.68614E+00
 303.15     0.7226      0.7233  -0.94860E-01   0.7276 -0.68708E+00
 313.15     0.7129      0.7138  -0.12478E+00   0.7180 -0.71529E+00
 333.15     0.6930      0.6942  -0.17662E+00   0.6984 -0.77320E+00
 353.15     0.6731      0.6738  -0.10218E+00   0.6780 -0.71841E+00
 373.15     0.6521      0.6523  -0.32137E-01   0.6566 -0.68114E+00
 393.15     0.6294      0.6296  -0.26585E-01   0.6340 -0.72159E+00
 413.15     0.6051      0.6052  -0.24581E-01   0.6098 -0.77774E+00
 433.15     0.5790      0.5789   0.19100E-01   0.5837 -0.80351E+00
 453.15     0.5489      0.5498  -0.15588E+00   0.5547 -0.10534E+01
 473.15     0.5122      0.5166  -0.84431E+00   0.5217 -0.18116E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.14106E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.78576E+00
------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.175) + CYCLOHEXANE (0.175) + HEXANE (0.650)

------------------------------------------------------------

0.1889      0.1753      0.6358


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)    H-B-T    ERROR(%)

 298.15     0.7032      0.7048  -0.23342E+00   0.7087 -0.77460E+00
 303.15     0.6988      0.7002  -0.19575E+00   0.7040 -0.73640E+00
 313.15     0.6892      0.6907  -0.21511E+00   0.6945 -0.75636E+00
 333.15     0.6696      0.6711  -0.22667E+00   0.6749 -0.77975E+00
 353.15     0.6496      0.6506  -0.16073E+00   0.6544 -0.74020E+00
 373.15     0.6289      0.6291  -0.28254E-01   0.6330 -0.64951E+00
 393.15     0.6065      0.6062   0.54416E-01   0.6103 -0.62339E+00
 413.15     0.5822      0.5816   0.10804E+00   0.5860 -0.64052E+00
 433.15     0.5557      0.5547   0.17150E+00   0.5594 -0.66151E+00
 453.15     0.5249      0.5248   0.13549E-01   0.5297 -0.91242E+00
 473.15     0.4869      0.4902  -0.67251E+00   0.4953 -0.16903E+01

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.17333E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.74708E+00
```

```
------------------------------------------------------------
ANALYSIS OF DATA FOR  BENZENE (0.100) + CYCLOHEXANE (0.100) + HEXANE (0.800)

------------------------------------------------------------

0.1089     0.1011     0.7900


TEMP.  DENSITY EXPT.  RACKETT   ERROR(%)     H-B-T    ERROR(%)

 298.15     0.6815     0.6834  -0.27770E+00   0.6861  -0.67262E+00
 303.15     0.6769     0.6787  -0.26920E+00   0.6814  -0.66444E+00
 313.15     0.6674     0.6692  -0.27602E+00   0.6719  -0.67388E+00
 333.15     0.6483     0.6497  -0.21061E+00   0.6524  -0.62569E+00
 353.15     0.6283     0.6291  -0.13345E+00   0.6320  -0.58134E+00
 373.15     0.6074     0.6075  -0.10617E-01   0.6105  -0.50771E+00
 393.15     0.5855     0.5844   0.19348E+00   0.5877  -0.36995E+00
 413.15     0.5613     0.5595   0.32936E+00   0.5631  -0.31685E+00
 433.15     0.5348     0.5321   0.50448E+00   0.5361  -0.24069E+00
 453.15     0.5036     0.5013   0.45891E+00   0.5056  -0.39719E+00
 473.15     0.4651     0.4650   0.30061E-01   0.4695  -0.94187E+00

PERCENT AVER. ABSOLUTE DEVIATION RACKETT = 0.22449E+00

PERCENT AVER. ABSOLUTE DEVIATION HBT = 0.49935E+00

OVERALL PER. AVERAGE ABS. DEVIATION RACKETT= 0.28567E+00

OVERALL PER. AVERAGE ABS.DEVIATION HBT = 0.60753E+00
```