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## P-x Measurements For 2-Ethoxyethanol and Four Chlorinated Hydrocarbons at 303.15 K

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P-x Measurements For 2-Ethoxyethanol and Four  
Chlorinated Hydrocarbons at 303.15 K

by

Salil Milan Pathare

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Master of Science in Chemical Engineering  
Department of Chemical Engineering  
College of Engineering  
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## TABLE OF CONTENTS

LIST OF TABLES	iii
LIST OF FIGURES	v
LIST OF SYMBOLS AND ABBREVIATIONS	vii
ABSTRACT	x
CHAPTER 1 INTRODUCTION	1
CHAPTER 2 EXPERIMENTAL METHOD	5
2.1 Theory of Approach	5
2.2 Apparatus	7
2.3 Procedure	11
2.3.1 Preparation of Chemical Sample	11
2.3.2 Degassing of Chemical	12
2.3.3 Evacuation of the Apparatus	13
2.3.4 Charging of the Equilibrium Cell	14
2.4 Materials	15
CHAPTER 3 DATA REDUCTION METHOD	16
3.1 Barker's Method	16
3.2 Equation Development	16
3.3 Modified Margules Model	22
CHAPTER 4 EXPERIMENTAL RESULTS	24

4.1 Calculation of Error Bars	39
CHAPTER 5 APPLICATION OF ASSOCIATION MODEL	47
5.1 Theory of Model	47
5.2 Results	55
CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS	63
6.1 Conclusions	63
6.2 Recommendations	63
REFERENCES	65
APPENDICES	68
Appendix I: Computer Programs for Binary Regression and Prediction of Data	69

## LIST OF TABLES

Table 1: Chemicals used and its Purity	15
Table 2: Comparison of Pure Component Vapor Pressures (kPa) Measured in the Present Study to those of Other Investigators at 303.15 K	26
Table 3: Total Pressure P as a Function of Liquid Phase Mole Fraction for Hexane (1) and 2-ethoxyethanol (2) System at 303.15 K	27
Table 4: Total Pressure P as a Function of Liquid Phase Mole Fraction for Carbon tetrachloride (1) and 2-ethoxyethanol (2) System at 303.15 K	28
Table 5: Total Pressure P as a Function of Liquid Phase Mole Fraction for Chloroform (1) and 2-ethoxyethanol (2) System at 303.15 K	29
Table 6: Total Pressure P as a Function of Liquid Phase Mole Fraction for 1, 2 Dichloroethane (1) and 2-ethoxyethanol (2) System at 303.15 K	30
Table 7: Total Pressure P as a Function of Liquid Phase Mole Fraction for Dichloromethane (1) and 2-ethoxyethanol (2) System at 303.15 K	31
Table 8: Regressed Constants for the Modified Margules Model	32
Table 9: Second Molar Virial Coefficients, $B_{ii}$ and $B_{ij}$ . And Saturated Liquid Volumes, $V_L$	33
Table 10: Values of $\frac{dP}{dT}$ for all the Components	40
Table 11: Regressed Constants for Different Models	55

Table 12: Average Deviation in Pressure (kPa) for each Component

56

## LIST OF FIGURES

Figure 1: Schematic of Experimental Apparatus	7
Figure 2: Schematic of Equilibrium Cell	10
Figure 3: Flowsheet for Barker's Method	21
Figure 4: Pressure P vs Liquid Mole Fraction $x_1$ and Vapor Mole Fraction $y_1$ for Hexane (1) and 2-ethoxyethanol (2) System at 303.15 K	34
Figure 5: Pressure P vs Liquid Mole Fraction $x_1$ and Vapor Mole Fraction $y_1$ for Carbon Tetrachloride (1) and 2-ethoxyethanol (2) System at 303.15 K	35
Figure 6: Pressure P vs Liquid Mole Fraction $x_1$ and Vapor Mole Fraction $y_1$ for Chloroform (1) and 2-ethoxyethanol (2) System at 303.15 K	36
Figure 7: Pressure P vs Liquid Mole Fraction $x_1$ and Vapor Mole Fraction $y_1$ for 1,2-Dichloroethane (1) and 2-ethoxyethanol (2) System at 303.15 K	37
Figure 8: Pressure P vs Liquid Mole Fraction $x_1$ and Vapor Mole Fraction $y_1$ for Dichloromethane (1) and 2-ethoxyethanol (2) System at 303.15 K	38
Figure 9: Difference of Experimental Values of the Present Study and Carmona's Values for Hexane (1) and 2-ethoxyethanol (2) System at 303.15 K	42
Figure 10: Comparison of Models for Carbon Tetrachloride (1) and 2-ethoxyethanol (2) at 303.15 K	43
Figure 11: Comparison of Models for Chloroform (1) and 2-ethoxyethanol (2) at 303.15 K	44



Figure 12: Comparison of Models for 1, 2 dichloroethane (1) and 2-ethoxyethanol (2) at 303.15 K	45
Figure 13: Comparison of Models for Dichloromethane (1) and 2-ethoxyethanol (2) at 303.15 K	46
Figure 14: Comparison of Regular Solution and Kretschmer-Wiebe models for the Binary System of Hexane (1) and 2-ethoxyethanol (2)	57
Figure 15: Comparison of Regular Solution and Kretschmer-Wiebe models for the Binary System of Carbon Tetrachloride (1) + 2-ethoxyethanol (2)	58
Figure 16: Comparison of Regular Solution and Kretschmer-Wiebe Models for the Binary System of Chloroform(1) and 2-ethoxyethanol (2)	59
Figure 17: Comparison of Regular Solution and Kretschmer-Wiebe Models for the Binary System of 1,2 dichloroethane (1) + 2-ethoxyethanol (2)	60
Figure 18: Comparison of Regular Solution and Kretschmer-Wiebe Models for the Binary System of Dichloromethane (1) and 2-ethoxyethanol (2)	61

## LIST OF SYMBOLS AND ABBREVIATIONS

- $A_{12}$  Parameter in the Modified Margules equation
- $A_{21}$  Parameter in the Modified Margules equation
- $B$  Second virial coefficient of a mixture,  $\text{cm}^3/\text{mol}$
- $B_{ii}$  Second virial coefficient of pure species  $i$ ,  $\text{cm}^3/\text{mol}$
- $B_{ij}$  Second virial cross coefficient,  $\text{cm}^3/\text{mol}$
- $C_m$  Dimensionless concentration  $\phi_m/r_m$  of stoichiometric species  $m$
- $C_{m1}$  Dimensionless concentration of monomeric species  $m$  in mixture
- $C_{m1}^0$  Dimensionless concentration of monomeric species  $m$  in pure stoichiometric species
- $C_{11}$  Concentration of unsolvated chlorinated hydrocarbon molecules
- $C_{2i}$  Concentration of the 2-ethoxyethanol monomers
- $C_{2i1}$  Concentration of 2-ethoxyethanol monomers that are solvated with a single hydrocarbon molecule
- $f$  Fugacity of pure liquid at temperature and pressure of mixture
- $f^L$  Fugacity of component in the liquid phase
- $f^V$  Fugacity of component in the vapor phase
- $G^E$  Excess Gibbs free energy
- $n_i$  Number of moles of a component
- $P$  Pressure, kPa

$p^{\text{sat}}$  Saturated vapor pressure, kPa  
 $p^{\text{exp}}$  Experimental pressure, kPa  
 $p^{\text{calc}}$  Calculated pressure, kPa  
 $R$  Universal gas constant  
 $r_i$  Measure of molecular size  
 $T$  Temperature, K  
 $V$  Volume,  $\text{cm}^3$   
 $V_i^{\text{L}}$  Saturated liquid volume,  $\text{cm}^3$   
 $x_i$  Liquid phase mole fraction  
 $y_i$  Vapor phase mole fraction  
 $\alpha_{12}$  Parameter in the Modified Margules method  
 $\alpha_{21}$  Parameter in the Modified Margules method  
 $\beta$  Physical interaction parameter in Association model  
 $K_{12}$  Solvation constant for hydrocarbon and 2-ethoxyethanol  
 $K_{21}$  Self-association constant for 2-ethoxyethanol  
 $\gamma_{12}$  Activity coefficient of component  $i$   
 $\delta_{12}$  Quantity as defined in equation 3.11  
 $\bar{\phi}_i$  Fugacity coefficient of  $i$  in mixture at  $T$  and  $P$   
 $\phi_i^{\text{sat}}$  Fugacity coefficient of pure component  $i$  at the temperature of the mixture and its vapor pressure at that  $T$   
 $\eta$  Parameter in the Modified Margules equation  
 $\Psi_m$  Total concentration of all complexes in the mixture

$\Psi_{purem}$  Total concentration of all complexes in the mixture in pure stoichiometric m

$\Phi$  Volume fractions of species i in liquid

## **P-x MEASUREMENTS FOR 2-ETHOXYETHANOL AND FOUR CHLORINATED HYDROCARBONS AT 303.15 K**

Salil Milan Pathare

### **ABSTRACT**

Total pressure measurements at 303.15 K are reported for the binary systems of 2-ethoxyethanol with carbon tetrachloride, chloroform, 1,2-dichloroethane and dichloromethane. Total pressure measurements for the system of hexane and 2-ethoxyethanol were also made to check the validity of the experimental apparatus and procedure. These measurements were taken according to the static method proposed by Van Ness (1975). Data reduction was accomplished using Barker's Method. The modified Margules equation was used as a model for the excess Gibbs free energy ( $G^E$ ) and parameter values were obtained by regression of the experimental data.

The obtained data were used to test the association model developed by Kretschmer and Wiebe (1967). In its original form, the Kretschmer-Wiebe model assumes self-association between molecules of 2-ethoxyethanol. An extended form of the Kretschmer-Wiebe model, in which cross-association of 2-ethoxyethanol with the halogenated hydrocarbon is postulated, was examined as well. The regular solution model, which results from the above theories when all

association is neglected, was also examined. It was found that the Kretschmer-Wiebe model was far superior to the regular solution model. However, the extended form of the Kretschmer-Wiebe model showed less improvement over the original form.

## **CHAPTER 1**

### **INTRODUCTION**

The design of separation processes in industry requires knowledge of the phase equilibrium behavior of different systems. Phase equilibrium thermodynamics is a subject of fundamental importance in many sciences, physical as well as biological, since so many processes are concerned with the interaction between different phases. It carries a special importance in chemical engineering because the manufacturing processes of most of the chemical products consist of phase contacting including extraction, absorption, distillation, leaching and adsorption. A large number of industrial processes involve vapor and liquid phases, although vapor-solid, liquid-solid, solid-solid are sometimes encountered.

Since distillation is the most popular separation method, vapor-liquid equilibrium receives the most attention. In vapor-liquid equilibrium, equilibrium between a liquid and vapor phase is brought about either by mass transfer between the phases or by chemical reaction within a phase or by both. The phase compositions depend on several variables, such as temperature and pressure and also on the chemical nature of the substances in the mixture. The data can be directly measured by experiments, but such measurements are difficult for binary systems and become increasingly difficult for

multicomponent systems. This is where thermodynamics plays an important role in vapor liquid equilibrium problems. It does not generate data but provides a mathematical framework, which allows maximum use of data.

The Distillation method is the oldest method for measuring vapor-liquid equilibrium. The vapors evolved from a distilling flask are condensed and collected in a receiver. Then the condensate returns to the distilling flask through a liquid conduit. This process continues until a steady state is reached, in which the compositions in both vessels do not change with time. Both compositions are measured analytically. In the present study, a static approach known as the total pressure method is used to determine vapor pressures of liquid solutions. Mixtures of known compositions are injected into the equilibrium cell from piston injectors. In this method, the equilibrium pressure  $P$  of a binary vapor-liquid mixture is measured as a function of liquid phase mole fraction  $x$  at constant temperature. The vapor phase mole fractions can also be derived from  $P$ - $x$  data thus giving the total  $P$ - $x$ - $y$  data for the entire system.

Correlation of vapor-liquid equilibrium data is generally accomplished indirectly through thermodynamic functions for the liquid phase. In particular, data reduction is done to yield a correlation for the activity coefficients of the liquid phase. Data reduction includes selecting an activity coefficient model to represent the data. In addition to the total pressure method, Van Ness (1972) developed a flexible model for the excess Gibbs free energy ( $G^E$ ) known as the modified Margules equation. All the binary systems in this study were



adequately fitted by the modified Margules equation proposed by Abbott and Van Ness (1975).

However the modified Margules equation is just a fitting model. It is a requirement of total pressure method that a model be flexible enough to represent the obtained data within experimental error since it is used in the data reduction procedure to correct the overall cell composition to liquid phase composition. After this we can use the data to test different models. These can be less accurate than the previous model but can be used to predict the thermodynamic behavior of ternary or higher order systems. There are many such models which can be used such as the Wilson (1964), NRTL (1968), and UNIQUAC (1975) equations. The model used here is the association model developed by Kretschmer and Wiebe (1954). This model, building on the Flory-Huggins (1944) model, attempted to quantify the interactions of hydrocarbons with alcohols by modeling the alcohols as long chain polymers linked by their hydrogen bonded hydroxyl groups. This theory was extended by Campbell to include any number of alcohols with any number of hydrocarbons. The model contained two parameters per binary system and this was an advantage.

In the present study, vapor-liquid equilibrium data were taken for binary systems of 2-ethoxyethanol and four chlorinated hydrocarbons which were carbon tetrachloride, chloroform, 1,2-dichloroethane and dichloromethane at 303.15 K. Data for the system 2-ethoxyethanol-hexane was experimentally determined first and compared with existing data to validate the procedure and apparatus. The data were in the form of pressure as a function of overall

composition in the equilibrium cell. As part of data reduction procedure, this data is converted to pressure as a function of liquid phase composition. The data reduction method used in this thesis is Barker's method, with the modified Margules equation used as the model. After data reduction was completed, the ability of the Kretschmer Wiebe association model to represent the data was assessed.

## CHAPTER 2

### EXPERIMENTAL METHOD

#### 2.1 Theory of Approach

Vapor-liquid equilibrium data are useful for obtaining the composition dependence of the activity coefficients for the liquid phase. As the activity coefficients for a given system are related to the excess Gibbs free energy,  $G^E$ , it is appropriate to build correlations around this function. Generally, the excess Gibbs free energy depends on temperature, pressure and the composition. However, for liquids, the dependence on pressure is weak and may be neglected. Hence VLE data that are measured at constant temperature are preferred over isobaric data for thermodynamic analysis.

A set of isothermal VLE data consists of measurements of pressures and compositions of the vapor and liquid phases. The fact that such data can be tested for thermodynamic consistency indicates an overdetermination of the equilibrium states. Hence it is not necessary to measure all of these variables. Since the vapor phase is less dense than the liquid phase, its composition is more difficult to determine. Thus, the measurement of vapor phase compositions is not considered and all calculations are based on pressure vs liquid phase compositions. When P-x data are measured, a thermodynamic consistency test cannot be performed as there are no redundant data.

It may seem that the measurement of only some of the data may not yield the same quality of information as a full set of P-x-y data. Van Ness (1973) has shown however that P-x data are more accurate than P-x-y data for the data reduction procedure. The data considered were both real (Van Ness and Abbott, 1975) and simulated (Van Ness, 1978). It was shown that correlations based on the full set of P-x-y data are virtually the same as correlations based only on P-x data. Since the values of vapor mole fractions ( $y$ ) are likely to be less reliable than that of liquid mole fractions ( $x$ ), the use of  $y$  values would introduce distortion in a correlation in which  $x$  is the independent variable. Hence P-x data are preferred to P-x-y data (Pradhan, 1991).

## 2.2 Apparatus

A schematic diagram of the apparatus is shown in Figure 1

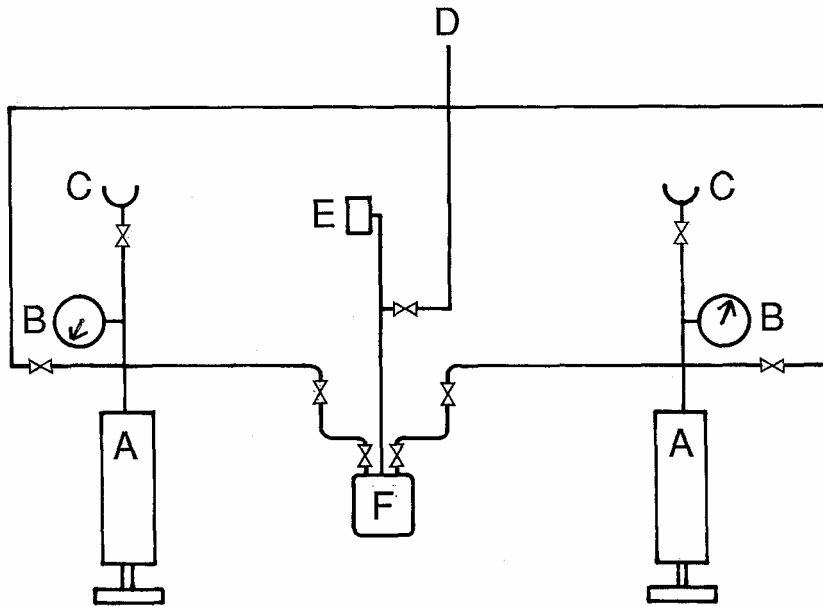


Figure 1: Schematic of Experimental Apparatus

A-piston injector, B-Bourdon gauge, C-fill tube, D-vacuum line  
E-Baratron pressure gauge, F-equilibrium cell

It includes two piston injectors (A) manufactured by Ruska Instrument Corporation (Model 2200) having capacities of approximately  $100 \text{ cm}^3$  each. The gauge can be read to within  $0.001 \text{ cm}^3$  which corresponds to 0.001 turns ( $1 \text{ turn} = 1 \text{ cm}^3$ ). These pumps were easy to use since the actual number of  $\text{cm}^3$  could be read directly from the numbering on the screw pump.

B represents a Bourdon gauge, which is present on both piston injectors screw pumps. After the initial charging of the screw pumps with their individual components, the operator has to ensure that all the material inside the pump is liquid. To achieve this state, the pump is turned until the volume is reduced, such that all the material inside is liquid. The Bourdon gauge will show a sudden increase at this point, indicating that there was no longer any space to compress the gas. Once a pure component in a piston injector is charged to the equilibrium cell, the valve must be opened between the cell and the pump. When this happens, the pump loses its high pressure and equilibrates with the pressure of the cell. Therefore it is important that, after material is added to the equilibrium cell from a piston injector, the pressure in the injector is brought back to a reproducible value to avoid any discrepancies in the determination of cell composition. Hence the pressure is maintained at 20 psig so that the development of the vapor phase is prevented.

C and D represent the sample bulb fill line and the overall vacuum line for the entire system, respectively. The Baraton pressure gauge is represented by E. The pressure inside the equilibrium cell (F) is measured to within 0.01 torr using this pressure gauge (high accuracy type 315-1000 torr). The lines between the pressure gauge

and the equilibrium cell are wrapped with heating tape to prevent condensation. Since the pressure sensor is sensitive to temperature, it is wrapped with a heating tape. The heating tape was further connected to a temperature controller (Omega model 49 proportional controller) and maintained at 343 K.

Details of the equilibrium cell are shown in Figure 2. It is made of Pyrex glass and has a volume of 130 cm<sup>3</sup>. In this figure, symbol A represents the water heater (Fisher model 7300) that is used to keep the system at a constant temperature of 303.15 K. It controls the temperature of the water bath in which the equilibrium cell is kept to within 0.02 K. The submersible stirrer B is used to drive the stirring bar C, which is kept inside the equilibrium cell. Symbol D is the line leading to the Baraton gauge and E is the vacuum line used to evacuate the system at the end of a given run.

Pure components are charged through lines (F) and Teflon valves (G) to the equilibrium cell. In order to eliminate the dead volume beneath the valves, stems are machined out of Teflon stock to the diameter of the dead space and attached to the Teflon valves. These force the liquid into the equilibrium cell instead of keeping it inside the dead volume (Pradhan, 1991).

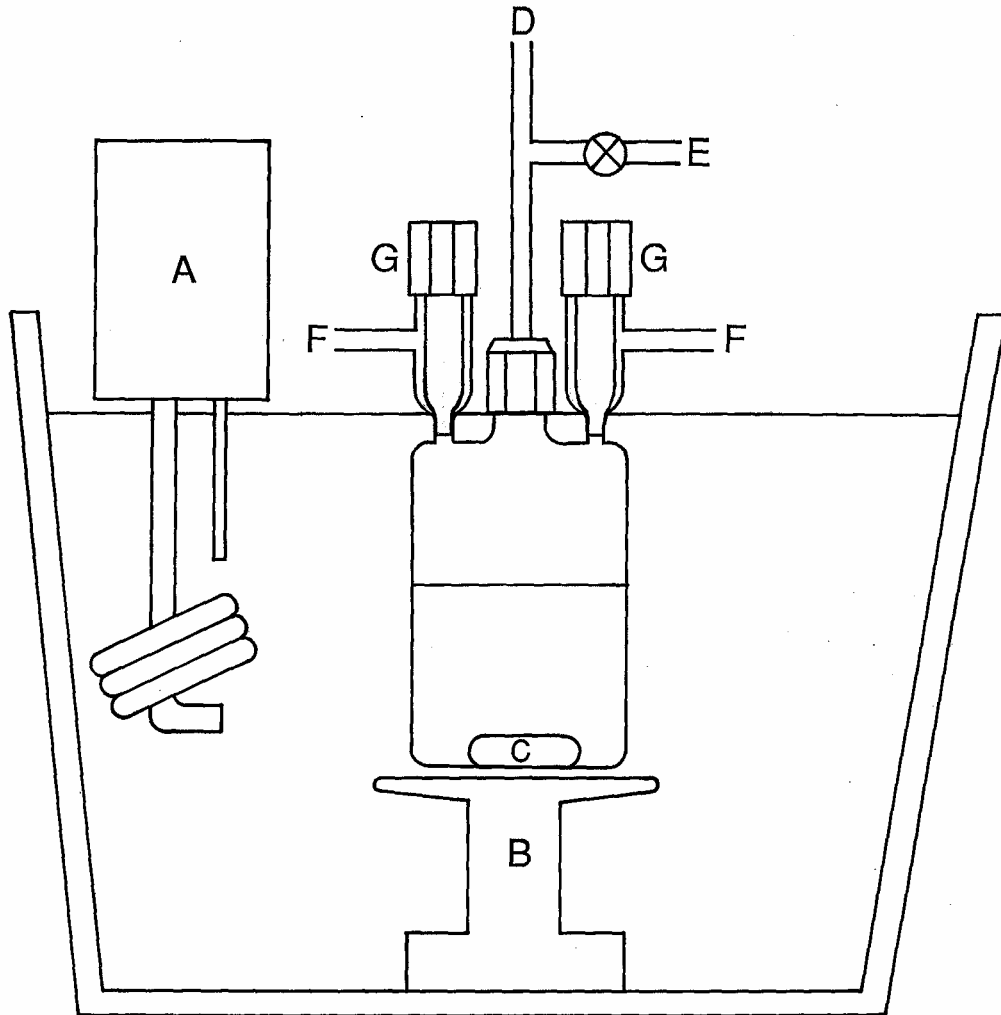


Figure 2: Schematic of Equilibrium Cell

A-heater circulator, B-submersible stirrer, C-stirring bar  
D-line to Baratron gauge, E-vacuum line, F-line to piston injector  
G-Teflon valves



## 2.3 Procedure

### 2.3.1 Preparation of Chemical Sample

Degassed liquid components are charged to the piston injectors from glass bulbs. The following procedure is used to prepare these samples.

First, an empty and dry bulb is evacuated for some time and its stopcock closed to keep the inside of the bulb under vacuum. The bulb is then connected to a special beaker, which has a jointed stem at its base. They were held together with the help of a joint clamp. The desired chemical is then poured into the beaker keeping in mind that the stopcock is still closed. Once the stopcock is opened, the chemical freely enters the bulb. If the chemicals used are toxic in nature, it is preferable to do this procedure under the hood.

This procedure is used for two reasons. Firstly it would take a long time to pour the chemicals into the bulb if it is done directly. Second, with a direct filling, there is a high possibility of spilling of the chemical and exposure of toxic chemicals to skin.

Using this method, the fill time is reduced considerably and there is no spillage since the chemicals are charged to the bulb directly from the beaker.

### 2.3.2 Degassing of Chemical

After filling the bulb, the chemical must be degassed. The bulb is attached to the vacuum pump via a liquid nitrogen trap. The system is first evacuated up to the stopcock, then the stopcock is opened and the air in the vapor phase of the bulb is removed by the vacuum pump. The stopcock is then closed and bulb is agitated for a number of times. Then the stopcock is opened and air is removed.

This procedure is repeated approximately 8 to 10 times. While performing this procedure, some liquid is lost from the glass bulb, but does not reach the vacuum pump as it gets retained in the liquid nitrogen trap. When the stopcock is opened initially, a noise is made by the vacuum pump. This noise is due to removal of air. But after repetitive measures, there is no noise and this indicates the complete removal of air. To confirm that all the air has been removed, the "click" test is performed as proposed by Van Ness and Abbott (1978). When a glass bulb containing a degassed liquid is agitated, a click sound is heard, resulting from a sudden collapse of trapped vapor under the liquid head. This test is a confirmation of thorough degassing.

Further evidence of chemical purity is provided by measuring its pure component vapor pressure. In the latter part of this thesis, it is shown that the vapor pressures measured in the present study are close to those of other investigators, indicating that the chemicals were pure.

### 2.3.3 Evacuation of the Apparatus

To begin, the entire system must first be evacuated of any residual liquids possibly left inside from previous run. In order to accomplish this, all of the valves on the entire apparatus, with the exception of those that are at the top of the piston injectors, are opened. A liquid nitrogen trap is then connected in series between the apparatus and the vacuum pump and the entire system is evacuated.

Next, the degassed samples were then connected to the Pyrex glass line which fed directly into the screw pumps. These lines were evacuated of any residual air in them. Then closing the valves between the screw pumps and rest of the apparatus, the liquid was allowed to pass into the piston injectors. When the screw pumps were turned all the way back to their original positions, the valve between the pumps and the glass bulb was then closed.

The screw pumps were turned so as to reduce the internal volume, as stated earlier, and force the contents to become liquid. At this point, a spike in pressure is seen in the bourdon pressure gauge. The other binary component was charged to the second injector using the same procedure. The valves between the piston-injectors and equilibrium cell were then opened so that the liquids flowed to the entrance of the equilibrium cell. Care was taken that the valves at the entrance to the equilibrium cell were still closed. The Baraton pressure gauge was checked constantly to be sure that there were no leaks.

#### 2.3.4 Charging of the Equilibrium Cell

Each pure component was stored in the piston injector. Approximately  $15 \text{ cm}^3$  of the first component (2-ethoxyethanol in this case) was added to equilibrium cell by opening the valve to the entrance of the equilibrium cell. After equilibration was reached, the vapor pressure was noted. Initially calculations are done to determine liquid densities at room temperature and then numbers of moles, and then volume, needed of the second component were calculated so as to reach a desired mole fraction in the cell.

A measured amount of the second component was then charged to the cell and pressure recorded. This procedure was repeated several times until approximately equal volumes of each component were present in the cell. The exact stopping point was determined for each individual run. When the last mole fraction is attained, the final pressure is noted. After this, the equilibrium cell is opened to atmosphere and the contents were extracted. The cell was then closed and again vacuum drawn on the entire system. This typically took close to an hour.

The second half of the isotherm is determined in the same manner except that the second component is charged first to the equilibrium cell. After its vapor pressure is determined, the composition is varied by adding successive amounts of the first component until the stopping point of the first half is reached. The pressures of this overlap point are compared to check whether they agree to within experimental error. This second run was normally done preferably on the same day or the next to ensure that the system did

not develop any abnormalities. It was seen that the equilibration time varied from chemical to chemical. This may be because some chemicals have very high vapor pressure as compared to others. In the present study, the vapor pressure of dichloromethane is high and comparatively it took more time to equilibrate than the other chemicals.

## 2.4 Materials

The following table gives the purity of all the chemicals used within this project. All chemicals used were obtained from Aldrich Chemical Company except hexane. Hexane was obtained from Fluka chemical.

Table 1: Chemicals used and its Purity

Chemical Name	Lot Number	Catalog Number	Purity*
Hexane	363519/1	52765	99.6%
Carbon Tetrachloride	01511DX	27065-2	99.97%
Chloroform	04359DG	27063-6	99.98%
1,2-Dichloroethane	03160LZ	27057-1	99.92%
Dichloromethane	06246BG	27056-3	99.96%
2-Ethoxyethanol	03049MO	25637-4	99.98%

\* In area percent, obtained by gas chromatography and reported by manufacturer

## CHAPTER 3

### DATA REDUCTION METHOD

#### 3.1 Barker's Method

In the present study, vapor liquid equilibrium data is obtained in the form of  $P$ - $n_1$ - $n_2$  where  $P$  is the pressure and  $n_1$  and  $n_2$  are the number of moles of components 1 and 2, respectively, in the equilibrium cell. The data are reduced using Barker's method, for which the objective function (OF) used is the sum of squares of the differences between the experimental and calculated pressures.

$$\text{OF} = \sum_i (P_i^{\text{exp}} - P_i^{\text{calc}})^2 \quad (3.1)$$

The regression and correction of data from overall cell composition to the liquid phase composition are done simultaneously.

#### 3.2 Equation Development

For a binary system, the fugacities for a liquid phase and vapor phase at an equilibrium temperature are same.

$$\bar{f}_i^L = \bar{f}_i^V \quad (i = 1, 2) \quad (3.2)$$

At low to moderate pressures, liquid phase fugacities are expressed in terms of activity coefficients and vapor phase fugacities in terms of fugacity coefficients.

$$\bar{f}_i^L = \gamma_i x_i f_i \quad (3.3)$$

$$\bar{f}_i^V = \bar{\phi}_i y_i P \quad (3.4)$$

Substituting equations (3.3) and (3.4) in (3.2) gives the following equation

$$\gamma_i x_i f_i = \bar{\phi}_i y_i P \quad (3.5)$$

Where  $\bar{\phi}_i$  = fugacity coefficient of i in vapor at temperature T and pressure P

$\gamma_i$  = activity coefficient of component i

$f_i$  = fugacity of pure liquid i at T and P of mixture

$$f_i = \phi_i^{sat} P_i^{sat} \exp \left[ \frac{V_i^L}{RT} (P - P_i^{sat}) \right] \quad (3.6)$$

Vapor phase nonidealities are accounted for by using the virial equation

$$\frac{PV}{RT} = 1 + \frac{BP}{RT} \quad (3.7)$$

For a binary mixture

$$B = y_1^2 B_{11} + y_2^2 B_{22} + 2y_1 y_2 B_{12} \quad (3.8)$$

where  $B_{11}$  and  $B_{22}$  are second virial coefficients for pure species 1 and 2 respectively and  $B_{12}$  is a second virial cross coefficient.

The following expressions are for the fugacity coefficients

$$\bar{\phi}_1 = \exp\left[\frac{P}{RT}(B_{11} + y_2^2 \delta_{12})\right] \quad (3.9)$$

$$\bar{\phi}_2 = \exp\left[\frac{P}{RT}(B_{22} + y_1^2 \delta_{12})\right] \quad (3.10)$$

where

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (3.11)$$



The quantity  $\phi_i^{sat}$  in equation (3.6) is the fugacity coefficient of pure i at the temperature of the mixture and at its vapor pressure at that temperature.

For the virial equation used, the expression for  $\phi_i^{sat}$  is

$$\phi_i^{sat} = \exp\left[\frac{B_{ii}P_i^{sat}}{RT}\right] \quad (3.12)$$

For a component i, equation (3.5) becomes

$$\gamma_i x_i \phi_i^{sat} P_i^{sat} \exp\left[\frac{V_i^L}{RT}(P - P_i^{sat})\right] = \bar{\phi}_i y_i P \quad (3.13)$$

Defining for convenience a property  $\Phi_i$  by

$$\Phi_i = \frac{\bar{\phi}_i}{\phi_i^{sat} \exp\left[\frac{V_i^L}{RT}(P - P_i^{sat})\right]} \quad (3.14)$$

leads to the equilibrium expressions

$$y_1 P = \frac{\gamma_1 x_1 P_1^{sat}}{\Phi_1} \quad (3.15)$$

$$y_2 P = \frac{\gamma_2 x_2 P_2^{sat}}{\Phi_2} \quad (3.16)$$

Adding equations (3.15) and (3.16) we get

$$P = \frac{\gamma_1 x_1 P_1^{sat}}{\Phi_1} + \frac{\gamma_2 x_2 P_2^{sat}}{\Phi_2} \quad (3.17)$$

For calculating pressures for a general multicomponent system, the equation can be generalized to

$$P = \sum_i \frac{\gamma_i x_i P_i^{sat}}{\Phi_i} \quad (3.18)$$

A very clear presentation of Barker's method is shown in figure 3.

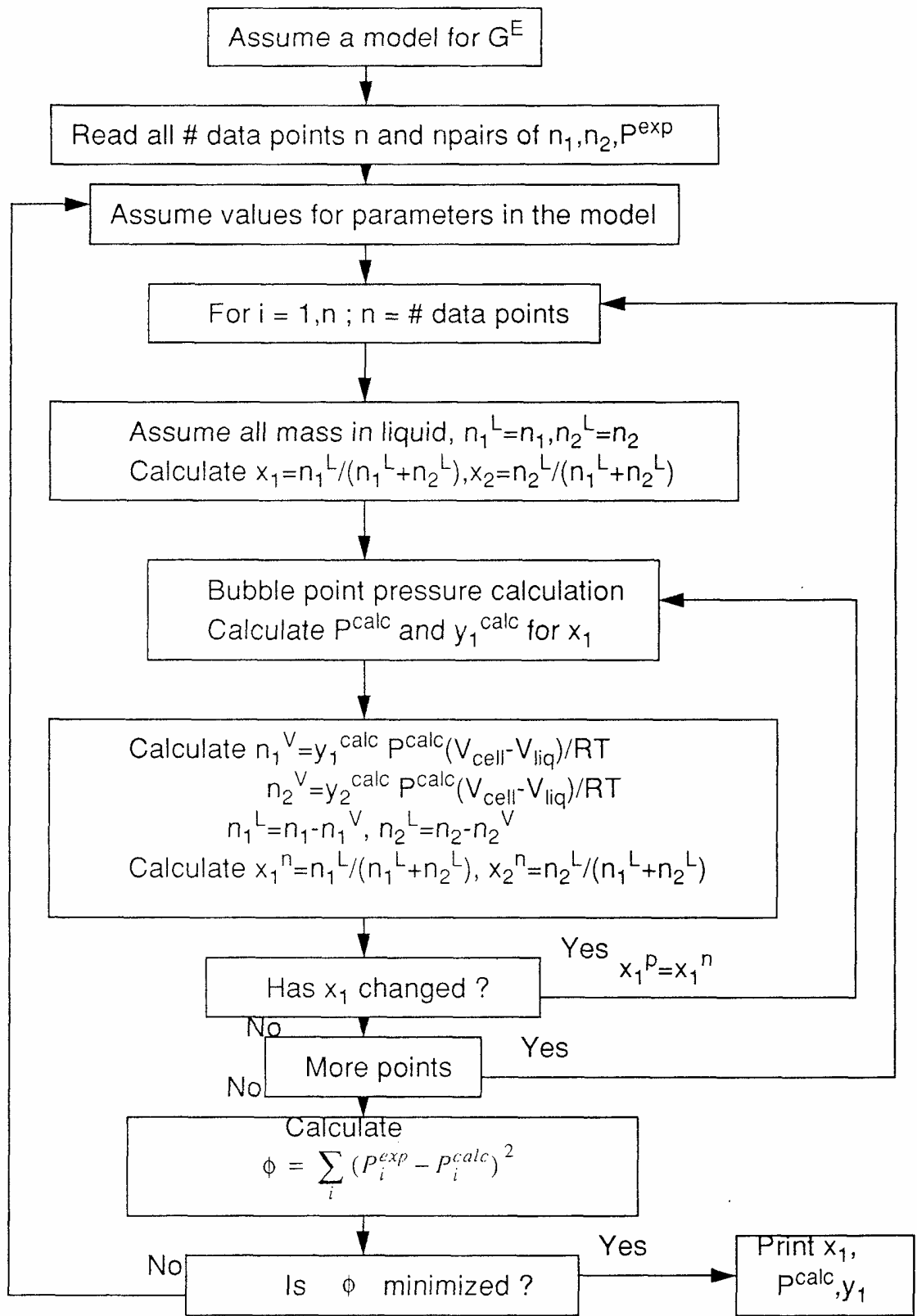


Figure 3: Flowsheet for Barker's Method (Pradhan, 1991)

In this approach, a model for  $G^E$  is assumed and guesses for parameters in the model are made. The experimental pressure values and the mole numbers are fed into the algorithm. All the mass in the equilibrium cell is assumed to be in liquid phase and based on this, the liquid phase compositions are calculated. Then calculated pressures and vapor mole fractions are obtained, followed by a loop that adjusts the liquid phase compositions due to the presence of the vapor phase. Once the phase compositions have stabilized, the objective function is calculated. If the objective function is minimized, the procedure is stopped otherwise new values of the parameters are assumed and the procedure is repeated until the function is minimized. In the present study, a FORTRAN program based on this algorithm was used to determine the compositions and pressure.

A new model of  $G^E$  is assumed, and the procedure is repeated, if the deviations between experimental values and calculated values of pressures are not within experimental error.

### 3.3 Modified Margules Model

In order to make use of Barker's method, it is necessary to incorporate a flexible  $G^E$  model, which can be fitted for a variety of systems within experimental error. The model considered in this study is the Modified Margules model. This model was developed by Van Ness (1975) while attempting to fit many different systems.

The modified Margules model is

$$\frac{G^E}{RTx_1x_2} = A_{21}x_1 + A_{12}x_2 - \frac{\alpha_{12}\alpha_{21}x_1x_2}{[\alpha_{12}x_1 + \alpha_{21}x_2 + \eta x_1x_2]} \quad (3.19)$$

The corresponding activity coefficients for a binary system are

$$\ln(\gamma_1) = x_2^2 \left[ A_{12} + 2(A_{21} - A_{12})x_1 - \frac{2\alpha_{12}\alpha_{21}x_1x_2}{\alpha_{12}x_1 + \alpha_{21}x_2 + \eta x_1x_2} + \frac{\alpha_{12}\alpha_{21}(\alpha_{12} + \eta x_2^2)x_1^2}{(\alpha_{12}x_1 + \alpha_{21}x_2 + \eta x_1x_2)^2} \right] \quad (3.20)$$

$$\ln(\gamma_2) = x_1^2 \left[ A_{21} + 2(A_{12} - A_{21})x_2 - \frac{2\alpha_{12}\alpha_{21}x_1x_2}{\alpha_{12}x_1 + \alpha_{21}x_2 + \eta x_1x_2} + \frac{\alpha_{12}\alpha_{21}(\alpha_{21} + \eta x_1^2)x_2^2}{(\alpha_{12}x_1 + \alpha_{21}x_2 + \eta x_1x_2)^2} \right] \quad (3.21)$$

The fifth parameter  $\eta$  is included only for the sake of completion. In reality, it is used only for systems which display high non-idealities that verge on phase splitting. In the present study,  $\eta$  is considered zero.

## CHAPTER 4

### EXPERIMENTAL RESULTS

Purity of the chemicals used in this study is verified by comparing the measured vapor pressures to previously measured values. Comparison of pure component vapor pressures measured in the present study to those of other experimenters is shown in Table 2. It is clearly shown from the table that the value for carbon tetrachloride is slightly less than the two values reported. On the other hand, the value for chloroform is slightly higher than the two values reported. The discrepancies are within the experimental error of the present study.

Values of second virial coefficients and saturated liquid volumes used are given in Table 9. Second virial coefficients were calculated using the Hayden-O'Connell (1975) correlation. Required constants for the chloroalkanes were obtained from Fredenslund et al (1977) and those for 2-ethoxyethanol were obtained as described by Carmona et al (2000). Solvation parameters for interactions between 2-ethoxyethanol and the chloroalkanes were obtained from Prausnitz et al (1980) and are 0, 0.1, 0 and 0 for carbon tetrachloride, chloroform, 1,2 dichloroethane and dichloromethane, respectively.

Saturated liquid volumes for 2-ethoxyethanol were obtained from smoothing values from Riddick et al (1986) and Venkatesulu et al (1997) while those for carbon tetrachloride, and chloroform were taken from the DIPPR database. Saturated liquid volumes for dichloromethane and 1,2 dichloroethane were taken from Riddick et al (1986) .

Experimental data is obtained in the form of P-n<sub>1</sub>-n<sub>2</sub> for five binary systems. Tables 3 to 7 show values of experimental and calculated pressures and liquid mole fraction. Regressed parameter values are shown in Table 8. Figures 4 to 8 depicts the plot of Pressure values vs. liquid mole fraction and vapor mole fraction for each binary system. These plots indicate how well the Margules model fits the P-x data.

The validity of the Margules model was examined by taking into consideration the experimental uncertainties. In the present study, these uncertainties were estimated to be 0.02 K in bath temperature, 0.001 in mole fraction and 0.1% of the pressure reading.

Table 2: Comparison of Pure Component Vapor Pressures (kPa)  
 Measured in the Present Study to those of Other  
 Investigators at 303.15 K.

Substance	Present work	DIPPR	Carmona (2000)	Riddick (1986)	Riddick& Antosik (1999)
2-ethoxyethanol	0.968		1.015		0.971
	0.975				
	0.984				
	0.981				
	0.973				
	0.976(avg)				
Hexane	24.850	25.076	24.938		
Carbon tetrachloride	18.826	18.898		18.903	
Chloroform	32.408	32.315		32.309	
Dichloromethane	70.486	71.003		70.909	
1,2 Dichloroethane	13.710			13.349	



Table 3: Total Pressure P as a Function of Liquid Phase Mole Fraction for Hexane (1) + 2-ethoxyethanol (2) System at 303.15 K

$x_1$	Experimental P (kPa)	Calculated P (kPa)	Calculated y
0.0000	0.972		
0.0293	6.097	6.159	0.846
0.0575	9.920	9.914	0.906
0.0980	13.809	13.801	0.934
0.1470	16.946	16.919	0.948
0.1973	19.001	18.989	0.955
0.2474	20.338	20.346	0.959
0.2976	21.248	21.264	0.961
0.3481	21.899	21.905	0.962
0.3981	22.354	22.359	0.964
0.4486	22.713	22.699	0.965
0.4476	22.684	22.694	0.965
0.4975	22.945	22.956	0.966
0.5474	23.177	23.169	0.966
0.5973	23.363	23.354	0.966
0.6473	23.523	23.523	0.968
0.6974	23.690	23.687	0.968
0.7475	23.867	23.853	0.969
0.7978	24.011	24.023	0.970
0.8482	24.205	24.203	0.972
0.8985	24.403	24.397	0.974
0.9386	24.578	24.577	0.977
0.9696	24.749	24.740	0.982
1.0000	24.846		

Table 4: Total Pressure P as a Function of Liquid Phase Mole Fraction for Carbon Tetrachloride (1) + 2-ethoxyethanol (2) System at 303.15 K

$x_1$	Experimental P (kPa)	Calculated P (kPa)	Calculated y
0.0000	0.980	-	-
0.0846	4.322	4.316	0.791
0.1313	5.979	5.971	0.856
0.1896	7.848	7.843	0.896
0.2499	9.552	9.551	0.920
0.3007	10.809	10.821	0.933
0.3501	11.897	11.913	0.942
0.3998	12.875	12.883	0.949
0.4501	13.742	13.744	0.955
0.4996	14.494	14.484	0.959
0.4989	14.488	14.475	0.959
0.5488	15.144	15.132	0.963
0.5987	15.719	15.707	0.966
0.6487	16.218	16.216	0.969
0.6986	16.663	16.666	0.972
0.7487	17.059	17.069	0.974
0.7886	17.351	17.363	0.976
0.8190	17.557	17.570	0.978
0.8762	17.934	17.934	0.981
0.9391	18.355	18.327	0.986
0.9724	18.583	18.569	0.991
1.0000	18.809	-	-

Table 5: Total Pressure P as a Function of Liquid Phase Mole Fraction for Chloroform (1) + 2-ethoxyethanol (2) System at 303.15 K

$x_1$	Experimental P (kPa)	Calculated P (kPa)	Calculated y
0.0000	0.984	-	-
0.0302	1.396	1.424	0.330
0.0630	1.987	1.971	0.534
0.1050	2.834	2.784	0.687
0.2042	5.235	5.209	0.856
0.2651	7.021	7.034	0.904
0.3094	8.474	8.506	0.927
0.3511	9.954	9.991	0.943
0.3995	11.792	11.810	0.957
0.4497	13.787	13.782	0.967
0.4997	15.833	15.795	0.975
0.5496	17.892	17.816	0.981
0.5487	17.761	17.780	0.980
0.5980	19.740	19.751	0.985
0.6486	21.708	21.711	0.988
0.6985	23.530	23.547	0.991
0.7484	25.238	25.259	0.993
0.7985	26.809	26.840	0.995
0.8486	28.284	28.285	0.996
0.8987	29.645	29.623	0.997
0.9390	30.749	30.672	0.998
0.9691	31.520	31.485	0.999
1.0000	32.403	-	-

Table 6: Total Pressure P as a Function of Liquid Phase Mole Fraction for 1, 2 Dichloroethane (1) + 2-ethoxyethanol (2) System at 303.15 K

$x_1$	Experimental P (kPa)	Calculated P (kPa)	Calculated y
0.0000	0.974	-	-
0.0444	1.664	1.636	0.431
0.0703	2.082	2.045	0.558
0.1010	2.585	2.549	0.657
0.1507	3.416	3.391	0.757
0.2170	4.534	4.534	0.833
0.2504	5.093	5.103	0.858
0.3069	6.016	6.041	0.889
0.3501	6.696	6.725	0.907
0.4000	7.439	7.470	0.922
0.4500	8.143	8.163	0.933
0.4999	8.794	8.799	0.943
0.5499	9.396	9.383	0.950
0.5493	9.380	9.376	0.950
0.5992	9.931	9.911	0.957
0.6493	10.436	10.406	0.962
0.6993	10.931	10.869	0.967
0.7491	11.341	11.311	0.972
0.7993	11.762	11.746	0.976
0.8491	12.173	12.186	0.982
0.8992	12.596	12.649	0.987
0.9393	12.971	13.045	0.992
0.9696	13.298	13.365	0.996
1.0000	13.707	-	-

Table 7: Total Pressure P as a Function of Liquid Phase Mole Fraction for Dichloromethane (1) + 2-ethoxyethanol (2) System at 303.15 K

$x_1$	Experimental P (kPa)	Calculated P (kPa)	Calculated y
0.0000	0.968	-	-
0.0355	2.403	2.625	0.644
0.0651	4.110	4.182	0.784
0.1068	6.696	6.637	0.871
0.1555	9.939	9.859	0.918
0.1953	12.819	12.743	0.940
0.2727	18.863	18.865	0.964
0.3182	22.676	22.688	0.973
0.3502	25.388	25.436	0.977
0.4033	29.987	30.043	0.982
0.4498	34.034	34.065	0.986
0.4981	38.165	38.167	0.988
0.5486	42.332	42.321	0.991
0.5995	46.346	46.317	0.992
0.5976	46.230	46.172	0.992
0.6474	49.894	49.868	0.994
0.6975	53.364	53.344	0.995
0.7476	56.547	56.562	0.995
0.7976	59.45	59.521	0.997
0.8481	62.212	62.278	0.997
0.8985	64.876	64.860	0.998
0.9388	67.000	66.902	0.998
0.9695	68.720	68.560	0.999
1.0000	70.474	-	-

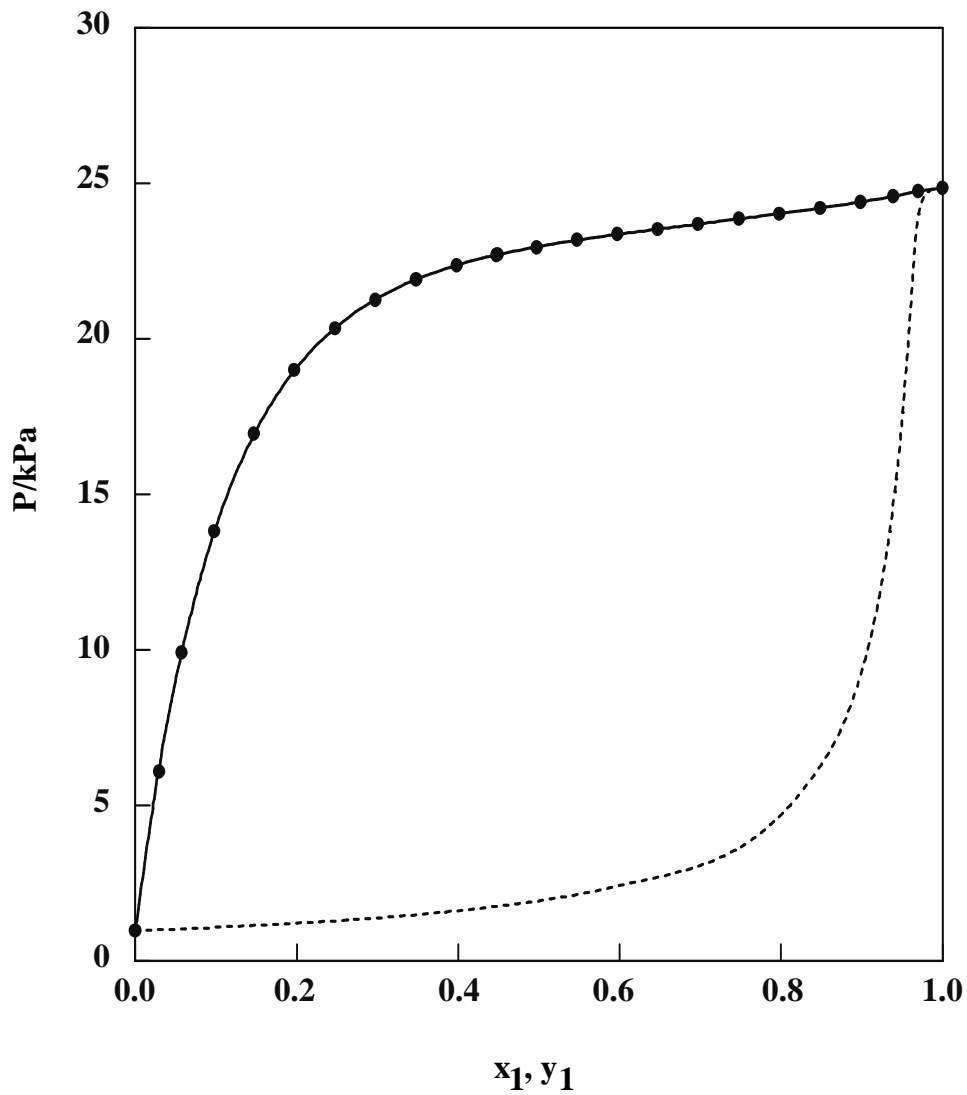
Table 8: Regressed Constants for the Modified Margules Model

System	$A_{12}$	$A_{21}$	$\alpha_{12}$	$\alpha_{21}$
Hexane + 2-ethoxyethanol	2.13049	3.30610	1.66405	8.86853
Carbon tetrachloride+2-ethoxyethanol	0.83441	2.29793	0.96064	6.31473
Chloroform+2-ethoxyethanol	-0.7876	0.1354	0.53533	1.6334
1,2 Dichloroethane+2-ethoxyethanol	0.10898	0.77531	-	-
Dichloromethane+2-ethoxyethanol	-0.4398	0.70325	0.52048	2.73650

Table 9: Second Virial Coefficients,  $B_{ii}$  and  $B_{ij}$ , and Saturated Liquid Volumes,  $V_L$

Component	$B_{ii}$ ( $\text{cm}^3/\text{mol}$ )	$B_{ij}$ ( $\text{cm}^3/\text{mol}$ )	$V_L$ ( $\text{cm}^3/\text{mol}$ )
Hexane	-1802	-1534	132.6
Carbon tetrachloride	-1622	-1442	97.702
Chloroform	-1143	-1342	81.01
1,2 Dichloroethane	-1265	-1279	79.916
Dichloromethane	-824	-1146	64.933
2-ethoxyethanol	-3584	<sup>1</sup>	97.833

<sup>1</sup> For this work, 2-ethoxyethanol is component 2 while the chlorinated hydrocarbons as component 1.



- Present work
- Margules fit to P-x data
- - - calculated  $y_1$

Figure 4: Pressure  $P$  vs Liquid Mole Fraction  $x_1$  and Vapor Mole Fraction  $y_1$  for Hexane (1) and 2-ethoxyethanol (2) System at 303.15 K.



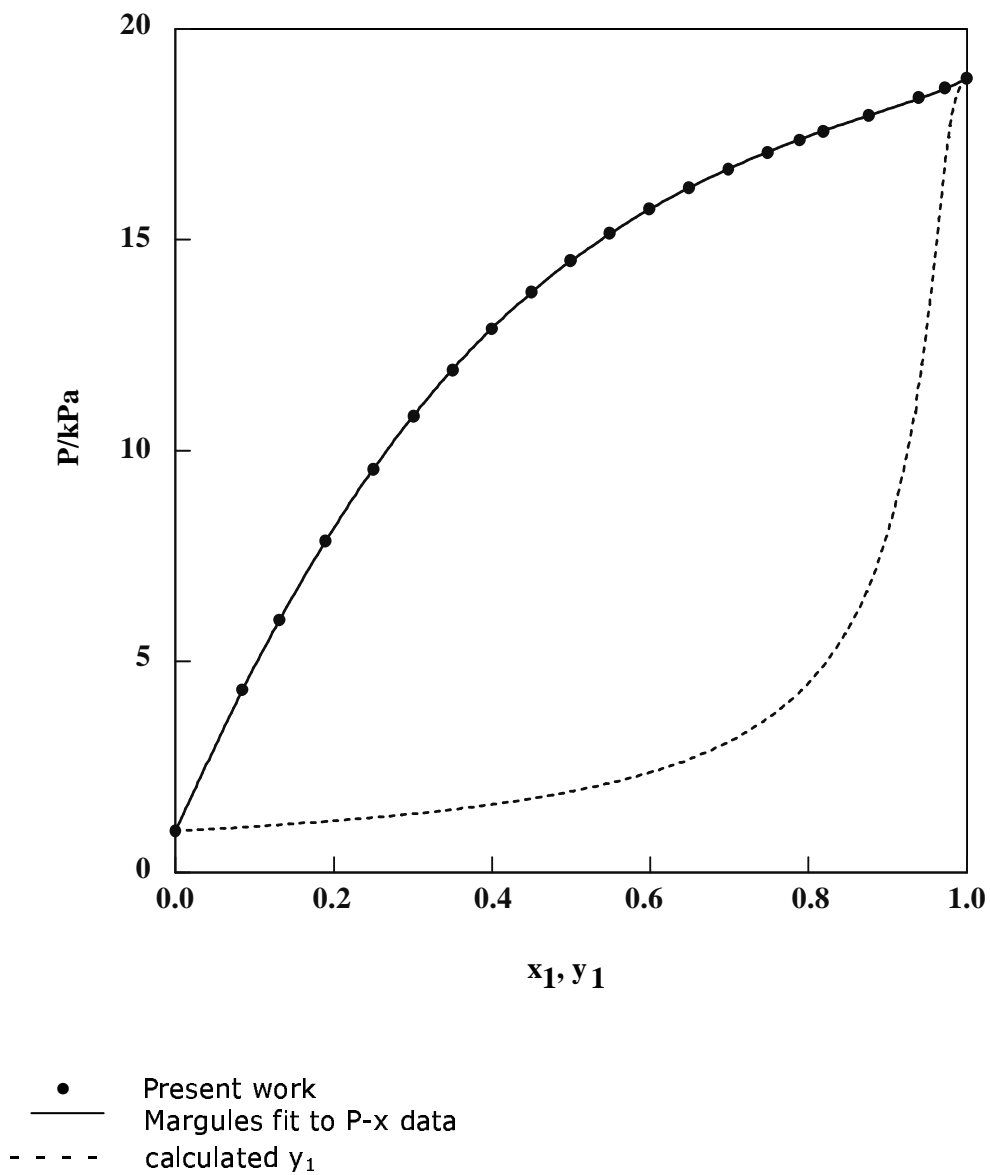


Figure 5: Pressure  $P$  vs Liquid Mole Fraction  $x_1$  and Vapor Mole Fraction  $y_1$  for Carbon Tetrachloride (1) and 2-ethoxyethanol (2) System at 303.15 K.

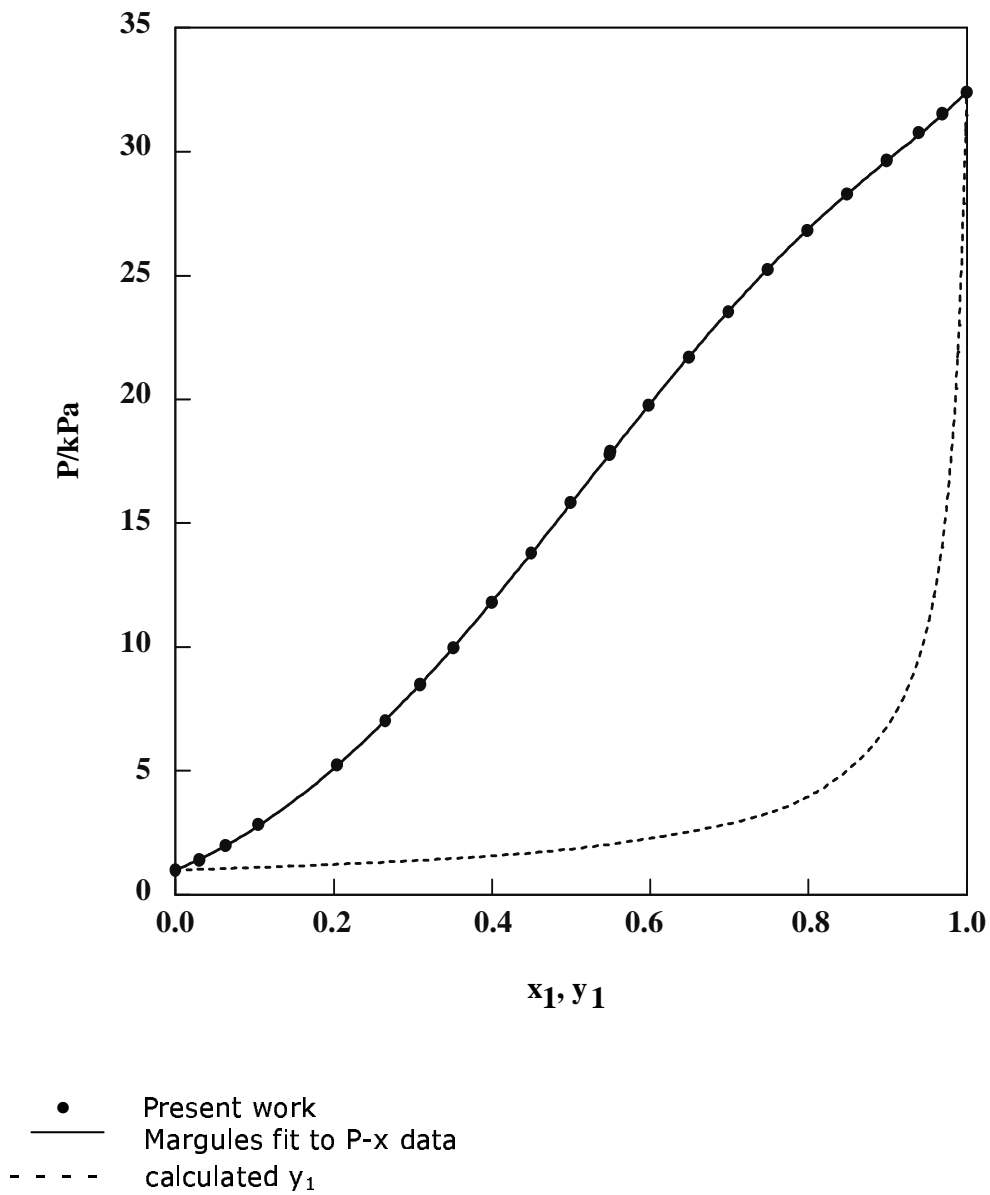
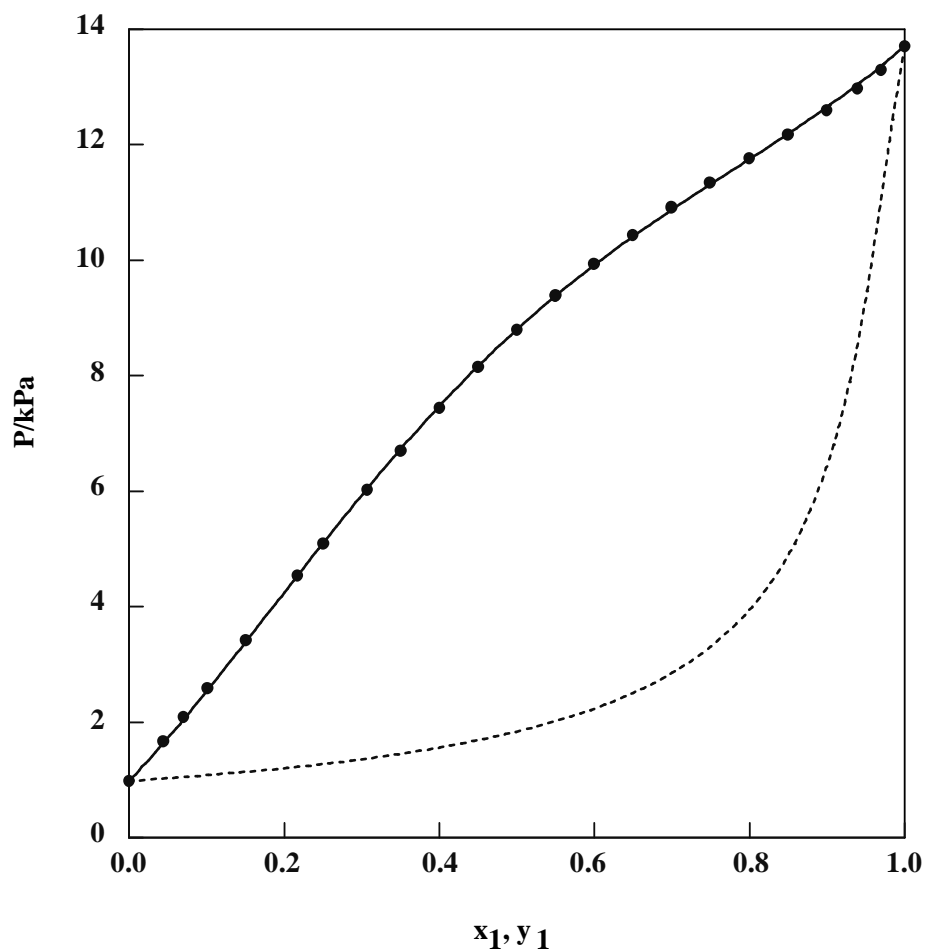


Figure 6: Pressure  $P$  vs Liquid Mole Fraction  $x_1$  and Vapor Mole Fraction  $y_1$  for Chloroform (1) and 2-ethoxyethanol (2) System at 303.15 K.



- Present work
- Margules fit to P-x data
- - - calculated y<sub>1</sub>

Figure 7: Pressure P vs Liquid Mole Fraction  $x_1$  and Vapor Mole Fraction  $y_1$  for 1,2-Dichloroethane (1) and 2-ethoxyethanol (2) System at 303.15 K.

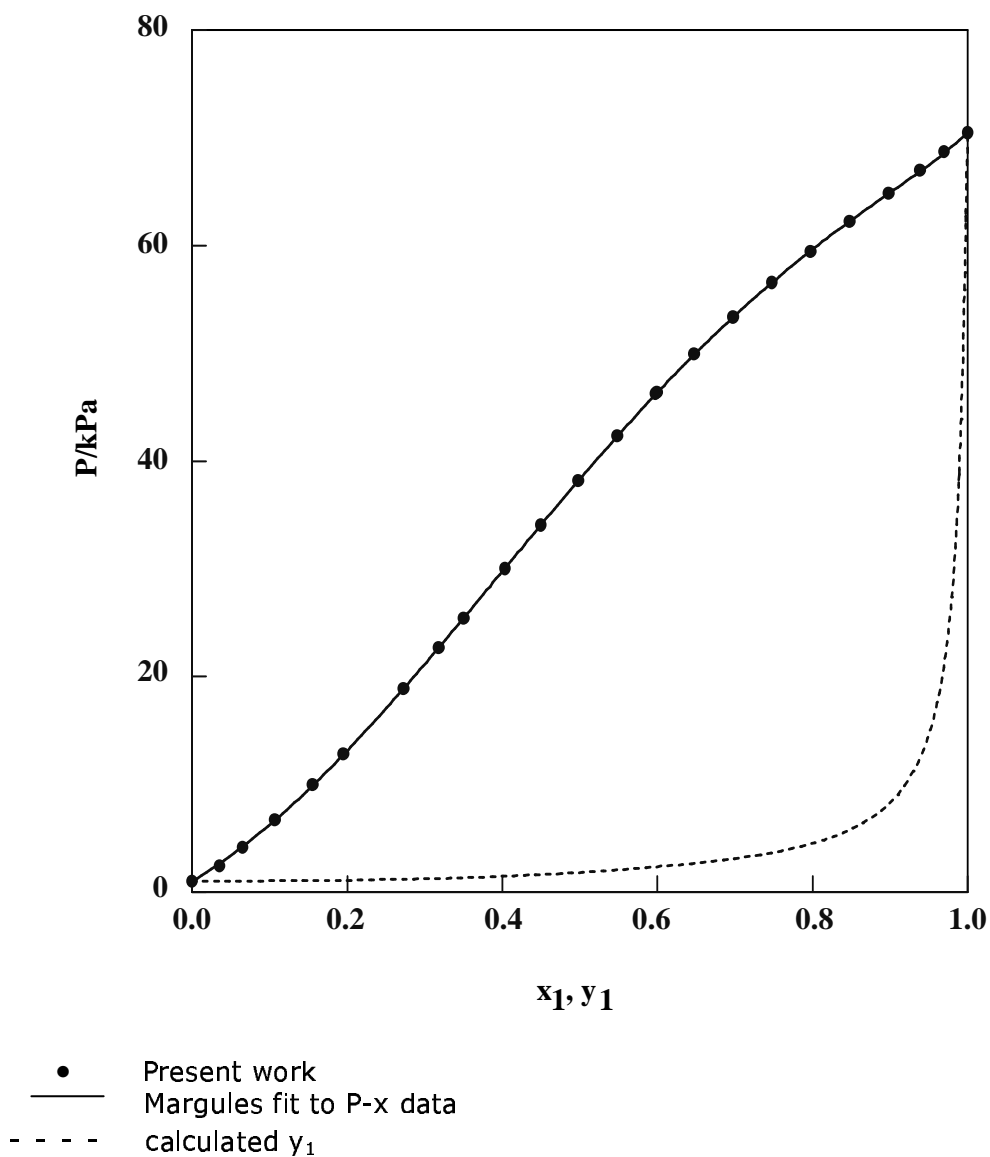


Figure 8: Pressure  $P$  vs Liquid Mole Fraction  $x_1$  and Vapor Mole Fraction  $y_1$  for Dichloromethane (1) + 2-ethoxyethanol (2) System at 303.15 K.

The uncertainty  $\Delta P$  in the measured variable  $P$  is a function of the three independent variables which are uncertainty in bath temperature, mole fraction and gauge reading. The following section shows the method for the calculation of error bars.

#### 4.1 Calculation of Error Bars

The equation for uncertainty in pressure is

$$\Delta P = \sqrt{\left(\frac{\partial P}{\partial T} \Delta T\right)^2 + \left(\frac{\partial P}{\partial x_1} \Delta x_1\right)^2 + \left(\frac{\partial P}{\partial P_{read}} \Delta P_{read}\right)^2} \quad (4.1)$$

Uncertainty in  $P$  due to uncertainty in bath temperature:  $\left(\frac{\partial P}{\partial T} \Delta T\right)$

$$\Delta T = 0.02K$$

Uncertainty in  $P$  due to uncertainty in mole fraction:  $\left(\frac{\partial P}{\partial x_1} \Delta x_1\right)$

$$\Delta x_1 = 0.001$$

Uncertainty in  $P$  due to uncertainty in gauge reading:  $\left(\frac{\partial P}{\partial P_{read}} \Delta P_{read}\right)$

$$\Delta P_{read} = 0.001P_{read}$$

The derivative  $\frac{\partial P}{\partial x_1}$  is estimated by central differences of the

experimental data. The calibration of the pressure gauge is

represented by  $P = 0.9638P_{read}$ . Therefore  $\frac{\partial P}{\partial P_{read}} = 0.9638$

We know

$$P = \frac{\gamma_1 x_1 P_1^s}{\Phi_1} + \frac{\gamma_2 x_2 P_2^s}{\Phi_2} \quad (4.2)$$

The temperature dependences of  $\gamma_i$  and  $\Phi_i$  are weak compared to those of the vapor pressures, so the derivative  $\frac{\partial P}{\partial T}$  may be estimated by partial differentiation.

$$\frac{\partial P}{\partial T} = \frac{\gamma_1 x_1}{\Phi_1} \frac{dP_1^s}{dT} + \frac{\gamma_2 x_2}{\Phi_2} \frac{dP_2^s}{dT} \quad (4.3)$$

where  $P_1^s$  and  $P_2^s$  are pure component vapor pressures at species 1 and 2. Values for  $\frac{dP_i^s}{dT}$  were estimated using vapor pressure data from the literature.

Table 10 shows the values of  $\frac{dP_i^s}{dT}$  for all the components in the present study.

Table 10: Values of  $\frac{dP}{dT}$  for all the Components

Component	$\frac{dP}{dT}$ ( kPa/K)	$\frac{dP}{dT}$ (torr/K)
2-Ethoxyethanol	0.0610	0.46
Carbon tetrachloride	0.8	6.0
Chloroform	1.34	10.0
Dichloromethane	2.72	20.4
1,2 Dichloroethane	0.61	4.6
Hexane	1.05	7.9

The following graphs shows the error plus and error minus lines for each system and the model tested on those systems. Error plus is  $\Delta P$  from uncertainty equation and error minus is  $-\Delta P$  from uncertainty equation. Points represent residuals  $P_{\text{exp}} - P_{\text{calc}}$ .

Figure 9 shows the plot of Pressure vs  $x_1$  for the binary system of hexane and 2-ethoxyethanol. The purpose of beginning the experiments with this binary system was to validate the apparatus and procedure. A comparison was made between the results of the present work and those of Carmona (2000). It was found that the results were approximately the same. The pressure is the difference of values between the readings taken by Carmona (2000) and the present study. The points lie between the error plus and error minus lines which suggests that the two studies agree to within the combined ranges of experimental error.

For the other systems, values are calculated using the three suffix, four suffix or Modified Margules model and plotted against liquid mole fraction. The objective of the graphs is to demonstrate the model which best fits the data. Figure 10, 11 and 13 show that the Modified Margules model fits better than the four suffix model. The pressures calculated using the Margules model are within the experimental error as compared to the four suffix model as they are scattered outside the error bars. For the system with 1,2 dichloroethane (figure 12), the four suffix model fits better than the three suffix. No improvement was observed when the modified Margules equation was applied.

The only reason for using the Modified Margules model in data reduction is that it is flexible enough to represent the data to within experimental error. In this procedure, the overall cell composition is corrected to liquid phase composition. After these corrections, the data can be tested for other solution models. In the next two chapters, we will see the application of a different model called the Kretschmer-Wiebe model to the obtained data.

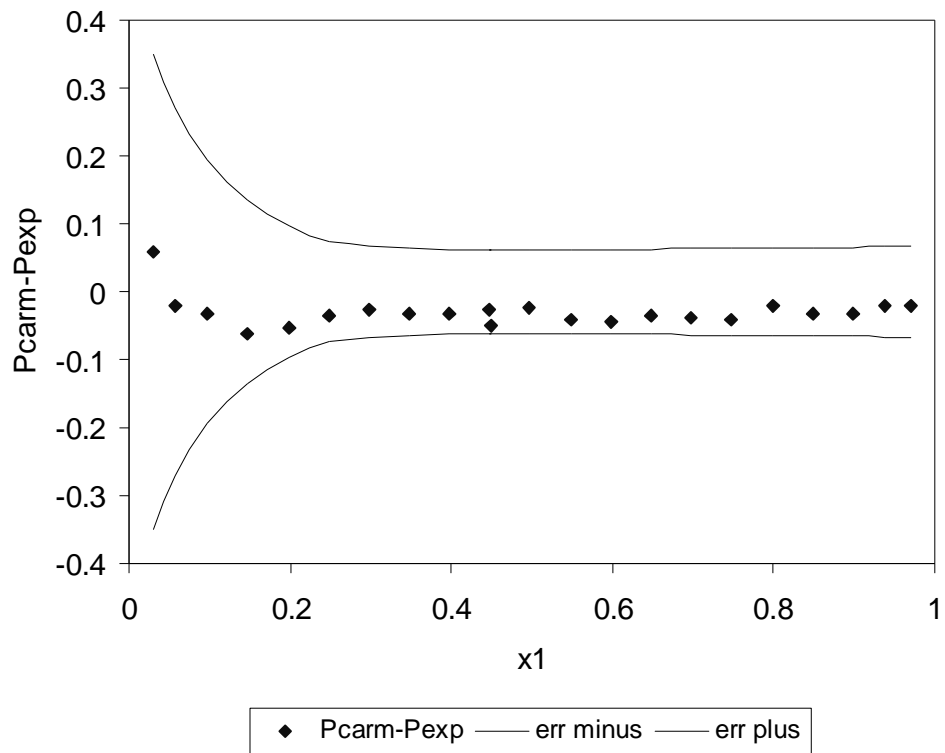


Figure 9: Difference of Experimental Values of the Present Study and Carmona's Values for Hexane (1) and 2-ethoxyethanol (2) System at 303.15 K



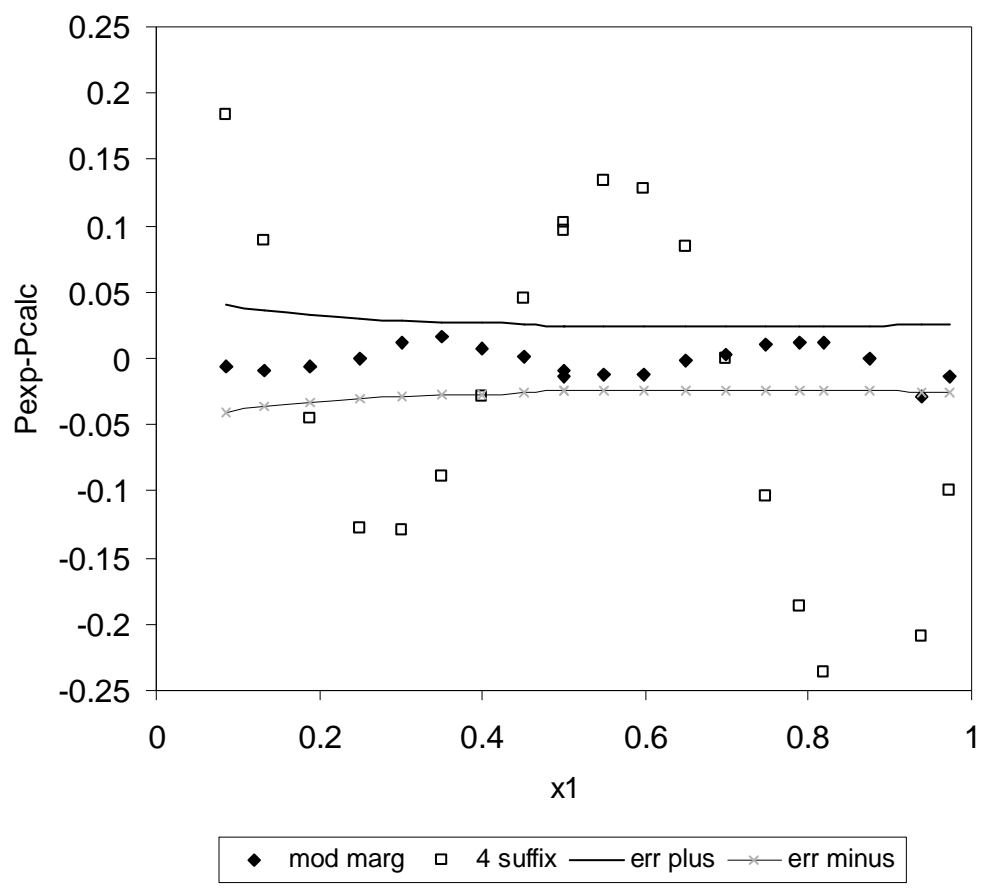


Figure 10: Comparison of Models for Carbon Tetrachloride (1) and 2-ethoxyethanol (2) System at 303.15 K

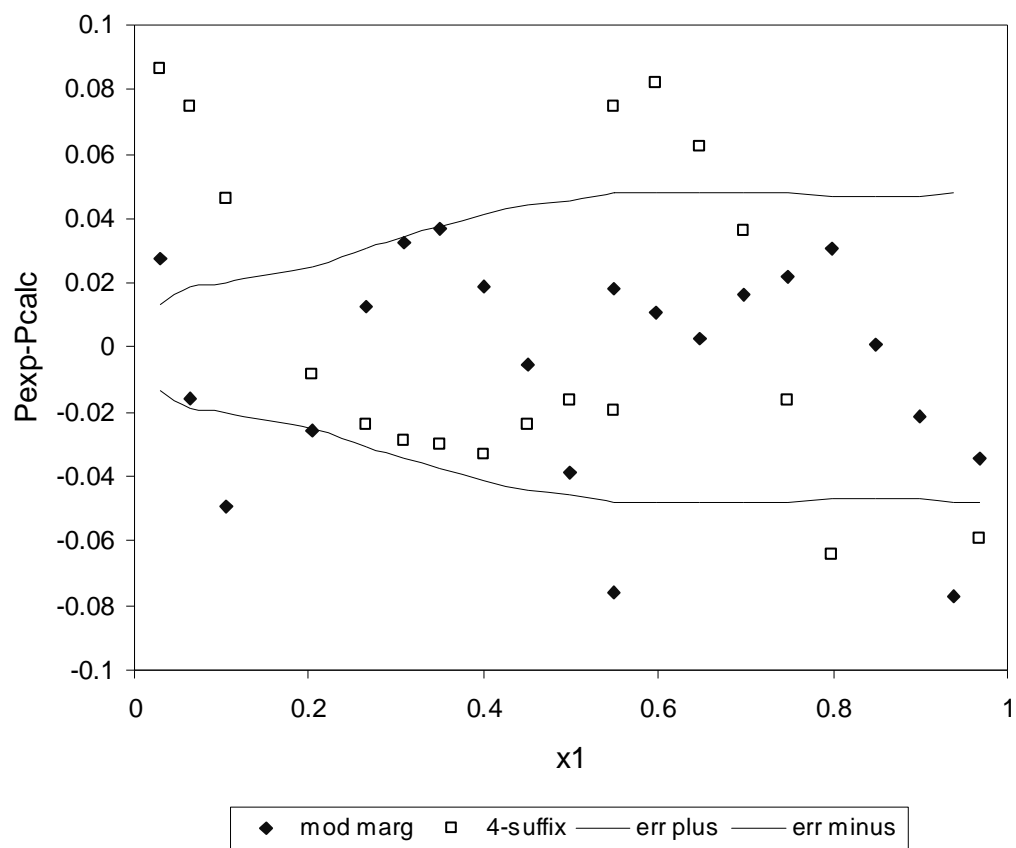


Figure 11: Comparison of Models for Chloroform (1) and 2-ethoxyethanol (2) System at 303.15 K

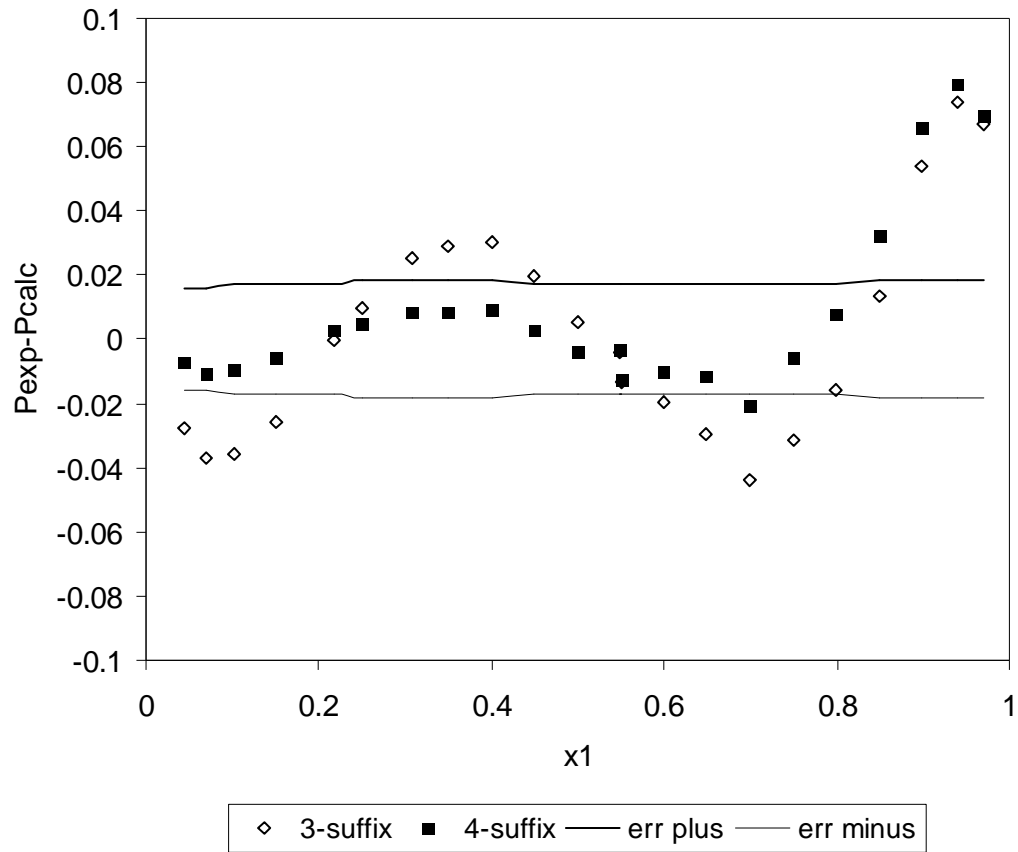


Figure 12: Comparison of Models for 1, 2 dichloroethane (1) and 2-ethoxyethanol (2) System at 303.15 K

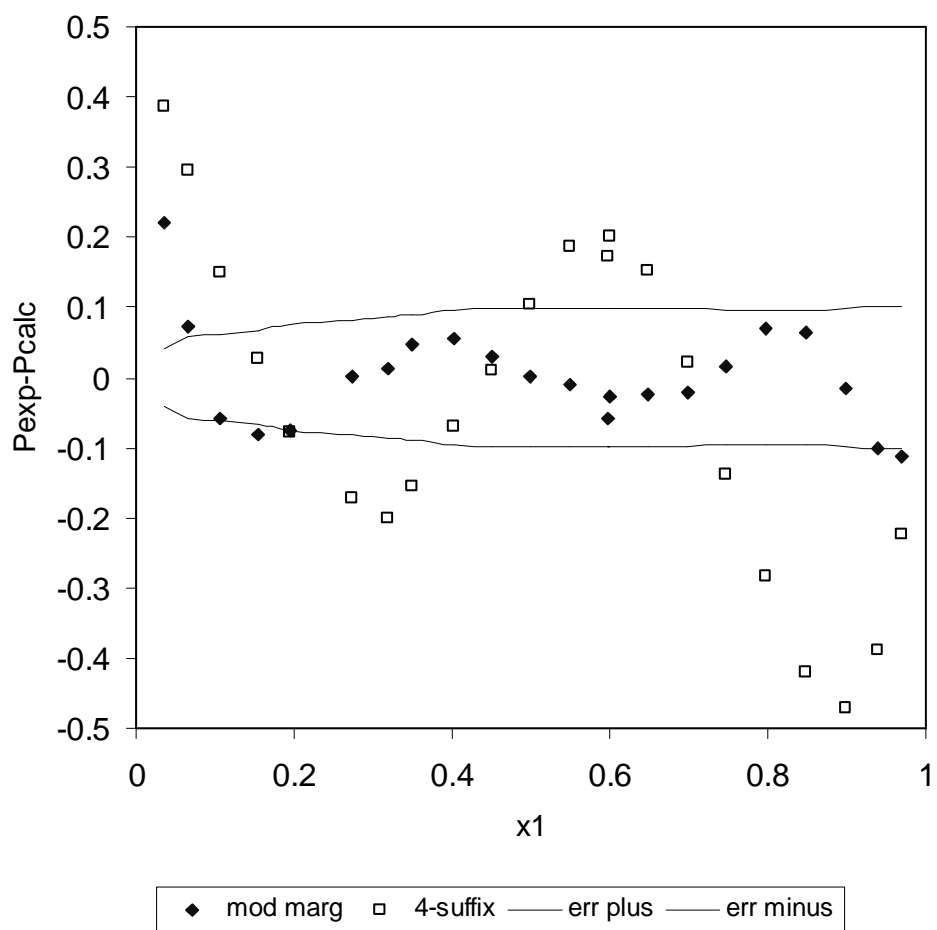


Figure 13: Comparison of Models for Dichloromethane (1) and 2-ethoxyethanol (2) at 303.15

## CHAPTER 5

### APPLICATION OF ASSOCIATION MODEL

#### 5.1 Theory of Model

Models are used in two different ways in this work. In the previous chapter we studied the application of the modified Margules equation, which is used solely for the purpose of reducing P-n<sub>1</sub>-n<sub>2</sub> data to P-x<sub>1</sub> data. The association model which we will be discussing presently is an example of a predictive (for multi-component systems) theoretical model and can be applied once the data reduction procedure is complete. The following equations will show the derivation of the association model for a binary system of components 1 and 2 where 1 is the chlorinated hydrocarbon and 2 is the alcohol.

The association model used here is an extension of one proposed by Kretschmer and Wiebe (1954). It is assumed that the Gibbs energy change upon mixing pure disordered species is assumed to be the sum of chemical and physical contributions.

$$\frac{n\Delta G_m}{RT} = \left( \frac{n\Delta G_m}{RT} \right)_{chemical} + \left( \frac{nG^E}{RT} \right)_{physical} \quad (5.1)$$

The chemical part of this model includes corrections to ideal mixing due to size differences and is described by using the Flory- Huggins

(1944) model. All of the sums seen in the Flory-Huggins model are over the true species of the components, which refers to monomers as well as any complexes. These true species should be differentiated from the stoichiometric species which are, for instance, hexane and 2-ethoxyethanol. A mathematical relation is developed later to relate true species to the stoichiometric species.

The Flory Huggins equations which gives the Gibbs free energy change,  $\Delta G^E$  of mixing is

$$\frac{n\Delta G_m}{RT} = \sum_i n_i \ln \Phi_i - \sum_i n_i \ln \left( \frac{r_i}{\sigma} \right) - \alpha \sum_i n_i (r_i - 1) \quad (5.2)$$

where:

$r_i$  is the measure of the molecular size

$\sigma (=1)$  is the symmetry neighbor

$\alpha = \ln (Z-1)$  where Z is the coordination number

$\Phi_i$  is the volume fraction of species i

For this binary system

$$\Phi_i = \frac{r_i x_i}{r_1 x_1 + r_2 x_2} \quad (5.3)$$

The quantities  $r_i$  are size factors defined as

$$r_i = \left( \frac{V_i^L}{V_{MeOH}} \right)_{303.15} \quad (5.4)$$

where  $V_i^L$  is the saturated liquid molar volume of species  $i$  at 303.15 K and  $V_{MeOH}$  is the saturated liquid molar volume of methanol at 303.15 K.

Campbell demonstrated that the activity coefficient of a (stoichiometric) species  $m$  in a mixture of associating and nonassociating components is given by

$$\ln \gamma_m = \ln \left( \frac{C_{m1}}{C_{m1}^0 x_1} \right) - r_m (\Psi - \Psi_{purem}) \quad (5.5)$$

where  $C_{m1}$  is the concentration of the monomeric form of stoichiometric species  $m$  in the mixture and  $C_{m1}^0$  is the concentration of monomeric form of species  $m$  in pure stoichiometric species  $m$ . The quantity  $\Psi$  is the total concentration of all complexes in the mixture and  $\Psi_{purem}$  is the total concentration of all complexes in pure stoichiometric  $m$ .

In the present study it is assumed that the 2-ethoxyethanol (2) molecule can associate to form chains and that the self association constant  $K_{22}$  for this reaction is independent of the chain length. It is also assumed that a chain of ethoxyethanol molecules may solvate with a single molecule of hydrocarbon (1) with a solvation constant  $K_{12}$  assumed to be independent of chain length.

Hence, the total concentration of all complexes is given by:

$$\Psi = C_{11} + \sum_{i=1}^{\infty} C_{2i} + \sum_{i=1}^{\infty} C_{2i1} \quad (5.6)$$

where  $C_{11}$  is the concentration of unsolvated chlorinated hydrocarbon molecules.  $C_{2i}$  is the concentration of the 2-ethoxyethanol chains of length  $i$  and  $C_{2i1}$  is the concentration of 2-ethoxyethanol chains of length  $i$  that are solvated with a single hydrocarbon molecule. Using chemical equilibria, the concentration of all complexes may be expressed in terms of  $C_{11}$  and the concentration  $C_{21}$  of 2-ethoxyethanol monomers as follows:

$$C_{2i} = C_{21} (K_{22} C_{21})^{i-1} \quad (5.7)$$

$$C_{2i1} = K_{12} C_{11} C_{21} (K_{22} C_{21})^{i-1} \quad (5.8)$$

Substituting equations (5.7) and (5.8) in (5.6) followed by putting the infinite series into closed forms yields:

$$\Psi = C_{11} + \frac{C_{21}(1 + K_{12}C_{11})}{1 - K_{22}C_{21}} \quad (5.9)$$

Now  $\Psi_{pure1} = C_{11}^0$  by substituting  $C_{11} = C_{11}^0$  and  $C_{21} = 0$

$$\Psi_{pure2} = \frac{C_{21}^0}{1 - K_{22}C_{21}^0} \text{ by substituting } C_{21} = C_{21}^0 \text{ and } C_{11} = 0$$



The physical contributions to the activity coefficients are assumed to be given by Scatchard-Hildebrand (or regular solution) expressions

$$\ln \gamma_{2_{phys}} = \frac{\beta_{12} r_2}{RT} \Phi_1^2$$

$$\ln \gamma_{1_{phys}} = \frac{\beta_{12} r_1}{RT} \Phi_2^2$$

These results for  $\Psi, \Psi_{pure1}, \Psi_{pure2}$  when substituted in equation (5.5) and added by physical contributions leads to equations (5.10) and (5.11)

$$\ln \gamma_1 = \ln \left( \frac{C_{11} r_1}{x_1} \right) + 1 - r_1 \left( C_{11} + C_{21} \frac{1 + K_{12} C_{11}}{1 - K_{22} C_{21}} \right) + \frac{\beta_{12} r_1}{RT} \Phi_2^2 \quad (5.10)$$

$$\ln \gamma_2 = \ln \left( \frac{C_{21}}{x_2 C_{21}^0} \right) - r_2 \left( C_{11} + C_{21} \frac{1 + K_{12} C_{11}}{1 - K_{22} C_{21}} - \frac{C_{21}^0}{1 - K_{22} C_{21}^0} \right) + \frac{\beta_{12} r_2}{RT} \Phi_1^2 \quad (5.11)$$

The concentrations  $C_{11}$  and  $C_{21}$  of the monomeric species may be related to the concentrations of the stoichiometric species 1 and 2 by mole balances.

For species 1,

$$C_1 = \frac{\Phi_1}{r_1} = C_{11} + \sum_{i=1}^{\infty} C_{2i1} \quad (5.12)$$

and for species 2,

$$C_2 = \frac{\Phi_2}{r_2} = \sum_{i=1}^{\infty} i C_{2i} + \sum_{i=1}^{\infty} i C_{2i1} \quad (5.13)$$

Substitution for  $C_{2i}$  and  $C_{2i1}$  using equations (5.7) and (5.8), followed by expressing the infinite series in closed form, yields

$$\frac{\Phi_1}{r_1} = C_{11} \left( 1 + \frac{K_{12} C_{21}}{1 - K_{22} C_{21}} \right) \quad (5.14)$$

$$\frac{\Phi_2}{r_2} = C_{21} \left( \frac{1 + K_{12} C_{11}}{(1 - K_{22} C_{21})^2} \right) \quad (5.15)$$

Equations (5.14) and (5.15) must be solved simultaneously by trial and error for  $C_{11}$  and  $C_{21}$ . The concentration  $C_{21}^0$  of monomeric 2-ethoxyethanol in pure 2-ethoxyethanol is also required in equation (5.11). It may be obtained from equation (5.15) by setting  $C_{11} = 0, \phi_2 = 1$  and  $C_{21} = C_{21}^0$ . These results in

$$\frac{1}{r_2} = \frac{C_{21}^0}{(1 - K_{22} C_{21}^0)^2} \quad (5.16)$$

In the present study, the binary systems of 2-ethoxyethanol with hexane and with carbon tetrachloride do not exhibit solvation. The association constant  $K_{12}$  associated with this bonding is therefore zero for these two binary systems. The binary systems of 2-ethoxyethanol with chloroform, 1,2-dichloroethane and dichloromethane would be expected to exhibit solvation. As a hydrogen bond forms between these unlike molecules, the formation of 2-ethoxyethanol chains stops. Therefore  $K_{12}$  is taken into consideration for these systems.

The original Kretschmer Wiebe model did not take solvation into account. It can be recovered from the extended Kretschmer Wiebe model given above by setting  $K_{12} = 0$

When  $K_{12}$  equals zero, equations (5.14) and (5.15) reduce to

$$\frac{\Phi_1}{r_1} = C_{11} \quad (5.17)$$

$$\frac{\Phi_2}{r_2} = \frac{C_{21}}{(1 - K_{22}C_{21})^2} \quad (5.18)$$

Equation (5.18) can be solved explicitly for  $C_{21}$ . The equation for  $C_{21}^0$  for this case is identical to the extended model and is given by equation (5.16), which can be solved explicitly for  $C_{21}^0$ . The results for  $C_{21}$  and  $C_{21}^0$  are

$$C_{21} = \frac{1 + \frac{2K_{22}\Phi_2}{r_2} - \sqrt{1 + \frac{4K_{22}\Phi_2}{r_2}}}{\left(\frac{2\Phi_2 K_{22}^2}{r_2}\right)} \quad (5.18)$$

$$C_{21}^0 = \frac{1 + \frac{2K_{22}}{r_2} - \sqrt{1 + \frac{4K_{22}}{r_2}}}{\left(\frac{2K_{22}^2}{r_2}\right)} \quad (5.19)$$

The original Kretschmer Wiebe model ( $K_{12} = 0$ ) was applied to all five systems in the following manner.

First it was applied to n-hexane and 2-ethoxyethanol to obtain  $K_{22}$  and  $\beta_{12}$ . Theoretically, since the self association constant  $K_{22}$  is characteristic only of 2-ethoxyethanol, it should not vary from system to system. Therefore, the Kretschmer Wiebe model was applied to the four chloroalkanes-ethoxyethanol binary systems by using the value of  $K_{22}$  obtained from the n-hexane system and treating  $\beta_{12}$  as the single adjustable parameter.

As a point of comparison, the regular solution model was also applied to the data sets treating  $\beta_{12}$  as the single adjustable parameter. This model neglects association of any type.

Finally the extended Kretschmer Wiebe model ( $K_{12} \neq 0$ ) was applied to the three systems for which it was expected to be important. Here two parameters ( $K_{12}$  and  $\beta_{12}$ ) were treated as adjustable for each system.

All regressions were done with MATLAB. Sample programs are given in Appendix A.

## 5.2 Results

The following table shows the values of  $K_{12}$ ,  $K_{22}$  and  $\beta_{12}$  for all the three models tested on each system.

Table 11: Regressed Constants for Different Models

Component	Regular Solution	Kretschmer Wiebe		Extended Kretschmer Wiebe		
		$\beta_{12}$	$K_{22}$	$\beta_{12}$	$K_{12}$	$K_{22}$
Hexane	1890.29	768.185	55.817		-	
Carbon tetrachloride	1351.18	79.6609	55.817*		-	
Chloroform	-279.37	-1666.8	55.817*	-1399	1.8	55.817
1,2 dichloroethane	654.989	-617.55	55.817*	404.26	12.353	55.817
dichloromethane	233.696	-957.56	55.817*	-859.5	0.5223	55.817

\* Obtained from system with hexane and used as non-adjustable parameter for other systems

The average deviation in pressure due to each of these models is shown in the next table. The objective of determining the average deviation in pressure is to identify which model fits the best to the data. According to the values, we can see that the average deviation in pressure is high for the regular solution model and is decreased to a large extent in Kretschmer-Wiebe model. The extended Kretschmer-Wiebe model does not bring a large change in deviation except in case of 1,2 dichloroethane where it changes from 0.2289 kPa to 0.0760 kPa.

Table 12: Average Deviation in Pressure (kPa) for each Component

Component	Regular Solution model	Kretschmer-Wiebe model	Extended Kretschmer Wiebe
Hexane	1.9765	0.2276	-
Carbon tetrachloride	0.906	0.0440	-
Chloroform	0.7648	0.2113	0.1734
1,2 Dichloroethane	0.2493	0.2289	0.076
Dichloromethane	1.9567	0.6503	0.6434

On the basis of the pressure values calculated due to these models, graphs are plotted between calculated pressure values for the regular solution model and Kretschmer-Wiebe model vs. the liquid mole fraction. The following graphs show a visual comparison of the two models.

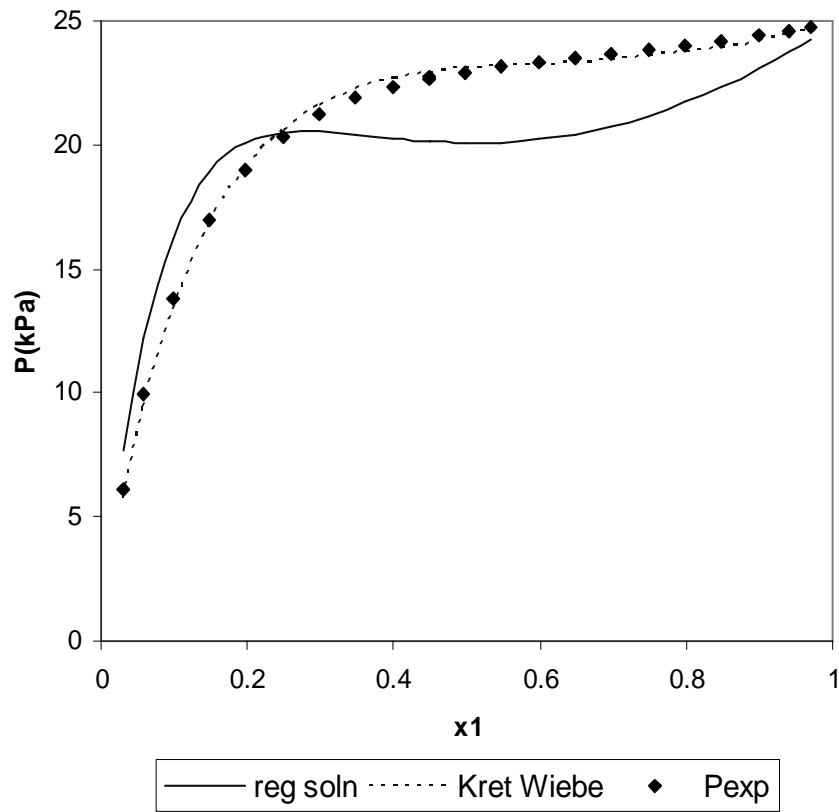


Figure 14: Comparison of Regular Solution and Kretschmer-Wiebe Models for the Binary System of Hexane (1) and 2-ethoxyethanol (2)

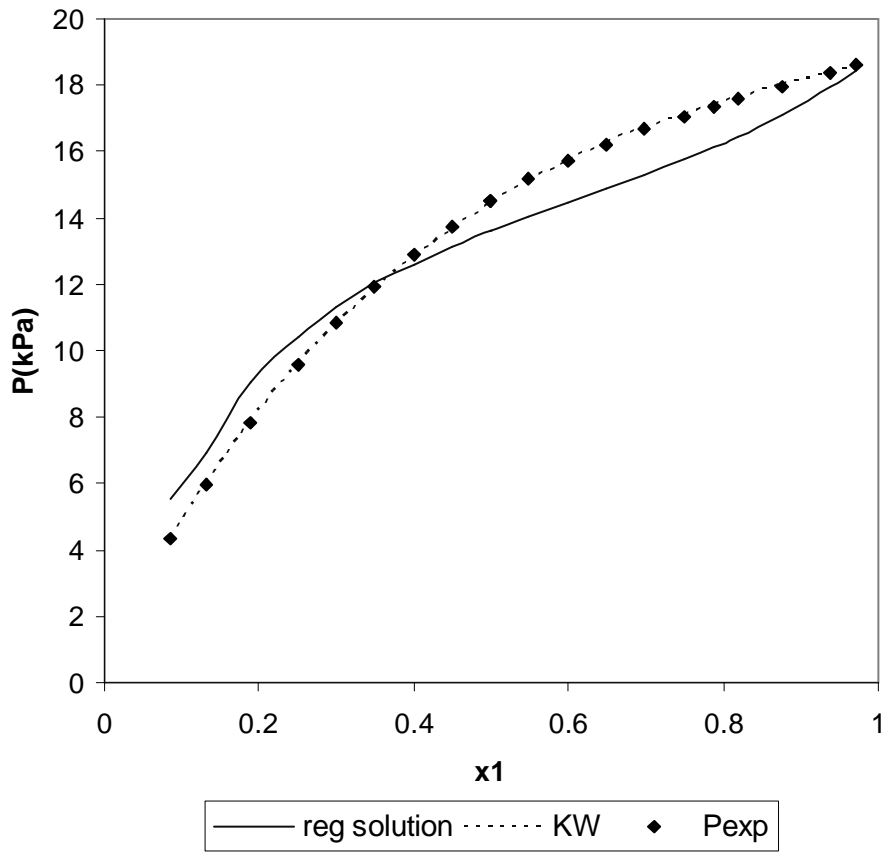


Figure 15: Comparison of Regular Solution and Kretschmer-Wiebe Models for the Binary System of Carbon Tetrachloride (1) + 2-ethoxyethanol (2)



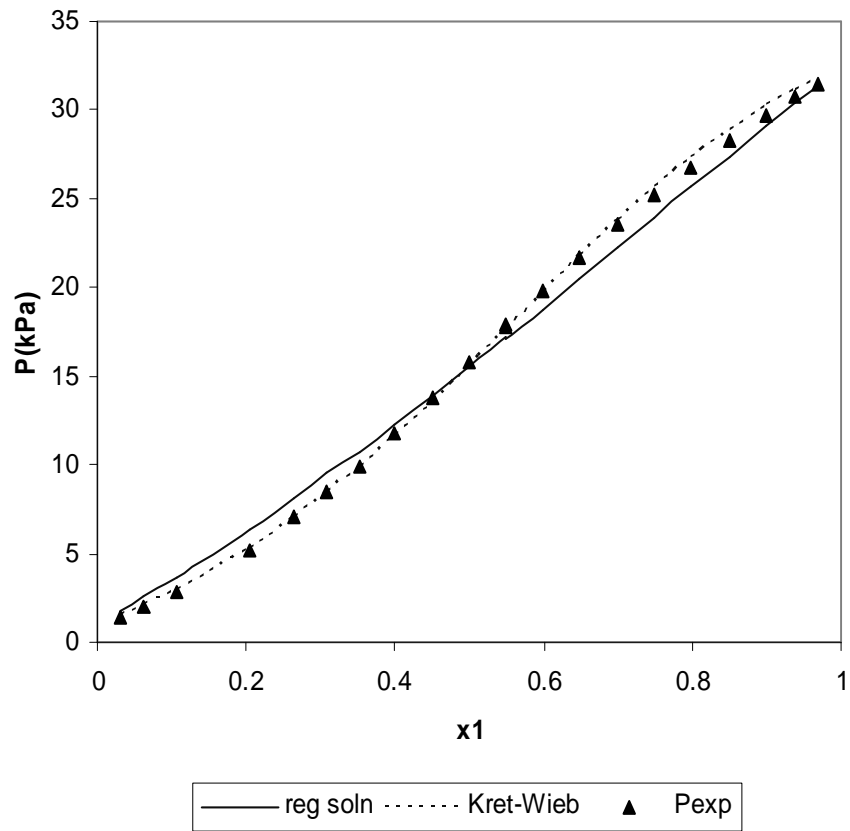


Figure 16: Comparison of Regular Solution and Kretschmer-Wiebe Models for the Binary System of Chloroform(1) and 2-ethoxyethanol (2)

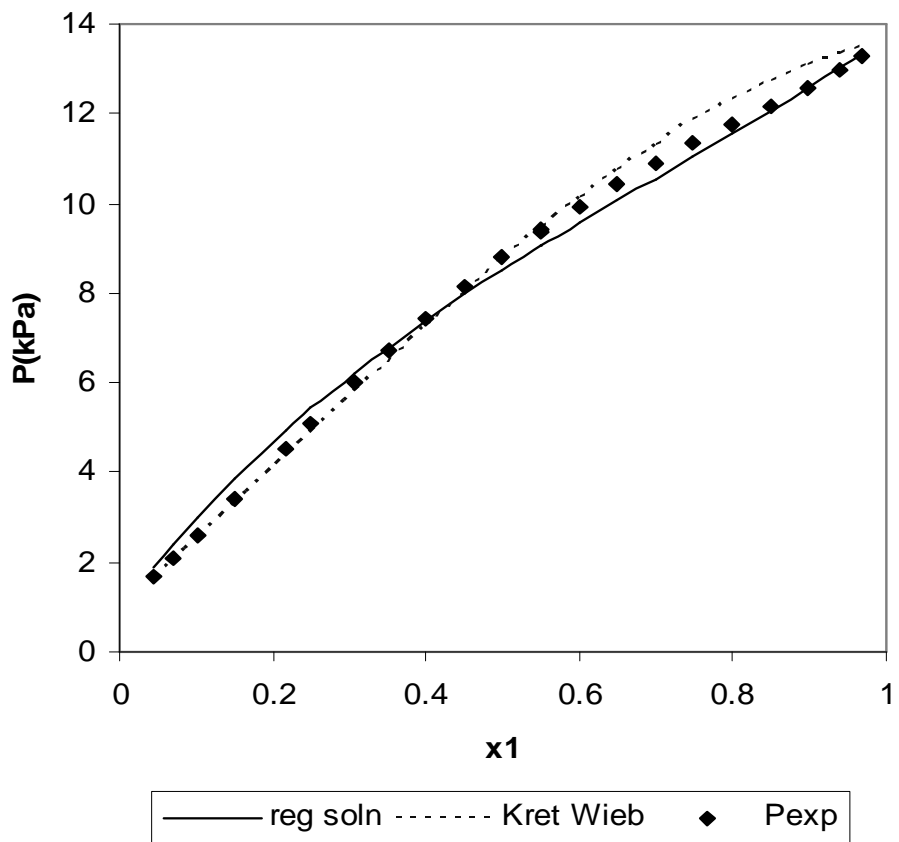


Figure 17: Comparison of Regular Solution and Kretschmer-Wiebe Models for the Binary System of 1,2 dichloroethane (1) + 2-ethoxyethanol (2)

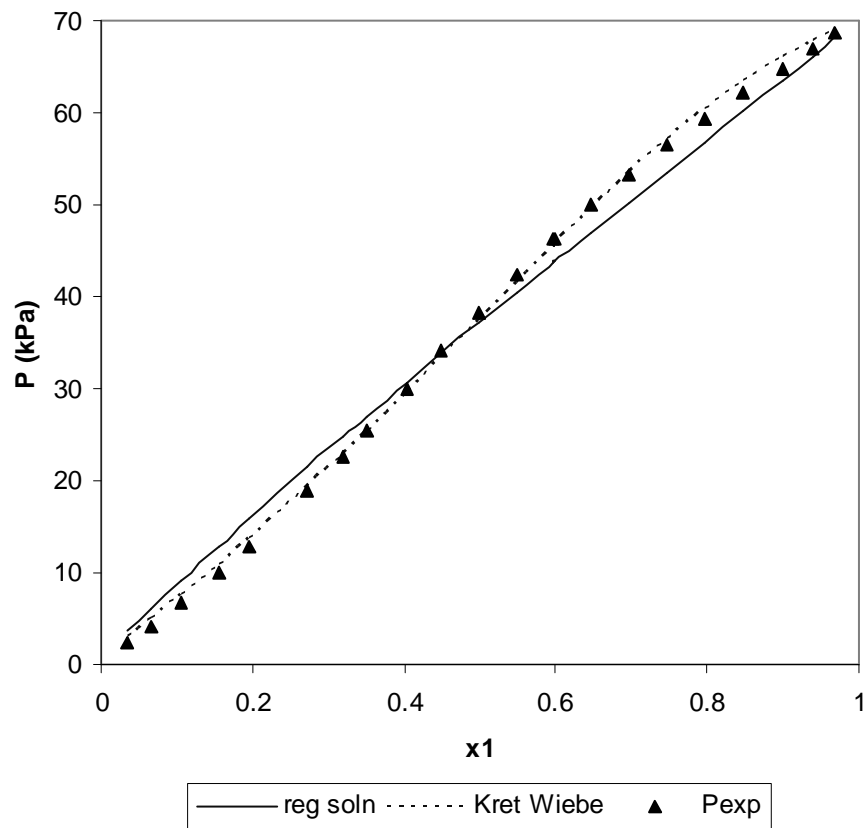


Figure 18: Comparison of Regular Solution and Kretschmer-Wiebe Models for the Binary System of Dichloromethane (1) and 2-ethoxyethanol (2)

Figures 14-18 depict the comparison between the experimental pressure values, regular solution pressure and Kretschmer-Wiebe pressure for each component of the system. Figures 14 and 15 show that the experimental pressure values and the Kretschmer-Wiebe values are approximately the same where as the pressure values from the regular solution model have a large deviation from each of them. Therefore for hexane and carbon tetrachloride, it is clearly shown the Kretschmer-Wiebe model has a good fit to the data.

For the other systems, not much difference between models is shown in the figures 16-18, but still it can be seen that the Kretschmer-Wiebe model has definitely a better fit than the regular solution model for these systems.

Another interesting thing found when working with the association model was in the behavior of the regressed constants. The comparison made between the Kretschmer-Wiebe and its extended form showed that the values of the physical constant  $\beta$  were very similar for the hydrocarbons except for 1,2 dichloroethane. It was interesting to note that for this component the  $\beta$  values for the Kretschmer-Wiebe (-617.55) and the extended Kretschmer-Wiebe (404.26) were quite different.

## CHAPTER 6

### CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 Conclusions

In the present study, vapor-liquid equilibrium data are reported for hexane and four chlorinated hydrocarbons with 2-ethoxyethanol at 303.15 K. Data reduction was accomplished using Barker's method. An association model developed by Kretschmer and Wiebe was then used to obtain the chemical equilibrium constant  $K$  and the physical equilibrium constant  $\beta$  for each binary mixture. The extended Kretschmer-Wiebe model and the regular solution model were also applied to the data. It was found that the Kretschmer-Wiebe model was far superior to the regular solution model. The graphs clearly depict that the pressure values calculated using Kretschmer-Wiebe model are in accordance with the experimental values. The extended form of Kretschmer-Wiebe model showed little improvement over the original form, even for systems where solvation was expected to be important.

#### 6.2 Recommendations

The apparatus designed by Van Ness was used to determine the vapor-liquid equilibrium data for the present study. There could be possibly made some changes to give more efficient result

It took a long time to draw vacuum on the equilibrium cell. The pump used is a normal vacuum pump which may be the reason for this. An absorption pump can be used instead to make this process faster as it would draw vacuum at a good speed. Also while pumping the liquid into the equilibrium cell, it is possible that the pressure may increase suddenly if the valve is not opened. Pressure relief valves would be appropriate near the piston injectors.

A possible direction of research is to explore the ability to predict the association constant based upon an easily measured property such as boiling point. Additionally, building on the predictive ability of the association model, it would be of interest to know whether or not the P-x data for a ternary system comprised of the components used in this study could be predicted based on the binary information found here.

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## **APPENDICES**

## Appendix I: Computer Programs for Binary Regression and Prediction of Data

Program 1: To calculate the regressed values of the chloroform (1) and 2-ethoxyethanol (2) system when  $K_{12}=0$  and  $K_{22}$  constant using the Kretschmer-Wiebe model.

```
%regression using K12=0 AND K22 constant  
function f=regress7(z)
```

```
P1s=32.403; %saturated pressure of chloroform(kPa)  
P2s=0.9838; %saturated pressure of 2-ethoxyethanol  
K22=55.8177;  
beta12=z(1);  
P=[ 1.3956 1.9875 2.834 5.235 7.021 8.474 9.954 11.792 13.787  
15.833 17.892 17.761 19.740 21.708 23.530 25.238 26.809 28.284  
29.645 30.749 31.520 ]; %total pressure values
```

```
x1=[ 0.0302 0.0630 0.1050 0.2042 0.2651 0.3094 0.3511 0.3995  
0.4497 0.4997 0.5496 0.5487 0.5980 0.6486 0.6985 0.7484 0.7985  
0.8486 0.8987 0.9390 0.9691]; %mol fraction
```

```
n=21;  
B11=-1143;%(cm3/mol)  
B22=-3584;  
B12=-1342;  
del12=2*(B12-B11-B22);  
T=303.15; %temperature at which reaction takes place  
R=8314; %universal gas constant  
RR=8.314;  
V1L=81.01; %molar volume of chloroform  
V2L=97.833; %molar volume of 2-ethoxyethanol  
V=40.9; %molar volume of methanol  
r1=V1L/V;  
r2=V2L/V;  
K12=0;
```

```
for a=1:n; x2(1,a)=1-x1(1,a);
```

Appendix I. (Continued)

eta1(1,a)=(r1\*x1(1,a))/((r1\*x1(1,a))+(r2\*x2(1,a)));      %volume  
fraction of hexane

eta2(1,a)=(r2\*x2(1,a))/((r1\*x1(1,a))+(r2\*x2(1,a)));      %volume  
fraction of ethoxyethanol

C11(1,a)=eta1(1,a)/r1;  
J(1,a)=(K22\*eta2(1,a))/r2;  
G(1,a)=(2\*(eta2(1,a)/r2)\*(K22^2));  
Z=2\*((K22^2)/r2);

C21(1,a)=((1+(2\*J(1,a)))-sqrt(1+(4\*J(1,a))))/G(1,a);  
C210=(((1+(2\*K22/r2))-sqrt(1+(4\*K22/r2)))/Z);

E(1,a)=(C11(1,a)\*r1)/x1(1,a);  
F(1,a)=((1+(K12\*C11(1,a)))/(1-(K22\*C21(1,a))));  
V1(1,a)=(C21(1,a)/(x2(1,a)\*C210));

N1(1,a)=(((beta12\*r1)/(RR\*T))\*(eta2(1,a)^2));  
K1=C210/(1-(K22\*C210));  
S1(1,a)=(((beta12\*r2)/(RR\*T))\*(eta1(1,a)^2));  
gam1(1,a)=exp(log(E(1,a))+1-  
(r1\*(C11(1,a)+(C21(1,a)\*F(1,a))))+N1(1,a));  
gam2(1,a)=exp(log(V1(1,a))-(r2\*(C11(1,a)+(C21(1,a)\*F(1,a))-  
K1))+S1(1,a));  
phi1=1;  
phi2=1;  
Pold=0;

Pcalc(1,a)=(((gam1(1,a)\*x1(1,a)\*P1s)/(phi1))+((gam2(1,a)\*x2(1,a)\*  
P2s)/(phi2)));  
X=abs(((Pcalc(1,a)-Pold)/(Pcalc(1,a))));

temp\_Pcalc=Pcalc(1,a);

if X>0.0001

    indicator=1;

    while indicator==1

        Pold=temp\_Pcalc;

        y1=(((gam1(1,a)\*x1(1,a)\*P1s)/((phi1)\*temp\_Pcalc)));

Appendix I. (Continued)

```
y2=1-y1;
M=exp(((Pcalc(1,a))/(R*T))*(B11+((y2^2)*del12)));
N=exp((B11*P1s)/(R*T));
K=exp(((V1L)/(R*T))*(temp_Pcalc-P1s));
S=exp(((temp_Pcalc/(R*T))*(B22+((y1^2)*del12))));
L=exp((B22*P2s)/(R*T));
Q=exp((V2L/(R*T))*(temp_Pcalc-P2s));

phi1=M/(N*K);
phi2=S/(L*Q);

temp_Pcalc=(((gam1(1,a)*x1(1,a)*P1s)/phi1)+((gam2(1,a)*x2(1,a)*
P2s)/phi2));
X=abs((temp_Pcalc-Pold)/(temp_Pcalc));

if X<=0.0001
    indicator=0;
    temp_Pcalcx(1,a)=temp_Pcalc;
else
    indicator=1;

end
end
end
ggg=size(temp_Pcalcx);
rrr=size(P);
end
SOS=0;
for i=1:n
    SOS=(SOS+((temp_Pcalcx(1,i)-P(1,i))^2))

end
f=SOS;
```

Appendix I. (Continued)

Call file for the main program

```
z=[100]; %initial guess
```

```
z=fminsearch('regress7',z);  
z
```

Program 2: To calculate the regressed values of the chloroform (1) and 2-ethoxyethanol (2) system when  $K_{12}$  not equal to zero and  $K_{22}$  constant using the Extended Kretschmer-Wiebe model.

```
function f=regress4(z)
```

```
P1s=32.403; %saturated pressure of chloroform(kPa)  
P2s=0.9838; %saturated pressure of 2-ethoxyethanol  
K22=55.8177;  
beta12=z(1);  
K12=z(2);  
P=[ 1.3956 1.9875 2.834 5.235 7.021 8.474 9.954 11.792 13.787  
15.833 17.892 17.761 19.740 21.708 23.530 25.238 26.809 28.284  
29.645 30.749 31.520]; %total pressure values
```

```
x1=[ 0.0302 0.0630 0.1050 0.2042 0.2651 0.3094 0.3511 0.3995  
0.4497 0.4997 0.5496 0.5487 0.5980 0.6486 0.6985 0.7484 0.7985  
0.8486 0.8987 0.9390 0.9691]; %mol fraction
```

```
n=21;  
B11=-1143;%(cm3/mol)  
B22=-3584;  
B12=-1342;  
del12=2*(B12-B11-B22);  
T=303.15; %temperature at which reaction takes place  
R=8314; %universal gas constant  
RR=8.314;  
V1L=81.01; %molar volume of chloroform  
V2L=97.833; %molar volume of ethoxyethanol
```

Appendix I. (Continued)

```

V=40.9;    %molar volume of methanol
r1=V1L/V;

r2=V2L/V;

for a=1:n
    x2(1,a)=1-x1(1,a);
    eta1(1,a)=(r1*x1(1,a))/((r1*x1(1,a))+(r2*x2(1,a))); %volume
fraction of hexane
    eta2(1,a)=(r2*x2(1,a))/((r1*x1(1,a))+(r2*x2(1,a))); %volume
fraction of ethoxyethanol

    C1(1,a)=eta1(1,a)/r1;
    C2(1,a)=eta2(1,a)/r2;
    C11=C1(1,a);
    dev=1.0;
    while dev>0.0001
        Xn=1+(K12*C11);
        J=((2*K22*C2(1,a))+Xn);
        G=((4*K22*C2(1,a)*Xn)+(Xn^2));
        Z=(2*(C2(1,a))*(K22^2));
        C21=(J-sqrt(G))/Z;
        C11new=C1(1,a)/(1+((K12*C21)/(1-K22*C21)));
        dev=abs((C11new-C11)/C11);
        C11=C11new;
    end

    C210=(((1+(2*K22/r2))-sqrt(1+(4*K22/r2)))/((2*(K22^2))/r2));
    E=(C11*r1)/x1(1,a);
    F=(((1+(K12*C11))/(1-(K22*C21))));
    V1=(C21/(x2(1,a)*C210));

    N1=(((beta12*r1)/(RR*T))*(eta2(1,a)^2));
    K1=C210/(1-(K22*C210));
    S1=(((beta12*r2)/(RR*T))*(eta1(1,a)^2));
    gam1(1,a)=exp(log(E)+1-(r1*(C11+(C21*F)))+N1);
    gam2(1,a)=exp(log(V1)-(r2*(C11+(C21*F)-K1))+S1);
    phi1=1;
    phi2=1;
    Pold=0;
    X=10;

```

## Appendix I. (Continued)

```
while X>0.0001

Pcalc=(((gam1(1,a)*x1(1,a)*P1s)/(phi1))+((gam2(1,a)*x2(1,a)*P2s)/
(phi2)));
y1=(((gam1(1,a)*x1(1,a)*P1s)/((phi1)*Pcalc));
y2=1-y1;
M=exp(((Pcalc)/(R*T))*(B11+((y2^2)*del12)));
N=exp((B11*P1s)/(R*T));
K=exp(((V1L)/(R*T))*(Pcalc-P1s));
S=exp(((Pcalc/(R*T))*(B22+((y1^2)*del12))));
L=exp((B22*P2s)/(R*T));
Q=exp((V2L/(R*T))*(Pcalc-P2s));

phi1=M/(N*K);
phi2=S/(L*Q);

temp_Pcalcx(1,a)=Pcalc;

X=abs((Pcalc-Pold)/(Pcalc));

Pold=Pcalc;

end
ggg=size(temp_Pcalcx);
rrr=size(P);
end
SOS=0;
for i=1:n
    SOS=(SOS+((temp_Pcalcx(1,i)-P(1,i))^2))
end
f=SOS;

Call file for regress4

z=[104.5,30]; %initial guess

z=fminsearch('regress4',z);
z
```



Appendix I. (Continued)

Program 3: To determine the calculated pressure, vapor mole fraction and average pressure deviation for the chloroform (1) + 2-ethoxyethanol (2) system.(  $K_{12}=0$ )

```
P1s=32.403; %saturated pressure of chloroform(kPa)
P2s=0.9838; %saturated pressure of 2-ethoxyethanol
K22=55.8177;
beta12=-1666.8;
P=[ 1.3956 1.9875 2.834 5.235 7.021 8.474 9.954 11.792 13.787
15.833 17.892 17.761 19.740 21.708 23.530 25.238 26.809 28.284
29.645 30.749 31.520 ]; %total pressure values
```

```
x1=[ 0.0302 0.0630 0.1050 0.2042 0.2651 0.3094 0.3511 0.3995
0.4497 0.4997 0.5496 0.5487 0.5980 0.6486 0.6985 0.7484 0.7985
0.8486 0.8987 0.9390 0.9691]; %mol fraction
```

```
n=21;
B11=-1143;%(cm3/mol)
B22=-3584;
B12=-1342;
del12=2*(B12-B11-B22);
T=303.15; %temperature at which reaction takes place
R=8314; %universal gas constant
RR=8.314;
V1L=81.01; %molar volume of chloroform
V2L=97.833; %molar volume of ethoxyethanol
V=40.9; %molar volume of methanol
r1=V1L/V;
r2=V2L/V;
K12=0;
```

```
for a=1:n
```

```
    x2(1,a)=1-x1(1,a);
    eta1(1,a)=(r1*x1(1,a))/((r1*x1(1,a))+r2*x2(1,a)); %volume
fraction of hexane
    eta2(1,a)=(r2*x2(1,a))/((r1*x1(1,a))+r2*x2(1,a)); %volume
fraction of ethoxyethanol
```

Appendix I. (Continued)

```

C11(1,a)=eta1(1,a)/r1;
J(1,a)=(K22*eta2(1,a))/r2;
G(1,a)=(2*(eta2(1,a)/r2)*(K22^2));
Z=2*((K22^2)/r2);

C21(1,a)=(((1+(2*J(1,a)))-sqrt(1+(4*J(1,a))))/G(1,a);
C210=(((1+(2*K22/r2))-sqrt(1+(4*K22/r2)))/Z);

E(1,a)=(C11(1,a)*r1)/x1(1,a);
F(1,a)=(((1+(K12*C11(1,a)))/(1-(K22*C21(1,a)))));
V1(1,a)=(C21(1,a)/(x2(1,a)*C210));

N1(1,a)=(((beta12*r1)/(RR*T))*(eta2(1,a)^2));
K1=C210/(1-(K22*C210));
S1(1,a)=(((beta12*r2)/(RR*T))*(eta1(1,a)^2));
gam1(1,a)=exp(log(E(1,a))+1-
(r1*(C11(1,a)+(C21(1,a)*F(1,a))))+N1(1,a));
gam2(1,a)=exp(log(V1(1,a))-(r2*(C11(1,a)+(C21(1,a)*F(1,a))-
K1))+S1(1,a));
phi1=1;
phi2=1;
Pold=0;

Pcalc(1,a)=(((gam1(1,a)*x1(1,a)*P1s)/(phi1))+((gam2(1,a)*x2(1,a)*
P2s)/(phi2)));
X=abs(((Pcalc(1,a)-Pold)/(Pcalc(1,a))));

temp_Pcalc=Pcalc(1,a);
if X>0.0001
    indicator=1;

    while indicator==1

        Pold=temp_Pcalc;
        y1=(((gam1(1,a)*x1(1,a)*P1s)/((phi1)*temp_Pcalc));
        y2=1-y1;
        M=exp(((Pcalc(1,a))/(R*T))*(B11+((y2^2)*del12)));
        N=exp((B11*P1s)/(R*T));
        K=exp(((V1L)/(R*T))*(temp_Pcalc-P1s));
        S=exp(((temp_Pcalc/(R*T))*(B22+((y1^2)*del12))));

```

Appendix I. (Continued)

```
L=exp((B22*P2s)/(R*T));
Q=exp((V2L/(R*T))*(temp_Pcalc-P2s));

phi1=M/(N*K);
phi2=S/(L*Q);

temp_Pcalc=((((gam1(1,a)*x1(1,a)*P1s)/phi1)+((gam2(1,a)*x2(1,a)*
P2s)/phi2));
X=abs((temp_Pcalc-Pold)/(temp_Pcalc));

if X<=0.0001
    indicator=0;
    temp_Pcalcx(1,a)=temp_Pcalc;
else
    indicator=1;

end
end
end
if X<=0.0001
    indicator=0;
    out_phi1(a,1)=phi1;
    out_phi2(a,1)=phi2;
    out_Pcalc(a,1)=temp_Pcalc;
    out_y1(a,1)=y1;

else
    indicator=1;

end
end
sum_delp=0;
for i=1:n

    output(i,1)=x1(i);
    output(i,2)=P(i);
    output(i,3)=out_Pcalc(i,1);
    output(i,4)=out_y1(i,1);
    output(i,5)=output(i,2)-output(i,3);
```

Appendix I. (Continued)

```
sum_delP=sum_delP+abs(output(i,5));  
  
end  
  
avg_delP=(sum_delP/n);  
disp('output using regressed values')  
disp('  x1    P    Pcalc    y1    delP')  
disp([output])  
avg_delP
```

Program 4: To determine the calculated pressure, vapor mole fraction and average pressure deviation for the chloroform (1) + 2-ethoxyethanol (2) system. (  $K_{12}$  not equal to zero )

```
P1s=32.403; %saturated pressure of chloroform(kPa)  
P2s=0.9838; %saturated pressure of 2-ethoxyethanol  
K22=55.8177;  
beta12=-1400;  
K12=1.8;  
P=[ 1.3956 1.9875 2.834 5.235 7.021 8.474 9.954 11.792 13.787  
15.833 17.892 17.761 19.740 21.708 23.530 25.238 26.809 28.284  
29.645 30.749 31.520]; %total pressure values  
  
x1=[ 0.0302 0.0630 0.1050 0.2042 0.2651 0.3094 0.3511 0.3995  
0.4497 0.4997 0.5496 0.5487 0.5980 0.6486 0.6985 0.7484 0.7985  
0.8486 0.8987 0.9390 0.9691]; %mol fraction  
  
n=21;  
B11=-1143;%(cm3/mol)  
B22=-3584;  
B12=-1342;  
del12=2*(B12-B11-B22);  
T=303.15; %temperature at which reaction takes place  
R=8314; %universal gas constant  
RR=8.314;  
V1L=81.01; %molar volume of chloroform  
V2L=97.833; %molar volume of ethoxyethanol  
V=40.9; %molar volume of methanol
```

Appendix I. (Continued)

r1=V1L/V;

r2=V2L/V;

for a=1:n

    x2(1,a)=1-x1(1,a);

    eta1(1,a)=(r1\*x1(1,a))/((r1\*x1(1,a))+(r2\*x2(1,a))); %volume  
fraction of hexane

    eta2(1,a)=(r2\*x2(1,a))/((r1\*x1(1,a))+(r2\*x2(1,a))); %volume  
fraction of ethoxyethanol

    C1(1,a)=eta1(1,a)/r1;

    C2(1,a)=eta2(1,a)/r2;

    C11=C1(1,a);

    dev=1.0;

    while dev>0.0001

        Xn=1+(K12\*C11);

        J=((2\*K22\*C2(1,a))+Xn);

        G=((4\*K22\*C2(1,a)\*Xn)+(Xn^2));

        Z=(2\*(C2(1,a))\*(K22^2));

        C21=(J-sqrt(G))/Z;

        C11new=C1(1,a)/(1+((K12\*C21)/(1-K22\*C21)));

        dev=abs((C11new-C11)/C11);

        C11=C11new;

end

C210=(((1+(2\*K22/r2))-sqrt(1+(4\*K22/r2)))/((2\*(K22^2))/r2));

E=(C11\*r1)/x1(1,a);

F=(((1+(K12\*C11))/(1-(K22\*C21))));

V1=(C21/(x2(1,a)\*C210));

N1=(((beta12\*r1)/(RR\*T))\*(eta2(1,a)^2));

K1=C210/(1-(K22\*C210));

S1=(((beta12\*r2)/(RR\*T))\*(eta1(1,a)^2));

gam1(1,a)=exp(log(E)+1-(r1\*(C11+(C21\*F)))+N1);

gam2(1,a)=exp(log(V1)-(r2\*(C11+(C21\*F)-K1))+S1);

phi1=1;

phi2=1;

Appendix I. (Continued)

```
Pold=0;
X=10;
while X>0.0001

Pcalc=(((gam1(1,a)*x1(1,a)*P1s)/(phi1))+((gam2(1,a)*x2(1,a)*P2s)/
(phi2)));
y1=(((gam1(1,a)*x1(1,a)*P1s)/((phi1)*Pcalc)));
y2=1-y1;

M=exp(((Pcalc)/(R*T))*(B11+((y2^2)*del12)));
N=exp((B11*P1s)/(R*T));
K=exp(((V1L)/(R*T))*(Pcalc-P1s));
S=exp(((Pcalc/(R*T))*(B22+((y1^2)*del12))));
L=exp((B22*P2s)/(R*T));
Q=exp((V2L/(R*T))*(Pcalc-P2s));

phi1=M/(N*K);
phi2=S/(L*Q);

temp_Pcalcx(1,a)=Pcalc;

X=abs((Pcalc-Pold)/(Pcalc));

Pold=Pcalc;

end
if X<=0.0001
    indicator=0;
    out_phi1(a,1)=phi1;
    out_phi2(a,1)=phi2;
    out_Pcalc(a,1)=Pcalc;
    out_y1(a,1)=y1;

else
    indicator=1;

end
end
sum_delP=0;
for i=1:n
```

Appendix I. (Continued)

```
output(i,1)=x1(i);
output(i,2)=P(i);
output(i,3)=out_Pcalc(i,1);
output(i,4)=out_y1(i,1);
output(i,5)=output(i,2)-output(i,3);
sum_delP=sum_delP+abs(output(i,5));
```

```
end
avg_delP=(sum_delP/n);
```

```
disp('output using regressed values')
disp('    x1    P    Pcalc    y1    delP')
disp([output])
avg_delP
```