The Thermodynamics of Liquids in Solution at 298 K and 1 atm

By

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ACKNOWLEDGEMENTS

The author gratefully makes the following acknowledgements:

- My supervisors, Professor Trevor Letcher and Professor Deresh Ramjugernath, under whose expert direction and support this work was carried out. I would like to thank them for the opportunities they have afforded me by taking me in as a student of theirs.

- Professor J. D. Raal, who is always a wealth of information and ideas

- The technical staff at The Departments of Chemistry and Chemical Engineering.

- My colleagues in the Department, Roger, Mark, Randhir, Daniel, Reshan, Kasuren, Prathika and Tyrone for their ideas and support.

- Mayesh Kasavan and Temple Road, without whom this would not have been possible.

- To my wife, Prevashni, for the making the past two years an absolute delight.

- To my late mom. Without you even the first would have been impossible

DEDICATION

For my family,
Daya, Shama, Sarika and Dylan.

"Work is a curse of the Drinking Class..." *Oscar Wilde*

Statement of Authorship

The work described herein was performed under the supervision of Professor T. M. Letcher in the Department of Chemistry and Professor D. Ramjugernath in the Dept. of Chemical Engineering, at the University of Natal Durban. The work is original unless otherwise stated in the text and has not been previously submitted in any form in candidature for a degree to any tertiary institution.

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Acknowledgement of Submission

This work has been submitted by the author with the full acknowledgement and agreement of both Professor T. M. Letcher and Professor D. Ramjugernath of the University of Natal Durban.

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ABSTRACT

For many years the problem of separating aliphatic and aromatic compounds has been at the forefront of the petroleum and oil refining industries. This separation is often effected using liquid-liquid extraction or extractive distillation. Both of these processes require the addition of a solvent to bring about separation.

The aims of this work were to investigate the use of "mixed" solvents, such as those used in the Arosolvan process, for their application in liquid-liquid extraction and extractive distillation as well as to provide related thermodynamic data for systems containing mixed solvents. In the last part of this work, a computer program was developed to theoretically predict the effectiveness of a number of solvents on a user-defined separation.

The solvents used for liquid-liquid extraction were chosen based on their similarities to those in the Arosolvan process and were of the form, {N-methyl-2-pyrollidone (NMP) + glycerol, a glycol or water} where the glycol was either monoethylene glycol (MEG), diethylene glycol (DEG) or triethylene glycol (TEG). The additives were combined in various mixing ratios to NMP to determine a mixing ratio for which the effect of the solvent is possibly optimized (a list of all solvents and mixing ratios used are presented in this work).

Solvent selectivity and the range of compositions over which separation could occur determined the effectiveness of the solvents. This work dealt with the separation of *n*-hexane and toluene. In order to determine the selectivity and range of compositions, the liquid-liquid equilibria (LLE) of systems containing *n*-hexane + toluene + solvent had to be determined. LLE was measured using a simple equilibrium cell at 298 K and 1 atm. The phase separation boundaries (binodal curves) were determined using a titration method.

The results obtained in this work showed an increase in the range of compositions over which the mixture of *n*-hexane and toluene could be separated (i.e a larger range of mixing ratios over which these components could be separated from each other) from the pure NMP solvent to the mixed solvent cases. This implies that there is a The range of compositions over which separation could be affected is given (for the solvents) in descending order:
NMP + 50% glycerol > NMP + 10% water > NMP + 30% MEG > NMP + 5% water > NMP + 30% glycerol > NMP + 10% glycerol > NMP + 10% MEG > NMP + 10% DEG > NMP + 10% TEG > NMP + 5% DEG > 100% NMP.

The selectivities of the solvents showed a remarkable increase from the pure NMP case to the mixed solvent cases. The maximum selectivity obtained for the NMP + 10% DEG system was over 1200 compared to a maximum selectivity of just 6 for the pure NMP system. The maximum selectivities obtained in descending order were as follows:
NMP + 10% DEG > NMP + 10% TEG > NMP + 10% glycerol > NMP + 10% MEG > NMP + 30% MEG > NMP + 50% glycerol > NMP + 10% water > NMP + 5% water > NMP + 30% glycerol > NMP + 5% DEG > 100% NMP.

The binodal curves were modelled using the Hlavaty, β-density and log-γ functions. The maximum standard deviations obtained were 0.075, 0.078 and 0.05 for each of the functions respectively. The equilibrium data was modelled using the UNIQUAC and NRTL thermodynamic models and showed excellent agreement. This work showed better agreement to the NRTL functions due to the fact that the non-randomness parameter, α_{ij}, may be chosen arbitrarily.

The results obtained in this work indicate that the use of mixed solvents greatly increases the effectiveness of NMP used for the separation of *n*-hexane and toluene. It is suggested that further studies be performed on a wider range of aliphatic and aromatic compounds in order to determine whether this is a generic behaviour or just true for *n*-hexane and toluene.

The effectiveness of each solvent for extractive distillation was determined by its separation factor. In order to determine separation factors, the activity coefficients at infinite dilution (IDACs) had to be measured. This was done using a gas-liquid chromatography technique. The solvents employed in this study were NMP, Glycerol, MEG, TEG, NMP + 10% glycerol, NMP + 10% MEG, NMP + 10% DEG, NMP + 10% TEG. The solutes used were: pentane, heptane, hexane, toluene and benzene.

The separation factors were determined for each alkane/aromatic pair per solvent. The pure solvent cases were then compared to the mixed solvent cases. The mixed solvents did not show results as promising for extractive distillation applications as they did for liquid-liquid extraction. TEG displayed the best selectivities for each of the alkane/aromatic separations except for the heptane/benzene pair, for which NMP + 10% glycerol proved to be the most effective solvent.

When compared to the results obtained from the original UNIFAC model, the IDACs obtained in this work showed up to a 99% deviation. This is due to the fact that the model does not work well for all types of molecules and does not predict the equilibrium of "unlike" molecules adequately.

It is suggested that other mixing ratios and different solvents be used to further investigate the effectiveness of mixed solvents for extractive distillation applications. It is further recommended that a computer aided data logging system be developed to determine residence times. This would not only provide more accurate results, but also provide a database for future reference.

The computer program that was developed using the original UNIFAC method contains a database of 28 commonly used industrial solvents. This program enables the user to compare graphically the effectiveness of each of the solvents on the desired separation. Due to the limitations of the original UNIFAC method, the program does not work well for all types of molecules. However, the model can be changed without altering the programming structure to include a modified version of the UNIFAC model depending on the users needs. The program although written from an extractive distillation standpoint can be extended to include liquid-liquid equilibrium predictions. The main benefit of such a program is to eliminate time-consuming experimental work required to narrow down a long list of solvents required for a particular separation by theoretically predicting the best solvents for the job. The solvent database can also be expanded when new solvents become available or the user needs change.

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LIST OF SYMBOLS

A = coefficient of Hlavaty Equation

B = coefficient of β function

C = coefficient of log-γ function

G = expression in NRTl equation (see Equation 2-17)

g = interaction parameter in NRTL (Equation 2-17)

M = molecular weight of i (unless otherwise defined)

n = number of data points

q = area parameter of component i used in UNIQUAC (Equation 2-23)

r = volume parameter of component i used in UNIQUAC (Equation 2-23)

R = universal gas constant = 8.314 $J.mol^{-1}$

$rmsd$ = root mean squared deviation

T = temperature

u = interaction parameter used in UNIQUAC equation (Equation 2-24)

v = liquid molar volume of

V = molar volume of component

x_i = mole fraction of component i

x_{ij} = mole fraction of i in j rich phase

x_{I}^{0} = mole fraction of n-alkane on x2=0 axis

x_{II}^{0} = mole fraction of n-alkane on x2=0 axis

x'_i = mole fraction of i in light phase

x''_i = mole fraction of i in the heavy phase

X = mass fraction

X_{ij} = mass fraction if i in j rich phase

z = coordination number used in UNIQUAC equation (Equation 2-23)

α = nonrandomness parameter used in NRTL equation (Equation 2-19)

σ = standard deviation

γ = activity coefficient

φ = volume fraction of component

Λ = parameter in Wilson equation (Equations 2-11, 2-12)

λ = interaction energy in Wilson equation (Equations 2-11, 2-12)

τ = parameter in NRTL equation (Equation 2-17)

= parameter in UNIQUAC equation (Equation 2-22)

*τ_{ij} has a different meaning in these two equations

ϑ = area fraction of component i

ln = natural logarithm

exp = exponential

Superscripts

C = combinatorial part of activity coefficient

E = excess quantity

L = liquid phase

R = residual part of activity coefficient

Subscripts

calc = calculated

exp = experimental

i, j, k, l, n = component i,j,k,l,n

CHAPTER
ONE

1. INTRODUCTION

1.1 Introduction

In this investigation, the separation potential of aromatic compounds from aliphatic compounds was undertaken. Liquid-liquid extraction involves the formation of two liquid phases by addition of a substance known as a solvent. Extractive distillation involves the addition of a solvent to a liquid mixture in order to alter the relative volatilities which enables a more efficient separation via distillation methods. Each technique is widely used in industry as revised by Lo *et al* [1982] and Seader and Henley [1998].

The selection of solvents is based on the selectivity or separation factor of the solvent. The selectivity and separation factor are a measure of the solvent's ability to separate components from one another in a binary or ternary mixture. In the case of liquid-liquid extraction the selectivity, S, is calculated from the weight fractions of the components at equilibrium:

$$S=\frac{\left[(\textit{weight fraction of component } 2)\big/(\textit{weight fraction of component } 1)\right]_{PHASE\ 1}}{\left[(\textit{weight fraction of component } 2)\big/(\textit{weight fraction of component } 1)\right]_{PHASE\ 2}} \tag{1-1}$$

where phases 1 and 2 represent the solvent-rich phase and the alkane-rich phase respectively, which are found at equilibrium. Component 1 refers to the aliphatic compound and component 2 refers to the aromatic compound (Letcher and Deenadayalu [1999]).

In the case of extractive distillation, the separation factor, β is calculated from the infinite dilution activity coefficients:

$$\beta=\frac{\gamma_i^{\infty}}{\gamma_j^{\infty}} \tag{1-2}$$

where γ_i^{∞} and γ_j^{∞} are the infinite dilutions activity coefficients of components i and j respectively (Perry and Green [1984]).

This thesis is divided into three parts, which reflect the three ways of approaching the prediction of the separating of aliphatic compounds from aromatic compounds.

a) **Liquid-liquid Extraction.** Since the adoption of liquid-liquid extraction as a separation technique towards the end of the nineteenth century, many industries have employed this technique as a means of separating the constituents of liquid mixtures. In the early days, the petroleum industry used liquid extraction as a means of refining kerosenes and from this beginning, developed a wide range of other extraction operations for hydrocarbon processing (Thornton [1992]). Liquid-liquid extraction is a process for separating components in solution by distributing them between two immiscible phases. This distribution or separation is effected by the addition of a third component to the liquid mixture. The third component may be a pure component or a mixture of constituents and is known as the solvent. The components that are to be separated from one another are known as the solutes (Seader and Henley [1998]). This process is often referred to in industry as solvent extraction (Lo *et al* [1982]). This method of extraction differs from other classical methods of separation in that it does not require the addition of large amounts of energy to achieve separation, for example: distillation requires the use of heat to produce a vapour phase; crystallization requires a cooling process to precipitate the solid phase. The implication of these energy considerations is that it could be far more economical to run a solvent extraction process as opposed to a distillation process. A disadvantage of solvent extraction is that the solvent needs to be separated (usually by distillation) after the solute in the final stage.

Separation by liquid-liquid extraction can be performed when the ratio or solubilities of the components to be separated, vary between the two phases, which are formed through the addition of the solvent. The simplest type of separation that can be performed is the use of a solvent to separate a binary mixture of liquids. This is similar to stripping or an adsorption step in distillation where mass is transferred from one phase to another (Scheitzer [1979]).

The success of a liquid-liquid extraction process is strongly dependant on the selection of the most appropriate solvent. The final choice of solvent will be a compromise between the properties, viz. selectivity, solvent capacity, cost of solvents, toxicological constraints, physical properties of the solvent and solutes and solvent recovery considerations (Perry and Green [1984]). These properties are discussed in Chapter 2 in greater detail. However, the most important solvent property is its ability to separate one component from the other. This property is known as the solvent selectivity and is simply calculated using the weight ratios of components at equilibrium using equation (1-1)

b) **Extractive distillation.** Extractive distillation refers to those processes in which high-boiling solvent is added to a distillation column to alter the relative volatilities of components in the main feed to the column. The alteration of these relative volatilities is desired because of:

- ➢ Similarities in the vapour pressures of the feed components or
- ➢ The presence of an azeotrope

In extractive distillation, as in liquid-liquid extraction, solvent selection is based on their separation factors, β. Gerster, Gorto and Eklund [1960], in their evaluation of pentane-pentene separation showed that a convenient way of illustrating the effect of a solvent on relative volatilities of two key components is the ratio of the key components infinite dilution activity coefficients (IDACS). This ratio is known as the separation factor, (Perry and Green [1984]) and is calculated using equation (1-2).

The determination of these separation factors can be obtained directly from vapour-liquid equilibrium measurement using an equilibrium still (Perry and Green [1984]). This method, however, is time consuming and costly to screen large numbers of solvents. Gas-liquid chromatography (GLC) is a faster and simpler experimental method for determination of IDACS according to Perry and Green [1984].

c) **Computer Modelling:** A convenient way of predicting IDACS is by use of the UNIFAC computational model. Following on this, separation factors can be predicted using equation (1-2), as we have discussed earlier

In this project it was decided to develop software containing a database of commonly used industrial solvents so that a user could view the effectiveness of each solvent for a desired separation of *n* components. A huge advantage of this method of predicting IDACs is that it saves one time in having to set up large numbers of experiments. Another advantage of this is that one may build on to the solvent database, as many solvents as one wishes without changing the program structure.

1.2 Solvents Investigated

The solvent may be a single compound or a mixture of two or more constituents. In this project a series of "mixed solvents" were investigated for the separation of aromatic and aliphatic compounds. On investigation of the Arosolvan systems in the literature it was found that good separation was effected using mixed solvents containing NMP + a glycol. It was, however, found that the solvent glycerol was not used even though it bore similar physical and chemical properties to the other glycols employed. It was also noted that insufficient data on *N*-methyl-2-pyrrolidone (NMP) solvent mixtures existed. It was thus decided to determine thermodynamic properties of NMP + a solvent in these types of liquid mixtures.

The solvent mixtures consisted of {N-methyl-2-pyrrolidone (NMP) + glycerol, a glycol or water}, an *n*-alkane and an aromatic. NMP is a dipolar aprotic solvent that is used for separation of low molecular weight monocyclic aromatic compounds from petroleum feedstock. The most popular of these processes is the Arosolvan Process (Lo *et al* [1983]), which uses as its solvents, monoethylene glycol (MEG) or water, as a mixture with NMP.

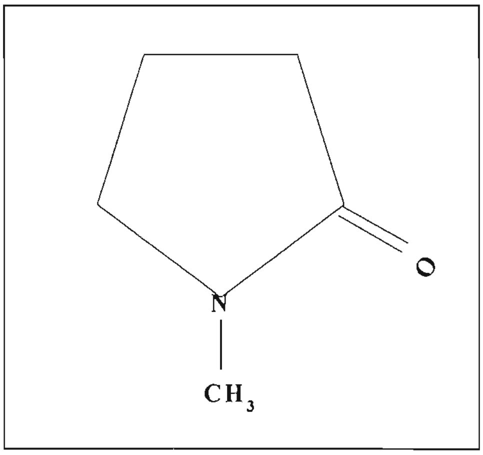
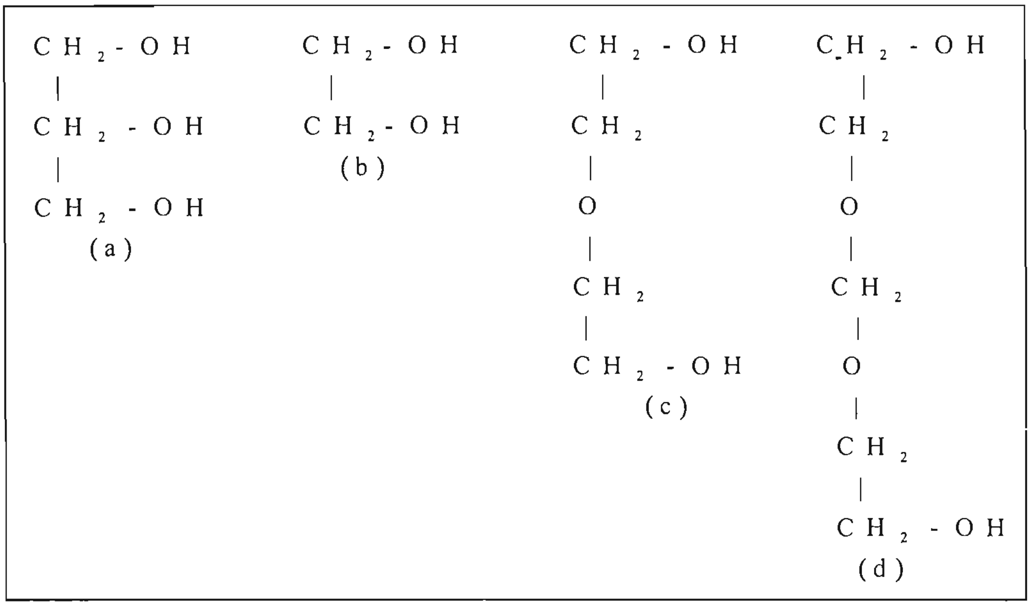


Figure 1-1: Structure of N-methyl-2-pyrrolidone (NMP)

The molecular structure of NMP is shown in Figure 1-1 above. NMP has many other uses and has been found to be an excellent dissociating solvent suitable for use in electrochemistry (Wuepper and Popov [1967], Dyke *et al* [1967], Breant [1971]). NMP has also been used as a dipolar aprotic medium for organic synthesis (Sowinski and Whitesides [1979]); as well as a solvent for the study of aromatic radicals and electron-transfer reactions using pulse radiolysis (Kadum *et al* [1986]). The polymer casting industry has also made use of NMP as a solvent (Guarino *et al* [1985]).

Over the years, NMP has proved to be an extremely important solvent in the solvent extraction industry.

The other solvents used in this analysis were chosen based on their similarities to the solvents used in the Arosolvan process, viz. MEG. The three polyhydroxy compounds, glycerol, diethylene glycol and triethylene glycol were chosen because of their structural (See Figure 1-2.) and physical similarities to monoethylene glycol, which proved to be so effective in the Arosolvan process.



$$\begin{array}{c} CH_2-OH \\ | \\ CH_2-OH \\ | \\ CH_2-OH \\ (a) \end{array} \qquad \begin{array}{c} CH_2-OH \\ | \\ CH_2-OH \\ (b) \end{array} \qquad \begin{array}{c} CH_2-OH \\ | \\ CH_2 \\ | \\ O \\ | \\ CH_2 \\ | \\ CH_2-OH \\ (c) \end{array} \qquad \begin{array}{c} CH_2-OH \\ | \\ CH_2 \\ | \\ O \\ | \\ CH_2 \\ | \\ O \\ | \\ CH_2 \\ | \\ CH_2-OH \\ (d) \end{array}$$

Figure 1-2: Structures of:

(a) glycerol, (b)monoethylene glycol (MEG), (c) diethylene glycol (DEG) (d) triethylene glycol (TEG)

Chapter 2 of this work deals with use of solvent extraction. The work made use of solvent mixtures of the type (NMP + a glycol), (NMP + glycerol) and (NMP + water) to separate an aliphatic compound (*n*-hexane) from an aromatic compound (toluene) were:. The pure NMP solvent was also investigated.

The study of extractive distillation contained in Chapter 3 employed solvents of the type (NMP + a glycol) or (NMP + glycerol) for the separation of aliphatic compounds (*n*-hexane, pentane and heptane) from aromatic compounds (toluene and benzene). The pure solvent NMP was also investigated along with glycerol, MEG and TEG and the effects were then compared to those results obtained from the mixed solvent cases.

The final part of this thesis (Chapter 4) deals with the simulation of extractive distillation systems using the UNIFAC group contribution methods. This program was written to incorporate a database of solvents commonly used in industry in order to compare the effects each have on a given separation. The aim of the program is to ultimately reduce the long hours spent on laboratory work narrowing down a list of solvents suited to a particular job.

CHAPTER

TWO

2. SELECTIVITY OF SOLVENTS LIQUID-LIQUID EQUILIBRIA

2.1 INTRODUCTION

In recent years, liquid-liquid extraction has been extensively used in industry for separation of aromatic and non-aromatic compounds. Several of these processes are discussed by Lo *et al* [1982]. It is often used as a precursor or cheaper alternative to distillation (Perry and Green [1984]).

In liquid-liquid extraction, a liquid feed of two or more components to be separated is contacted with a second liquid phase called the solvent. The solvent must be immiscible or only partially miscible with one or more components of the liquid feed and completely or partially miscible with one or more of the other components in the liquid feed. Thus the solvent which, is a single chemical species or a mixture (as in our case), partially dissolves certain components of the liquid feed, effecting at least a partial separation of the liquid feed. The components of the liquid feed are known as the solutes (Seader and Henley [1998]).

The success of a liquid-liquid extraction process is strongly dependent on the selection of the most appropriate solvent. Several properties govern the choice of a solvent for a particular separation. These properties were outlined by Perry and Green [1984] as follows:

(1) *Solvent selectivity.* The ability to separate or selectivity of a solvent is the mole (or mass)-ratio of two components in the extraction-solvent/solvent-rich phase divided by the mole-ratio of the same components in the feed-solvent/alkane-rich phase (see equation 2-27). The separation power of a solvent is governed by the deviation of the selectivity S from unity. A value of $S = 1$ gives no separation. A large or small value of S indicates good separation. (Perry and Green [1984])

(2) *Capacity.* This refers to the amount of solvent usage.

(3) *Toxicity.* Low toxicity from solvent-vapour inhalation or skin contact is preferred because of potential exposure during the repair of solvent extraction equipment, or if

connections in a plant are broken during solvent transfer. Also low toxicity to fish and bio-organisms is preferred when extraction is used as a pretreatment for wastewater before it enters a bio-treatment plant and with final effluent discharge to a stream or lake. (Perry and Green [1984])

(4) *Solvent solubility.* A low solubility of extraction solvent in the raffinate generally leads to a high relative-volatility in a raffinate stripper or a low solvent loss if the raffinate is not desolventized. A low solubility of feed solvent in the extract leads to a high relative separation and, generally, to low solvent-recovery costs. (Perry and Green [1984])

(5) *Recoverability.* The extraction solvent must generally be recovered from the extract stream and from the raffinate stream in an extraction process. Since distillation is often the preferred method for recovery, the relative volatility of the extraction-solvent to non-solvent components should be significantly greater or less than unity. A low latent heat of vapourisation is desirable for a volatile solvent. (Perry and Green [1984])

(5) *Range of Separation.* It is important that a solvent be able to separate a liquid-mixture over a large composition range.

However, the most important property for solvent selection is the solvent-selectivity, S. The value of S is obtainable directly from liquid-liquid equilibrium (LLE) results. It is therefore of vital importance to determine a systems liquid-liquid equilibrium before a solvent may be selected for a particular separation process (Ferreira *et al* [1984]).

Often, a solvent may prove more effective when it is mixture of two components as in the well-known Arosolvan Process (Mueller and Hoefeld [1971]), which uses *N*-methyl-2-pyrrolidone (NMP) mixed with a glycol or water as a solvent. Solvents of this nature have been studied with a great deal of interest (Somekh and Friedlander [1970], Rawat and Gulati [1976], Rawat and Prasad [1980], Nagpal and Rawat [1981], Lo *et al* [1982], Ferreira *et al* [1984], Naidoo and Letcher [2001]). Of particular interest to us is the work by Rawat and Prasad [1980], Nagpal and Rawat [1980], Ferreira, Barbosa and Medina [1984]). The work performed by them showed that mixed-solvent systems could be represented and modelled as "pseudo-ternary" systems.

Details of mixed solvent systems relevant to this work found in literature are given in Table 2-1 below. These systems include solvents that contain NMP, glycerol, a glycol or water as one of its constituents.

Solvent	**Solute**	**Raffinate**	**Reference**
NMP + monoethylene glycol	Heptane	Toluene	Lo *et al* [1993] Ferreira, Barbosa and Medina [1983]
NMP + water	Heptane	Benzene	Nagpal and Rawat [1980]
Tetraethyleneglycol + water	Heptane	Benzene	Rawat and Prasad [1980]
NMP + monoethylene glycol	Benzene + hexane	Toluene	Nagpal and Rawat [1980]
Monoethylene glycol +epsilon-carprolactam	Hexane	Toluene	Wisniak and Abraham [1984]
Monoethylene glycol + diethylene glycol monoethyl ether	Potassium carbonate	Water	Wisniak and Abraham [1984]
Monoethylene glycol + 1-methylnaphthalene	Methanol	Tetradecane	Wisniak and Abraham [1984]
Diethylene glycol + epsilon-carprolactam	Hexane	Benzene	Wisniak and Abraham [1984]
Diethylene glycol + epsilon-carprolactam	Toluene	Water	Wisniak and Abraham [1984]
NMP + monoethylene glycol	Benzene + hexane	Toluene	Nagpal and Rawat [1980]
Diethylene glycol + naphthalene	Heptane	Benzoylthiphene	Wisniak and Abraham [1984]
{Sulfolane + water}	Heptane	Benzene	Rawat and Prasad [1980]
{Triethylene glycol + water}	Heptane	Benzene	Rawat and Prasad [1980]

Table 2-1: Available data for systems with mixed solvents containing NMP, monoethylene glycol, diethylene glycol, triethylene glycol or glycerol

In order to compare the relative selectivities of the solvents, *n*-hexane and toluene were used as the aliphatic compound and aromatic compound respectively throughout each of the experiments. Table 2-2 lists the "pseudo-ternary" systems examined in this study.

Solvent	**Solute**	**Raffinate**
*NMP	*n*-hexane	Toluene
NMP + 10%(w/w) glycerol	*n*-hexane	Toluene
NMP + 30%(w/w) glycerol	*n*-hexane	Toluene
NMP 50%(w/w) glycerol	*n*-hexane	Toluene
NMP + (10%(w/w) Monoethylene glycol	*n*-hexane	Toluene -
NMP + 30%(w/w) monoethyleneglycol	*n*-hexane	Toluene
NMP + 5 %(w/w) diethyleneglycol	*n*-hexane	Toluene
NMP + 10%(w/w) diethyleneglycol	*n*-hexane	Toluene
NMP + 10%(w/w) triethyleneglycol	*n*-hexane	Toluene
NMP + 5%(w/w) water	*n*-hexane	Toluene
NMP + 10%(w/w) water	*n*-hexane	Toluene

*Test system previously published by Letcher and Naicker [1998]

Table 2-2: Systems for which liquid-liquid equilibria were determined at 298 K and 1 atm

The systems mentioned in Table 2-2 have not been measured previously unless otherwise stated. This Chapter extends the available literature data to include systems given in Table 2-2 and other available techniques for the measurement of liquid-liquid equilibrium data are discussed. The results obtained from measurements undertaken in this work are presented in later in this chapter.

The binodal curve data obtained in this work were modelled using the β, log-γ and Hlavaty equations. The results of the modelling are presented in Chapter 2.6.1 (page 32). The tie-line data obtained in this work were modelled using the UNIQUAC and NRTL equations and the results from the modelling are given in Chapter 2.6.2.

2.2 TERNARY LIQUID-LIQUID EQUILIBRIUM REPRESENTATION

Most ternary systems are obtained under isothermal conditions, and each set of data covers a range of ternary compositions. Such data sets are conveniently represented on triangular diagrams by use of either equilateral or right-angle triangles:

2.2.1 Equilateral Triangles

It is convenient to represent ternary systems by using triangular coordinates as shown in Figure 2-2-1. There are many different types of ternary systems. That exhibited in Figure 2-1 is of a Type I classification. For the various types of ternary systems refer to Chapter 2.2.3 (p 11) A property of an equilateral triangle is that the sum of the perpendicular distances from any point within the triangle to the three sides is equal to the altitude of the triangle. Hence, by letting the altitude represent 100% composition, any ternary composition may be represented by a point within the triangle (see Appendix A-1 for more detail).

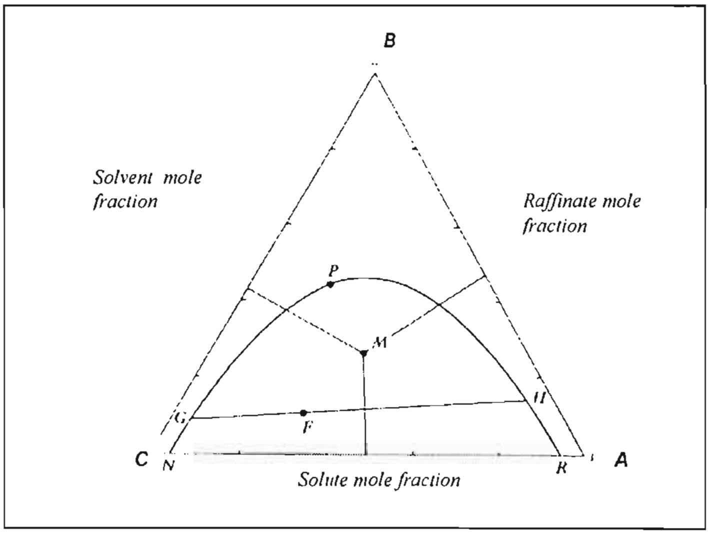


Figure 2-1: Equilateral triangle representation for ternary liquid-liquid equilibria

Referring to Figure 2-1; each corner of the triangle represents a pure component, defined as *A*, *B* or *C*. For a point within the triangle *M*, the perpendicular distance from *M* to base *BC* represents the amount of component *B* in the mixture. Similarly, the amounts of components *A* and *C* can be obtained by the perpendiculars from point *M* to bases *BC* and *AB* respectively. Any point on a side of the triangle represents a binary mixture. The curve *NPR* within the triangle represents the boundary of the two-phase region for this type of system. The various types of ternary systems are discussed below. The curve *NPR* is defined as the system binodal curve and is specific to one particular temperature. The line *GH* joining points on the binodal curve is defined as a tie-line and joins points representing the liquid phases in equilibrium. The limit of immiscibility is represented by point *P* and is defined as the "plait point". This point represents (theoretically) the point at which the two liquid phases at equilibrium have the same composition. As more of component B is added to the system, the tie-lines get shorter and as a result, the points in equilibrium get closer together. As the length of the tie-line diminishes to zero, the system becomes completely miscible.

2.2.2 Right Angle Triangles

An alternative to equilateral triangles is to use rectangular coordinates (right-angle triangles) as illustrated in Figure 2-2. The composition at point M is defined in the same way as for equilateral triangles, but the scales are not equal. For example, the binary mixture CA changes from 0 to 1.0 over the length AB which is equal to $(\sqrt{2})CA$. All other concepts and points are defined exactly as those for equilateral triangles. This method has been used previously (Ferreira, Ferreira and Medina [1983], Ferreira, Barbosa and Medina [1983]). This type of diagram is not in common use due to the unequal weighting of each of the components on the diagram.

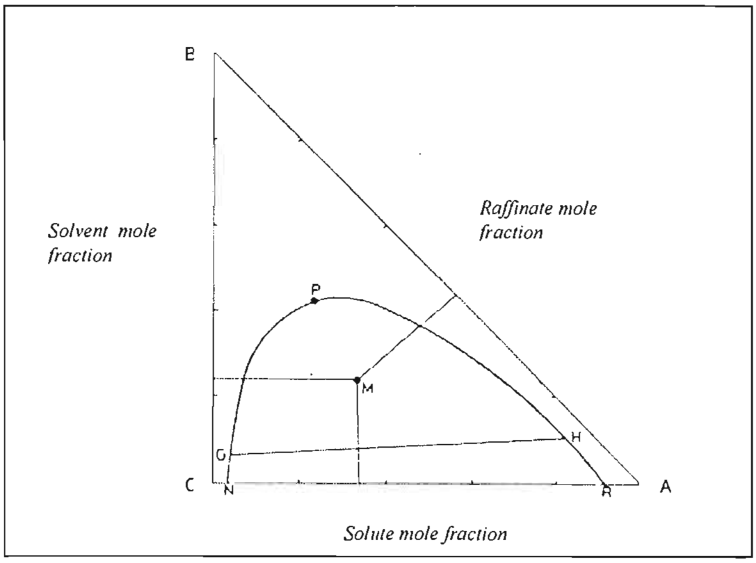


Figure 2-2: Rectangular coordinates for representation of ternary liquid-liquid equilibria.

2.2.3 Types of typical Ternary Systems

Ternary liquid-liquid systems have been divided into three types, which are dependant on the mutual solubility of the three constituent components (Thornton [1992]) Refer to Figures 2-3 and 2-3-1 for the three main types of ternary systems. In a type I system, one pair of components are partially miscible in each other, i.e. components A and C. In a system of type II, there exists two pairs of partially miscible components, A and C along with A and B. A type III system is one in which there are three pairs of partially miscible constituents, and three phases are present. The three vertices of the inner triangle represent the compositions of the three phases. If one applies the phase rule to such a system, it produces zero degrees of freedom at constant temperature and pressure and is called an invariant system.

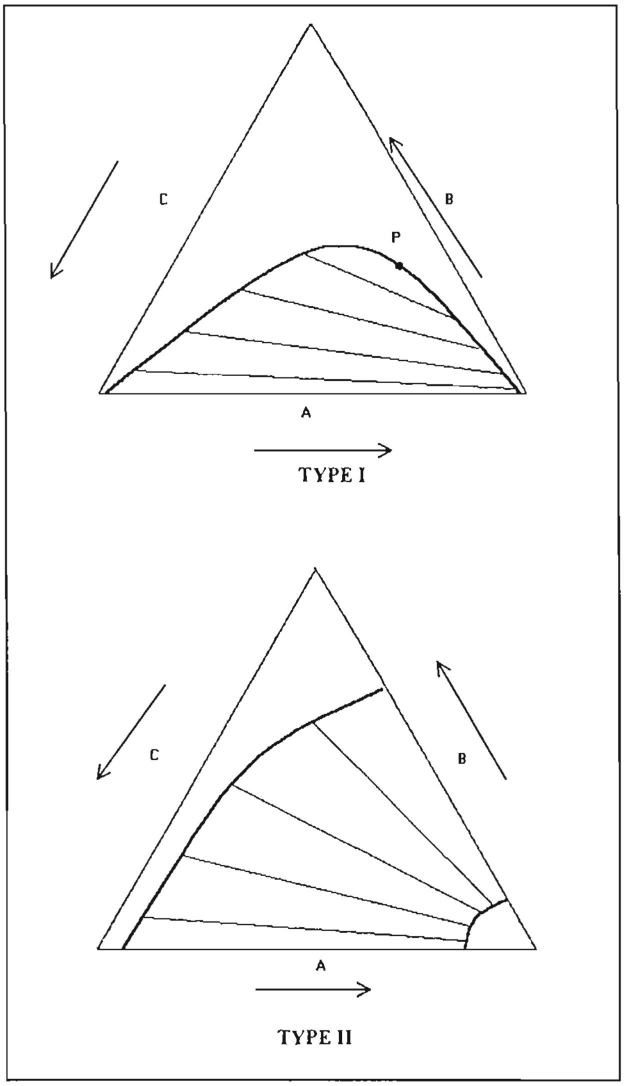


Figure 2-3: Types of triangular Ternary Phase Diagrams

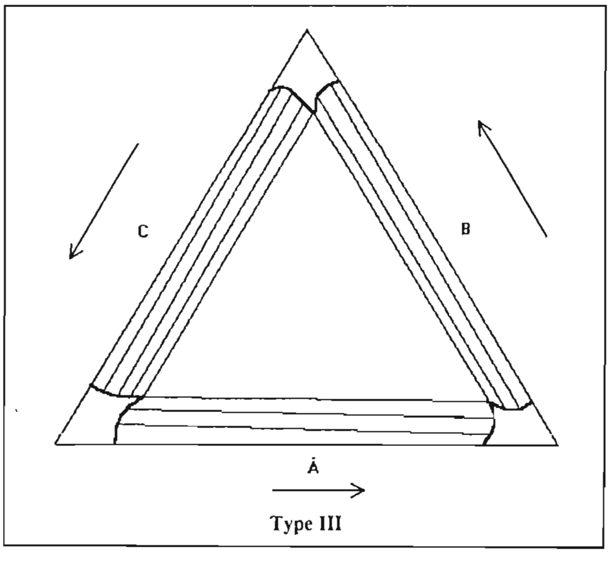


Figure 2-3 (*contd.*) : Types of triangular Ternary Phase Diagrams

2.3 AVAILABLE TECHNIQUES FOR DETERMINATION OF LIQUID-LIQUID EQUILIBRIUM DATA:

2.3.1 Cell Equilibration:

(See Figure 2-4)

This technique is a simple means of determining liquid-liquid equilibrium data. An equilibration cell is illustrated below in Figure 2-4. A small total volume of about 15-20ml is used (Lo *et al* [1983]). Due to the small mass of the solution, it is easy to maintain a constant temperature with by circulating a thermostatic fluid (usually water) inside the jacket surrounding the sample flask. In order to achieve complete phase equilibria, good mixing between the two phases is necessary. A magnetic stirrer at the bottom of the flask is used to achieve proper mixing. The purpose of vigorous agitation is to increase the contact area between the two phases. The mixture is then allowed to settle so that the two phases may separate (Lo *et al* [1983], Thornton [1998]). Once the phases are allowed to equilibrate for approximately 48 hours, samples from each phase are withdrawn via the septum using a syringe. These are then analyzed, usually by gas-chromatography. This procedure yields the full equilibrium data in terms of binodal curves and tie-lines (see Figure 2-5).

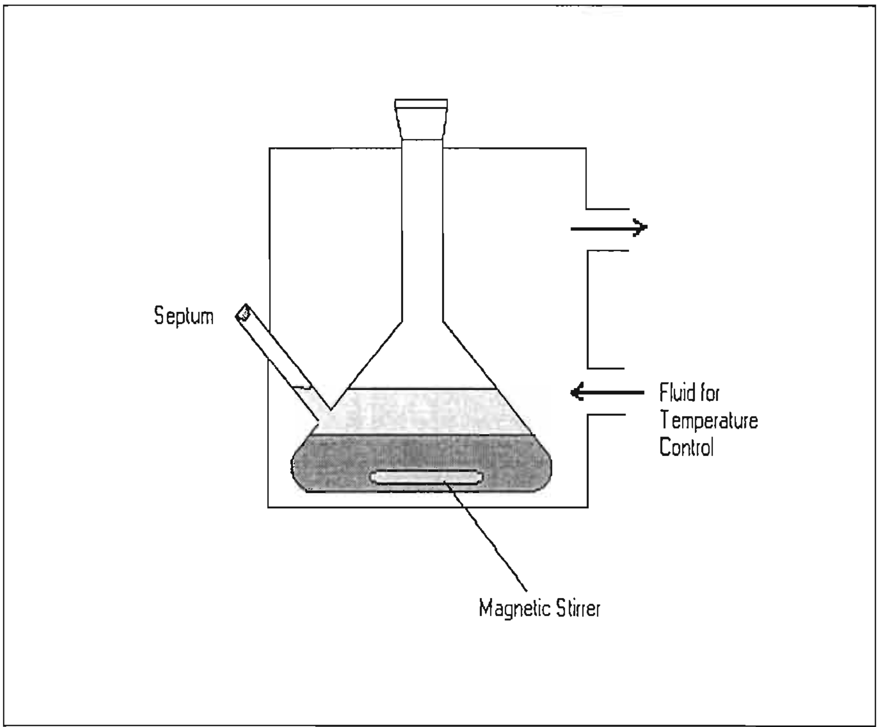


Figure 2-4: Simple Equilibration Cell for Liquid-liquid Equilibrium data.

By suitable choice of the overall composition charged to the cell, the full composition range can be covered. Once the tie-lines have been determined, it is then possible to draw the binodal curve, which is the locus of points indicating the solubility limits of the system.

An advantage of this technique is that it is relatively simple. This technique has a number of disadvantages though, as outlined by Newsham [1992]

- Equilibrium time may be long, although the problem is minimized by stirring.
- Settling times may be very long, especially if secondary dispersions (i.e. secondary phases within another phase) are formed or if the phases have similar densities.
- If the temperature of the experiment differs from ambient temperature, phase separation may occur on withdrawing of the sample for analysis.
- If a sample is stored prior to analysis, the vapour space of the sample bottle must be kept to a minimum since the composition of the vapour phase can be very different from that of the liquid.
- Entrainment of one phase may occur as a result of introducing the syringe needle into the system.

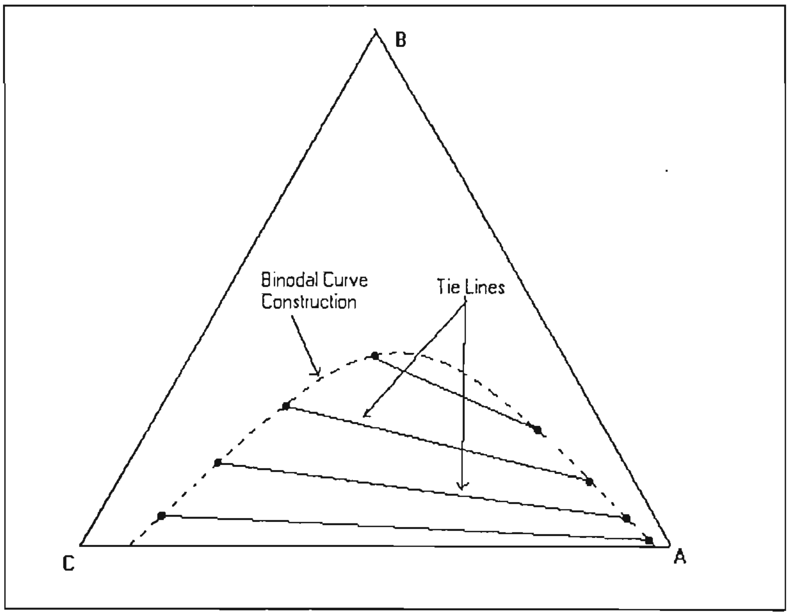


Figure 2-5: Tie-lines obtained from cell-equilibration method of analysis

A more sophisticated device for obtaining equilibrium data is the AKUFVE (Swedish acronym for "apparatus for continuous measurement of partition factors in solvent extraction") presented by Reindhardt and Rydberg [1969]. Davis *et al* [1976] have suggested a modification to this apparatus the measurement of systems displaying high phase ratios. The AKUFVE system is discussed later.

2.3.2 Titrimetry

Another simple technique for determination of ternary liquid-liquid equilibria exists that avoids use of expensive analytical equipment. It depends only on simple titration and material balances and has been described by Newsham and Ng [1972], Letcher *et al.* [1986] and Thornton [1992].

The method involves the determination of the systems solubility limits followed by the determination of the tie-lines (Alders [1959], Treybal [1963] and Francis [1963]). The determination of the binodal curve is done by titrating a mixture of known composition with a third component. The titration end-point is detected by the onset or disappearance of turbidity, depending on the starting mixture.

2.3.2.1 Determination of the binodal curve

(a) Binary mixture of known composition is prepared using two soluble components e.g. A and B (Figure 2-6). These compositions are indicated on side AB of the triangular phase diagram in Figure 2-5.

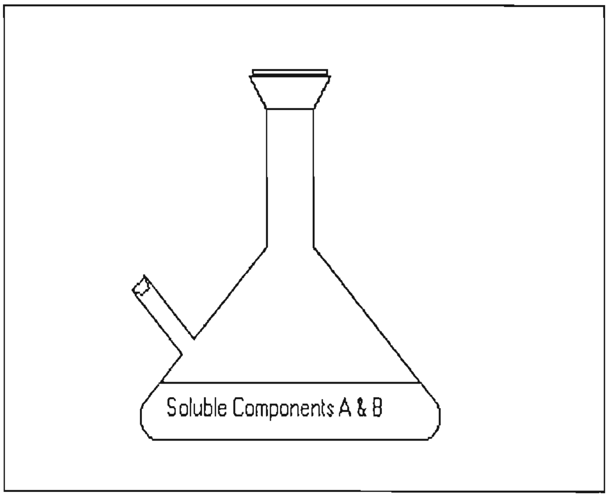


Figure 2-6: A binary mixture of A and B

(b) A known amount of a third component is added to the mixture of A and B until the onset of turbidity or murkiness. This indicates the formation of a second liquid phase. This is illustrated diagrammatically in Figure 2-7 overleaf.

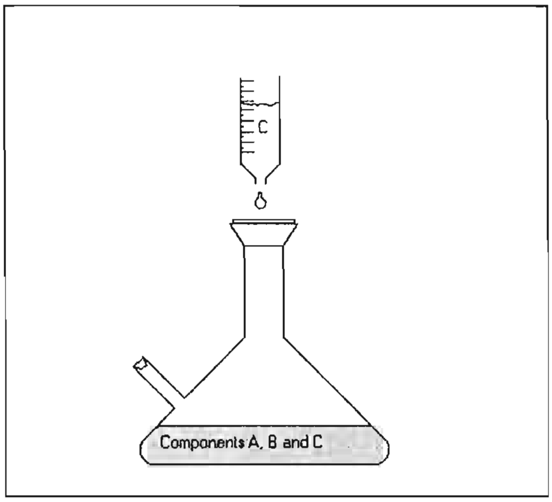


Figure 2-7: Formation of a turbid mixture on addition of a third component.

Figure 2-8 indicates graphically, the path of the titrations, on a triangular phase diagram. Side AB of the triangle consists only of mixtures of components A and B as in step (a) above. Upon titration, the liquid mixture then moves into the ternary region of the diagram, until the onset of turbidity, which is also known as the titration end-point. This end-point indicates the formation of the second phase and the locus of these points is called the solubility or binodal curve. For compositions near the C-rich region, binary mixtures of C and B are titrated with component A.

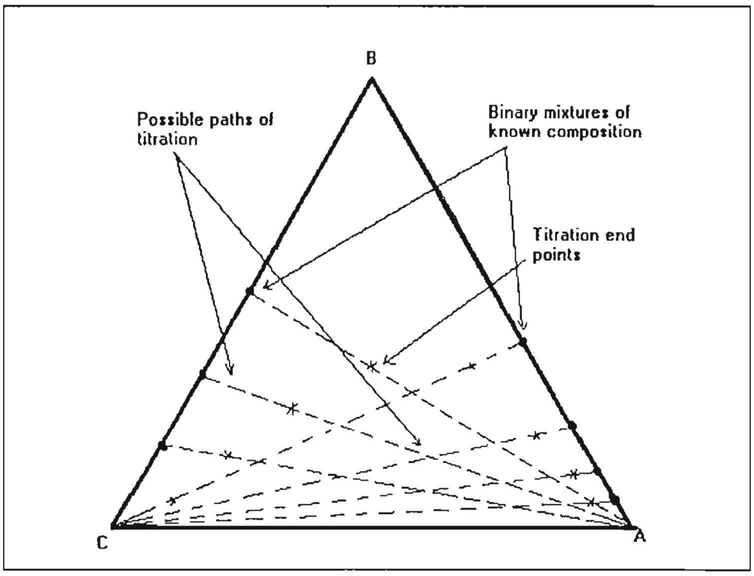


Figure 2-8: Graphical representation of the titration method of determining the binodal curve for a ternary system

2.3.2.2 Determination of tie-lines from the titration method:

Once the binodal curve has been found, it is then possible to determine the position of the tie-lines and the plait-point. Tie-lines are lines on the triangular phase diagram that join compositions of the two phases formed at equilibrium. The tie-lines are determined by preparing a mixture with a composition lying within the binodal curve (or two-phase region). Once this is done, the mixture is allowed to settle (or equilibrate). The two phases formed are then analyzed separately and the tie-lines can be constructed. It should be noted that the tie-lines must begin and end on the binodal curve and pass through the point of the original mixture composition. The use of this technique provides a useful check on the binodal curve.

The plait-point is a point where the phases formed at equilibrium have identical compositions. At this point, the value of the selectivity is exactly unity and no separation can be effected. Plait-points may be determined using the methods presented in Chapter 2.5.1.

The titration method does present a drawback when working with volatile components. If a volatile component is added to the liquid mixture, evaporation into the atmosphere occurs thereby creating an error in terms of the masses in the mixture. This problem was overcome by injecting the volatile component directly into the liquid mixture thereby minimizing evaporation leading to more accurate mass determination.

2.3.3 Equipment of Raal and Broukaert [1992]

Figure 2-9 represents the equilibrium cell that was used in the work of Raal and Broukaert [1992], for the measurement of binary liquid-liquid equilibria to obtain full data in terms or tie-lines and solubility limits. Raal and Broukaert employed a glass, stainless steel and Teflon equilibrium cell. This version of the equilibrium cell used a mechanical stirrer which was driven by a pulley from the to of the cell. The top of this cell was sealed using a Teflon block with O-ring fits as indicated in the diagram. Water is passed at a vigorous rate through the jacket of the cell, from a constant-temperature water-bath. The Teflon block was engineered such that the water used for temperature regulation passed through passages engineered into the block itself, thereby ensuring a highly isothermal environment. Temperature was monitored using a Pt-100 thermocouple. Sampling was carried out using a syringe inserted through a shaped aperture in the Teflon block end-piece. Temperature gradients are effectively eliminated using the Teflon block and water passages (this is important since liquid-liquid equilibrium data is relatively sensitive to temperature, particularly near the critical solution temperature). Raal and Broukaert [1992] measured the liquid-liquid equilibrium for the water/methyl-butanol system. A few of their data-points are presented in Raal and Muhlbauer [1998]. The apparatus used was relatively cost effective to construct and maintain and equilibrium was established in a short space of time. The onset or disappearance of turbidity, which indicates the formation of a second liquid phase, was based on the visual judgment of the user.

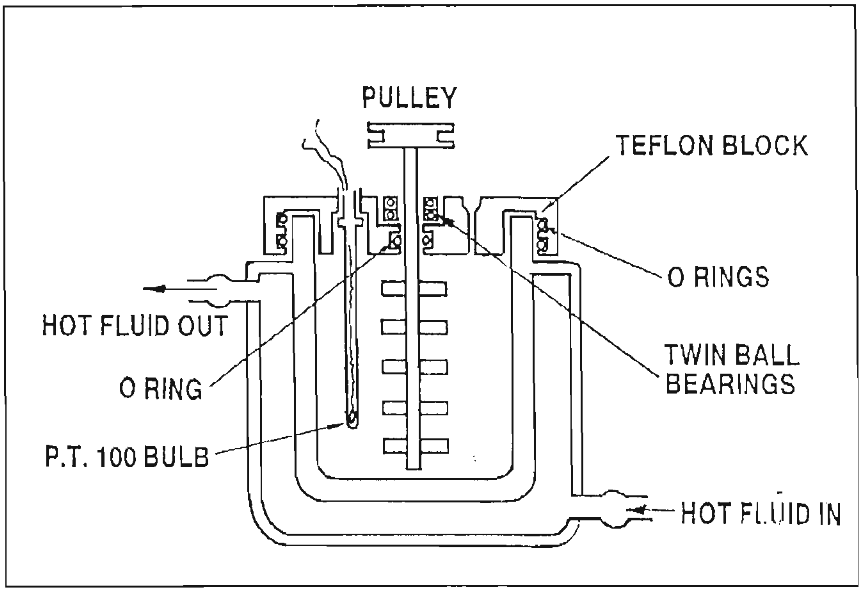


Figure 2-9: Equilibrium cell for direct measurement by Raal and Broukaert [1992]

2.3.4 Apparatus of Ochi et al [1993]

Ochi *et al* [1993] made provisions for minimizing or eliminating the uncertainty of the formation of a turbid solution by using a photocell. The photocell accurately detects the intensity or change in intensity of a primary light source or of scattered light. The equipment made use of a He-Neon laser light source and a selenium cell. Figure 2-10 represents a comprehensive picture of the apparatus.

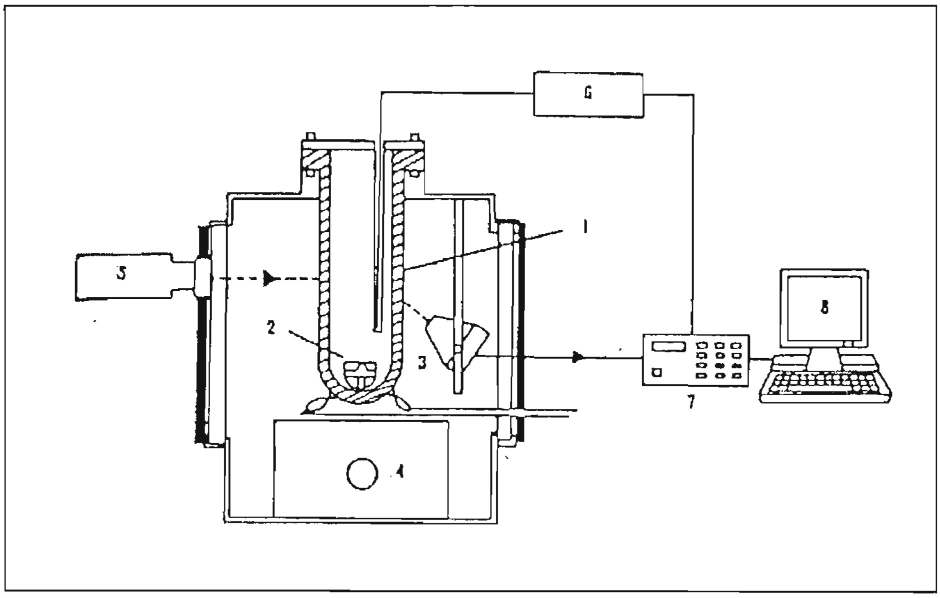


Figure 2-10: Apparatus of Ochi *et al* [1993]: (1) -Equilibrium vessel (pressure glass with film heater); (2) - stirrer; (3) -Light sensor (photocell); (4) - magnetic stirrer; (5) - Optical System (He-Neon laser); (6) - Thermometer; (7) - digital multimeter; (8) - personal computer.

An example of how to eliminate hte error of visual visual judgment was presented by Ochi *et al* [1993]. This apparatus produced very accurate data, including tie-lines and solubility data, up to and including the critical solution temperature (Raal and Mulhbauer [1998]). The systems for which liquid-liquid equilibria were measured are aniline + *n*-hexane and furfural + cyclohexane.

The method employed by Ochi *et al* was used for the determination of binary liquid-liquid equilibrium data but the concept could be used in the determination of ternary liquid-liquid equilibrium data.

2.3.5 The Rifai and Durandet Method [1962]

An extremely clever but simple method was developed by Rifai and Durandet [1962], which eliminated the need for determining the point at which turbidity is achieved. The method may be classified as a titration method, since known amounts of one substance were added to another. Figure 2-11 shows a schematic diagram of their apparatus. The method requires measurement of two phase volumes in a calibrated capillary column. The point of immiscibility is determined from the measured volumes and a linear plot of the volume of the second phase against the mass of the second component. A more comprehensive description of the procedure is given by Raal and Muhlbauer [1998].

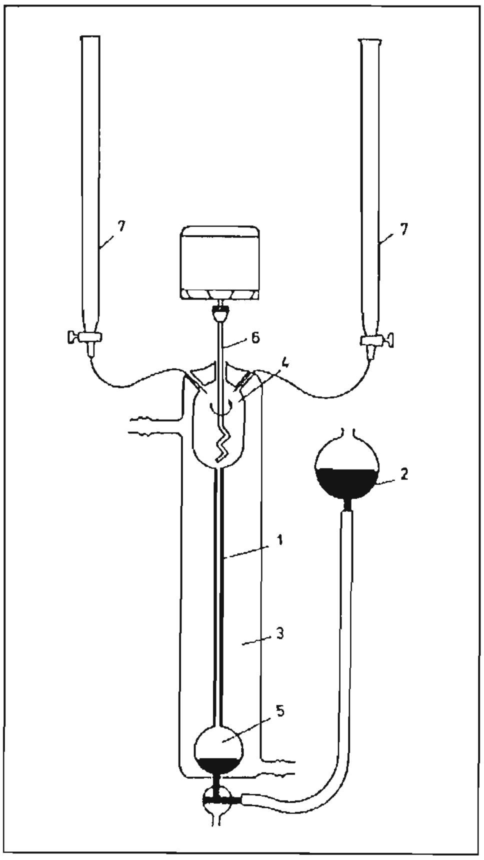


Figure 2-11: Apparatus for determining the phase separation point by method of Rifai and Durandt [1962]: (1) graduated capillary tube; (2) mercury stock bottle; (3) thermostatting tube; (4); (5) stock bottles; (6) stirrer; (7) micro-burettes.

This method has been extremely useful since the judgment of the point of turbidity is avoided by simple arithmetic and accurate measurement of volumes at a relatively low cost. The equipment however can be expensive to maintain due to the delicate nature of some of the glassware involved in the construction.

The experimental apparatus and procedures mentioned in Chapters 2.3.3 through 2.3.5 work well for the measurement of binary liquid-liquid equilibria as a function of temperature; however, they are not well suited for the measurement of ternary systems. Provisions for the measurement of ternary systems can be made by the introduction of a flow system. A flow system was designed by Reinhardt and Rydberg [1969] specifically for this purpose and is discussed in the preceding section.

2.3.6 Continuous Measurement: The AKUFVE System (Reinhardt and Rydberg [1969]).

The AKUFVE system shown in Figure 2-12 was used by Reinhardt and Rydberg [1969] for rapid determination of distribution and liquid-liquid equilibrium curves in a very short time (Lo *et al* [1982]). The two liquid phases were mixed in the mixing chamber and were separated into two outgoing pure phases in the centrifuge. Each phase passed the flow meter, sampling valve, and on-line detectors (spectrophotometers in an external loop) and was then returned by way of the heat exchanger to the mixing vessel. Chemical reagents were added to the mixing chamber when desired. The mixing chamber was of the dynamic stirrer type or static Kenics mixer (Anderson and Spink [1970]). The latter was used for short mixing times (<1s).

During sampling, usually 0.1 to 0.5ml was withdrawn at the sampling valve. For on-line measurements, they employed a radioactive tracer to detect the elements under investigation. The detector cell used could be a flexible rubber tube wound around a scintillation crystal, which was encased in a lead shield.

For on-line pH-measurement, combined glass electrodes, which were housed in a glass pocket, are used. The AKUFVE method employed two different models of centrifuge viz. the H-33 and the H-10 depending on the systems under investigation. A cutaway of the H-centrifuge is given in Figure 2-13. The H-10 centrifuge was preferred when the use of chemicals was expensive, dangerous, or otherwise undesirable (Reinhardt and Rydberg [1969]). The H-33 was easier to handle when one performed routine laboratory work; also, sampling removed a small fraction of the total liquid volume. Heat developed as a result of the acceleration and retardation of the liquids in the centrifuge; thus heat exchangers were necessary for constant-temperature work, especially with the H-33 centrifuge. The total liquid (both phases) volume of an AKUFVE system with the use of the H-33 was approximately 500ml, while the H-10 required only around 100ml.

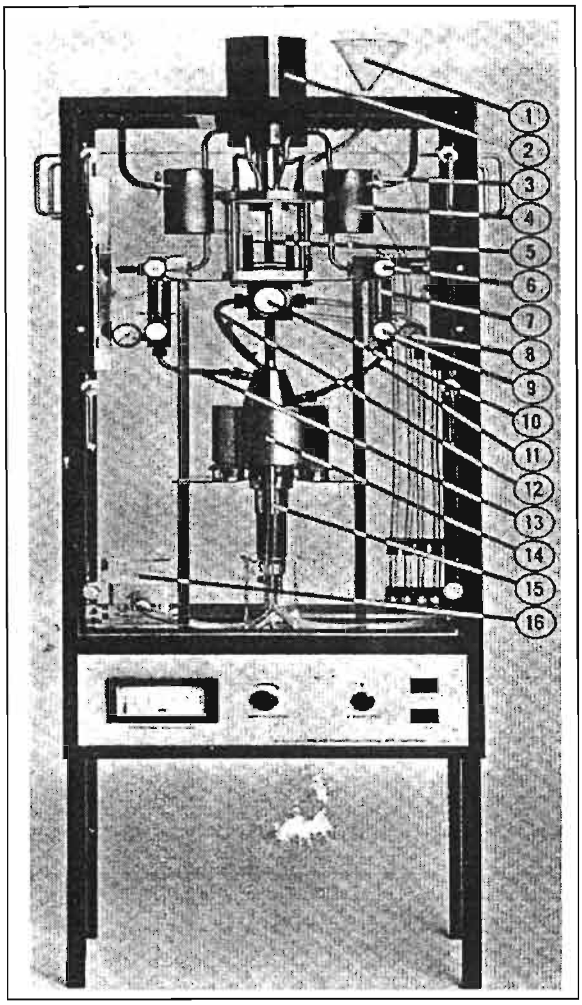


Figure 2-12: The AKUFVE system with H-33 centrifuge: (1) main feed inlet; (2) stirrer motor; (3) Sampling valve; (4) heat exchanger; (5) mixer; (6) valve to detector or mixer; (7) flow meter; (8) pressure gauge; (9) throttling valve; (10) valve "centrifuge-closed-drain" ; (11) centrifuge outlet, light phase; (12) centrifuge inlet; (13) centrifuge outlet, heavy phase; (14) centrifuge; (15) centrifuge (air) motor; (16)

2.3.6.1 Data Collection.

The primary purpose of the original AKUFVE system was to obtain accurate distribution data in a minimum amount of time. For the system shown in Figure 2-14, complete mixing equilibrium (not necessarily chemical equilibrium) is obtained within one minute. In order to measure the concentration of the species of interest in each phase, along with temperature, reagents added etc., as often as once per minute, a data logger was required (Anderson *et al* [1969], Anderson and Spink [1970]). When taking samples for external (or off-line) measurements, an operator could normally collect a sample of each phase in approximately 3 minutes (Lo *et al* [1982]). The data logger could be connected to an on-line computer (Reindhardt and Rydberg [1973]). Automatic burettes have been connected to the AKUFVE systems in more elaborate schemes. However, even in simple sampling for off-line measurements, the AKUFVE provides more exact data in a shorter time than seems achievable with simpler techniques (Lo *et al* [1982]).

The AKUFVE system made provision for the judgement error that occurs when determining the point of turbidity by employing the H-centrifuge. This occurred by way of the two phases separating as soon as they are formed. Equilibrium is attained in extremely short time and the data obtained are very accurate (Lo *et al* [1983]). The accuracy obtained was usually greater than 1% and has made the AKUFVE system useful for the determination of equilibrium constants (Liljenzin and Stary [1970], Spink and Okuhara [1974], Allard *et al* [1974]) and thermodynamic constants (Allard *et al* [1974], Liljenzin *et al* [1969], Flett and Spink [1977], Rydberg [1974]).

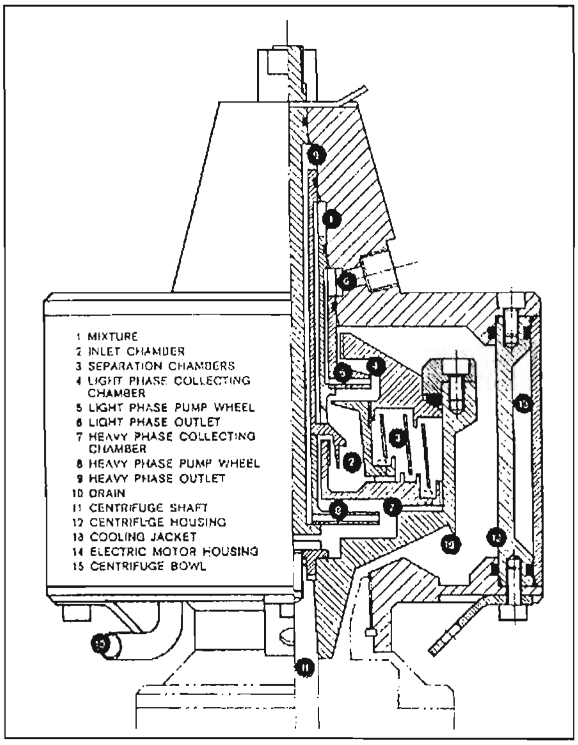


Figure 2-13: Cutaway of the H- centrifuge.

The systems measured by the AKUFVE method are too many to mention (Lo *et al* [1983]). The systems concerned were measured mainly in the interest of the separation of aromatic compound from non-aromatic compounds.

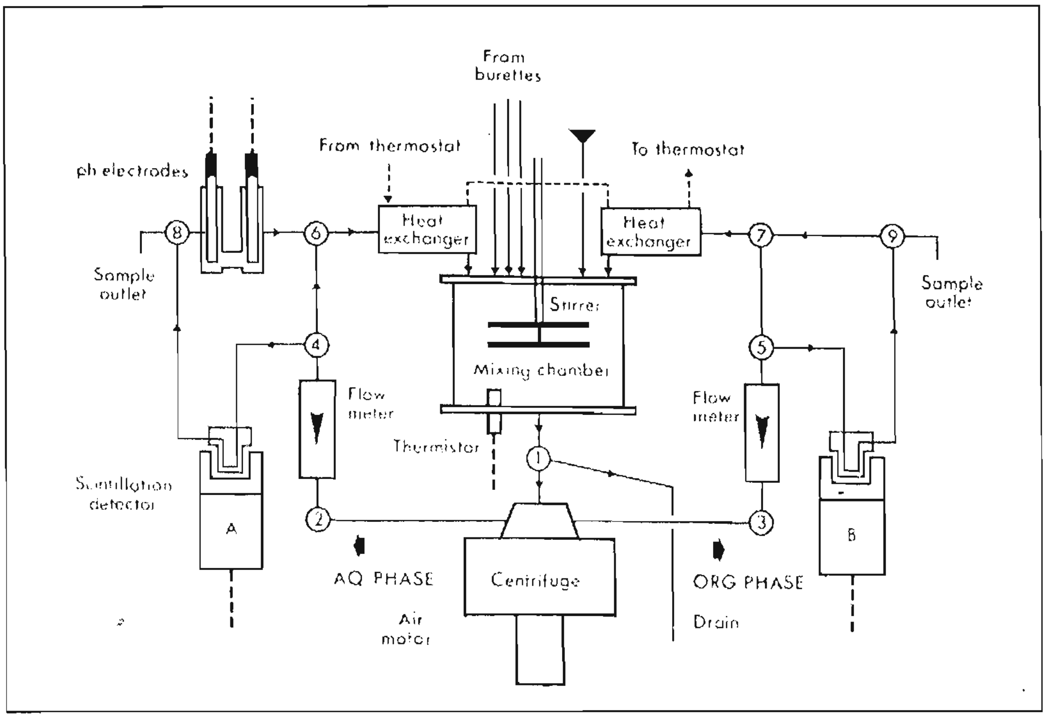


Figure 2-14: Diagram of the AKUFVE liquid flow system. (o) Represents the valves.

2.3.7 Apparatus of Rawat and Prasad [1980]

Rawat and Prasad [1980] measured the LLE for benzene + *n*-heptane systems using the solvents TEG, tetraethylene glycol, and Sulfolane containing water. These experiments were conducted at elevated temperatures of 383, 393, 394.5 and 418 K, where literature data is scarce (Rawat and Prasad [1980]).

The cell employed by Rawat and Prasad was a metallic pressure cell (Figure 2-15). The cell had two sight glasses for viewing of the interphase level; a jacket for the circulation of thermostatic fluid; a thermowell for the thermometer and a screw tube that enabled the introduction of the solvent or hydrocarbon feed.

The solvent and hydrocarbon feed of known weight and compositions were charged into the cell and the charging tube was then plugged with a nut wrapped in polytetraflouroethylene (teflon) tape. The set-point temperature was maintained by circulating heating oil around the still through Teflon tubing. This enabled temperature control to within 1 K of the desired temperature. Rawat and Prasad [1980] used the needle valve for sample extraction. Small volumes of each phase were discarded in order to avoid the overlapping of the different phases.

This cell enabled rapid determination of tie line and solubility limits. It also kept the disturbance of equilibrium to a minimum during sampling. Provisions were made for overlapping of phases during sampling

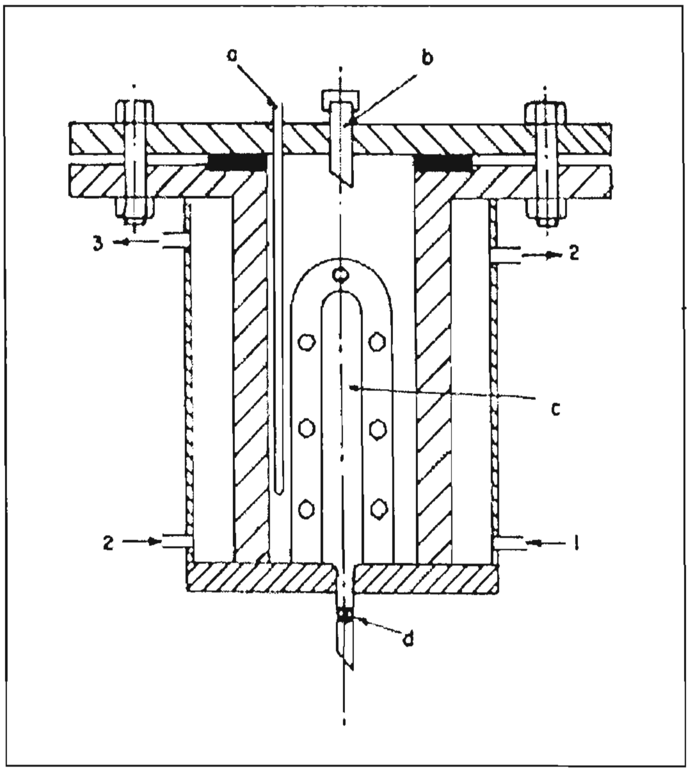


Figure 2-15: Equilibrium still used by Rawat and Prasad [1980]: (a) Thermometer pocket, (b) screw charging tube, (c) sight glasses, (d) needle valve.

The cell was used for elevated temperature and pressure determination of equilibria and could be used with no modification for systems at room temperature. The onset of turbidity was based on the judgement of the user and no provisions were made to nullify or limit this. Settling times could have been long if the two phases had very similar densities (a problem that was overcome by use of a centrifuge for separating the phases) (Reinhardt and Rydberg [1969]).

This experimental set-up provides full equilibrium results in terms of tie-lines and binodal curves.

The equipment mention above was not economically feasible to construct and in some cases showed large settling times for certain systems. However, it could be very useful for determining the equilibrium of systems at elevated temperatures, which is especially important in the petroleum industry (Rawat and Prasad [1980]).

2.4 EXPERIMENTAL PROCEDURE AND EQUIPMENT.

2.4.1 Experimental Procedure

(a) **Binodal curves and refractive index calibration curves:**

Points on the binodal curve were determined using a method adapted from that of Briggs and Comings [1943]. The third component was added to a mixture of known composition of the other two components in 100 cm^3 long necked flasks until one drop caused the clear solution to become turbid or cloudy. The flasks were well immersed in a water bath of constant temperature of 298 K and were shaken continuously. The added component was dispensed using a weighed gas-tight syringe, which was fitted with a needle capable of dispensing a drop weighing less than 0.01 g.

It is possible to use any physical property for composition analysis. Refractive indices were used since they are quick and easy to determine. Gas chromatography was not used since NMP has a vapour pressure and would exhibit very long retention times.

To relate the compositions on the binodal curve to the tie-lines compositions, refractive index measurements were made for each of the mixtures on the binodal curve. One drop of a component was added to the mixture to restore miscibility before measurements were made. This was done to ensure that phase separation did not take place on the lens of the refractometer. A calibration curve for each system was obtained by dropping a perpendicular from the point on the binodal curve to the *n*-hexane composition axis of the phase diagram.

b) **Determination of tie-line data:**

Tie-lines were determined from carefully made solutions in the immiscible region of the phase diagram. The flasks were well shaken and left for approximately twenty-four hours for the mixture to separate into two phases at 298 K. Refractive index measurements were then taken of each of the two separated phases by carefully withdrawing samples using a hypodermic syringe. The refractive index measurements were related to compositions on the binodal curve using the calibration curve. Each tie-line on the phase diagram was checked to ensure that it passed through the composition of the feed point. This process is show graphically in Figure 2-16.

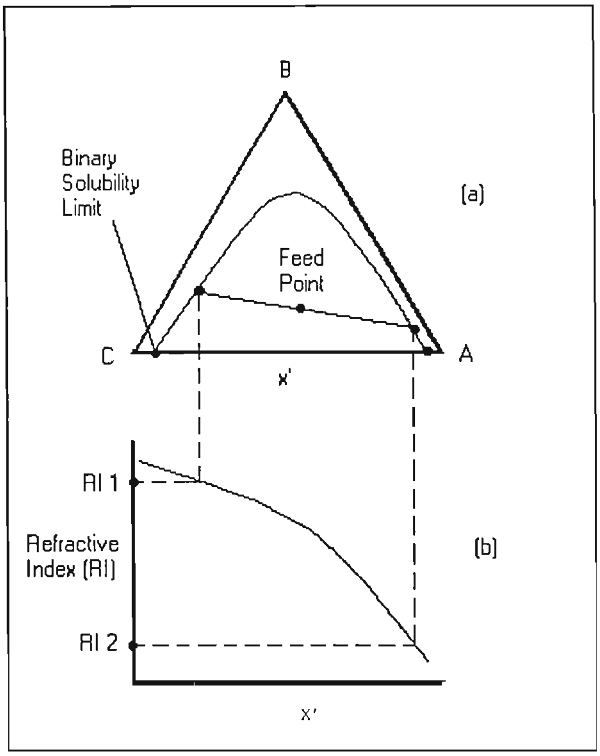


Figure 2-16: Graphical representation of tie-line determination. (a) Binodal Curve, (b) Refractive Index Calibration Chart.

2.4.2 Equipment Used

Figure 2-17 represents a schematic diagram of the equipment used for the determination of liquid-liquid equilibria for systems investigated in this work. This equipment has been used previously to good effect (Letcher *et al* [1986], Letcher and Siswana [1992], Naicker [1997], Letcher and Naicker [1998], Letcher and Deenadayalu [1999], Naidoo, *et al* [2001], Harris [2001]). An insulated water bath was used to provide a constant-temperature environment. This temperature was maintained to within 0.05 K using the following set-up: a light bulb was used as a low capacity heater and was connected to a Tronac temperature controller. The temperature was monitored using a Hewlett Packard quartz thermometer. This temperature was maintained to within 0.05 K using the following set-up: a light bulb was used as a low capacity heater and was connected to a Tronac temperature. The temperature was monitored using a Hewlett Packard quartz thermometer. Masses were recorded (in grams) using an electronic Metler balance accurate to the forth decimal point. Titrations were performed using a weighed syringe and needle. For accurate mass measurement, the syringe was weighed before and after titration. Refractive index measurements were taken using a Bellingham and Stanley Abbe refractometer.

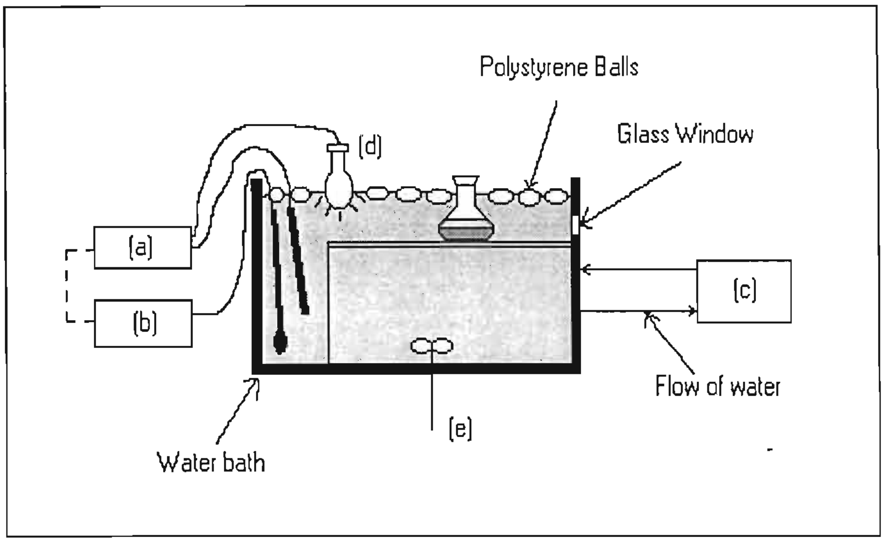


Figure 2-17: Schematic diagram of equipment used in this work. (a) Tronac PTC-41 Temperature Controller, (b) Hewlett Packard 2804A, quartz thermometer, (c) Bellingham and Stanley Abbe Refractometer, (d) Light Bulb, (e) Mechanical Stirrer.

2.5 DETERMINATION OF PLAIT POINTS

The plait-point is a point on the solubility/binodal curve at which a tie-line has equal compositions in both the alkane-rich phase and the solvent-rich phase. In the case of many systems in literature, only a few tie lines have been determined experimentally (Treybal [1963]). Direct interpolation on the triangular plot of such data, particularly extrapolation to yield plait-points, leads to inaccurate results (Treybal [1963]) due to human errors in construction. This will become more apparent in the following section. As a result, many methods have been developed to overcome paucity in tie-line data. Two such methods are described below:

2.5.1 Graphical Interpolation on the triangular plot (Treybal [1963]):

In Figure 2-18, *DE* is a tie line with *DG* drawn parallel to *CB*, and *EF* parallel to *AC*; the two constructed lines intersect at *H*. A tie line conjugation curve *PHJ* is drawn through several such constructed point intersections from the other tie lines available. From any point on the conjugation curve, two constructed lines parallel to *AC* and *BC* will intersect the binodal cure at concentration corresponding to conjugate solutions and may be joined with a tie line. The curve *PHJ* is not a straight line, although the curvature is very small, and it passes through the binodal curve at the plait point *P*.

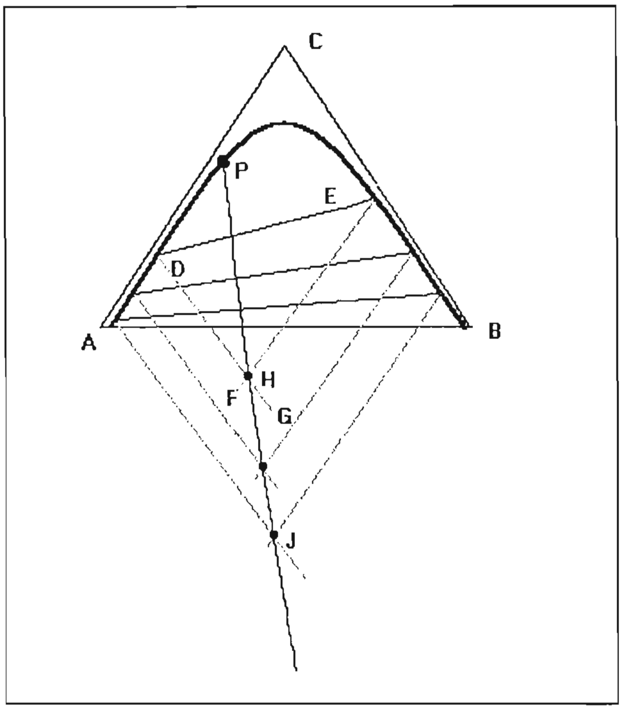


Figure 2-18: Graphical interpolation of tie lines.

The method described above is very useful for determining plait points when the tie-lines are close to it. This method takes up a large amount of space and a modification to avoid this is show in Figure 2-19.

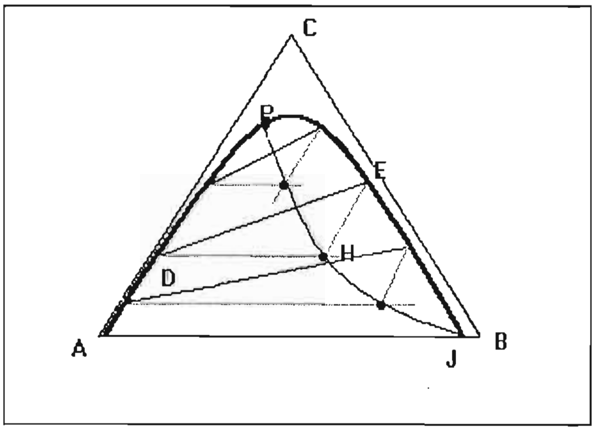


Figure 2-19: Modification of graphical interpolation of tie lines (Treybal [1963])

2.5.2 The Treybal Plot (Treybal [1963]):

In this instance, a graph using the binodal curve and the tie-lines is used to determine the location of the plait point. This type of plot requires that the weight distribution of component *C* in each phase be plotted. Next, for each experimental point on the binodal curve, the weight distribution of component *C* relative to component *B* is plotted against the weight distribution of component *C* relative to component A, on the same set of axes. These plots are drawn on a double logarithmic set of coordinates as proposed by Hand [1930]. Once this is done we arrive at a plot similar to that shown in Figure 2-20.

X_A, X_B and X_C are the weight fractions of A, B and C on the binodal curve, and X_{CB} is the weight fraction of C in the B rich phase, X_{CA} is the weight fraction of C in the A rich phase, X_{BB} is the weight fraction of B in the B rich phase and X_{AA} is the weight fraction of A in the A rich phase. The intersection of the two curves indicates the plait point and this composition can then be determined by simple arithmetic.

Type II systems (Figure 2-3, p12) cannot be represented by Treybal plots. They exhibit two partially miscible binary pairs and therefore we get either $\frac{X_C}{X_B}$ or $\frac{X_C}{X_A} = 0$ and since we are plotting on a logarithmic scale, we arrive at an undefined region. This is consistent with the fact that the plait points of Type II systems lie outside the phase diagram and are in mathematical terms imaginary.

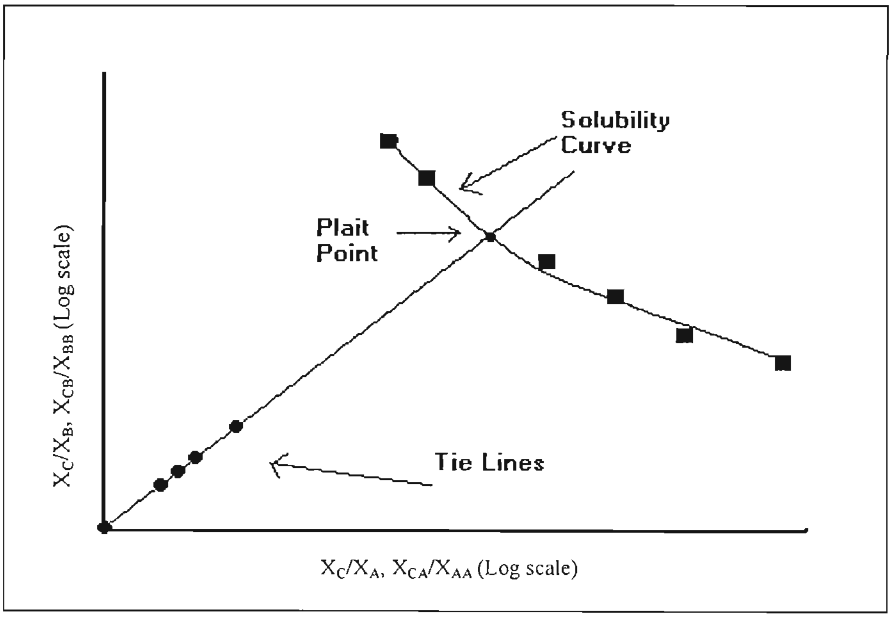


Figure 2-20: Treybal Plot for Plait Point Determination (Treybal [1963])

The plait-points for the systems investigated were determined graphically using the Treybal plot and by the construction method. This was done in order to check whether or not the two methods correlate well with one another. The Treybal plots for all systems investigated are presented in Figures 2-34 through 2-42 (p56-60). Compositions of all plait points, which were found using these Treybal plots are presented in Table 2-5 (p61)

2.5.2 Distribution Curves

There are many methods for plotting of conjugate solution concentrations against each other. The reason for these types of graphs is for the purpose of correlating data and to facilitate interpolation (Treybal [1963]). Such plots should preferably be rectilinear in nature, since it would not only facilitate interpolation, but two determined tie-lines could be used to predict all other tie-lines.

A plot of the mass-concentration of component *C* (toluene) in the *A*-rich phase (solvent) against the concentration of *C* (toluene) in the *B*-rich phase (*n*-hexane), was made on rectangular coordinates. Figure 2-21 shows typical distribution curves along with their corresponding phase diagrams. In all cases, the intersection of the distribution curve with the $y = x$ line indicates the plait point (*G*). As we have discussed earlier, Type II systems do not exhibit a plait point.

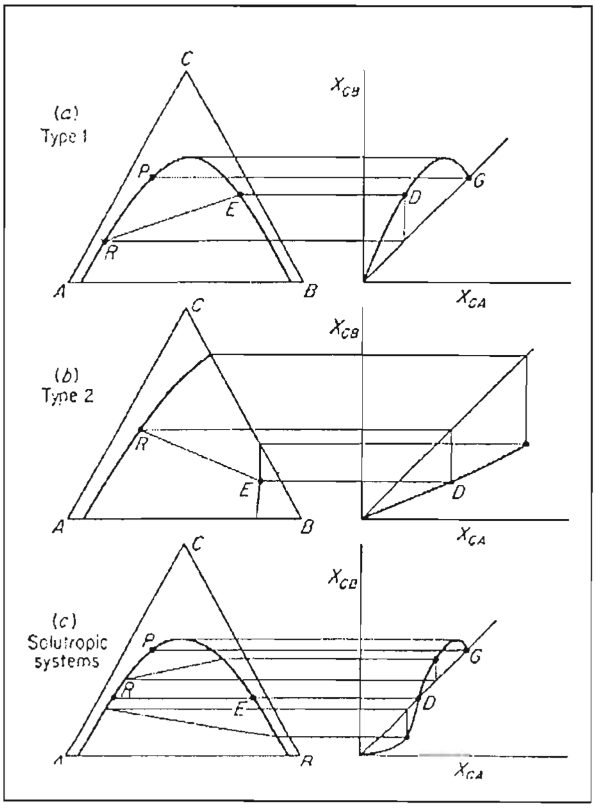


Figure 2-21: Typical Distribution curves and corresponding phase diagrams (Treybal [1963])

In a solutropic system as that illustrated in Figure 2-21 (c), a horizontal tie-line is exhibited. This horizontal tie-line means that the composition of the aromatic is exactly the same in both equilibrium phases. This corresponds to point *D* in the distribution diagram alongside it.. The ratio $\frac{X_{CB}}{X_{CA}}$ corresponds to the distribution coefficient, *m*, where X_{CB} is the mass-concentration of component *C* in the *B*-rich phase and X_{CA} is the mass-concentration of *C* in the *A*-rich phase. The value of this ratio decreases with increasing concentration of component *C* and comes to unity at the plait point. The distribution curves for all systems investigated are given in Figures 2-43 to 2-52(p62-67). Distribution diagrams are important in the design of separation processes because they show the distribution of a particular component in each phase. This can be useful when designing solvent recovery operations or distillation operations to recover the aromatic compound from the solvent.

2.6 THEORETICAL CONSIDERATIONS

As with any experimental work, it was required that the results obtained in this work be correlated with theory. This provides one with a measure of accuracy of the experimental technique as well as the equipment used. Theoretical correlation also provides a means of reproducing the results later on without having to perform rigorous experimental work. In the case of liquid-liquid equilibria it was necessary to correlate two sets of results for each system investigated viz. the binodal curves and the tie-line data measured. The three methods by which the binodal curves for our systems were correlated were developed by Hlavaty [1972], Schultz *et al* [1973] and Letcher *et al* [1989]. These models are known as the Hlavaty equation, the β function and the log-γ function respectively. These models were based purely on mathematical models and have no thermodynamic basis. The correlation of tie-line data is based on the thermodynamics of the systems under investigation and was carried out using the NRTL and UNIFAC thermodynamic models.

2.6.1 Binodal Curve Correlation

The binodal curves were correlated using the Hlavaty equation, the β and the log-γ functions (Hlavaty [1972]) and the set of equations used to correlate these binodal curves are listed below.

The Hlavaty equation (Hlavaty [1972]):

$$x_2 = A_2 x_A \ln x_A + A_1 x_B \ln x_B + A_3 x_A x_B \qquad (2\text{-}1)$$

The β function as represented by Schultz *et al* [1973]:

$$x_2 = B_2 (1 - x_A) B_1 x_A B_3 \qquad (2\text{-}2)$$

The log-γ function (Letcher *et al* [1989]):

$$x_2 = C_2(-\ln x_A)C_1 x_A C_3 \tag{2-3}$$

In the above equations, the following terms apply:

$$x_A = \frac{(x_1 + \frac{1}{2}x_2 - x_1^0)}{(x_{11}^0 - x_1^0)} \tag{2-4}$$

and

$$x_B = \frac{(x_{11}^0 - x_1 - \frac{1}{2}x_2)}{(x_{11}^0 - x_1^0)} \tag{2-5}$$

where x_1 refers to the mole fraction of the *n*-alkane, x_2 refers to the mole fraction of the aromatic hydrocarbon and x^0_{11} and x^0_1 are the values of x_1 on the binodal curve which cuts the $x_2 = 0$ axis. These equations summarize the binodal curve data and have been discussed extensively by Letcher and Siswana [1989]. The coefficients A_i, B_i, C_i determined using equations (2-1) to (2-5) simultaneously, as well as the standard deviations for each function are given in Table 2-6 (p68).

The standard deviation is defined as follows:

$$\sigma = \left[\frac{\Sigma\left\{x_{2\,calc} - x_{2\,exp}\right\}^2}{n-3}\right]^{0.5} \tag{2-6}$$

where n is the number of data points and 3 is the number of coefficients.

Data on the binodal curves have all been represented in terms of the mass fractions.

The solvent mixture of the systems under investigation was treated as a single component. The solvent mixture (in the case of mixed solvents) molar mass was calculated as a combination of both components making up the solvent i.e. one component in the solvent mixture was not ignored. All modelling was performed using mole fractions as indicated.

2.6.2 Tie-line correlation: Thermodynamic correlating Equations

The tie-lines measured for the systems under investigation were correlated using the NRTL and UNIQUAC equations. Although these sets of data were presented in mass fractions, for thermodynamic modeling, however, they were easily converted to mole fractions. The third component of most of the systems under investigation contained two constituents. The molar mass of this component was considered to be made up of both constituents according to the mixing ratios. The modeling of LLE using UNIQUAC and NRTL models has been done previously (Renon and Prausnitz [1968], Abrams and Prausnitz [1975], Ferreira *et al* [1983], Letcher and Deenadayalu [1999], Letcher and Deenadayalu [2000], Naidoo *et al* [2001]). In the discussion that follows, the more common liquid-liquid equilibrium correlations will be outlined, together with those used in this work and the results obtained are presented in Table 2-7.

The condition of equality of activities of a component in two-liquid phases (Appendix A-3) in equilibrium suggests that analytic representation of the activity coefficients may be used to correlate liquid equilibrium data (Lo *et al* [1983]). Although, almost any of the large number of correlating equations available for activity coefficients could be used, a large number of the simpler forms are unable to properly describe the highly non-ideal behaviour of systems that exhibit phase separation.

The thermodynamic basis of liquid-liquid equilibrium lies with the activity coefficient and this causes some doubt about some of the assumptions made (Appendix A-3) or models used to generate the correlating equations (Lo *et al* [1983]). This becomes important when equilibrium data are to be extrapolated or used to predict the behaviour of systems with added components (Renon and Prausnitz [1968], Abrams and Prausnitz [1975], Lo *et al* [1983]).

The three main methods of correlation are:

(a) The Wilson equation
(b) The NRTL equation and
(c) The UNIQUAC equation

Each of these models is discussed in the next section.

2.6.2.1 The Wilson Equation

The generation of correlating equations that have been most successful in representing liquid-liquid equilibrium data began with the Wilson equation (Wilson [1964]), i.e. equations that used the local compositions concept. The Wilson equation in its original form was unable to handle the case of liquid phase splitting. The equation depended on the two-liquid theory proposed by Scott

[1956]. Scott's theory regarded the mixture as being made up of hypothetical fluids- one for each component. The fluid consisted of cells each having a molecule of the corresponding component at its center (Scott [1956]). The local composition x_{ij} within a cell was defined as the composition of molecules of component j surrounding a molecule of component i. Wilson made the proposition that local and overall compositions in terms of mole fractions are related by

$$\frac{x_{ij}}{x_{ii}} = \frac{x_j \exp\left(\frac{-\lambda_{ij}}{RT}\right)}{x_i \exp\left(\frac{-\lambda_{ii}}{RT}\right)} \tag{2-7}$$

where R is the Universal Gas Constant and T is the system temperature in K.

where λ_{ij} is the interaction energy between a molecule of component i and a molecule of component j. Wilson then used this expression to calculated the effective volume fraction around a molecule of each type, and he then utilized

$$\frac{g^E}{RT} = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} \tag{2-8}$$

in the equation for athermal mixtures ($h^E = 0$). ϕ_i represents the average segment fraction and is related to the pure component structural parameters.

This gives

$$\frac{g^E}{RT} = -x_1 \ln\left(x_1 + \Lambda_{12} x_2\right) - x_2 \ln\left(\Lambda_{21} x_1 + x_2\right) \tag{2-9}$$

In Equation (2-9),

$$\Lambda_{12} = \frac{v_2}{v_1}\exp\left[\frac{-(\lambda_{12}-\lambda_{11})}{RT}\right] \tag{2-10}$$

$$\Lambda_{21} = \frac{v_1}{v_2}\exp\left[\frac{-(\lambda_{12}-\lambda_{22})}{RT}\right] \tag{2-11}$$

where v_i is the liquid molar volume of component i

The corresponding activity coefficient expression is:

$$\ln\gamma_1 = -\ln(x_1+\Lambda_{12}) - x_2\left[\frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}} - \frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}}\right] \tag{2-12}$$

The expression for γ_2 is obtained by interchanging the subscripts of Equation (2-12). The multicomponent form of the Wilson equation takes the form:

$$\ln\gamma_k = -\ln\left[\sum_{j=1}^{n} x_j\Lambda_{kj}\right] + 1 - \sum_{i=1}^{n}\frac{x_i\Lambda_{ik}}{\sum_{j=1}^{n} x_j\Lambda_{ij}} \tag{2-13}$$

However, as outlined earlier, the Wilson equation was unable to predict phase splitting. This was demonstrated by Wilson himself and by Renon and Prausnitz [1968]. Wilson recognized the failure of his equation to predict partial miscibility regardless of the parameter values. To overcome this he multiplied the excess free-energy expression (Equation 2.9) by a constant. He did not offer any theoretical explanation or physical justification for his decision, but later Renon and Prausnitz [1969] provided a derivation based on the integration of an excess enthalpy expression that justified this assumption by Wilson.

Hiranuma [1975] investigated the effect of the value of the multiplication constant on the quality of correlation of different systems. He suggested that specified values be used for each constituent binary parameter. He indicated that the value of the constant seemed to be influenced by the degree of hydrogen bonding for systems with association and/or solvation, but dispersion effects seemed to be negligible.

Katayama [1973] indicated that the three parameter Wilson equation for excess free-energy could have at most two points of inflection in the binary range, while the NRTL equation (discussed later) could have up to four. This meant that the miscibility gap predicted by the Wilson equation was unique. This was an advantage when it was being used to generate equilibrium data.

Sorensen *et al.* [1979] reviewed many modifications to the Wilson equation and deduced that none of the modifications displayed any advantage over the NRTL or UNIQUAC equations and therefore it was undertaken to employ these in this study. Furthermore, the Wilson equation does not account for phase splitting in a system.

2.6.2.2 The NRTL Equation

The Wilson and other local composition equations were examined by Rēnon and Prausnitz [1969]. They sought to modify two steps common to the derivation of these equations. These steps were the relationship between local and overall mole fractions (Equation 2-8) and the use of mole fractions to give local volume fractions for inclusion in Equation (2-9).
They proposed that Equation (2-9) be modified to the following:

$$\frac{x_{21}}{x_{11}} = \frac{x_2 \exp\left(\frac{-\alpha_{12}\lambda_{21}}{RT}\right)}{x_1 \exp\left(\frac{-\alpha_{12}\lambda_{11}}{RT}\right)} \tag{2-14}$$

Where the single constant α_{12} is a measure of the non-randomness of the mixture of components 1 and 2. Secondly, they related the free energy directly to the molecular interactions, giving

$$g^E = x_1 x_{12}\left(\lambda_{21} - \lambda_{11}\right) + x_2 x_{12}\left(\lambda_{12} - \lambda_{22}\right) \tag{2-15}$$

The final forms of the multicomponent NRTL equations are:

$$\ln\gamma_i = \frac{\sum_{j=1}^{m}\tau_{ji}G_{ji}x_j}{\sum_{l=1}^{m}G_{li}x_l} + \sum_{j=1}^{m}\frac{x_j G_{ij}}{\sum_{l=1}^{m}G_{lj}x_l}\left(\tau_{ij} - \frac{\sum_{n=1}^{m}x_n\tau_{nj}G_{nj}}{\sum_{l=1}^{m}G_{lj}x_l}\right) \tag{2-16}$$

where,

$$\lambda_{ij} = \frac{\left(g_{ji} - g_{ii}\right)}{RT} \tag{2-17}$$

$$G_{ji} = \exp\left(\alpha_{ji}\tau_{ji}\right) \tag{2-18}$$

and

$$\tau_{ii} = \tau_{jj} = 0$$
$$G_{ii} = G_{jj} = 1$$

with

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

(Renon and Prausnitz [1969]).

An important property of the NRTL equation was that, just like the Wilson equation, only binary interaction parameters are required for multi-component prediction. The Wilson equation had only two parameters per binary interaction whereas the NRTL equation employed three parameters. This increased flexibility should improve the representation of the more non-ideal systems. According to Renon [1969], a value of α that provided a measure of the non-randomness of the mixture lay between 0.2 and 0.5. Lower values of α are useful when dealing with phase splitting. Renon showed that with values greater that 0.426, phase splitting did not occur. Therefore a universal value of α_{ij} = 0.3 was used for our calculations. Further investigations on the values of α greater than 0.426 were carried out by Heidemann and Mandhane [1973], Mattelin and Verhoeye [1975] and Tassios [1976], however their investigations fall outside the scope of this work and will not be discussed here.

2.6.2.3 The UNIQUAC Equation

The UNIQUAC Equation proposed by Abrams and Prausnitz [1975], has had similar success to that of the NRTL equation in terms of correlating and predicting liquid-liquid equilibrium data. The equation was derived by introducing local area fractions of the molecules as the primary concentration variables into the quasichemical analysis by Guggenheim [1952] with molecular size and shape parameters obtained from pure components data. The multicomponent forms of the equations that resulted are:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{2-19}$$

Where the superscripts C and R represent the combinatorial and residual parts of the activity coefficient, with:

$$\ln \gamma_i^C = \ln \frac{\varphi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\vartheta_i}{\varphi_i} + l_i - \frac{\varphi_i}{x_i} \sum_j x_j l_j \tag{2-20}$$

$$\ln \gamma_i^R = q_i \left[1 - \ln\left(\sum_{j=1}^{m} \vartheta_j \tau_{ji} \right) - \sum_{j=1}^{m} \frac{\vartheta_j \tau_{ij}}{\sum_{k=1}^{m} \vartheta_k \tau_{kj}} \right] \tag{2-21}$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \qquad z = 10 \tag{2-22}$$

In equations (2-20) and (2-21),

$$\vartheta_i = \frac{q_i x_i}{\sum_j q_j x_j} \qquad \text{(area fraction of component i)}$$

$$\varphi_i = \frac{r_i x_i}{\sum_j r_j x_j} \qquad \text{(volume fraction of component i)}$$

and

$$\tau_{ji} = \exp - \left(\frac{u_{ji} - u_{ii}}{RT} \right) \tag{2-23}$$

$$\tau_{ii} = \tau_{jj}$$

where q_i and r_i are area and surface parameters of component i respectively and z is the coordination number. The generation of pure component parameters r and q is identical for the UNIQUAC functional group activity coefficient (UNIFAC) discussed later in this work. The local composition equations generally have parameters in the form of Equation (2-23) and provide some temperature dependence of the activity coefficients. Since this work is performed at constant temperature, the temperature dependence of these parameters will not be discussed here.

The equations and algorithms used in the calculation of the composition of the liquid phases follow the method proposed by Walas [1985]. The objective function *F(P)* used to minimize the difference between the experimental and calculated concentrations is defined as:

$$F(P) = \sum_{i=1}^{n} \left[x'_{1i} - x'_{1i}(calc)[PT]\right]^2 - \left[x'_{2i} - x'_{2i}(calc)[PT]\right]^2 + \left[x''_{1i} - x''_{1i}(calc)[PT]\right]^2 + \left[x''_{2i} - x''_{2i}(calc)[PT]\right]^2 \qquad (2\text{-}24)$$

Where P is the set of parameters vector, n is the number of experimental points, x'_{ji}, x'_{ji} (calc) are the experimental and calculated values for one phase respectively and x''_{ji} and x''_{ji} (calc) are the experimental and calculated values of the other phase.

The NRTL equation was optimized for all parameters. The parameters for the both models are given in Table 2-7 along with the root mean squared deviation values defined below, which can be taken as the measure of accuracy of the correlating equation.

$$rmsd = \sqrt{\left(\sum_{i}\sum_{l}\sum_{m} \frac{\left[x_{ilm}^{exp} - x_{ilm}^{calc}\right]^2}{6k}\right)} \qquad (2\text{-}25)$$

where x is the mole fraction and the subscripts *i, l, m* designate the component, phase, and tie-line respectively and k is the number of interaction parameters. Figure 2-22 outlines the basic calculation procedure used for calculation of the model parameters.

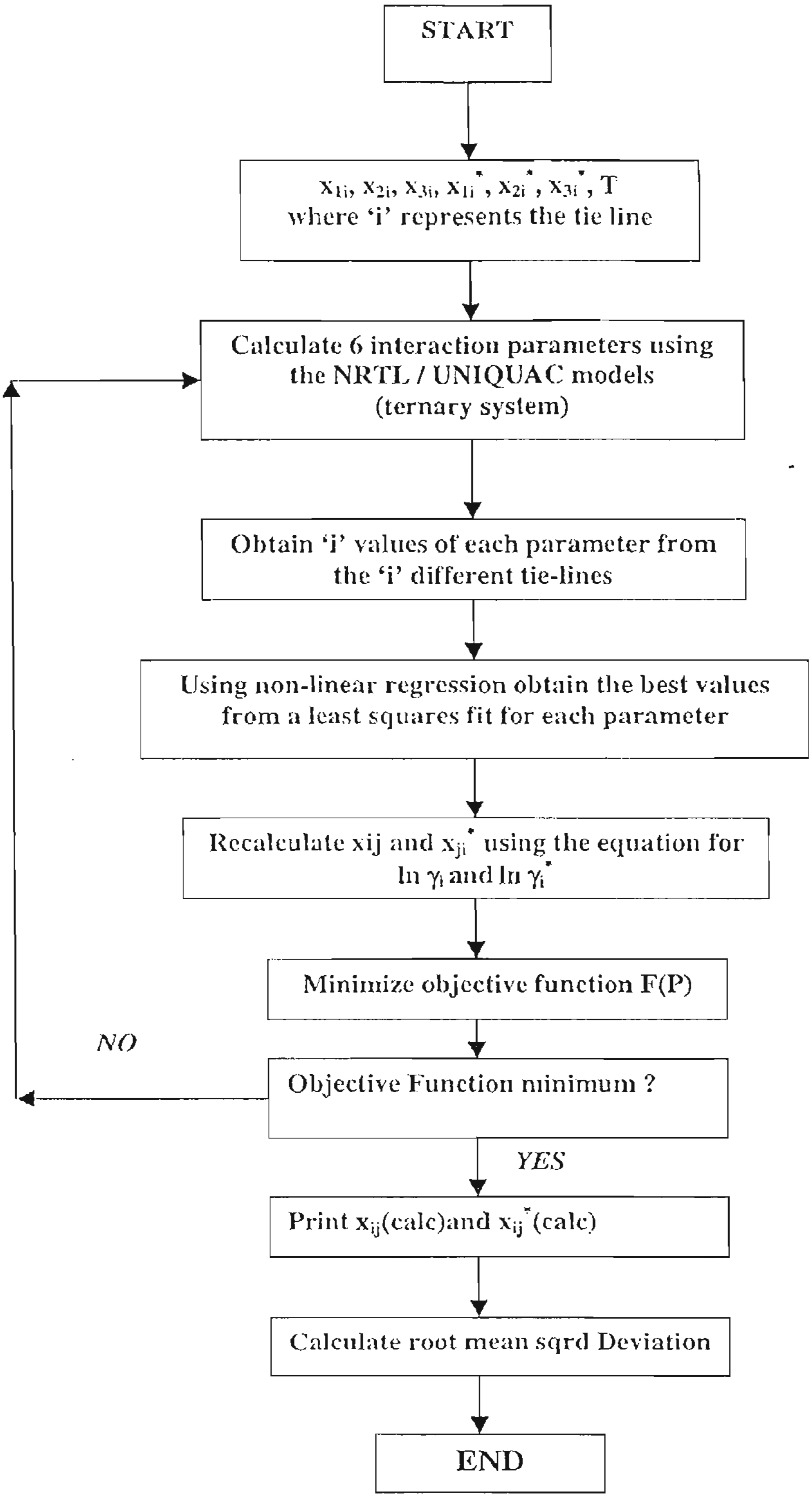


Figure 2-22: Flow diagram for basic calculation of NRTL and UNIQUAC model parameters.

2.7 RESULTS

The Table 2-3 below indicates the compositions of the points on the binodal curves, determined from experiment, of each of the systems for which liquid-liquid equilibria were measured. All results are represented in terms of mass fractions X_i.

X_1	X_2	X_1	X_2
NMP		NMP + 10%(w/w) Glycerol	
0.909	0.000		
0.856	0.040	0.972	0.000
0.804	0.064	0.806	0.175
0.742	0.102	0.723	0.260
0.667	0.118	0.647	0.338
0.620	0.126	0.562	0.424
0.415	0.129	0.424	0.553
0.214	0.059	0.370	0.603
0.155	0.000	0.230	0.701
		0.089	0.332
		0.102	0.117
		0.096	0.062
		0.102	0.000
NMP + 30%(w/w) Glycerol		NMP+50%(w/w) Glycerol	
0.953	0.000	0.969	0.000
0.762	0.197	0.004	0.994
0.628	0.319	0.483	0.482
0.494	0.455	0.772	0.196
0.581	0.360	0.205	0.762
0.024	0.475	0.082	0.901
0.021	0.326	0.047	0.937
0.020	0.409	0.001	0.996
0.017	0.000	0.004	0.993
0.130	0.670	0.001	0.999
		0.011	0.000
		0.000	0.221
		0.010	0.106
NMP + 10%(w/w) MEG		30%(w/w)MEG	
0.983	0.000	0.944	0.000
0.095	0.000	0.108	0.000
0.877	0.097	0.479	0.486
0.643	0.314	0.591	0.379
0.622	0.318	0.765	0.183
0.567	0.361	0.061	0.273
0.335	0.429	0.080	0.168
0.128	0.228	0.019	0.811
0.401	0.441	0.278	0.706
0.364	0.444	0.210	0.769

Table 2-3: Compositions of points on the binodal curves at 298 K and 1 atm for mixtures: {NMP + solvent}(X_3) + *n*-hexane (X_1) + toluene (X_2). $X_3 = 1 - X_1 - X_2$

X_1	X_2	X_1	X_2
5% (w/w) DEG		10% (w/w) DEG	
0.145	0.000	0.086	0.000
0.225	0.117	0.185	0.221
0.305	0.191	0.207	0.245
0.512	0.233	0.288	0.411
0.538	0.232	0.439	0.464
0.603	0.223	0.436	0.468
0.737	0.157	0.461	0.447
0.831	0.088	0.600	0.376
0.935	0.000	0.854	0.123
		0.990	0.000
10% (w/w) TEG		5% (w/w) water	
0.991	0.000	0.916	0.000
0.894	0.089	0.478	0.483
0.703	0.277	0.596	0.362
0.590	0.335	0.787	0.157
0.478	0.314	0.335	0.812
0.366	0.251	0.139	0.814
0.139	0.095	0.055	0.485
0.080	0.059	0.047	0.361
0.072	0.000	0.047	0.165
		0.067	0.796
		0.067	0.000
NMP+10% (w/w) water			
0.982	0.000		
0.950	0.040		
0.939	0.045		
0.852	0.133		
0.603	0.386		
0.489	0.490		
0.368	0.616		
0.294	0.684		
0.120	0.875		
0.034	0.171		
0.029	0.107		
0.021	0.032		
0.020	0.971		
0.012	0.000		
0.010	0.981		
0.000	0.568		

Table 2-3 (*contd*): Compositions of points on the binodal curves at 298 K and 1 atm for mixtures: {NMP + solvent} (X_3) + *n*-hexane (X_1) + toluene (X_2).

The compositions of the conjugate solutions that make up the tie lines are given in Table 2-4.

alkane rich layer			solvent rich layer	
X'$_1$	X'$_2$	Solvent	X"$_1$	X"$_2$
		NMP		
0.846	0.041		0.192	0.042
0.800	0.070		0.239	0.077
0.744	0.095		0.311	0.106
0.643	0.155		0.276	0.156
		10% (w/w) Glycerol		
0.465	0.520		0.101	0.040
0.356	0.613		0.097	0.098
0.322	0.642		0.097	0.133
0.225	0.694		0.090	0.272
		30% (w/w) Glycerol		
0.871	0.077		0.017	0.052
0.816	0.137		0.020	0.073
0.684	0.266		0.020	0.121
0.500	0.440		0.020	0.226
0.400	0.534		0.020	0.298
0.286	0.617		0.020	0.387
		50% (w/w) Glycerol		
0.844	0.118		0.012	0.039
0.604	0.356		0.012	0.106
0.501	0.462		0.006	0.153
0.243	0.731		0.006	0.209
		10% (w/w) MEG		
0.939	0.038		0.095	0.023
0.815	0.163		0.095	0.023
0.686	0.273		0.095	0.023
0.499	0.402		0.095	0.023
0.296	0.439		0.095	0.023

Table 2-4: Compositions of tie-lines on the binodal curves at 298 K and 1 atm for mixtures: {NMP + solvent}(X_3) + *n*-hexane(X_1) + toluene(X_2). $X_3 = 1 - X_1 - X_2$

alkane rich layer			solvent rich layer	
X'1	X'2	Solvent	X"1	X"2
		30% (w/w) MEG		
0.732	0.213		0.099	0.076
0.509	0.461		0.094	0.106
0.394	0.587		0.080	0.188
0.253	0.726		0.057	0.298
0.159	0.800		0.032	0.441
		5% (w/w) DEG		
0.800	0.113		0.161	0.036
0.711	0.168		0.177	0.058
0.596	0.219		0.186	0.073
0.393	0.226		0.214	0.109
		10% (w/w) DEG		
0.699	0.294		0.100	0.029
0.657	0.337		0.110	0.048
0.550	0.405		0.118	0.126
0.386	0.452		0.194	0.250
		10% (w/w) TEG		
0.909	0.077		0.085	0.041
0.842	0.150		0.085	0.041
0.765	0.224		0.085	0.041
0.690	0.280		0.085	0.041
0.585	0.325		0.085	0.041
		5% (w/w) water		
0.147	0.813		0.047	0.563
0.349	0.635		0.059	0.457
0.519	0.447		0.070	0.303
0.695	0.250		0.076	0.139
		10% (w/w) water		
0.852	0.132		0.028	0.073
0.729	0.256		0.034	0.139
0.587	0.395		0.031	0.219
0.370	0.614		0.025	0.351
0.200	0.786		0.017	0.439

Table 2-4 (*contd)*: **Compositions of tie-lines on the binodal curves at 298 K and 1 atm for mixtures: {NMP + solvent}(X_3) + *n*-hexane(X_1) + toluene(X_2). $X_3 = 1 - X_1 - X_2$**

The binodal curves for these systems are presented in Figures 2-23 through 2-33. The refractive index calibration charts for determination of plait points a given in Appendix A-2 and are represented as Figures A-2 to A-12. The distribution curves are presented in Figures 2-23 through 2-32.

2.7.1 The Binodal Curves

Figure 2-23: Binodal Curve for X_1 (n-hexane) + X_2 (toluene) + X_3 (N-methyl-2-pyrollidone) at 298 K and 1atm

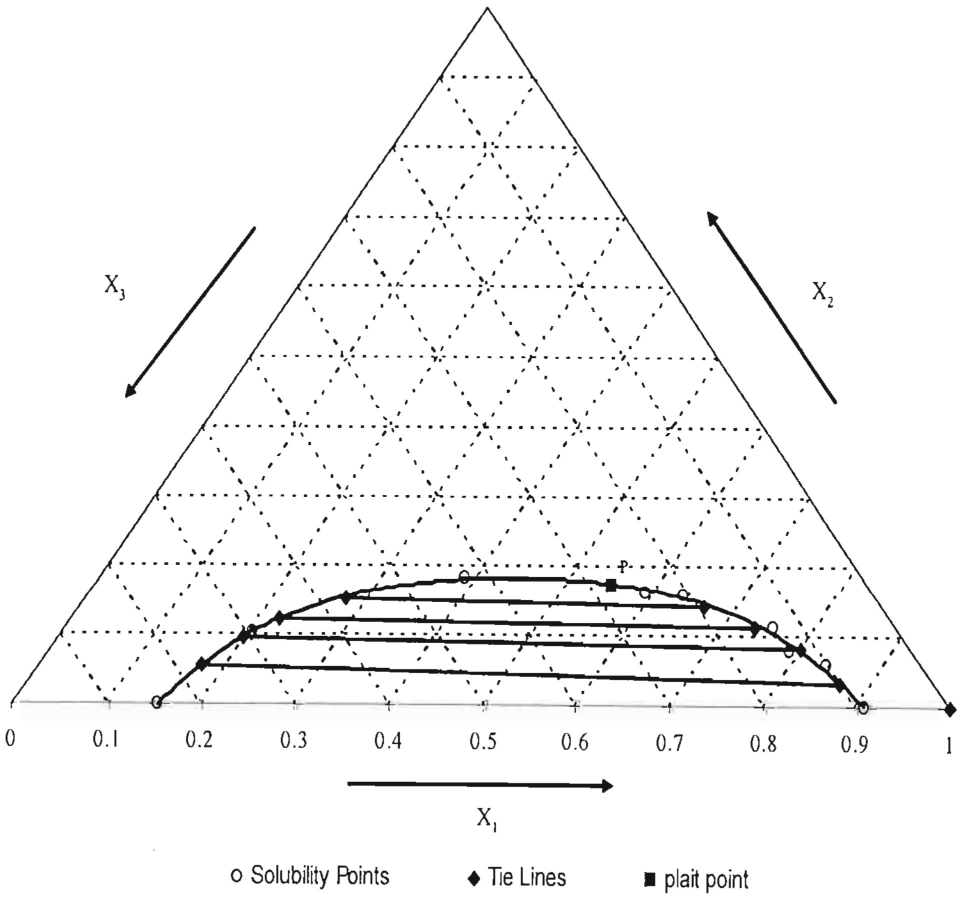
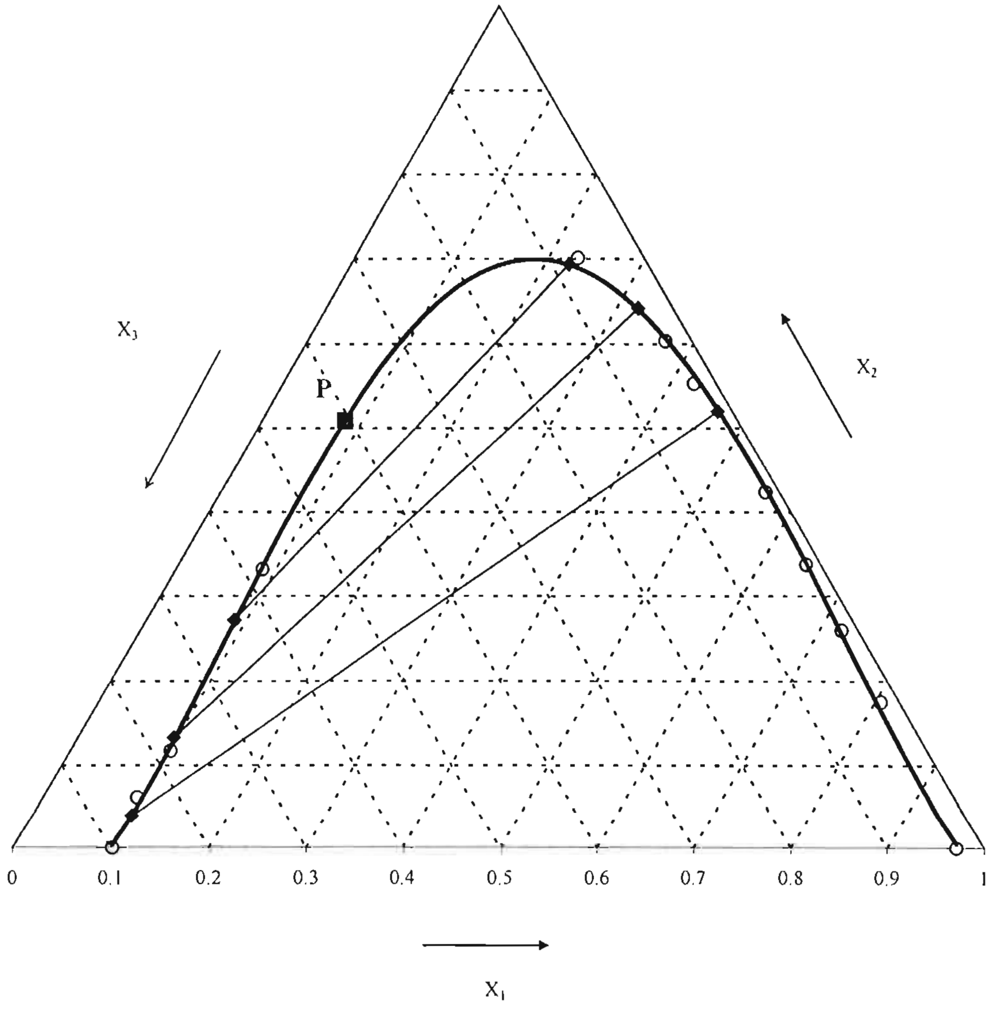


Figure 2-24: Binodal Curve For X_1(*n*-hexane) + X_2(toluene) + X_3(NMP + 10% w/w Glycerol) at 298 K and 1 atm



○ Solubility Points ◆ Tie-Lines ■ Plait Point

Figure 2-25: Binodal Curve For X_1(n-hexane) + X_2(toluene) + X_3(NMP + 30% (w/w) Glycerol) at 298 K and 1 atm

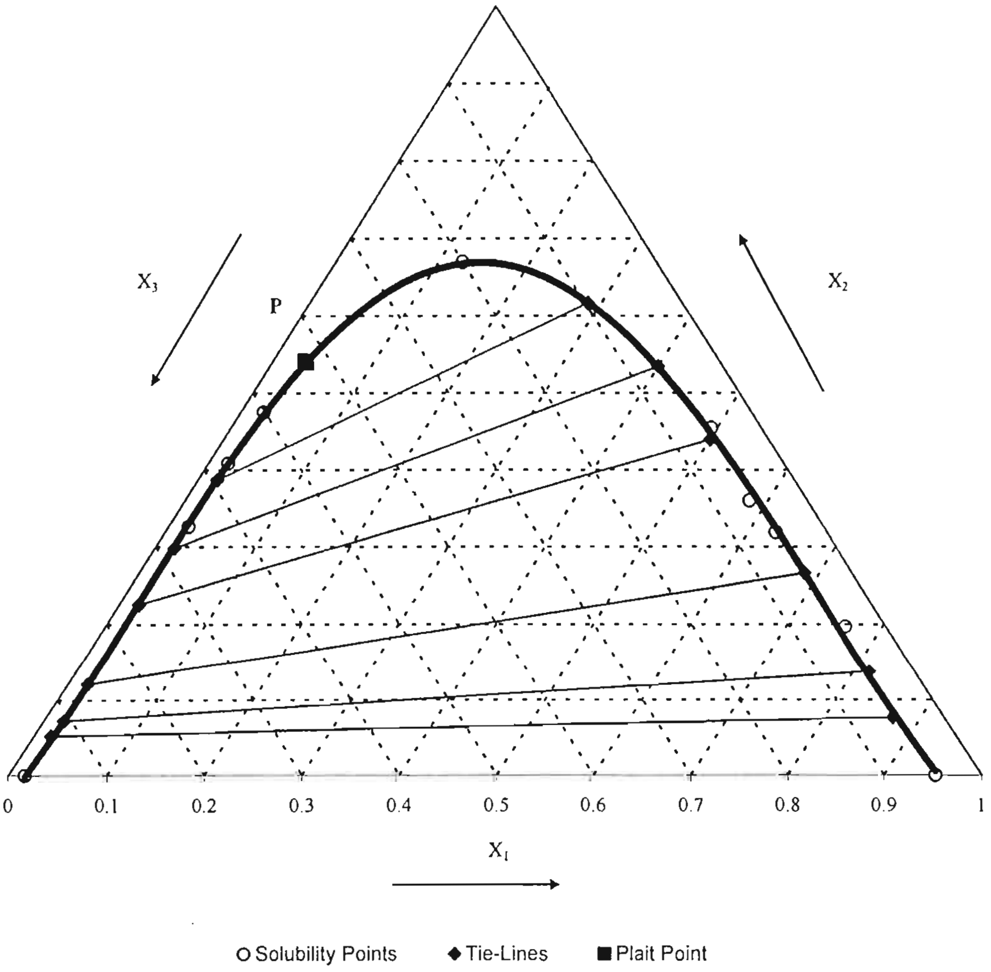


Figure 2-26: Binodal Curve For X_1(*n*-hexane) + X_2(toluene) + X_3(NMP + 50% (w/w) Glycerol) at 298 K and 1 atm

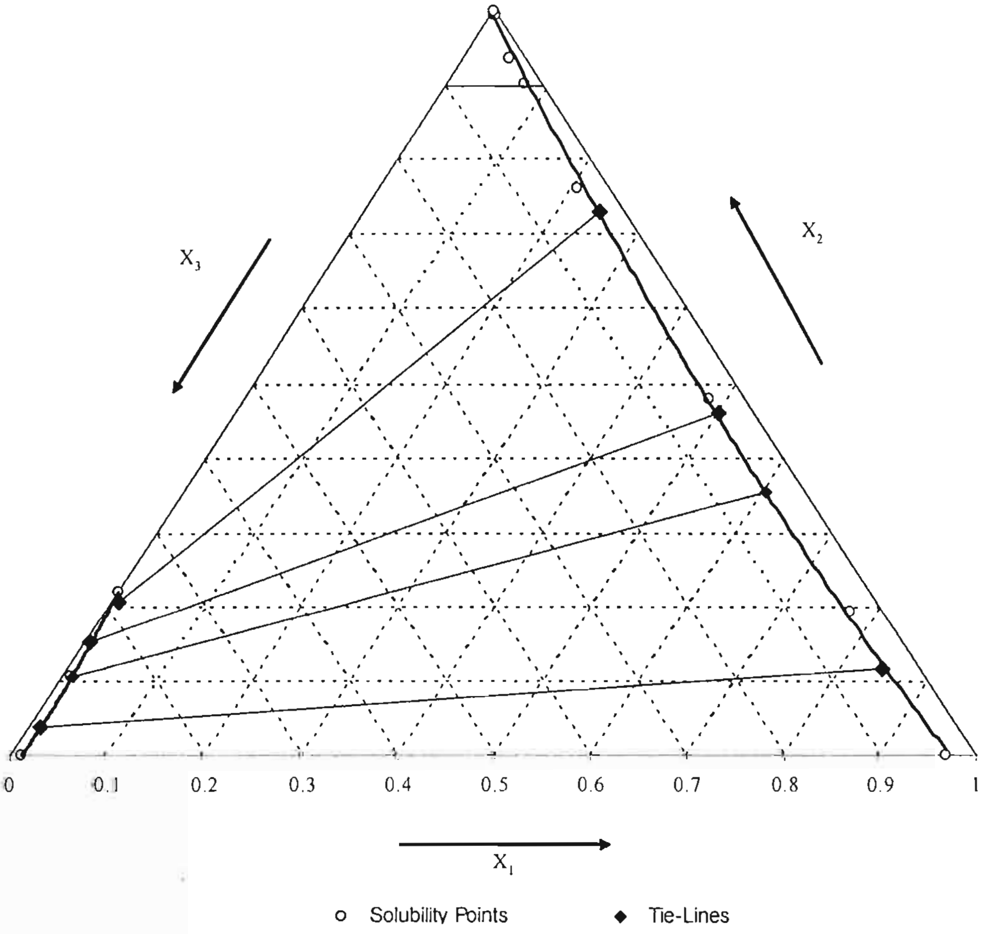


Figure 2-27: Binodal Curve for X_1(*n*-hexane) + X_2(toluene) + X_3(NMP + 10% w/w MEG) at 298 K and 1 atm

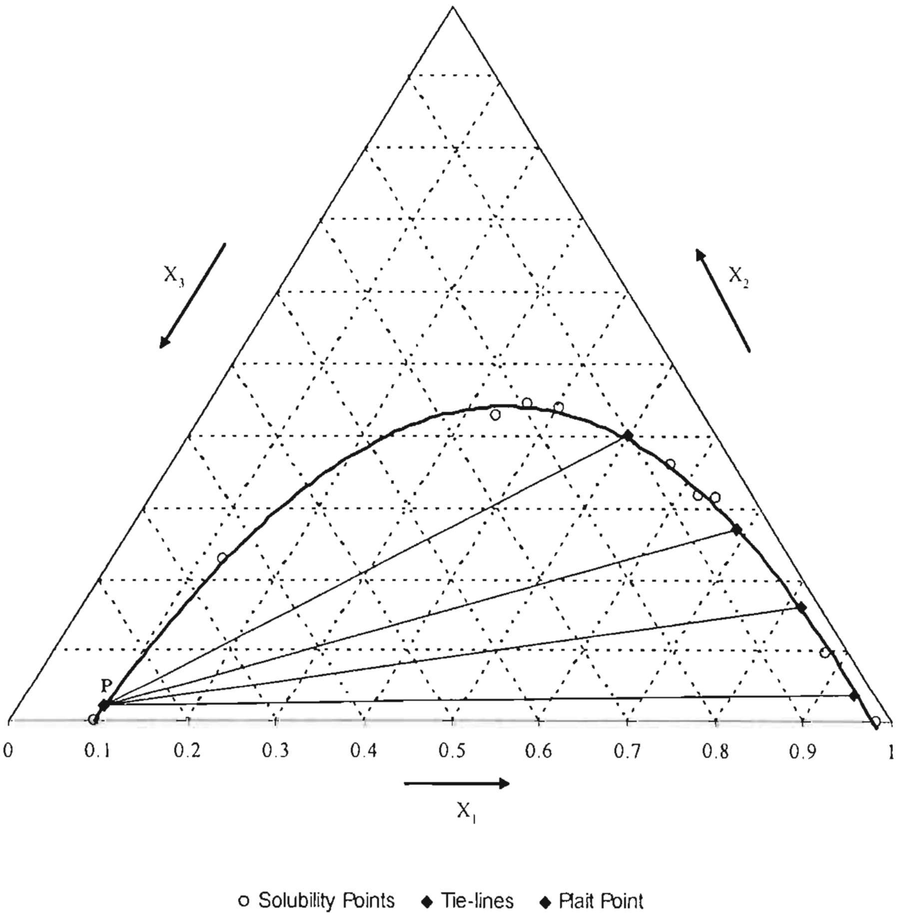


Figure 2-28: Binodal Curve for X_1(*n*-hexane) + X_2(toluene) + X_3(NMP + 30% (w/w) MEG) at 298 K and 1 atm

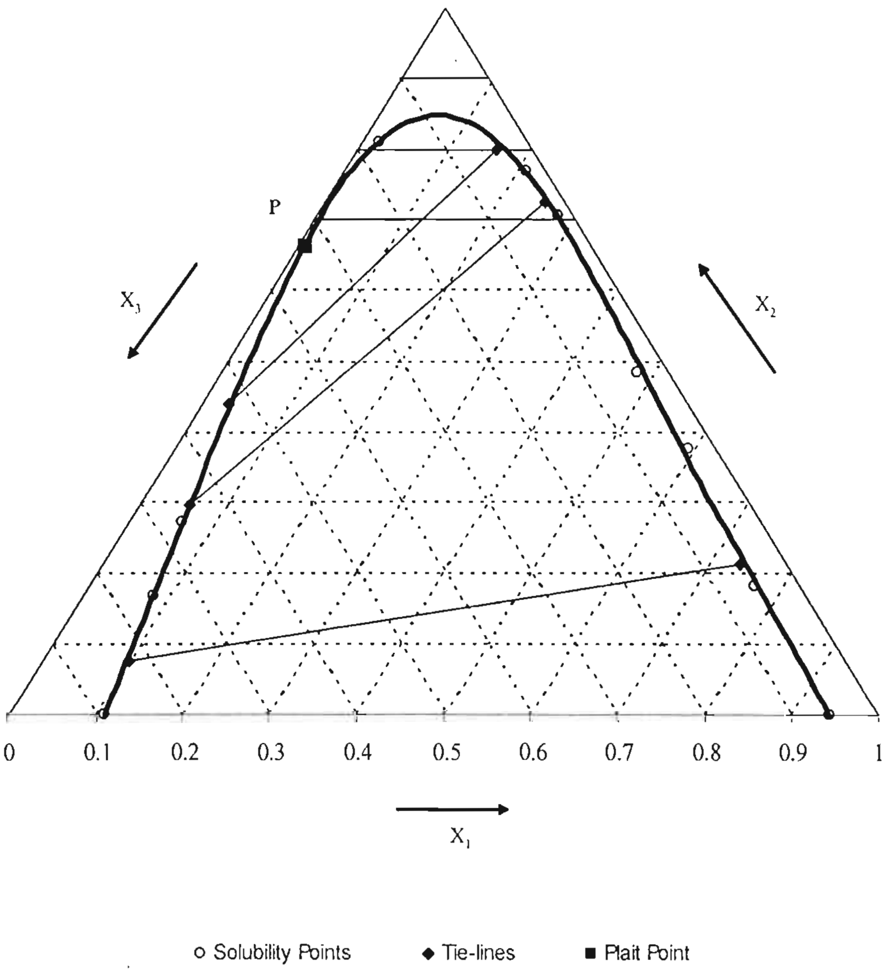


Figure 2-29: Binodal Curve for X_1 (*n* -hexane) + X_2 (toluene) + X_3 { NMP+ 5% (w/w) DEG } at 298 K and 1atm

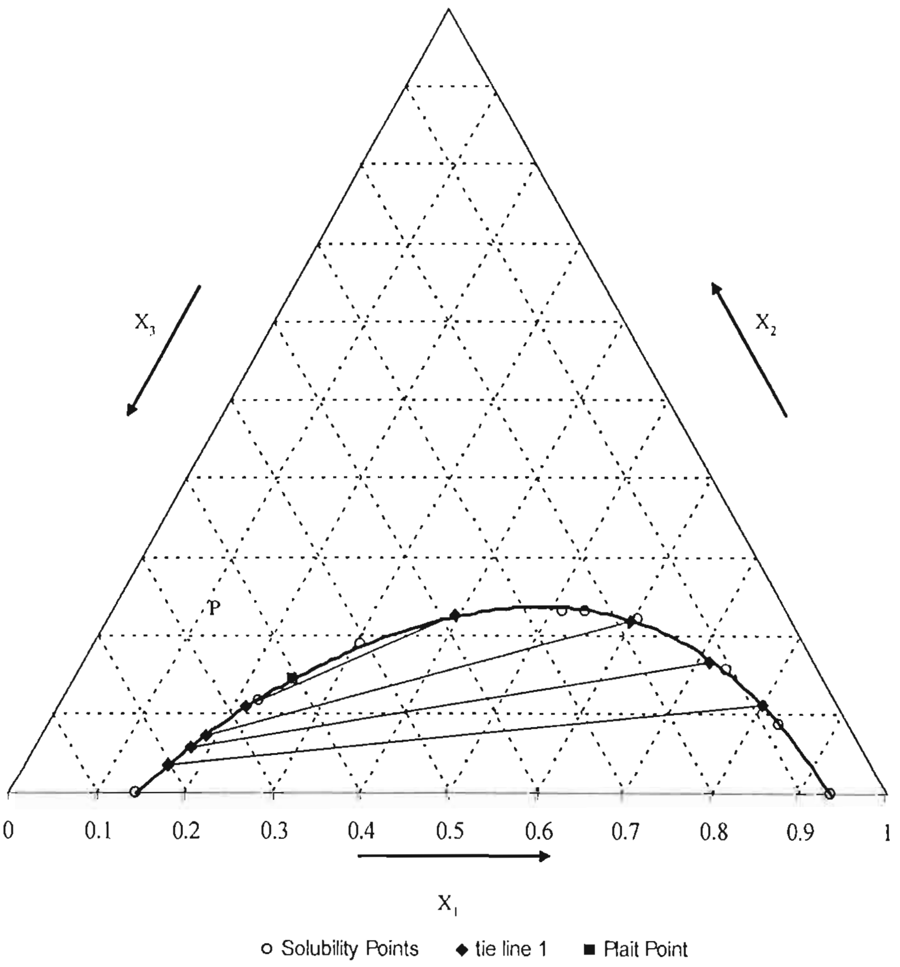


Figure 2.30: Binodal Curve for X_1(*n* -hexane) + X_2(toluene) + X_3 (NMP + 10% (w/w) DEG) at 298 K and 1 atm

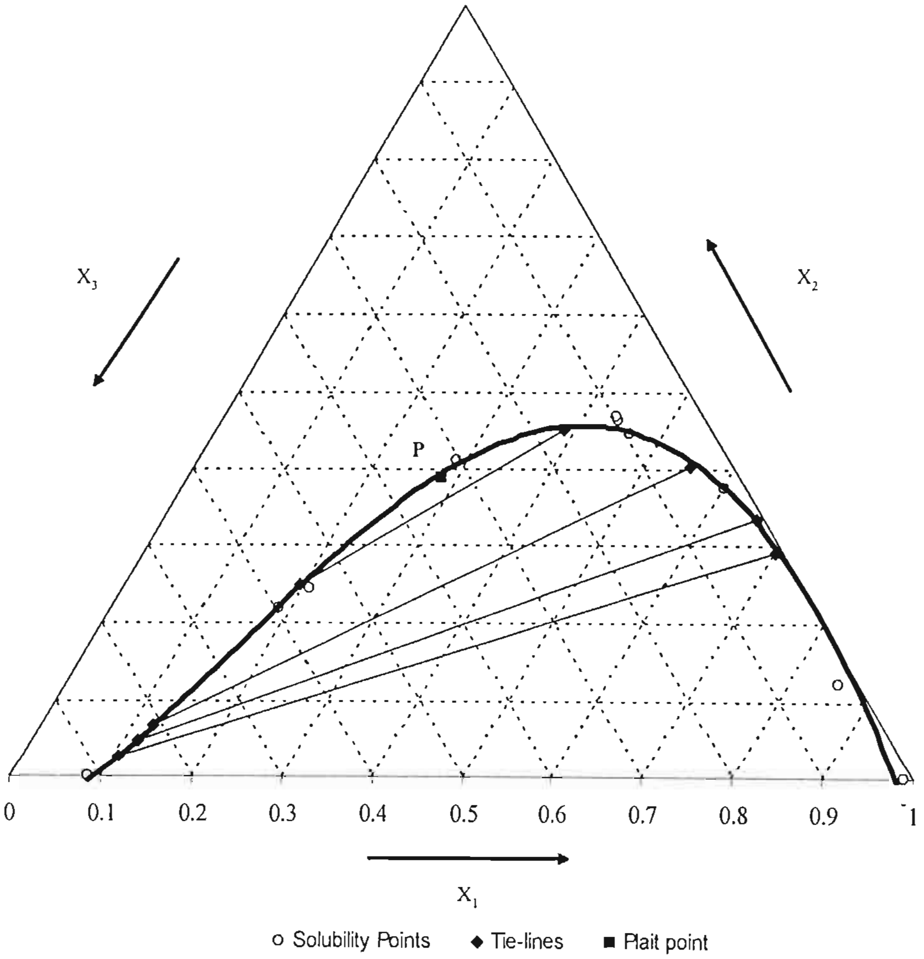


Figure 2-31: Binodal Curve of X_1(*n*-hexane) + X_2(toluene) + X_3(NMP + 10% (w/w) TEG) at 298 K and 1 atm

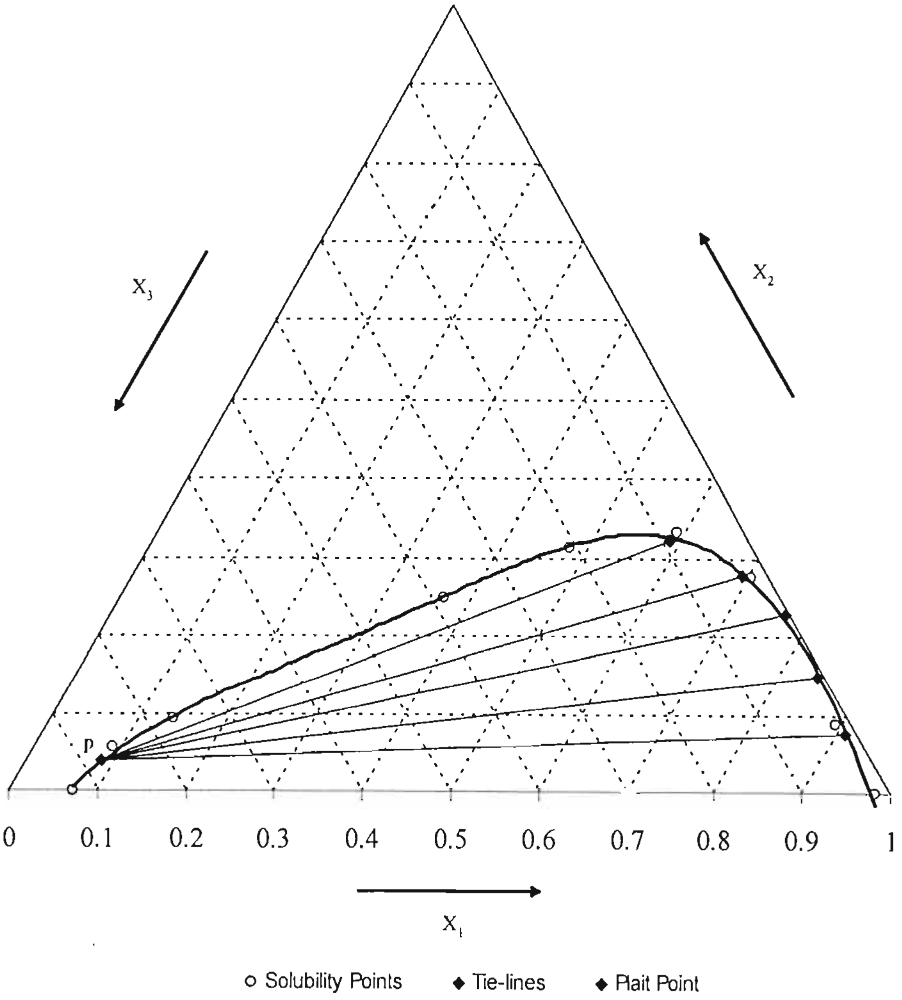


Figure 2-32: Binodal Curve For X_1(*n*-hexane) + X_2(toluene) + X_3\{ NMP + 5% (w/w) water\} at 298 K and 1 atm

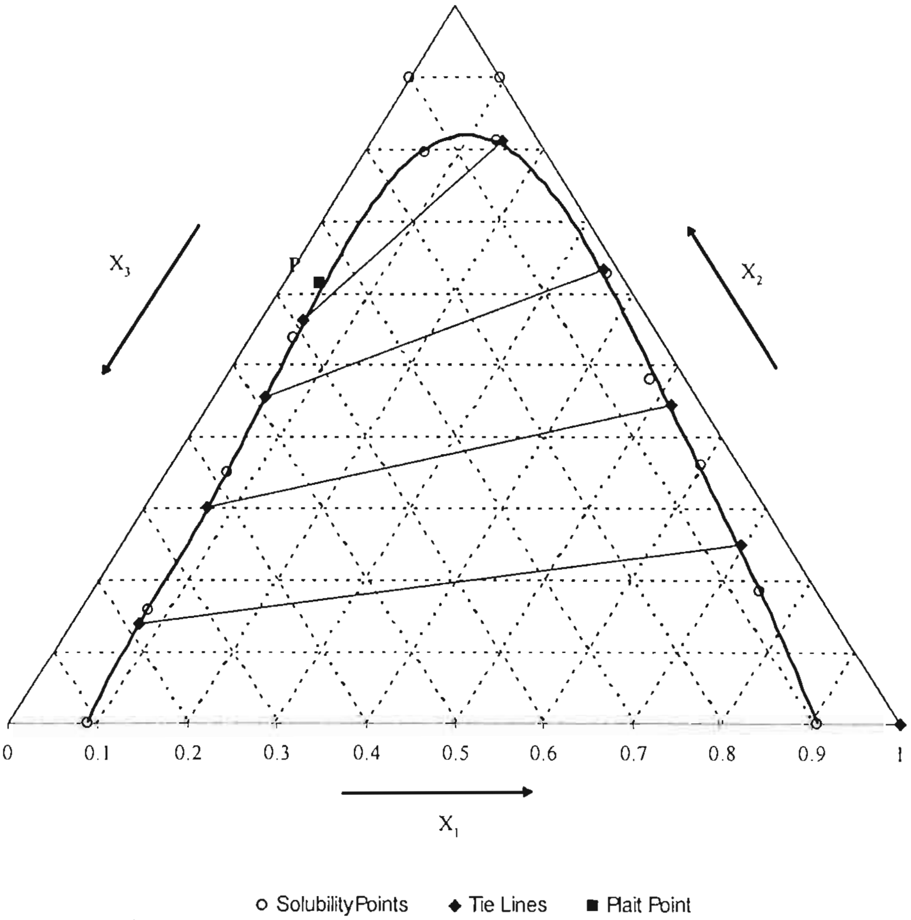
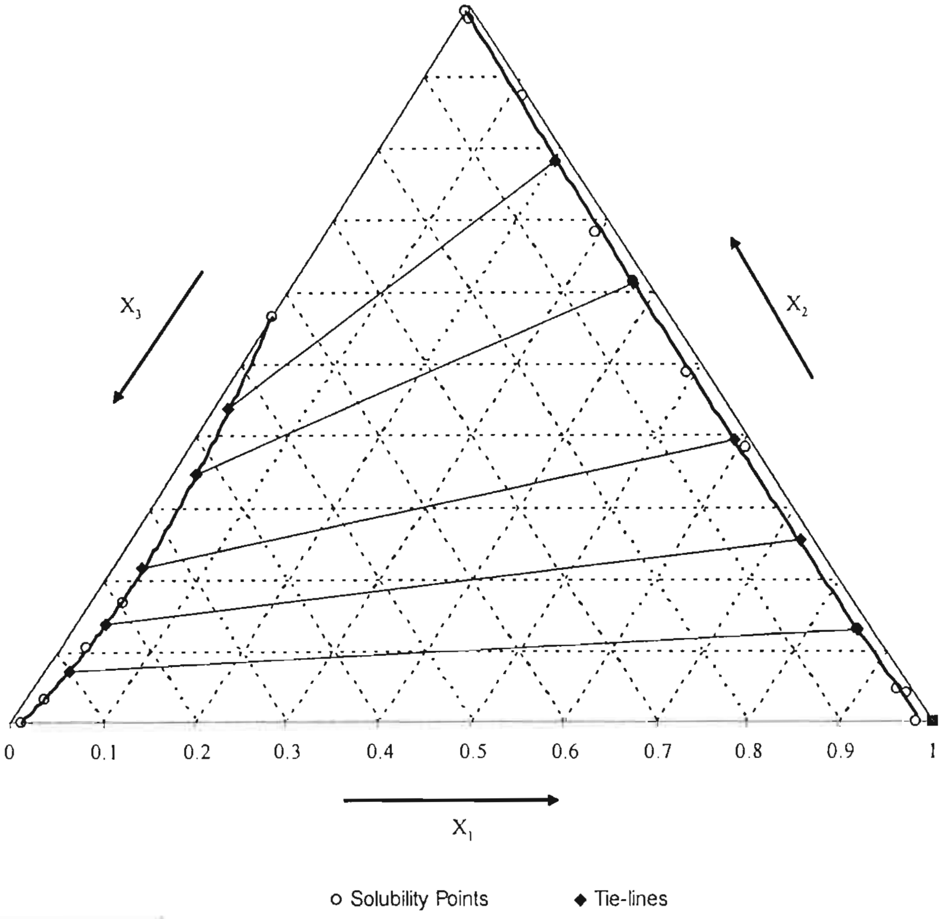


Figure 2-33: Binodal Curve of X_1(*n*-hexane) + X_2(toluene) + X_3{NMP + 10% (w/w) Water} at 298 K and 1 atm



2.7.1 The Treybal Plots

Figure 2-34: Treybal Plot for *n*-hexane + toluene + NMP at 298 K and 1 atm

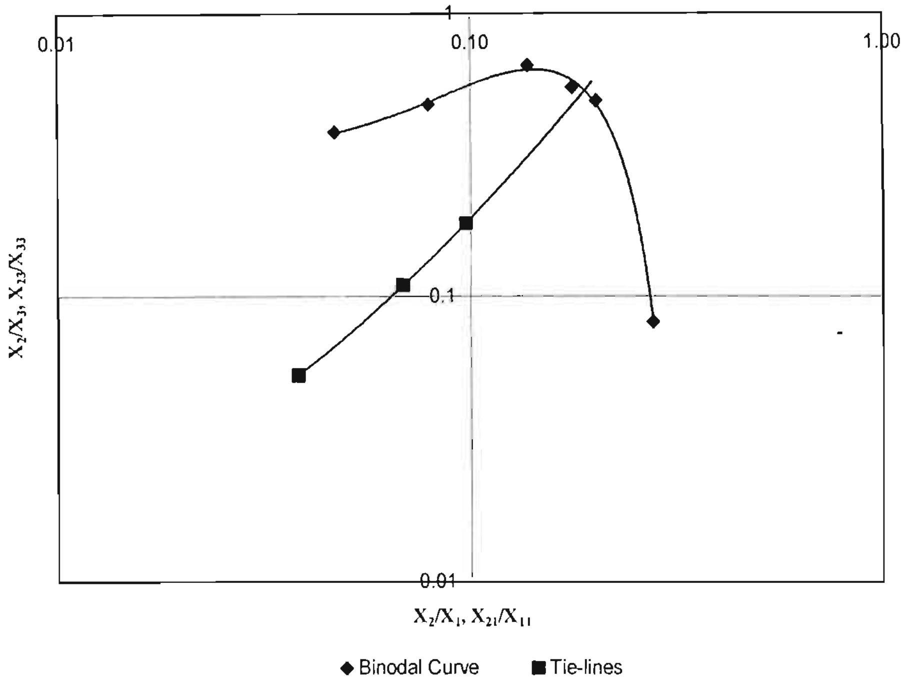


Figure 2-35: Treybal plot for *n*-hexane + toluene + {NMP + 10% Glycerol} at 298 K and

1 atm

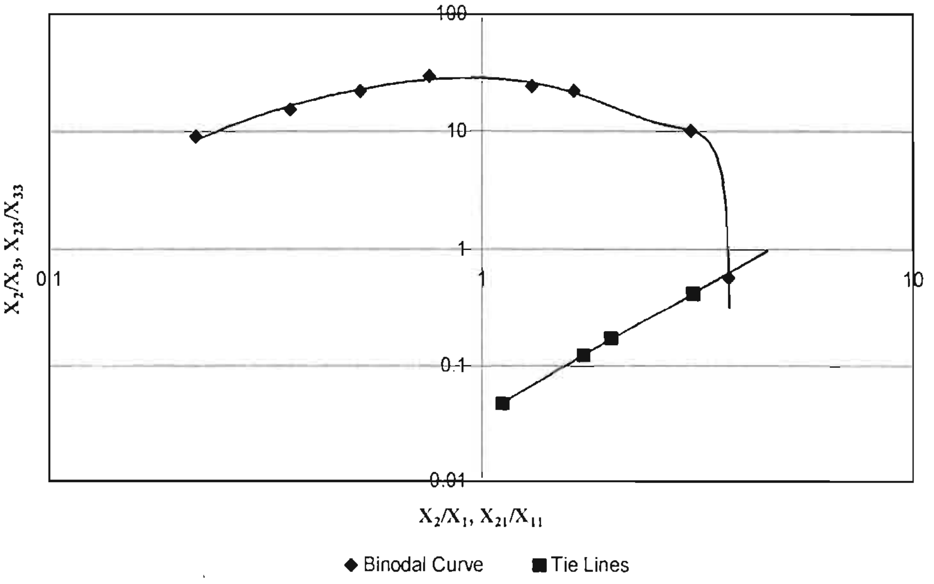


Figure 2-36: Treybal Plot for *n*-hexane + toluene + {NMP + 30% Glycerol} at 298 K and 1 atm

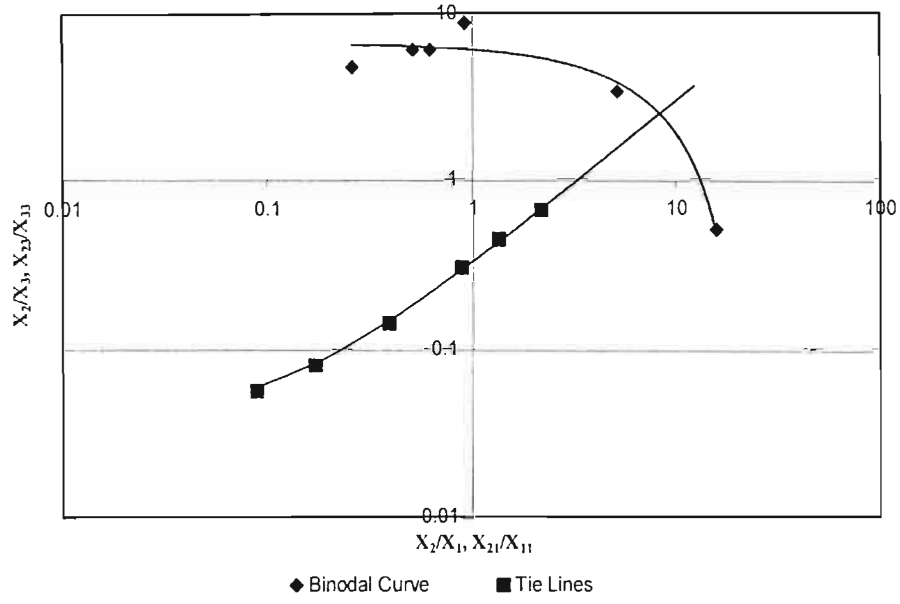


Figure 2-37: Treybal Plot for *n*-hexane + toluene + {NMP + 10% MEG} at 298 K and

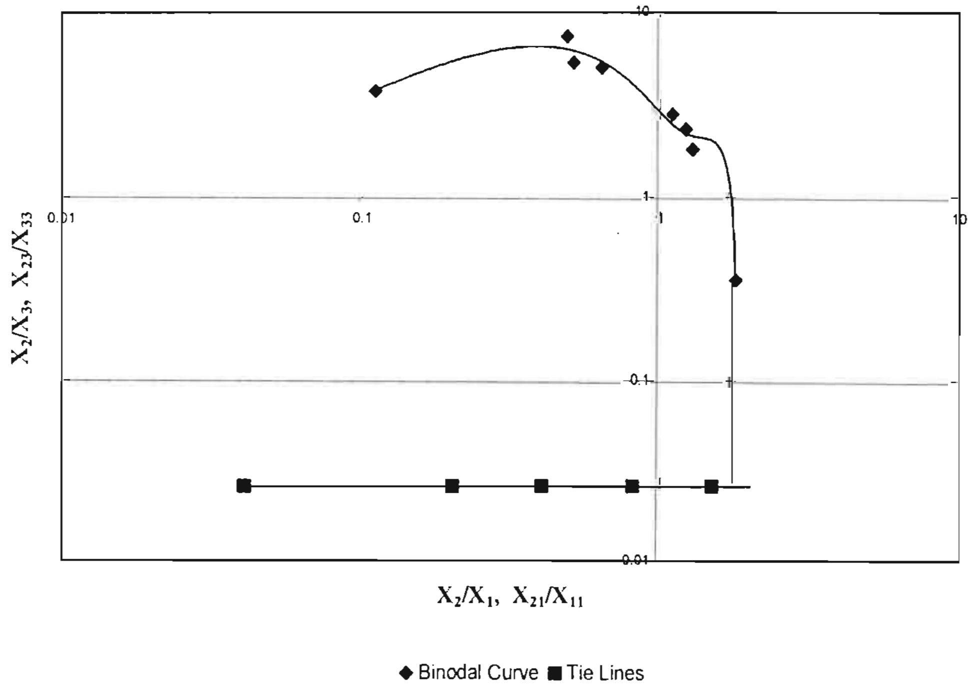


Figure 2-38: Treybal Plot for *n*-hexane + toluene + {NMP + 30% MEG} at 298 K and

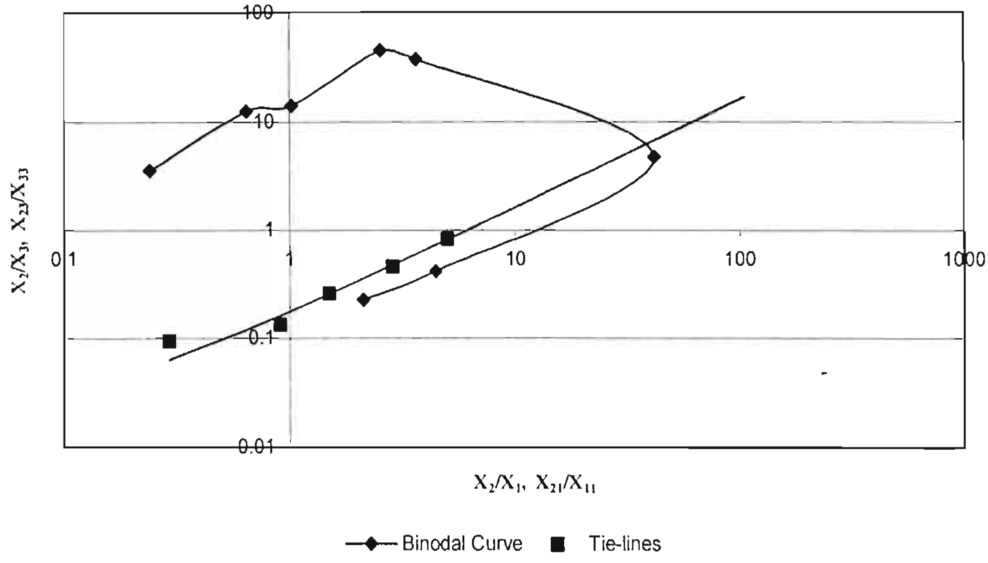


Figure2-39: Treybal Plot for *n*-hexane + toluene + {NMP + 5% DEG} at 298 K and 1 atm

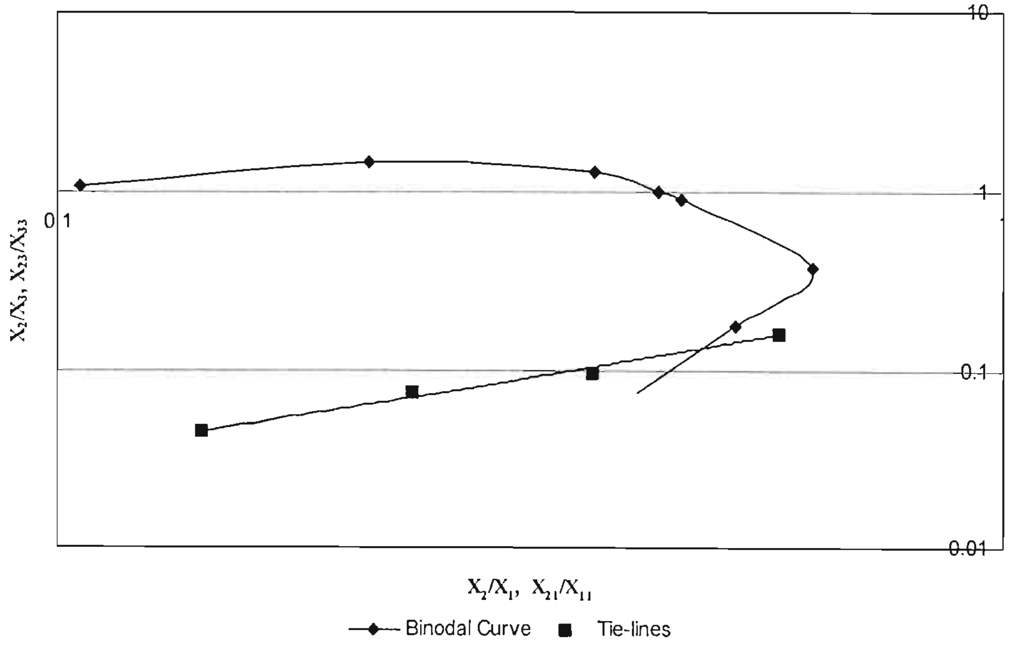


Figure 2-40: Treybal Plot for *n*-hexane + toluene + {NMP + 10% DEG} at 298 K and

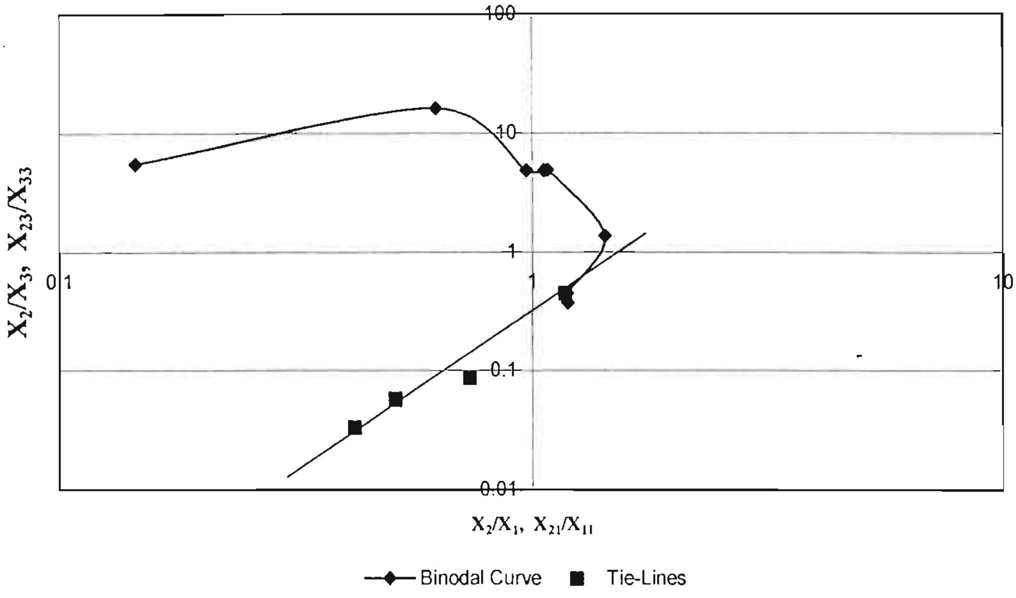


Figure 2-41: Treybal Plot for *n*-hexane + toluene + {NMP + 10% TEG} at 298 K and

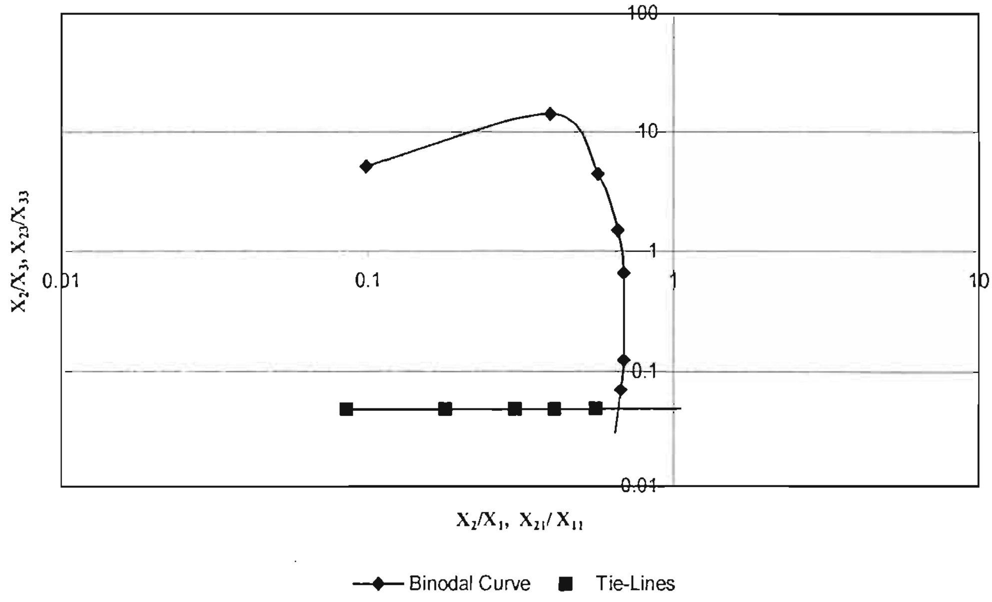
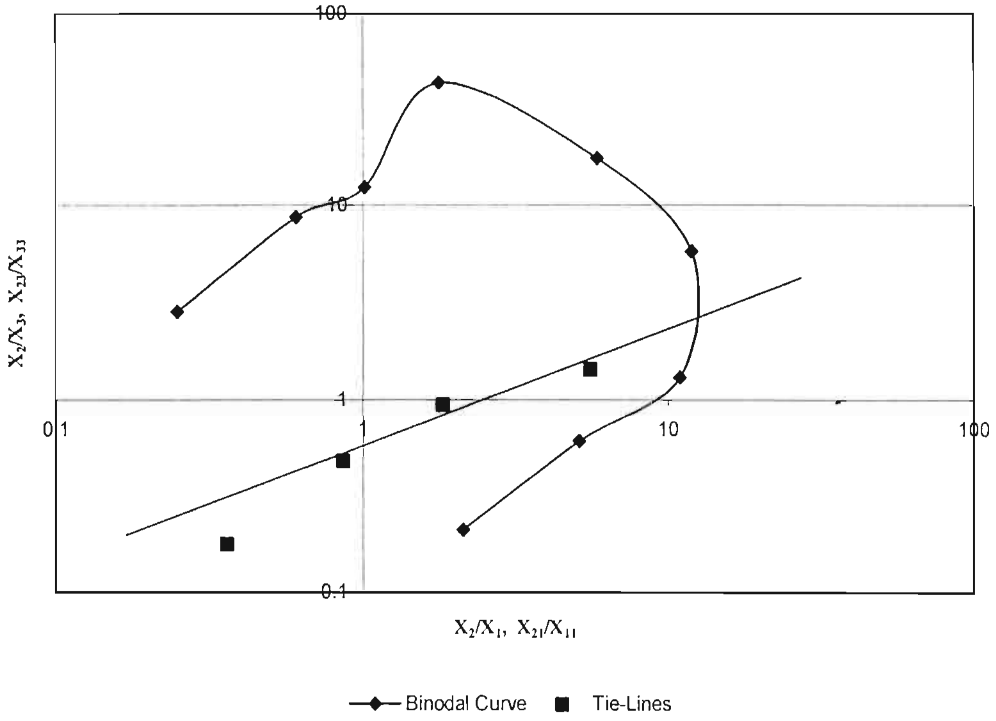


Figure2-42: Treybal Plot for *n*-hexane + toluene + {NMP + 5% Water} at 298 K and



X_1	Solvent	X_2
0.566	NMP	0.133
0.086	10% (w/w) Glycerol	0.509
0.034	30% (w/w) Glycerol	0.540
imaginary	50% Glycerol (lies outside triangle)	imaginary
0.095	10% (w/w) MEG	0.023
0.009	30% (w/w) MEG	0.661
0.250	5% (w/w) DEG	0.145
0.301	10% (w/w) DEG	0.419
0.085	10% (w/w) TEG	0.042
0.041	5% (w/w) water	0.615
imaginary	10% (w/w) water (lies outside triangle)	imaginary

Table 2-5: Compositions of Plait Points at 298 K and 1 atm for the systems {NMP + solvent} + *n*-hexane (X_1) + toluene (X_2). $X_3 = 1 - X_1 - X_2$, where X_i refers to the mass fraction of component *i*

2.7.2 The Distribution Curves

Figure 2-43: Distribution Curve for *n*-hexane + toluene + NMP at 298K and 1 atm

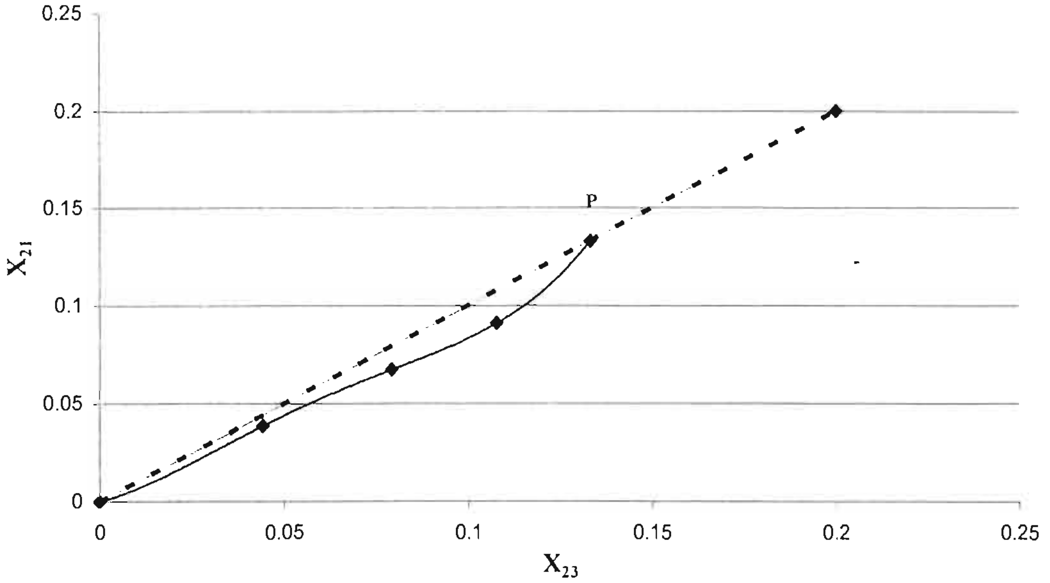


Figure 2.44: Distribution curve of *n*-hexane + toluene + {10% (w/w) glycerol + NMP} at 298K and 1 atm

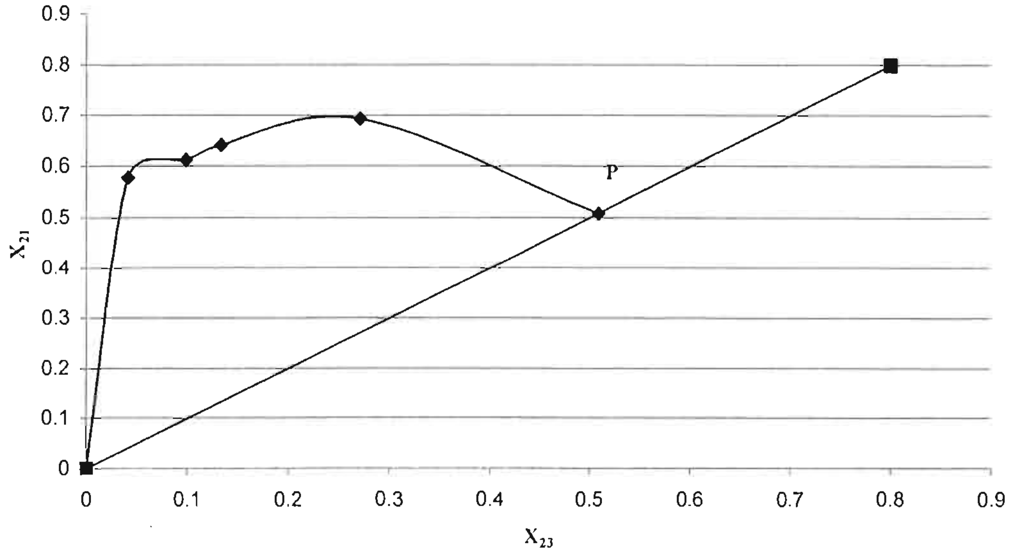


Figure 2-45: Distribution Curve of *n*-hexane + toluene + { 30%(w/w) Glycerol + NMP} at 298 K and 1 atm

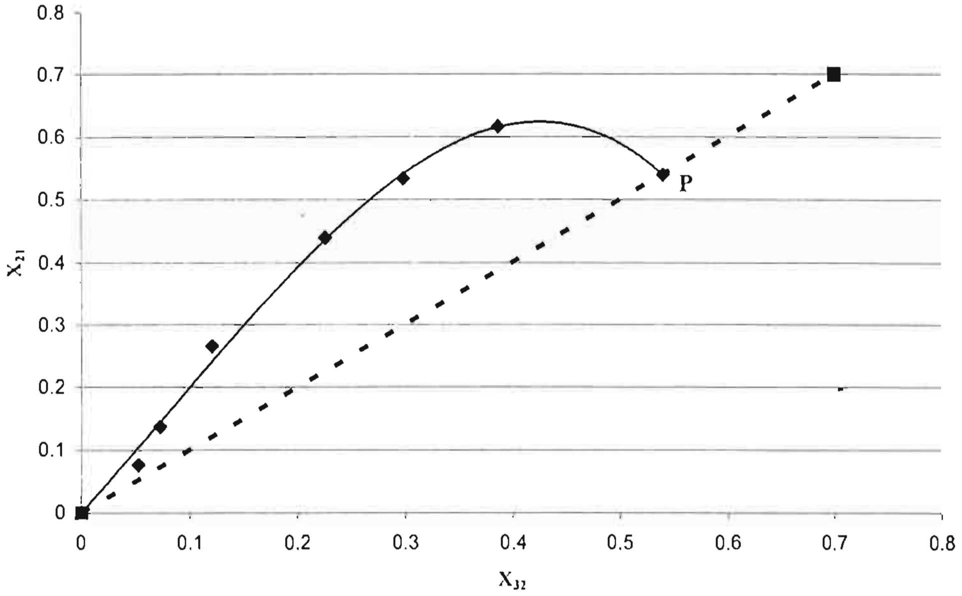


Figure 2-46: Distribution Curve of *n*-hexane + toluene + {50% (w/w) Glycerol + NMP} at

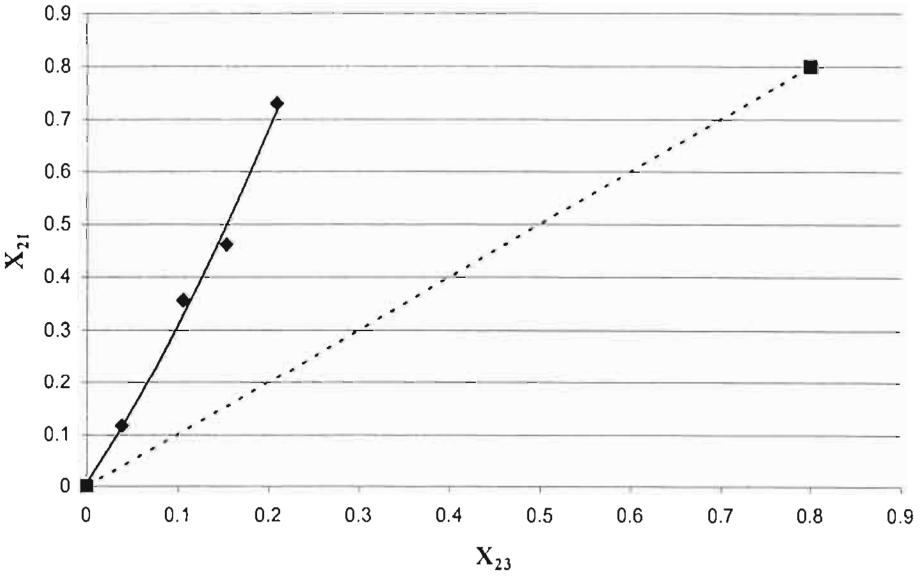


Figure 2-47: Distribution Curve of *n*-hexane + toluene + {10% (w/w) MEG + NMP} at 298 K and 1 atm

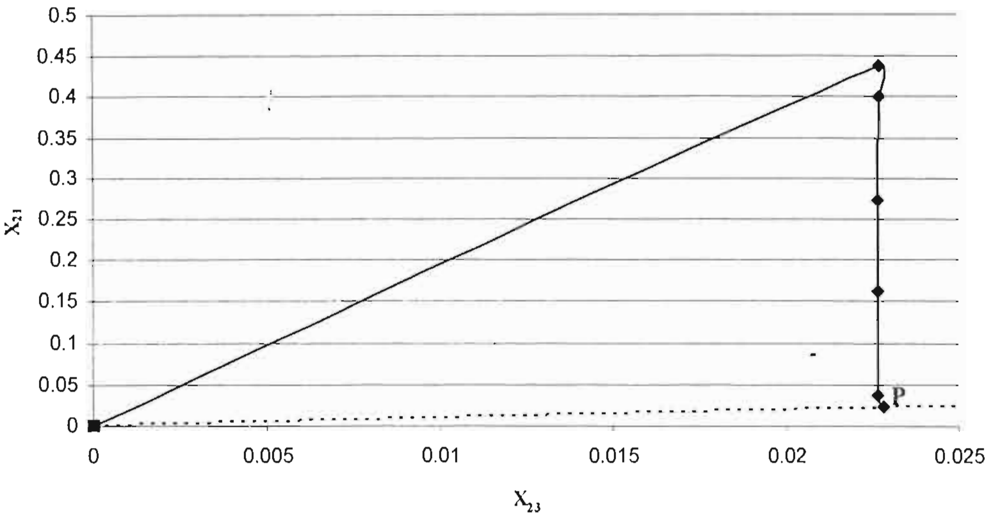


Figure 2-48: Distribution Curve of *n*-hexane + toluene + {30% (w/w) MEG + NMP} at 298K and 1 atm

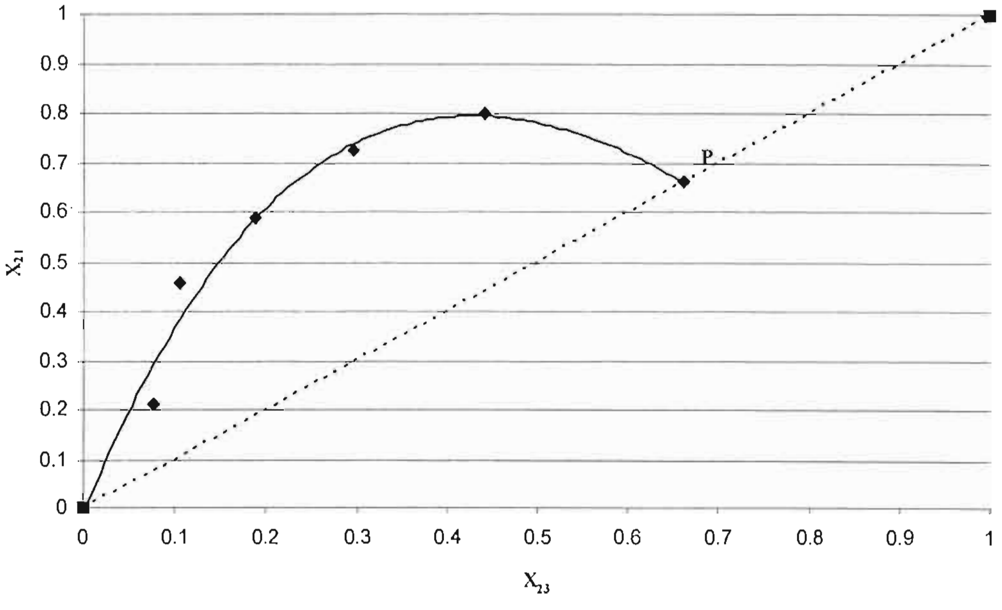


Figure 2-49: Distribution Curve for *n*-hexane + toluene + {NMP + 5% (w/w) DEG} at 298K

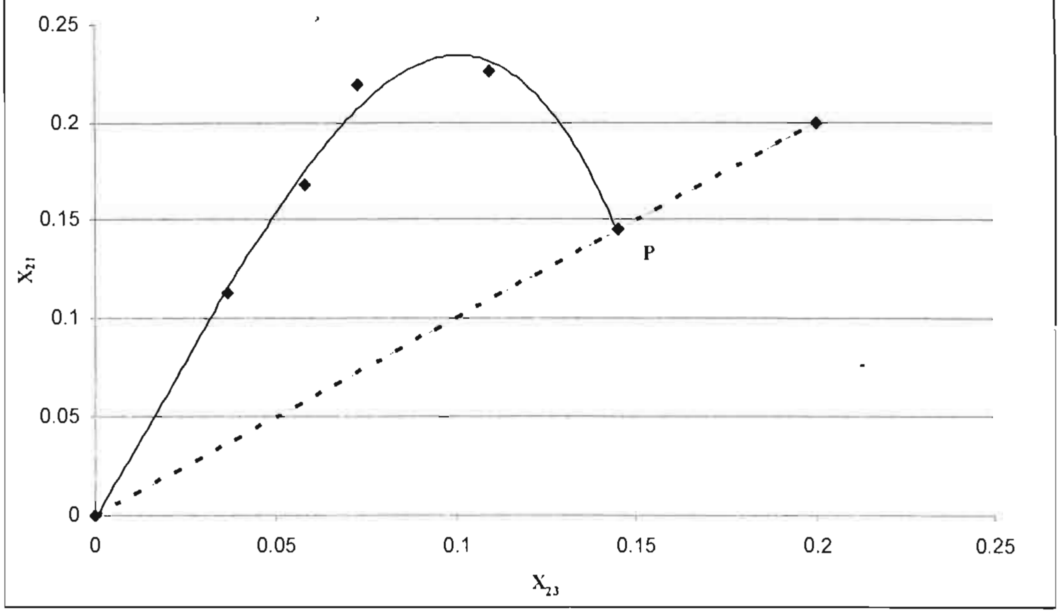


Figure 2-50: Distribution Curve for *n*-hexane + toluene + {NMP + 10% (w/w) DEG} at 298 K and 1 atm

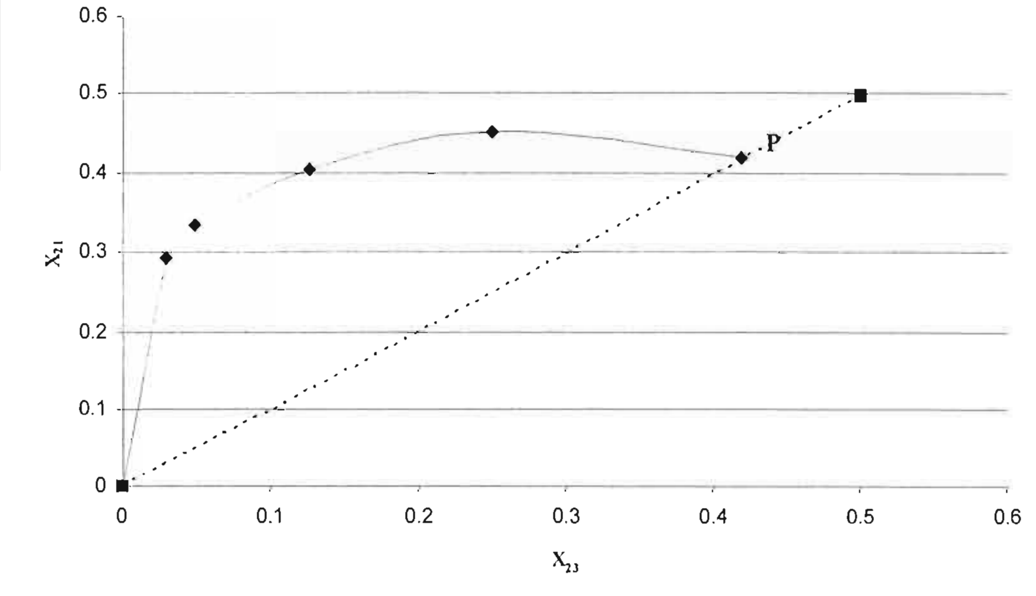


Figure 2-51: Distribution Curve of *n*-hexane + toluene + {NMP + 10% (w/w) TEG} at 298 K and 1 atm

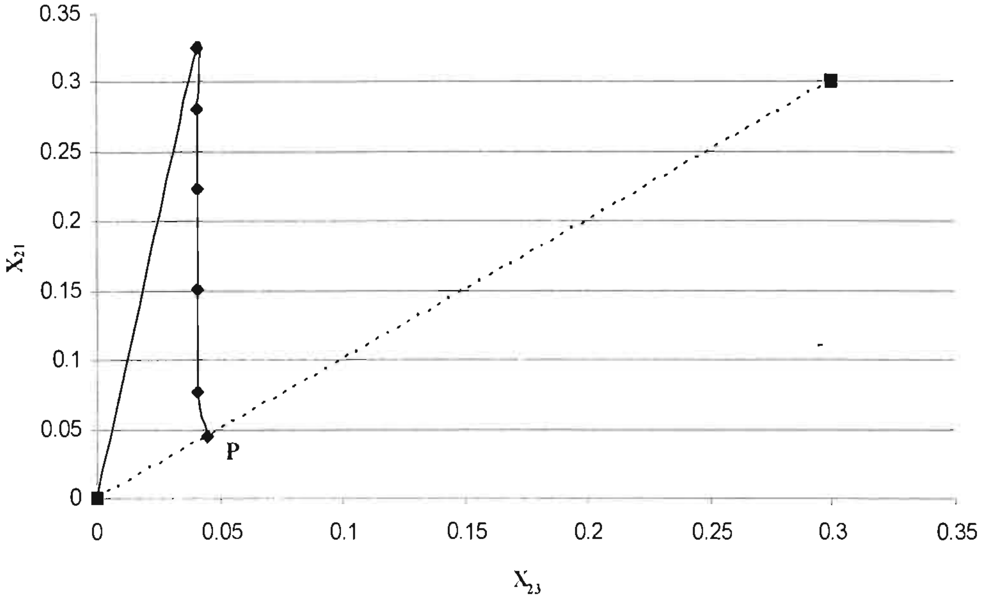


Figure 2-52: Distribution Curve of n-hexane + toluene + {NMP + 5% (w/w) water} at 298 K and 1 atm

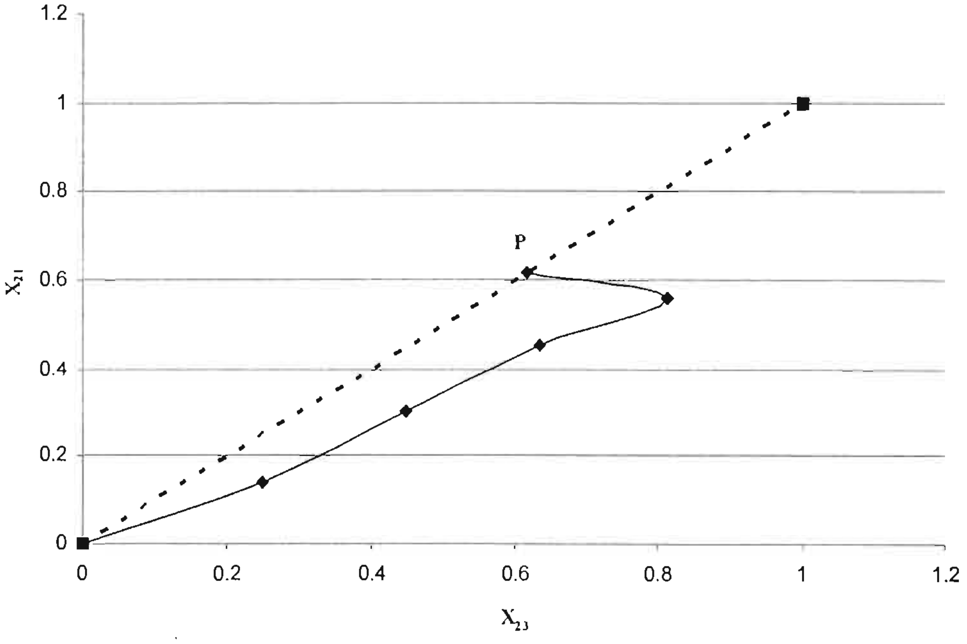
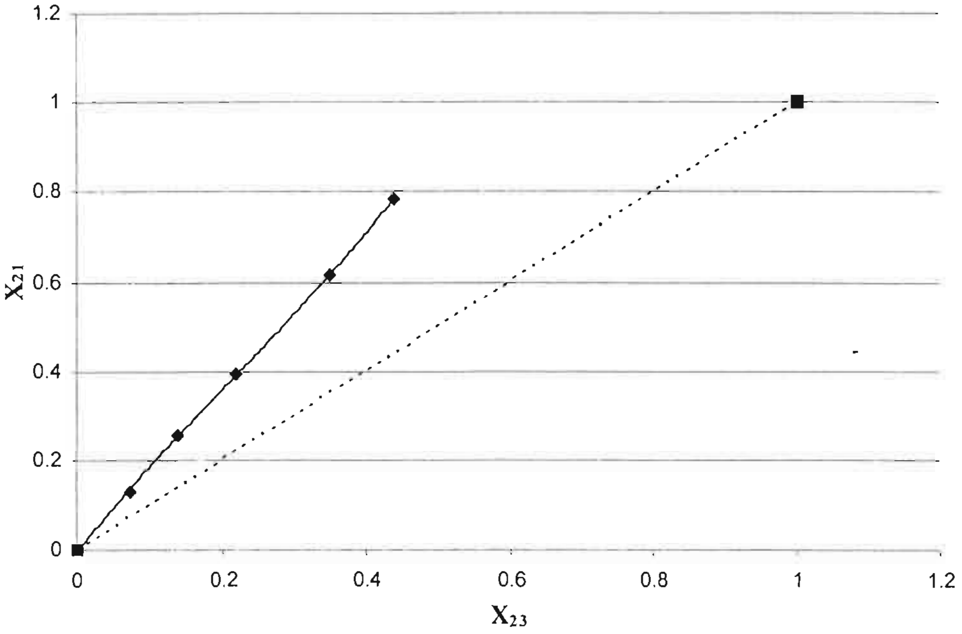


Figure 2-52: Distribution Curve for {NMP + 10%(w/w) water} + n-hexane + toluene at 298 K and 1 atm.



2.7.3 Modelling Results

2.7.3.1 Hlavaty Modelling

Solvent	A_1	A_2	A_3	B_1	B_2	B_3	C_1	C_2	C_3
NMP	-0.515	-0.529	-0.786	0.315	0.454	0.510	0.295	0.430	0.646
NMP + 10% glycerol	1.045	0.604	4.993	3.496	1.137	1.297	3.083	1.086	1.677
NMP + 30% glycerol	1.031	1.295	5.826	4.298	1.402	1.333	3.917	1.364	1.875
NMP + 50% glycerol	1.896	2.340	8.900	4.160	1.127	1.338	3.796	1.101	1.824
NMP + 10% MEG	0.201	-0.009	2.046	2.133	1.088	1.142	2.001	1.065	1.564
NMP + 30% MEG	1.512	2.746	9.120	8.362	1.836	1.531	6.963	1.754	2.172
NMP + 5% DEG	0.101	-0.259	0.729	0.956	0.881	1.114	0.908	0.862	1.459
NMP + 10% DEG	1.536	0.323	4.420	3.929	1.313	1.772	3.680	1.290	1.459
NMP + 10% TEG	-0.027	-0.941	-0.172	0.974	0.740	0.929	0.883	0.700	1.166
NMP + 5% Water	1.451	1.014	6.562	4.250	1.197	1.291	3.773	1.148	1.715
NMP + 10% Water	1.926	2.040	8.996	4.145	1.134	1.328	3.724	1.105	1.714

		ERROR	
Solvent	Hlavaty	β	γ
NMP	0.011	0.010	0.0009
NMP + 10% glycerol	0.013	0.015	0.016
NMP + 30% glycerol	0.012	0.011	0.010
NMP + 50% glycerol	0.011	0.009	0.007
NMP + 10% MEG	0.008	0.010	0.011
NMP + 30% MEG	0.022	0.014	0.013
NMP + 5% DEG	0.003	0.004	0.004
NMP + 10% DEG	0.013	0.011	0.012
NMP + 10% TEG	0.023	0.032	0.033
NMP + 5% Water	0.022	0.025	0.027
NMP + 10% Water	0.050	0.078	0.075

Table 2-6. Hlavaty coefficients A_i, B_i, C_i and Error Hlavaty, β and γ for systems containing *n*-hexane (X_1) + toluene (X_2) + {NMP + solvent} at 298 K and 1 atm. $X_3 = 1 - X_2 - X_1$

2.7.3.2 UNIQUAC and NRTL

		Parameters (J.mol^{-1})					
component		NRTL			UNIQUAC		
ij	ji	g_{ij} - g_{ji}	(rmsd)	g_{ji} - g_{ij}	Δu_{ij}	(rmsd)	Δu_{ji}
			0.058	NMP		0.010	
1-2	2-1	-346.690		1333.480	0.009		0.187
1-3	3-1	3060.870		3771.620	-0.148		0.148
2-3	3-2	-5789.610		-2472.670	0.079		0.216
			0.127	NMP + 10%(w/w) glycerol		0.149	
1-2	2-1	-4237.700		-1803.240	0.127		-0.143
1-3	3-1	-249.010		966.860	-0.013		0.000
2-3	3-2	2225.380		2798.740	0.032		0.072
			0.088	NMP + 30%(w/w) glycerol		0.112	
1-2	2-1	-4826.230		-1700.650	-3649.110		-2053.730
1-3	3-1	3382.680		7194.030	-355.100		1749.210
2-3	3-2	1742.770		400.820	2230.030		2080.780
			0.008	NMP + 50%(w/w) glycerol		0.306	
1-2	2-1	-141.103		13394.512	0.969		0.960
1-3	3-1	5327.013		14664.089	2.489		2.664
2-3	3-2	5938.046		3419.631	0.848		-1.049
			0.155	NMP + 10%(w/w) MEG		0.224	
1-2	2-1	-182.730		1792.790	0.015		-0.036
1-3	3-1	2396.460		1757.240	0.077		0.008
2-3	3-2	111.750		-3916.020	-0.281		0.063
			0.096	NMP + 30%(w/w) MEG		0.226	
1-2	2-1	-4066.470		-784.520	0.079		0.005
1-3	3-1	2873.560		1720.560	0.004		0.004
2-3	3-2	1962.900		1474.820	0.005		0.009
			0.034	NMP + 5%(w/w) DEG		0.041	
1-2	2-1	5030.192		3930.558	645.417		-166.966
1-3	3-1	3237.229		3045.507	2285.927		-145.550
2-3	3-2	2080.734		5039.584	1542.112		263.913

Table 2-7: Values of the parameters for the NRTL and UNIQUAC Equations as well the root mean squared deviation (rmsd).

component		Parameters $(J.mol^{-1})$					
		NRTL			UNIQUAC		
ij	ji	$g_{ij} - g_{ii}$	(rmsd)	$g_{ji} - g_{ij}$	Δu_{ij}	(rmsd)	Δu_{ji}
			0.067	NMP + 10%(w/w) DEG		0.173	
1-2	2-1	-9799.320		-540.310	0.057		0.007
1-3	3-1	3221.240		4335.130	0.046		0.050
2-3	3-2	3632.670		-1626.280	-0.020		0.001
			0.042	NMP + 10%(w/w) TEG		0.207	
1-2	2-1	-3315.880		-7291.060	0.026		0.035
1-3	3-1	6151.530		3101.040	-0.049		-0.087
2-3	3-2	3609.390		-2515.940	0.054		0.095
			0.014	NMP + 5%(w/w) water		0.199	
1-2	2-1	-2041.249		5879.660	33.737		31.547
1-3	3-1	15348.487		5785.214	6.848		4.420
2-3	3-2	5303.926		-86.044	-55.234		-19.899
			0.148	NMP + 10%(w/w) water		0.186	
1-2	2-1	-1637.790		-2378.530	-0.168		-0.017
1-3	3-1	2817.350		2478.740	0.076		0.076
2-3	3-2	-1726.380		523.090	0.014		0.046

Table 2-7(contd) : Values of the parameters for the NRTL and UNIQUAC Equations as well the root mean squared deviation (rmsd).

2.8 DISCUSSION

In order to verify that the experimental apparatus being used could adequately measure the liquid-liquid equilibria of the systems under investigation, it was necessary to measure the LLE of a system for which data was available in literature and determine how closely our experimental apparatus and procedure could reproduce the results. The system chosen as the test system was previously measured by Letcher and Naicker [1998] and contained *n*-hexane toluene and NMP. All data were measured at 298 K and 1 atm.

2.8.1 Literature Comparison

The only data presented in this work that has been measured previously is the-system, (NMP + *n*-hexane + toluene). This work was done earlier by Letcher and Naicker [1998], using experimental methods and equipment identical to those employed in this work. The binodal curve obtained in the work done by Letcher and Naicker is plotted together with the binodal curve obtained in this work in Figure 2-53. The data presented in this work showed a maximum deviation of 0.004 mass fractions from that of Letcher and Naicker. Although the work done by Letcher and Naicker has been presented in the form of mole fractions, the conversion to mass fractions for comparisons was easily performed using Equation 2-7.

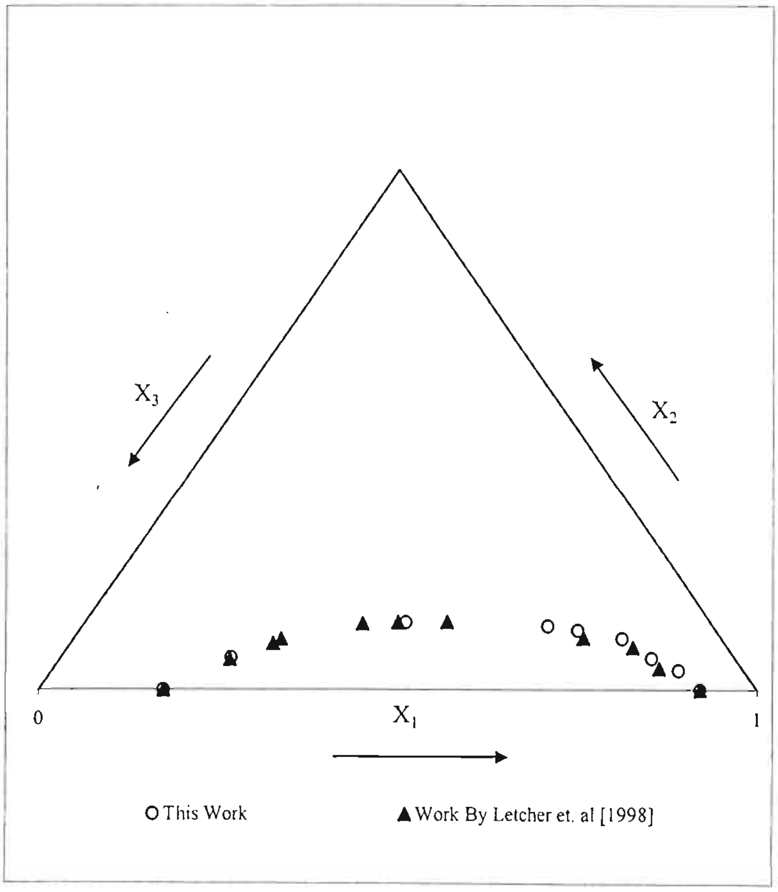


Figure 2-53: Literature Comparison of Solubility curves for NMP + *n*-hexane + toluene at 298 K and 1atm:

in this work are plotted on the same phase diagram in Figure 2-54. The tie-line data exhibited a maximum deviation of 0.03 mass fractions while the deviation in the plait point was found to be approximately 0.04 mass fractions.

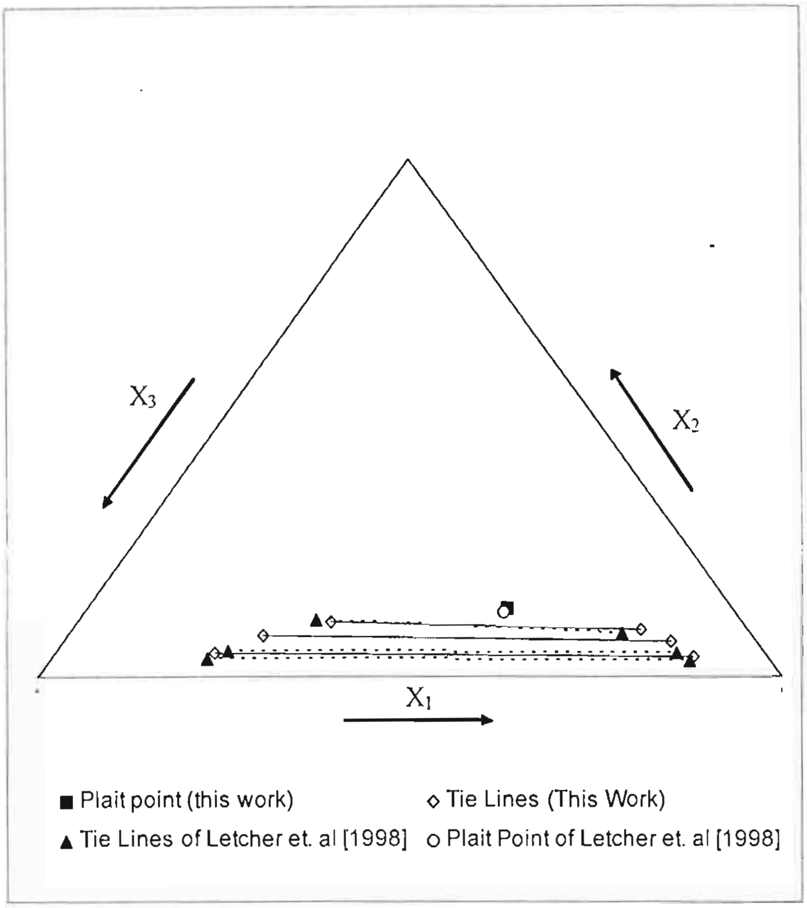


Figure 2-54: Literature Comparison of Tie lines and Plait Points for NMP + n-hexane + toluene at 298 K and 1atm

2.8.2 This Work

The aim of this work was to extend present available literature data on systems of the type {NMP + glycerol, a glycol or water}, as well as to obtain a better understanding of mixed solvents containing {NMP + glycerol, a glycol or water} for the separation of aromatic compounds and aliphatic compounds. In this work, the subscripts 1 and 2 represent *n*-hexane and toluene respectively. These components were used throughout each of the experiments as the aliphatic and aromatic components respectively due to time constraints.

This discussion is based on two important facts:

(1) The basis of solvent selection is the solvent selectivity, which is calculated from tie-line data using simple arithmetic according to Equation 2-27 below (Letcher and Deenadayalu [1999]).

$$S = \frac{\left(X_2 / X_1\right)_{\text{Solvent Rich Phase}}}{\left(X_2 / X_1\right)_{\text{Alkane Rich Phase}}} \qquad (2\text{-}26)$$

Where X_1 and X_2 are the mass fractions of *n*-hexane and toluene respectively. A value of $S = 1$ gives no separation whilst a value of S far greater or far less than 1 indicates good separation. The case of S = 1 occurs only at the plait-point of the system. Selectivities calculated from Equation 2-26 are reported in Table 2-8 overleaf

(2) The extent of the two-phase region (the region encompassed by the binodal curve) indicates the range of compositions over which separation using liquid-liquid extraction may be performed at the temperature under consideration.

N-methyl-2-pyrollidone (NMP) is used as one of the components in the solvent for each of the experiments. The second component in this solvent mixture was either glycerol, MEG, DEG, TEG or water, added in various weight fractions to NMP. In this discussion, each system will therefore be referred to by the solvent additive used in that particular system. For example, the system containing {NMP + 10 %(w/w) glycerol} + *n*-hexane + toluene will be referred to as the 10% glycerol system. The test system, NMP + *n*-hexane + toluene will be referred to as the "base" system and is used as the basis for our discussion

(i) The base system exhibits a small, flat binodal curve (Figure 2-23), which represents a small range over which the separation of *n*-hexane and toluene can occur. The maximum selectivity obtained for this system was found to be almost 6. This system will henceforth be referred to as the "base" system. The 10% glycerol system showed a large increase in the size of the two-phase region (Figure 2-24) and hence an increase in the composition range over which separation can occur. The maximum selectivity calculated for this system was approximately 750, indicating an increase of more than a hundred fold compared to the base system, proving that the addition of glycerol to NMP is more effective compared to using just NMP for the separation of n-hexane and toluene.

Solvent	NMP	10%/w/w) Glycerol	30% (w/w) Glycerol
Selectivities			26
	6	747	37
	5	159	38
	3	102	24
	3	20	19
			10

Solvent	50% (w/w) Glycerol	10% (w/w) MEG	30% (w/w) MEG
Selectivities	75	65	42
	74	291	113
	69	257	118
	106	156	75
		64	23

Solvent	5% (w/w) DEG	10% (w/w) DEG	10 % (w/w) TEG
Selectivities	29	1224	124
	18	964	433
	12	54	1080
	4	6	205
			77

Solvent	5% (w/w) water	10% (w/w) water
Selectivities	14	98
	41	101
	27	72
	26	68
		69

Table 2-8: Selectivities for systems containing *n*-hexane + toluene + a solvent at 298 K and 1 atm

(ii) Figure 2-25 shows a slight increase in the two-phase region for the 30% glycerol system compared to that of the 10% glycerol system. The selectivity for this system was approximately 40. These results show that a larger amount of solvent additive (glycerol) is not necessarily desirable.

(iii) The 50% glycerol system exhibits a two-phase region that encompasses almost the entire triangular phase diagram (Figure 2-26) indicating the largest range of compositions over which separation can occur thus far encountered in this study. However the selectivity calculated was greater than that of the 30% glycerol but still less than that of the 10% glycerol system, at a value of around 110.

(iv) The next solvent additive investigated was monoethylene glycol (MEG). The two-phase region for the 10% MEG system (Figure 2-27) was larger than the base system, but still smaller than all the glycerol systems investigated. Its selectivity had a maximum value of about 300, which was larger than all systems thus far investigated except for the 10% glycerol system.

(v) The 30% MEG system displayed an increase in the size of the two-phase region (Figure 2-28), being only smaller than the 50% glycerol system, indicating a large composition range for separation. The maximum selectivity showed a decrease from the previously mentioned MEG system to about 120. From our above discussion it can be seen that the selection of the solvent is likely to be a trade-off between the range over which separation can occur and the selectivity of the solvent.

(vi) A 5% DEG system was investigated and showed a binodal curve, which was only slightly larger than that of the base system (Figure 2-29). The selectivity obtained from this system had a maximum value of below 30. This system showed a small region for separation, and selectivity only larger than that of the base system and smaller than all other system studied.

(vii) On investigation of a 10% DEG system, it was discovered that the two-phase region did not show a large increase. It was found to be about the same size as the 10% MEG system and exhibited a slight skewing to the right of the triangular diagram (Figure 2-30). The selectivity however showed a phenomenal increase to a value of just below 1230.

(viii) The binodal curve of the 10% TEG system (Figure 2-31) also showed a slight skewing to the right. The size of the two-phase region showed a small decrease compared to that of the 10% DEG system. The selectivity of the 10% TEG system was only smaller than the 10% DEG system and larger than all other systems mentioned above. It had a value of approximately 1100.

(ix) The two-phase region of the 5 % water system was found to be relatively large (Figure 2-32), however the system exhibited a poor selectivity with a maximum of 41.

(x) On increasing the amount of water added to 10% mass fraction, the binodal curve increased to cover almost the entire phase diagram (Figure 2-33), indicating a very large range of separation compositions. This system showed a selectivity of around 100, which was relatively poor.

It was observed, that as a rule of thumb, it is desirable to have a system with tie-lines sloping towards the solvent rich region. This indicated a larger selectivity than systems with relatively flat or horizontal tie-lines.

The size of the two-phase regions in decreasing order of magnitude is as follows:
50% glycerol > 10% water > 30% MEG > 5 % water > 30% glycerol > 10 % glycerol > 10 % MEG > 10% DEG > 10% TEG > 5% DEG > 100% NMP.

The maximum selectivity's in decreasing order of magnitude are:
10% DEG > 10% TEG > 10% glycerol > 10% MEG > 30% MEG > 50% glycerol > 10% water > 5% water > 30% glycerol > 5 % DEG > 100% NMP.

All systems showed excellent correlation with the Hlavaty equations for the binodal curves. The maximum standard deviations obtained were 0.05, 0.078 and 0.075 for the Hlavaty, log-β and log-γ functions respectively. For all Hlavaty coefficients and standard deviations thereof see Table 2-6 in Chapter 2.7.3.1

The systems investigated show good correlation with the thermodynamic correlating equations viz. the NRTL and UNIQUAC equations. The systems showed slightly better correlation with the NRTL equations. This is possibly because a universal value for the non-randomness parameter α_{ij} = 0.30 may be chosen. All parameters and standard deviations for both sets of equations are given in Table 2-7 in Chapter 2.7.3.2.

In light of the fact that the system investigated were in essence, quaternary systems and were modeled as pseudo-ternary systems, they showed excellent agreement with theoretical considerations for ternary systems.

CHAPTER
THREE

3. EFFECTIVENESS OF SOLVENTS IN EXTRACTIVE DISTILLATION

3.1 INTRODUCTION

In Chapter 2 the potential of mixtures containing *N*-methyl-2-pyrollidone with the addition of a glycol, glycerol or water was investigated as a solvent for the separation of *n*-alkanes from aromatic hydrocarbons in liquid-liquid extraction. The aim of this part of the study was to investigate the effectiveness of these solvents in extractive distillation (Schweitzer [1979]).

Aromatic compounds are central to the plastic, synthetic-fibre and synthetic-organic compound producing industries. For this reason, the separation and production of aromatic compounds from liquid mixtures is of paramount importance to industry. Separation is usually achieved by extractive distillation or solvent extraction, where both techniques require a solvent highly selective to the aromatic compounds.

Extractive distillation is a separation technique that utilizes a high boiling solvent to alter the liquid-phase activity coefficients of one or more components in the mixture, so that the relative volatilities of the compounds to be separated from each other becomes more favourable. The solvent is also useful for breaking an azeotrope in the feed component, should one exist (Seader and Henley [1998]).

The effectiveness of a solvent in an extractive distillation process is referred to as the separation factor. The selection of a solvent depends primarily on its separation factor for a desired separation (Perry and Green [1984]). The effect of a solvent on the relative volatilities of the two key components is conveniently represented by the ratio of the infinite dilution activity coefficients (IDACs) of the two key components. This ratio is known as the separation factor of the solvent, β (Gerster, Gorto and Eklund [1960], Tiegs *et al* [1986]).

Vapour-liquid equilibrium stills may be used to determine the effectiveness of solvents. However, gas liquid chromatography (GLC) has been found to be a cheaper and faster alternative and was used in this study for the determination of IDACs (Perry and Green [1984]).

Data that has been found in the literature that bear similarity to this work are displayed in Table 3-1 overleaf. The solvents for which IDACs have been measured in this work are shown in Table 3-2. Data for the following systems measured at 298 K and 1 atm are available in literature and are of significant interest to us.

Solute	**Solvent**	**Reference**
Pentane	NMP	Smiley [1980]
Hexane	NMP	Muller *et al* [1976]
Hexane	Monoethylene glycol	Vernier *et al* [1976]
Hexane	Triethylene glycol	Arancibia *et al* [1980]
Heptane	NMP	Muller *et al* [1976]
Heptane	Monoethylene glycol	Opris [1981]
Heptane	Triethylene glycol	Alessi [1971]
Benzene	NMP	Kikic [1976]
Benzene	Monoethylene glycol	Arancibia *et al* [1982]
Benzene	Triethylene glycol	Arancibia *et al* [1980]
Toluene	NMP	Popescu *et al* [1967]
Toluene	Monoethylene glycol	Arancibia *et al* [1982]
Toluene	Triethylene glycol	Arancibia *et al* [1980]

Table 3-1: Systems for which data is available in literature

As was deduced in Chapter 2, the mixed solvent showing the most significant improvement compared to the pure solvent case, in the selectivity of an aromatic compound for the solutes investigated case was that of a mixture containing (NMP+10%(w/w) solvent). Initially, solvent mixtures of NMP + a glycol or glycerol were investigated. Thereafter, the pure component solvents (NMP, glycols and glycerol) were investigated. This was done to facilitate comparisons between the pure and mixed solvent separation factors for extractive distillation

Solutes	**Solvents**
Pentane	N-methyl-2-pyrollidone (NMP)
Hexane	Glycerol
Heptane	Monoethylene glycol (MEG)
Toluene	Triethylene glycol (TEG)
Benzene	NMP + 10%(w/w) glycerol
	NMP + 10%(w/w) MEG
	NMP + 10%(w/w) DEG

Table 3-2: Components used for determining activity coefficients at infinite dilution at 298 K and .1 atm

understand some general concepts of the infinite dilution activity coefficient. The activity coefficient was introduced as a correction factor used on ideal liquid solutions in order to describe real liquid solutions (Winnick [1977]). The activity coefficient, γ_i, of component *i* is defined in terms of the fugacities in solution, $\hat{f}$, as:

$$\gamma_i = \frac{\hat{f}_i}{x_i \hat{f}_i} \tag{3-1}$$

And in a real liquid solution:

$$\mu_i = \mu_i^0 + RT \ln \gamma_i x_i \tag{3-2}$$

The standard state of the liquids used in this study as defined by the Lewis Randall rule was such that as $x_i \rightarrow 1.0$, $\gamma_i \rightarrow 1.0$. The activity coefficient, as $x_i \rightarrow 0$, is known as the infinite dilution activity coefficient or the limiting activity coefficient and is denoted, γ_i^∞. In general, the dilute region will demonstrate the largest deviation from ideality. Alessi *et al.* [1991] noted the following: in a binary mixture of *i* and *j*, the infinite dilution region is described in physical chemistry terminology as the region in which a molecule of type *i* is completely surrounded by molecules of type *j* so that the molecular interaction occurring are only those between molecule *i* and the surrounding molecules *j* and exclude any interaction between two molecules of *i*.

3.2 DETERMINATION OF INFINITE DILUTION ACTIVITY COEFFICIENTS

IDACs have generated large amounts interest over the past few decades (Harris [2001]). This had led to the ongoing study and development of new and improved ways of measuring or determining IDACs. The following are a few of the more popular techniques available for the measurement of IDACs (Harris [2001]):

- Differential Ebulliometry (Gautreaux and Coates [1955])
- Gas Liquid Chromatography (GLC) (Letcher [1978])
- Dew-Point method (Suleman and Eckert [1994])
- Headspace chromatography (Hussman *et. al* [1985])
- Differential pressure (Pividal *et. al* [1992])
- Inert gas stripping (Leroi *et. al* [1977])
- Inverse solubility (Letcher *et.al* [1978])

The three most popular techniques, which were defined by Abbot [1986] and summarized by Raal and Muhlbauer [1998], will be discussed below in brief detail.

3.2.1 Differential Ebulliometry.

The thermodynamic basis for direct experimental measurement of infinite dilution activity coefficients was pioneered by Gautreaux and Coates [1955), who developed thermodynamically exact relationships for the following four sets of data measurements.

- Isobaric temperature-liquid composition data
- Isobaric temperature-vapour composition data
- Isothermal pressure-liquid composition data
- Isothermal pressure-vapour composition data

The most common means of data measurements for IDACs are isobaric and isothermal temperature liquid composition measurements, (Raal and Muhlbauer [1998]). The calculation of infinite dilution activity coefficients for these cases is given below in Equations (3-3) and (3-4) respectively.

$$\gamma_1^{\infty} = \frac{p_2^{sat}}{p_1^{sat}}\left\{1 - \left(\frac{\partial T}{\partial x_1}\right)_P^{\infty}\left(\frac{d\ln p_2^{sat}}{dT}\right)\right\} \tag{3-3}$$

$$\gamma_1^{\infty} = \frac{p_2^{sat} + \left(\frac{\partial P}{\partial x_1}\right)_T^{\infty}}{p_1^{sat}} \tag{3-4}$$

Where γ^{∞} is the activity coefficient at infinite dilution, p_i^{sat} is the vapour pressure of component i, T is the system temperature. P is the system pressure and x_i is the liquid mole fraction of component i.

3.2.1.1 Experimental Apparatus of Thomas *et al* [1982]

Thomas *et al* [1982] developed a compact ebulliometer (Figure 3-1) that consisted of the following special features:

(1) The inside of the vertical heater tube had a layer of fused ground glass to provide nucleation sites to facilitate smooth boiling.

(2) It had a separate jacket built over the top portion of the equipment to facilitate good temperature control.

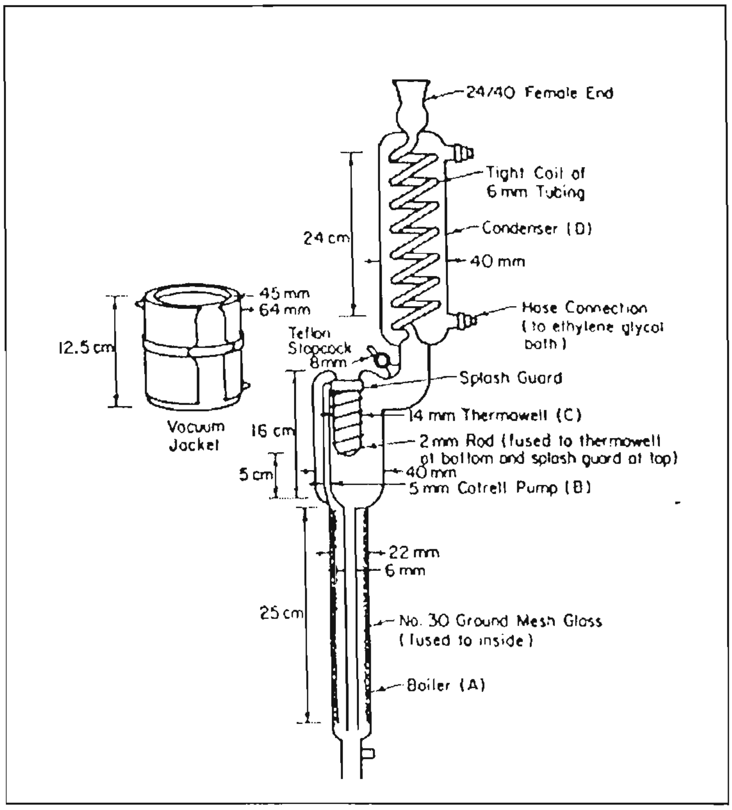


Figure 3-1: Differential Ebulliometer used in the experimental work of Thomas et. al. [1982]

Thomas *et al* [1982] used five ebulliometers simultaneously and studied an exceptionally large number of systems. A comprehensive list of these systems is given by Raal and Muhlbauer [1998]. Their work proved to be relatively accurate and exhibited a maximum uncertainty in the IDACs of ± 15%. This uncertainty was based on the standard deviation of the fit to the $\left(\frac{dT}{dx_1}\right)_p^{\infty}$ expressions, the sensitivity of the change in the value of γ_i^{∞} to the changes in the slope, and on the magnitude of the holdup correction. The construction and maintenance of such equipment can be excessively costly.

3.2.1.2 Apparatus of Null [1980]

A large amount of effort, in terms of experimental work, may be avoided by placing several ebulliometers in series. This was illustrated by Null [1980] who used three ebulliometers in series with each other. Figure 3-2 is a schematic of his experimental apparatus setup.

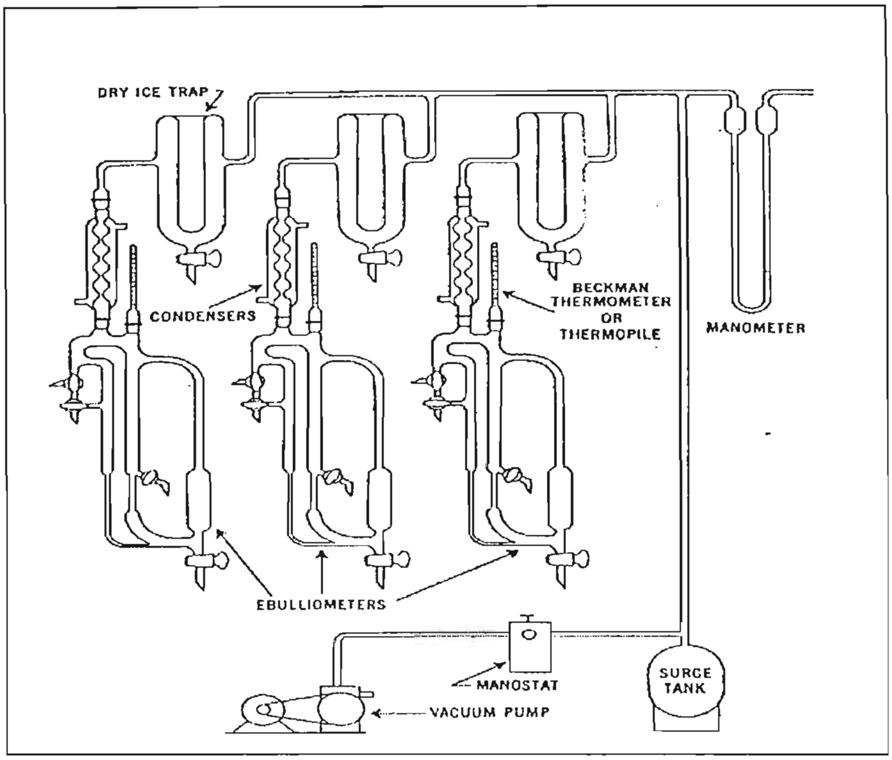


Figure 3-2: Schematic diagram of three ebulliometers used in series by Null [1980]

Although ebulliometric methods provide relatively good results, they do present some limitations. They become problematic when the system is very viscous or if one component is almost completely non-volatile (Raal and Muhlbauer [1998]). More complications arise at extremely low vapour pressures since as

$p_1^{sat} \rightarrow 0, \gamma_1^{\infty}$ becomes indeterminate. Systems that present a limited liquid mutual solubility also present a problem when using ebulliometry. For these reasons, ebulliometry could not be used as an experimental method for the systems under investigation in this study.

3.2.2 Gas liquid Chromatography

Gas liquid chromatography (GLC) has been used and has produced the best results for determination of infinite dilution activity coefficients using a volatile solute in a non-volatile solvent, and could be extended to systems for which the solvent is moderately volatile (Bayles *et al* [1993] and Thomas *et al* [1982a].

This method was developed by Everett *et al* [1965], and not only was it easy to use and maintain, but was also cost effective and simple to construct and operate. GLC has an added advantage in that the solutes need not be purified before use since the impurities are easily separated within the column.

As mentioned above, numerous systems have been measured by this method which has proven to have an estimated inaccuracy of less than 5% (Raal and Muhlbauer [1998]), which can be reduced to around 2% by using the refined theory presented by Letcher [1980]). Approximately 88% of the nearly 2100 data points reported by Bastos et. al [1985] have been determined by GLC (Harris [2001]). Figure 3-3 shows a simplified schematic of a typical GLC setup.

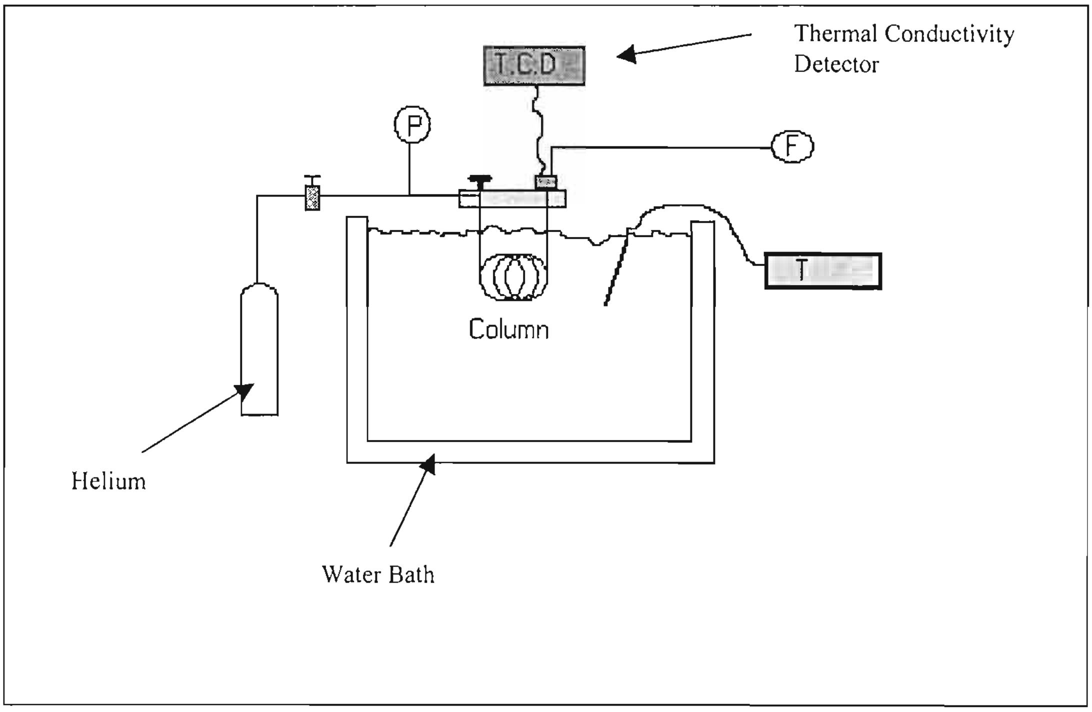


Figure 3-3: Simple schematic of gas liquid chromatographic equipment; T- column temperature, F - gas flow rate and P - inlet Pressure

The basic equation defining IDACs in GLC is:

$$\ln \gamma_{13}^{\infty} = \frac{n_3 R T}{V_N p_1^0} + C_1 + C_2 \tag{3-5}$$

$$\text{with } V_N = f\left(P_o, P_i, U, T_w, t_R, t_G\right) \tag{3-6}$$

C_1 and C_2 are gas phase correction terms based on the virial coefficients (Cruickshank et. al [1966]). Subscripts *1,2* and *3* refer to the solute, carrier gas and solvent respectively. The quantities that had to be determined via experimentation are presented in Chapter 3.5.1.

3.2.3 Inert Gas Stripping Method (Leroi et. al. [1977])

The idea of inert gas stripping came from Fowlis and Scott [1963]. In this procedure, developed by Leroi *et al* [1977], a flow of inert gas was passed through a liquid mixture such that it "stripped" the more volatile component from its very dilute solution in the heavier solvent. The inert gas, which contains traces of the solute, was then analysed using gas chromatography. The concentration-time profile, which resulted from this analysis, was then used to determine the activity coefficients at infinite dilution. The method could be applied to a non-volatile or volatile solvent provided that it is less volatile than the solute. The dilutor flask used by Leroi *et. al.* [1977] is shown in Figure 3-4 overleaf.

Leroi *et al* [1977] performed experiments with solutes of *n*-hexane and benzene. With these they investigated 10 different solvents. According to Raal and Muhlbauer [1998], these results gave exceptionally good reproducibility, but, however, differed from those results obtained from GC retention time methods, particularly for highly non-ideal systems. This was attributed to the interaction with the solid Chromosorb within the column in the GC studies. It is possible to extend this method for a solute in a multicomponent mixture.

The apparatus used here is a relatively cost effective to operate, however in the event of breakages (as with all precision glass instruments), can be especially costly to repair and maintain.

The set of general equations used for calculation of IDACs from this technique are outlined below in detail. The following equations are used to calculate the infinite dilution activity coefficients using the inert gas-stripping method:

For a non-volatile solvent:

$$\ln \frac{A}{\left(A_{sol}\right)_{t=0}} = -\frac{D}{RT}\frac{p_{sol}^{0}}{N}\gamma^{\infty} t \tag{3-7}$$

For a volatile solvent:

$$\ln \frac{A}{\left(A_{sol}\right)_{t=0}} = \left[\frac{\gamma^{\infty} p_{sol}^{sat}}{p_{s}^{sat}} - 1\right] \ln\left[1 - \frac{P}{P - p_{s}^{sat}} . \frac{D\, p_{s}^{0}}{N_{o} R T} . t\right] \tag{3-8}$$

Where γ^{∞} is the infinite dilution activity coefficient, p^{sat} is the saturated vapour pressure, T is the system temperature, x is the liquid mole fraction, D is the carrier gas flowrate, P is the system pressure, N is the number of moles of solvent in the still, t is the time and A is the area of the solute GC curve at time t. Subscript *sol* refers to the solute and *s* to the solvent. A typical schematic of the inert gas stripping process is shown in Figure 3-5.

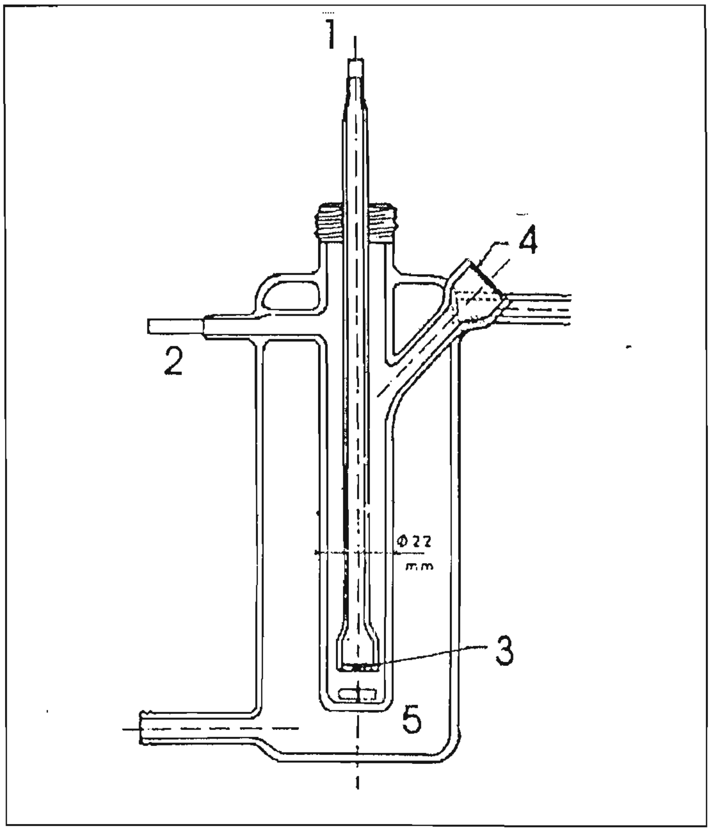


Figure 3-4: Dilutor Flask of Leroi et. al. [1977]:
1,2 = inert gas inlet and outlet; 3 = fine porosity fritted disk; 4 = septum holder; 5 = magnetic stirrer

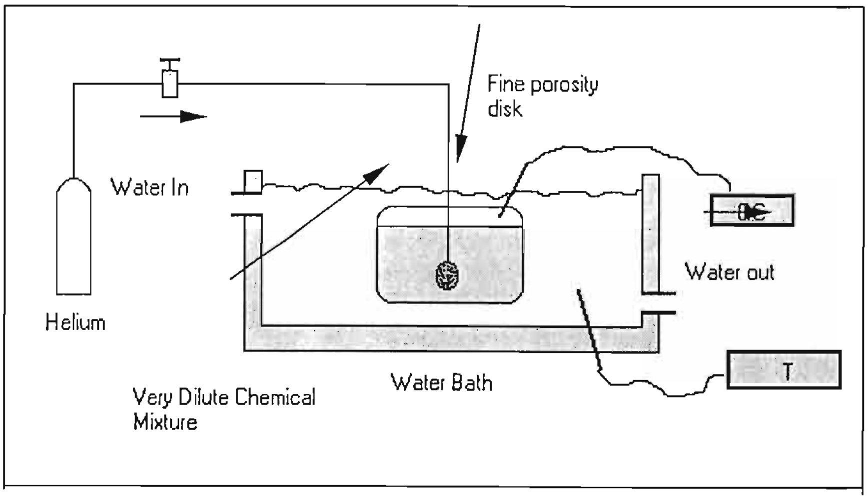


Figure 3-5: Schematic of Inert Gas Stripping Method

Due to the relevant equipment being readily available, gas-liquid chromatography was used to determine the IDAC's for systems considered in this work. This technique also provides rapid and accurate determination of infinite dilution activity coefficients.

3.3 EXPERIMENTAL TECHNIQUE EMPLOYED

The concept of GLC was first introduced by Martin and Synge [1941]. James and Martin [1952] proved how useful the technique could be as an analytical tool, and extended liquid-liquid theory to cover GLC. They also indicated that retention volumes could yield valuable physico-chemical information. Later Martin [1956] and Hoare and Purnell [1956] indicated the potential of GLC to study the behaviour of a volatile solute in a non-volatile solvent, and hence the measurement of activity coefficients (γ_i) by GLC.

GLC (as used in this study) is an analytical technique involving two immiscible phases that have a common interface. These are a stationary liquid or solvent phase and a mobile gas phase, where the gas phase is allowed to flow over the stationary liquid phase. The stationary liquid phase is characterized by having a large surface area and is coated onto an inert solid support such as diatomaceous earth (celite), which is then packed into the column. The gas is then allowed to flow between the coated celite particles.

The nature of gas-liquid chromatography limits the choice of liquid mixtures that one could use. The solute must be volatile if retention times are to be reasonable. The solvent must be a liquid at the experimental temperature, with a low vapour pressure so as not to seep out of the column during experimentation. GLC provides an easy means of studying the thermodynamics of liquids that fall within the above restrictions. A volatile solute would be partitioned between the stationary solvent phase and the mobile gas phase while being eluted. A small amount of solute was introduced into the column inlet. A solute peak was carried through the column by the mobile phase and was recorded using a detector connected to the column outlet. Cruickshank et al [1966] noted that the solute peak velocity, past a point in the GLC column depended on, (1) the local distribution coefficients between the two phases; (2) the local gas velocity and (3) the ratio of the local specific volumes of the gas and liquid phases. A concentration/time profile of the solute was recorded by the detector from the time it was introduced into the column to the time of its emergence.

3.3.1 Experimental variables/parameters.

The following variables are required to be determined from experiment :

- n_3 = number of moles of solvent
- P_o = the outlet pressure = atmospheric pressure
- P_i = inlet pressure
- U = flow rate
- t_g = the retention time for inert gas to pass through column
- t_r = solute retention time

3.3.2 Temperature Control (*T*)

The activity coefficient is a function of the solute vapour pressure (Equation 3-5), and it is therefore important that the column temperature be accurately known. A stirred, well-insulated water bath along with a Tronac temperature controller provided good temperature control to within 0.01 K of the set-point temperature. The temperature controller was connected to a simple on/off relay using a light bulb as a low capacity heater. A 2 m length of 4.2 mm bore copper tubing was used as a pre-column to ensure that the temperature of the carrier gas was at the same temperature as the column.

Temperature control is extremely important because of the solute vapour-pressure dependency on temperature. A deviation of 0.05 K in column temperature translates to an uncertainty of 0.003 Pa. This in turn results in an uncertainty in γ_{13}^{∞} of approximately 0.26 %. In this work the uncertainty due to temperature fluctuations is less than 0.08%.

3.3.3 Pressure Measurement (P_i and P_o)

The inlet pressure was measured using a wide bore mercury barometer (15mm in diameter) and a cathetometer and read to approximately 0.01mmHg. The outlet or atmospheric pressure was determined using a normal barometer. It was estimated that the inlet and outlet pressure were known to within 0.03 mmHg.
The error in P_i and P_o would translate to an error in J_3^2 and this presented an error of $9\mathrm{x}10^{-6}$ in γ_{13}^{∞} (Whitehead [1999]).

3.3.4 Flow Rate Measurement

Flow rate was calculated using a calibrated soap bubble flow meter. The flow meter consisted on a 100ml calibrated cylinder .The flow meter was connected upstream of the detector. The flow meter (Figure 3-6) that was used was constructed as follows: The top of the flow meter was open to the atmosphere. The gas inlet to the cylinder was positioned just above the soapy water solution. A rubber teat was used in order to displace the soap solution. The flow rate was measured with an accuracy of 0.5ml.s^{-1}

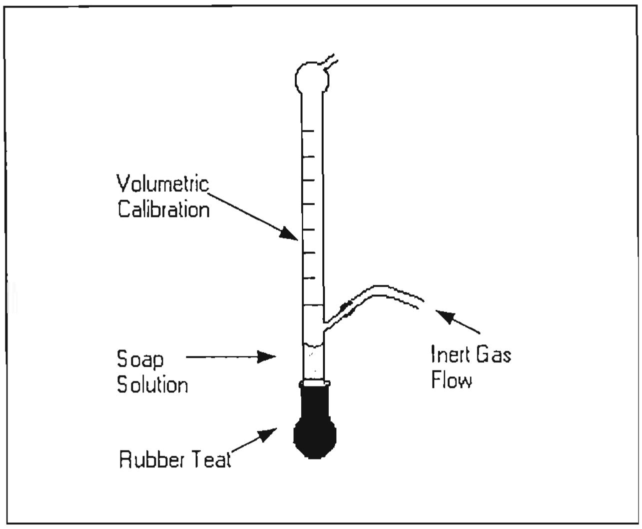


Figure 3-6: Bubble flow meter used to measure flowrate, U.

3.3.5 Determination of the number of moles of solvent, n_3

The calculations of activity coefficients at infinite dilution are extremely sensitive to n_3 and so care is taken to make sure that n_3 is determined with the utmost accuracy. The following procedure was employed:

- A round bottom flask was accurately weighed
- Celite was added to the flask and weighed
- A rough estimate of the amount of solvent to be added to the celite, to achieve the required loading percentage, was made up.
- Solvent is added to the celite and weighed
- Diethyl ether is added to the mixture to distribute the solvent evenly in the celite, and the total mass is noted.
- The diethyl ether was then removed using a rotary evaporator. The mixture was constantly re-weighed to determine if all the diethyl ether was removed.
- A funnel was then weighed with the round-bottomed flask containing the mixture.
- The funnel was used to fill the column with the celite and solvent
- The funnel was then weighed together with the round-bottomed flask to determine the exact amount of solvent and celite transferred to the column.

The mass of the constituents was known to 0.001g. . If we consider NMP as the solvent this translates to accuracy in n_3 of approximately 1×10^{-5} moles This resulted (worst case) in an uncertainty of less than 0.05% in γ_{13}^{∞}

3.3.6 Infinite dilution range

A typical injection volume of $0.05\mu L$ was used. If we consider toluene, this corresponds to 4.7×10^{-7} moles. A typical column used for our investigation contained on average 3×10^{-3} moles. It is reasonable to assume that the solute is exposed to 30% of the solvent at any time. This corresponds to a mole fraction of 4.7×10^{-4}, which is within the limits suggested by Alessi *et al* [1991] as the infinite dilution region.

3.3.7 Determination of true retention times, t_g and t_r.

Peaks achieved during experimentation were spread and not confined to a small area; therefore it was necessary to estimate where the true retention time would have been.

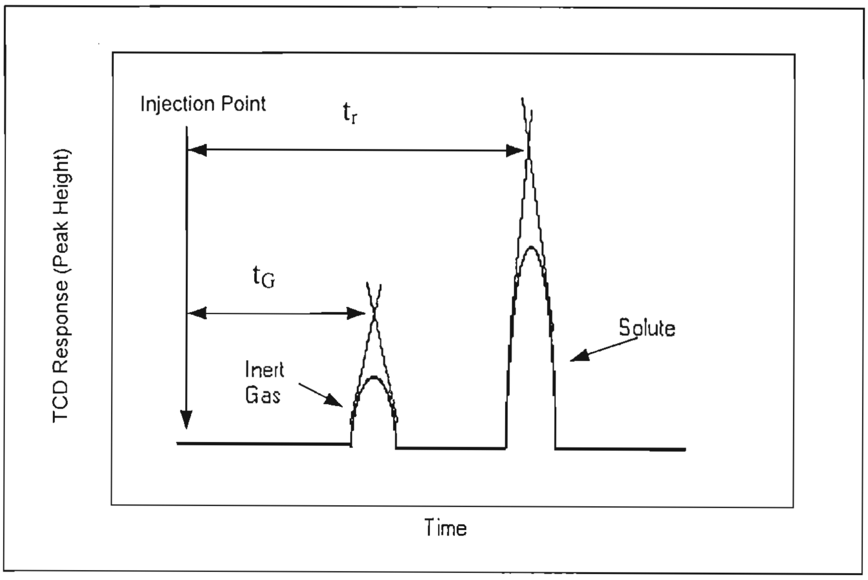


Figure 3-7: Chromatogram showing TCD response vs. time

This was done by defining the true retention time as the time from injection to the intersection of the tangents of the peak (Letcher [1978]). This time was accurate to 0.2 seconds over a period of 10 to 6000 seconds. The chromatogram constructions are shown in Figure (3-7).

3.3.8 Apparatus Used

Copper and Stainless steel columns of 4.2mm bore were used. The columns were between 0.3 and 1.2 m in length. Figure 3-8 is a schematic diagram of the equipment employed.

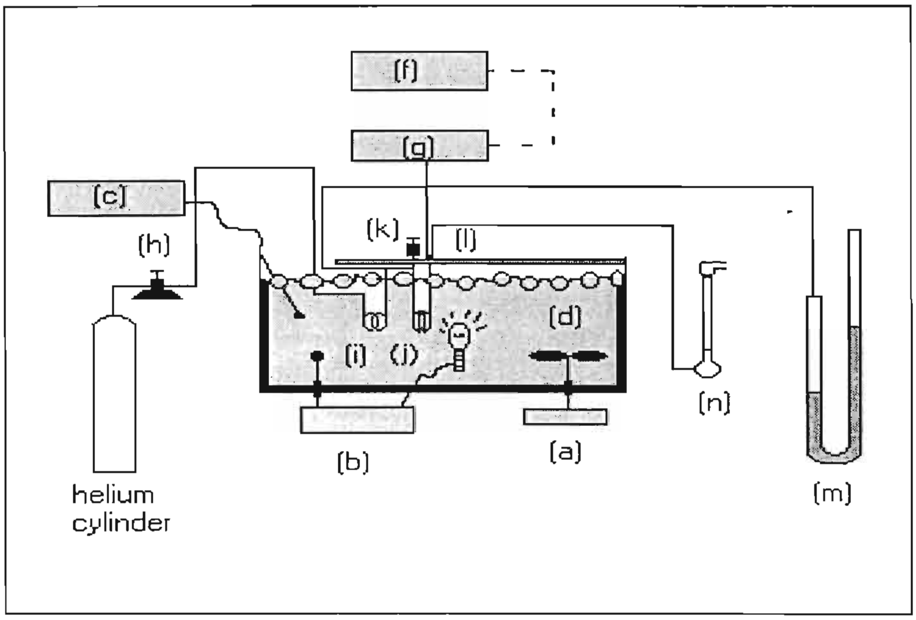


Figure 3-8: Schematic Diagram of Equipment used in this work:
(a) Stirrer; (b) Tronac PTC-41 Temperature Controller; (c) Hewlett Packard 2804A Quartz Thermometer; (d) Constant temperature water; (f) Kipp and Zonoen Chart recorder; (g) Gow-Mac Instrument Co. Series 350 Power Supply Unit; (h) Negretti Zambra Needle Valve; (i) Pre-Column made of copper; (j) Column; (k) Injection port; (l) Thermal Conductivity detector; (m) Mercury manometer; (n) Soap bubble meter

3.4 THEORETICAL CONSIDERATIONS

3.4.1 Development of Calculation

The calculation of activity coefficients at infinite dilution is made possible via thermodynamic manipulation of experimental data. A partition for distribution coefficient, K_L, was defined by Conder & Young [1979] as follows:

$$K_L = \frac{q}{c} = \frac{C_L}{C_w} \qquad (3\text{-}9)$$

In the above expression, c is the concentration of solute in the mobile gas phase. The term q is the concentration of solute in the liquid phase, when solute is distributed between a gas and a liquid at equilibrium. At equilibrium, the solute free energy is at a minimum and the chemical potential would be equal in the mobile (M) and liquid (L) phases, therefore the following applies:

$$\mu_i^L = \mu_i^M \tag{3-10}$$

From the equation:

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{3-11}$$

by replacing the activities by concentration then substituting into equation (3-8) we get:

$$\mu_i^{0L} + RT \ln C_L = \mu_i^{0M} + RT \ln C_M \tag{3-12}$$

$$\therefore \ln \frac{C_L}{C_M} = \left(\frac{\mu_i^{0M} - \mu_i^{0M}}{RT} \right)$$

These give us the following expression from the use of equation (3-7):

$$K_L = \frac{C_L}{C_M} = \exp\left[\frac{\Delta \mu_i^0}{RT} \right] \tag{3-13}$$

Since, ideally, $\Delta\mu_i$ is a constant, K_L is also a constant due to the fact that R and T are also constants in the above expression. The net retention volume V_N is related to K_L and the volume of the stationary phase V_L by:

$$V_N = K_L V_L \tag{3-14}$$

This can be used to calculate the partition coefficient at mean column pressure (Laub and Pecsok [1978]). A simple derivation for the activity coefficient is outline below, without taking into account the gas-phase imperfections. Consider equation (3-7). If we let V_g and V_l be the volumes of the gas and liquid phase respectively then we may rewrite the expression for K_L as:

$$K_L = \frac{x\, n_3\, V_g}{y\, n_2\, V_l} \tag{3-15}$$

Where n_3 is the number of moles of solvent in the liquid phase and n_2 is the number of moles of carrier in the mobile phase. x and y are the mole fractions of the solute in the liquid and mobile phases respectively. The activity coefficient at any concentration is defined by:

$$p_1 = \gamma_1 x_1 p_1^0 \tag{3-16}$$

The solute pressure is p_1 and p_1^0 is the saturated vapour. The solute pressure may be expressed in terms of the total pressure P as follows:

$$p_1 = y_1 P \tag{3-17}$$

Using equations (3-14) and (3-15) and substituting into equation (3-13) gives:

$$K_L = \frac{P\, n_3\, V_g}{\gamma_1\, P_1^0\, n_2\, V_l} \tag{3-18}$$

Assuming gas phase ideality where $PV = nRT$, we get:

$$\gamma_{13}^{\infty} = \frac{n_3 R T}{p_1} \cdot \frac{1}{V_l K_L} \qquad (3\text{-}19)$$

Now substituting (3-12) into equation (3-17). Also, $V_g \equiv V_l$, we get the expression:

$$\gamma_{13}^{\infty} = \frac{n_3 R T}{V_N P_1^0} \qquad (3\text{-}20)$$

Using this equation to calculate γ_{13}^{∞} from net retention volumes, V_N, provides only a rough estimate of γ_{13}^{∞}. If one requires greater accuracy, gas phase imperfections and compressibility must be taken into account. In order to simplify the theory we have assumed that the mobile phase is insoluble in the stationary liquid phase and that the solute equilibrates between the stationary and mobile phases. Further developments of equation (3-18) by Everett [1965], Cruickshank *et al* [1966] and Cruickshank *et al* [1969] required that the procedure take into account the gas imperfections and compressibility through the column. This led to the Equation (3-21) used by Desty *et al* [1962] and later by Letcher *et al* [1978]

$$\ln \gamma_{13}^{\infty} = \left[\frac{n_3 RT}{V_N P_1^0}\right] - \left[\frac{\beta_{11} - v_1^0}{RT}\right] P_1^0 + \left[\frac{\left(2\beta_{12} - v_1^{\infty}\right) J_2^3 P_o}{RT}\right] \qquad (3\text{-}21)$$

Where P_o is the outlet pressure and is equal to atmospheric pressure $J_1^3 P_o$ is the mean column pressure, n_3 is the amount of solvent in the column at temperature T, P_1^o is the vapour pressure of the solute, β_{11} is the 2nd virial coefficient of the pure solute, β_{12} is the mixed 2nd virial coefficient of the solute (1) and the carrier gas (2), v_1^o is the molar volume of the solute v_1^{∞} is the partial molar volume at ∞ dilution in the solvent so $v_1^{\infty} = v_1^o$. The equation, however, is not applicable to highly polar solvents.

The net retention volume, V_N, is given by

$$V_N = J_3^2 . U_o (t_r - t_g) \qquad (3\text{-}22)$$

Where

$$J_i^j = (J_j^i)^{-1}$$

and t_r and t_g are the retention times for the solute and unretained gas respectively. U_o is the volumetric flow rate of carrier gas expressed in terms of column temperature and was corrected for the vapour pressure of water as follows:

$$U_o = u\left(1 - \frac{P_w}{P_o}\right) \frac{T}{T_f} \qquad (3\text{-}23)$$

where T_f is the temperature of the flow meter, P_w is the vapour pressure of water at T_f and U is the flow rate ($m^3.s^{-1}$) measure at a soap bubble flow meter.

Everett [1965] outlined an expression for the gas compressibility factor J_2^3 and is given by

$$J_2^3 = \frac{2}{3}\left[\frac{\left(\frac{P_i}{P_o}\right)^3 - 1}{\left(\frac{P_i}{P_o}\right)^2 - 1}\right] \tag{3-24}$$

where P_i is the column pressure that was measured using a mercury manometer.

The theory for the determination of γ_1^∞ for moderately volatile solvents was developed by Bayels, Letcher and Moolan [1993]. They proposed that the first term of Equation (3-19) be replaced by:

$$\ln\left[\frac{n_3RT - P_3'U_ot}{VNP_1^o}\right]$$

Using this, we arrive at the following expression for $\ln\gamma_{13}^\infty$

$$\ln\gamma_{13}^\infty = \ln\left[\frac{n_3RT - P_3'U_ot}{VNP_1^o}\right] + C \tag{3-25}$$

where

$$C = \left[\frac{(\beta_{11} - \upsilon_1^o)P_1^o}{RT}\right] + \left[\frac{(2\beta_{12} - \upsilon_1^\infty)J_2^3P_o}{RT}\right] \tag{3-26}$$

U_o is kept constant throughout the experiment and the number of moles of solvent lost from the column, $n_3^{\cdot}$, is given by $\frac{P_3'U_ot}{RT}$ where P_3' is the partial pressure of the solvent in the gas at the column outlet and this the time elapsed from the start of the carrier gas flow into the column.

3.4.2 Calculation of Virial Coefficients

The virial coefficients were calculated using McGlashan and Potters' [1962] equation

$$\frac{\beta_{ij}}{V_{c_{ij}}} = 0.43.0.886\left(\frac{T_{c_{ij}}}{T}\right) - 0.694\left(\frac{T_{c_{ij}}}{T}\right)^2 - 0.0375\left(n_{ij}' - 1\right)\left(\frac{T_{c_{ij}}}{T}\right)^{4.5} \tag{3-27}$$

where T_c is the critical temperature, n' is the number of carbon atoms and V_c is the critical volume. For β_{12}, the Lorentz rule (Conder and Young [1979]) and the Hudson and McCoubrey [1960] mixing rules were applied:

$$T_{c_{ij}} = \frac{128\left(T_{c_{ii}}T_{c_{jj}}\right)^{\frac{1}{2}}\left(I_{c_{ii}}I_{c_{jj}}\right)^{\frac{1}{2}}\left(V_{c_{ii}}V_{c_{jj}}\right)^{\frac{1}{2}}}{I_{c_{ij}}} \qquad (3\text{-}28)$$

with

$$I_{c_{ij}} = \left(I_{c_{ii}} + I_{c_{jj}}\right)^{\frac{1}{2}}\left(V_{c_{ii}}^{\frac{1}{3}} + V_{c_{jj}}^{\frac{1}{3}}\right)^{6} \qquad (3\text{-}29)$$

$$V_{c_{ij}} = \left(V_{c_{ii}}^{\frac{1}{3}}.V_{c_{jj}}^{\frac{1}{3}}\right)^{\frac{3}{8}} \qquad (3\text{-}30)$$

and

$$n'_{ij} = \frac{\left(n'_i + n'_j\right)}{2} \qquad (3\text{-}31)$$

Further, I represents the ionization energies, P_i^o the vapour pressures V_i^o represents the molar volumes. These values are given in appendix B-1 (Table B-1) for all solutes, helium and water Vapour pressures were calculated using the Antoine equation:

$$\log P = A - \frac{B}{t + c} \qquad (3\text{-}32)$$

In the above equation, P is the pressure in *mmHg* and t, the temperature in Kelvin. Antoine constants for all components used are given in Appendix B-1, Table B-2.

3.4.3 Prediction of Infinite Dilution Activity Coefficients

As with liquid-liquid equilibria, many models exist for prediction of infinite dilution activity coefficients. Some of the models are empirical in nature and others are more complicated and consider fundamental molecular nature. Harris [2001] outlined the methods, which are very common and included empirical and molecular bases. They are:

3.4.3.1 Modified separation of Cohesive Energy

Thomas and Eckert [1984] proposed a model that was based on regular solution theory. It was meant for calculation of γ^{∞}'s from pure component only. A detailed review of this method is given by Ried and Prausnitz [1986] and Malanowski and Andetetko [1992]. Below is the general equation used in this method.

$$\ln \gamma_i^{\infty} = \frac{v_i}{RT}\left[\lambda_j - \lambda_i\right]^2 + \frac{q_j^2 q_i^2 \left(\lambda_j - \lambda_i\right)^2}{\psi_i} + \frac{\left(\alpha_j - \alpha_i\right)\left(\beta_j - \beta_i\right)}{\xi_j} \tag{3-33}$$

where subscripts *i* and *j* represent the solute and solvent respectively, v_i is the liquid molar volume at *20°C*, λ is the dispersion parameter, q is the induction parameter, τ is the polar parameter, α is acidity parameter and β is the basicity parameter, ψ accounts for the difference in polarity between *i* and *j* and ξ accounts for the degree of hydrogen bonding.

The parameters $\alpha, \beta, \tau, \xi, q, v$ are obtained from Ried and Prausnitz [1986]. The term d_{12} is the Flory-Huggins combinational term that accounts for the difference in molecular size of *i* and *j* and is calculated as follows:

$$d_{12} = \ln\left(\frac{v_2}{v_1}\right)^{aa} + 1 - \left(\frac{v_2}{v_1}\right)^{aa} \tag{3-34}$$

aa is also obtained from Ried and Prausnitz [1986]. $\alpha, \beta, \tau, \xi, \psi$ and aa are all temperature dependent.

3.4.3.2 Analytical Solution of Groups (ASOG)

This method is based on the fact that there are far fewer functional groups than there are chemicals (Wilson and Deal [1962] and Wilson [1964]). For this reason, parameters determined for functional groups can be used to calculate activity coefficients for any chemical mixture. The functional groups of the molecule are assessed and each group contributes to the activity coefficients.

The following are the general equations and principles used in the method.

$$\ln \gamma_i = \ln \gamma_i^{s} + \ln \gamma_i^{G} \tag{3-35}$$

with

$$\ln \gamma_i^s = 1 - R_i + \ln R_i \qquad (3\text{-}36)$$

where in the above expression,

$$R_i = \frac{S_i}{\sum S_j x_j}$$

S_i is the size fraction of component *i* in the mixture, γ_i^G is the group activity coefficient and is the functional group contribution to the overall γ.

3.4.3.3 Universal quasi-chemical functional group activity coefficient (UNIFAC)

The UNIFAC method is presented in detail in Chapter 4 and so will just be discussed in brief in this section. This method is a functional group simulation developed by Fredenslund [1975] based on the UNIQUAC model (see Chapter 2.6.2) proposed by Abrams [1975] and is by far the more superior model compared to the previous two discussed in this work thus far.

The basic principles are:
The activity coefficient is made up of a combinatorial part, *C*, and a residual part, *R*; therefore we have an equation of the form:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad (3\text{-}37)$$

Where $\ln \gamma_i^C$ and $\ln \gamma_i^C$ are the combinatorial and residual terms respectively.
These are defined as:

$$\ln \gamma_i^C = f\left(q_i, x_i, \Phi_i, Z, \theta_i, l_i\right) \qquad (3\text{-}38)$$

Where the bracketed terms are the UNIFAC model parameters and are calculated using the respective equations in Chapter 4.2.

$$\ln \gamma_i^R = f(\nu_k^{(i)}, \Gamma_k, \Gamma_k^{(i)}) \qquad (3\text{-}39)$$

Again, the terms in brackets are the model parameters whose defining equations are detailed in Chapter 4.2.

3.5 RESULTS

The activity coefficients at infinite dilution of the hydrocarbon solutes, γ_{13}^{∞}, in each of the solvents along with the number of moles of solvent in each column, n_3, the volumetric flowrate, U_0, and temperature, T, of the columns is presented in Table 3-3 below.

Solute	T K	n_3 mmol	$10^6 U_o$ $m^3.s^{-1}$	γ_{13}^{∞}
		NMP		
pentane	298.20	2.78	1.37	13.67
hexane	298.20	2.78	1.28	27.13
heptane	298.20	2.78	1.28	31.29
benzene	298.20	2.78	1.33	1.42
toluene	298.20	2.78	1.36	1.17
Solute	T K	n_3 mmol	$10^6 U_o$ $m^3.s^{-1}$	γ_{13}^{∞}
		Glycerol		
pentane	298.20	5.40	1.56	560
hexane	298.20	5.40	1.57	85.13
heptane	298.20	5.40	1.57	234.1
benzene	298.20	5.40	1.57	52.08
toluene	298.20	5.40	1.57	14.74
Solute	T K	n_3 mmol	$10^6 U_o$ $m^3.s^{-1}$	γ_{13}^{∞}
		monoethylene glycol		
pentane	298.20	7.52	1.32	1528
hexane	298.20	7.52	1.33	1012
heptane	298.20	7.52	1.32	211.9
benzene	298.20	7.52	1.33	19.78
toluene	298.20	7.52	1.33	63.02
Solute	T K	n_3 mmol	$10^6 U_o$ $m^3.s^{-1}$	γ_{13}^{∞}
		triethylene glycol		
pentane	298.20	3.70	1.69	251.6
hexane	298.20	3.70	1.70	52.43
heptane	298.20	3.70	1.70	25.18
benzene	298.20	3.70	1.70	0.76
toluene	298.20	3.70	1.69	0.65

Table 3-3: Amount of solvent, n_3, on each column; the volumetric flowrate U_0 and the activity coefficients of hydrocarbon solutes at infinite dilution, γ_{13}^{∞}, in each of the solvents indicated,

Solute	T K	n_3 mmol	10^6Uo $m^3.s^{-1}$	γ_{13}^{∞}
		NMP + 10%(w/w) glycerol		
pentane	298.20	3.10	1.29	28.46
hexane	298.20	3.10	1.27	27.06
heptane	298.20	3.10	1.31	42.34
benzene	298.20	3.10	1.26	1.00
toluene	298.20	3.10	1.19	1.32

Solute	T K	n_3 mmol	10^6Uo $m^3.s^{-1}$	γ_{13}^{∞}
		NMP + 10%(w/w) MEG		
pentane	298.20	3.00	1.95	19.47
hexane	298.20	3.00	1.90	17.95
heptane	298.20	3.00	1.95	26.01
benzene	298.20	3.00	1.81	1.11
toluene	298.20	3.00	1.84	1.31

Solute	T K	n_3 mmol	10^6Uo $m^3.s^{-1}$	γ_{13}^{∞}
		NMP + 10%(w/w) DEG		
pentane	298.20	3.20	1.64	123.3
hexane	298.20	3.20	1.64	77.79
heptane	298.20	3.20	1.64	239.7
benzene	298.20	3.20	1.64	4.49
toluene	298.20	3.20	1.64	50.76

Solute	T K	n_3 mmol	10^6Uo $m^3.s^{-1}$	γ_{13}^{∞}
		NMP + 10%(w/w) TEG		
pentane	298.20	2.70	1.97	14.08
hexane	298.20	2.70	1.92	15.93
heptane	298.20	2.70	1.86	17.50
benzene	298.20	2.70	1.90	1.07
toluene	298.20	2.70	1.83	1.05

Table 3-3 (*cont.*): **Amount of solvent, n_3, on each column; the volumetric flowrate U_0 and the activity coefficients of hydrocarbon solutes at infinite dilution, γ_{13}^{∞}, in each of the solvents indicated,**

3.6 DISCUSSION

It was necessary, before beginning experimentation, to determine the accuracy with which the equipment could predict activity coefficients at infinite dilution. Pentane was used as a solute at infinite dilution in a hexadecane solvent since hexadecane exhibits a low volatility and pentane a typical, volatile solute. Table 3-4 displays the results obtained for the test system calculations.

	Solute	Solvent	$\ln \gamma_{13}^{\infty}$	Reference
RUN 1	pentane	hexadecane	0.891	
RUN 2	pentane	hexadecane	0.919	
Literature	pentane	hexadecane	0.92	Tiegs et al [1986]

Table 3-4: Literature Comparison of test system with solvent, hexadecane and solute pentane

From the first run of our experiment, the value obtained for the test system showed a 3.2 % deviation from the literature. The equipment was thoroughly checked and it was found that there was a leak at the sample injection port. The joint was then sealed with thread sealant tape and properly tightened so that the septum did not completely block the flow of helium through the column. The next experimental test run proved to be much more successful, showing a 0.1 % deviation from literature (Tiegs et. al. [1986]).

3.6.1 Using infinite dilution activity coefficients for Solvent selection

The ability of a solvent to separate one component from another in a binary mixture is called its separation factor. The separation factor is calculated from the ratio of the infinite dilution activity coefficients (IDACs) of the two components to be separated. The use of GLC has long been used as a rapid and convenient method for evaluation of solvent separation factors for extractive distillation (Rawat *et al* [1972] and Rawat *et al* [1976])

Following the suggestion that gas liquid chromatography could be utilized as a relatively simple technique for studying the interaction of a volatile solute with a volatile or moderately volatile solvent (Martin [1956]), follow-up papers were published to correlate solvent effects in GLC with the partition coefficient, the solute vapour pressure and IDACs (γ_i^{∞}) (Pierotti *et al* [1956] and Porter *et al* [1956]). Porter *et al* [1956] showed that within experimental error, γ_i^{∞} and static partition coefficient were of the same magnitude. Porter *et al* [1956] suggested that separation of the partition coefficient; the solute vapour pressure and the activity coefficient could lead to a number of important observations.

Solvency can be rated by the solubility of one or more solutes at a given temperature; the basis of this evaluation can be summarized as follows. The activity coefficient at infinite dilution may be rewritten as:

$$\gamma_i^{\infty} = \frac{n_3 R T}{K_L V_L p_i^{\bullet}} \tag{3-40}$$

For extraction purposes, the limiting separation or separation factor, β_{12}, can be written as follows:

$$\beta_{12} = \left(\frac{\gamma_1^{\infty}}{\gamma_2^{\infty}}\right) \cdot \left(\frac{\gamma_2^{0}}{\gamma_1^{0}}\right) ; \; \frac{\gamma_1^{\infty}}{\gamma_2^{\infty}} \tag{3-41}$$

Where the approximation only holds true if the activity coefficients in the non-polar phase, γ_i^0, have very similar values. The infinite dilution relative volatility of a solute 1 to solute 2, α_{12}^{∞}, for extractive distillation could be written as:

$$\alpha_{12}^{\infty} = \frac{K_L(2)}{K_L(1)} = \frac{\gamma_1^{\infty}}{\gamma_2^{\infty}} \cdot \frac{p_1^{\bullet}}{p_2^{\bullet}} \tag{3-42}$$

The solvent separation factors, β, of the aromatic hydrocarbons for each alkane is given in Table (3-5) overleaf.

The separation factors obtained for each alkane/aromatic binary pair is given in Table 3-5. It should be noted that due to the nature of the separation factor, the larger the deviation from unity, the better the separation factor (the better the solvent). i.e. as β -> 1, the poorer the solvents separation factor. The pure solvents case, TEG, displayed the best separation factors for each of the alkane/aromatic mixtures except for the benzene/heptane separation, for which the {NMP + 10% glycerol} solvent proved the most effective.

The separation factors for each alkane/aromatic pair investigated in decreasing order of effectiveness are:

Pentane/toluene: TEG, Glycerol, MEG, NMP + 10% Glycerol, NMP + 10% MEG, NMP + 10% TEG, NMP; NMP + 10% DEG.

Hexane/toluene: TEG, NMP, NMP + 10% Glycerol, MEG, NMP + 10% MEG, NMP + 10% TEG, Glycerol, NMP + 10% DEG.

Heptane/toluene: TEG, NMP + 10% Glycerol, NMP, NMP + 10% MEG, NMP + 10% TEG, Glycerol, NMP + 10% DEG, MEG.

Pentane/benzene: TEG, MEG, NMP + 10% Glycerol, NMP + 10% DEG, NMP + 10% MEG, NMP + 10% TEG, Glycerol, NMP.

Hexane/benzene: TEG, MEG, NMP + 10% Glycerol, NMP, NMP + 10% MEG, NMP + 10% DEG, NMP + 10% TEG, Glycerol.

Heptane/benzene: NMP + 10% Glycerol, NMP + 10% DEG, TEG, NMP + 10% TEG, NMP + 10% MEG, NMP, MEG, Glycerol.

Solvent	β_{i-j}^{∞}					
i	**toluene**			**benzene**		
j	pentane	hexane	heptane	pentane	hexane	heptane
NMP	0.09	0.04	0.04	0.10	0.04	0.05
Glycerol	0.03	0.17	0.06	0.09	0.61	0.22
monoethylene glycol	0.04	0.06	0.30	0.01	0.02	0.09
triethylene glycol	0.00	0.01	0.03	0.00	0.01	0.03
NMP + 10%(w/w) glycerol	0.05	0.05	0.03	0.04	0.04	0.02
NMP + 10%(w/w) MEG	0.07	0.07	0.05	0.06	0.06	0.04
NMP + 10%(w/w) DEG	0.41	0.65	0.21	0.04	0.06	0.02
NMP + 10%(w/w) TEG	0.07	0.07	0.06	0.08	0.07	0.03

Table 3-5: Separation factors, β_{ij}^{∞} of Solvents for aromatic hydrocarbons, toluene and benzene

3.6.2 Comparison to Literature

Table 3-6 lists the literature values of the infinite dilution activity coefficients available, along with those obtained in this study. The NMP solvent showed a minimum deviation of 0.1 % and a maximum of 17%. The monoethylene glycol solvent did not show very good agreement with literature except in the case of toluene where a deviation of 2% was noted. The triethylene glycol solvent also did not show extremely good agreement with literature. It should be noted however that in most cases, a wide range of values for γ_i^{∞} were reported in literature at a specific temperature indicating a large standard deviation. It is therefore not unexpected that the values obtained in this work vary largely from those fund in the literature.

Solvent: **NMP**

Solute	T K	$\gamma_{13}^{\infty EXP}$	$\gamma_{13}^{\infty Lit}$	Reference	Method
pentane	298.2	13.67	13.80	Smiley [1980]	GLCI
hexane	298.2	27.13	23.00	Muller et al. [1976]	GLCI
heptane	298.2	31.29	28.00	Muller et al. [1976]	GLCI
benzene	298.2	1.42	1.00	Kikic [1976]	GLCR
toluene	298.2	1.17	1.30	Popescu et. al. [1967]	GLCI

Solvent: **Glycerol**

Solute	T K	$\gamma_{13}^{\infty EXP}$	$\gamma_{13}^{\infty Lit}$	Reference	Method
pentane	298.2	560	n.a		
hexane	298.2	85.13	n.a		
heptane	298.2	234.1	n.a		
benzene	298.2	52.08	n.a		
toluene	298.2	14.74	n.a		

Solvent: **monoethylene glycol**

Solute	T K	$\gamma_{13}^{\infty EXP}$	$\gamma_{13}^{\infty Lit}$	Reference	Method
pentane	298.2	1528	n.a		
hexane	298.2	1012	685.0	Vernier et. al. [1969]	GLCI
heptane	298.2	211.9	556.0	Opris [1981]	GLCI
benzene	298.2	19.78	32.30	Arancibia et. al [1982]	GLCI
toluene	298.2	63.02	61.70	Arancibia et. al [1982]	GLCI

Solvent: **triethylene glycol**

Solute	T K	$\gamma_{13}^{\infty EXP}$	$\gamma_{13}^{\infty Lit}$	Reference	Method
pentane	298.2	251.6	n.a		
hexane	298.2	52.43	67.10	Arancibia et. al [1980]	GLCI
heptane	298.2	25.18	98.5	Alessi et. al [1971]	GLCI
benzene	298.2	0.76	3.80	Arancibia et. al [1980]	GLCI
toluene	298.2	0.65	6.01	Arancibia et. al [1980]	GLCI

Table 3-6: Literature Comparison of Infinite Dilution Activity Coefficients

Key:*n.a =not available
GLCI = gas-liquid chromatography without gas phase correction.
GLCR= gas-liquid chromatography with gas phase corrections

3.6.3 Thermodynamic Modelling.

Since we have used solvents that are made up of more than one component, it was necessary to models the systems using ternary UNIFAC equations.

The use of the classic UNIFAC model showed extremely poor results. This is due to the fact that the original UNIFAC was meant for use with "like" molecules. The modelling of this work shows similar deviations to that obtained by Harris [2001]. The activity coefficients showed up to a 99% deviation from that obtained by experiment. Table 3-7 shows the values of the infinite dilution activity coefficients obtained from the UNIFAC method.

			γ_{13}^{∞}		
Solute:	pentane	hexane	heptane	toluene	benzene
Solvent					
NMP	6.82	9.12	11.95	1.81	12.61
Glycerol	22.53	40.50	71.30	19.06	0.97
Triethylene Glycol	2.11	2.53	2.97	1.08	1.24
Monoethylene Glycol	1.53	1.63	1.70	1.36	1.74
NMP + 10%(w/w) Glycerol	9.73	16.30	26.76	4.94	3.71
NMP + 10%(w/w) MEG	2.17	2.71	3.32	1.04	0.94
NMP + 10%(w/w)DEG	2.18	2.78	3.48	0.91	0.82
NMP + 10% (w/w)TEG	2.24	2.92	3.73	0.85	0.76

Table 3-7: Values of Infinite Dilution Activity Coefficients Predicted by UNIFAC method.

These values also show a large deviation from those values obtained from literature. It should be noted that these values obtained from the modeling equations also differ greatly from those obtained from literature (see Table 3-6 for comparisons to literature).

CHAPTER
FOUR

4. PROGRAMMING: SOLVENT SELECTION USING UNIFAC

4.1 INTRODUCTION

As was discussed in Chapter 2 and 3, liquid-liquid equilibrium and activity coefficient data are essential for the design and commissioning of separation equipment and processes. The measurement of such data is relatively rapid if one has an indication of the solvents that would be or have proven to be effective for the separation process under investigation. However, a problem arises when such information is limited, inconclusive or unavailable. How would, then, one narrow down the solvents for which such separation data should be measured? It would be impractical and time consuming to investigate all possible solvents for that a particular separation. It would, therefore, be very useful to have some preliminary means for narrowing down the solvent selection. It would also be advantageous to have some way of trying out new solvent molecules without going through rigorous experimental procedures.

For the reasons mentioned above, a computer program was constructed that aided in solvent selection. The program was required to have the ability to compare the effectiveness of various common solvents for the user defined separation need as well as allow the user to use his or her own solvent molecules when necessary. At present, the UNIFAC model is the only generalized method for the prediction of liquid-liquid equilibrium behaviour and was used as the basis of this program. The solvents were compared on the basis of their selectivities derived from the infinite dilution activity coefficients.

4.2 THE UNIFAC MODEL

Since chemical process design is often concerned with separation of fluid mixtures, design engineers must frequently estimate liquid phase activity coefficients. In those cases where phase equilibrium data are available, those estimates are easily made. In many cases, where the required experimental data is unavailable, it is difficult to make even rough estimates on a rational basis.
The fundamental idea of a solution-of-groups model is to utilize existing phase equilibrium data for predicting phase equilibria of systems for which no experimental data are available. In concept, the UNIFAC model follows Derr and Deal's [1969] analytical solution of groups (ASOG) model, where activity coefficients in mixtures are related to interactions between structural groups. Their method entailed suitable reduction of experimentally obtained activity coefficient data to obtain parameters characterizing interactions between pairs of structural groups in non-electrolytes, and use of these parameters to predict activity coefficients for other systems which have not been studied experimentally.

Derr and Deal [1969] separated the molecular activity coefficient into two parts. The first part provided the contribution due to the difference in molecular sizes and the second part made provisions for the contribution due to molecular interactions. The first change was established by using the athermal Flory-Huggins equation and the second change was established using the Wilson equation which was applied to the functional groups of the molecules. Derr and Deal [1969] removed the arbitrariness of the activity coefficient by combining the solution-of-groups (ASOG) concept with the UNIQUAC equations (Chapter 2.5). The UNIQUAC model was useful in that it contained two parts; the residual part: which is due to energy considerations; and the combinatorial part: This is essentially due to differences in size and shape of the molecules in a mixture. The group sizes and interaction surface areas were then introduced from independently obtained pure component data.

Over the years that followed, many other improvements and developments were made to the UNIFAC model. Although there were too many changes in that time period to discuss all of them, some of the more important developments to the model will be discussed later.

4.3 DEVELOPMENT OF EQUATIONS

Abrams and Prausnitz [1975] show that the UNIQUAC equation gives good representation of both vapor-liquid and liquid-liquid equilibria for binary and multi-component mixtures containing a variety of non-electrolytes such as hydrocarbons, ketones, esters, water, amines, alcohols, nitrites etc.

The UNIFAC equations are based on the UNIQUAC equations, which are discussed in detail in Chapter 2.5 => $\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R$ (Equation (2-20)). The combinatorial part of the activity coefficient is given by:

$$\ln\gamma_i^C = \ln\frac{\varphi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\vartheta_i}{\varphi_i} + l_i - \frac{\varphi_i}{x_i\sum_j x_j l_j} \qquad (4\text{-}1)$$

With z = 10 and

$$\vartheta_i = \frac{q_i x_i}{\sum_i q_i x_i} \qquad (4\text{-}2)$$

$$\varphi_i = \frac{r_i x_i}{\sum_i r_i x_i} \qquad (4\text{-}3)$$

By using the following definitions:

$$L_i = \frac{q_i}{\sum_i q_i x_i} \qquad (4\text{-}4)$$

and

$$J_i = \frac{r_i}{\sum_i r_i x_i} \qquad (4\text{-}5)$$

With

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \qquad (4\text{-}6)$$

We arrive at the expression:

$$\ln\gamma_i^C = 1 + J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}\right). \qquad (4\text{-}7)$$

For the combinatorial term of the UNIFAC model, which is identical to that of the UNIQUAC model.

The residual term of the activity coefficient is replaced by

$$\ln\gamma_i^R = \sum_k \nu_k^{(i)}\left[\ln\Gamma_k - \ln\Gamma_k^{(i)}\right] \tag{4-8}$$

Where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group *k* in a reference solution containing only molecules of type *i* (Fredenslund, Jones and Prausnitz [1975]); (*i*) is the number of subgroups of type *k* in a molecule of species *i*. The relevance of the assumption is explained in detail by Fredenslund, Jones and Prausnitz [1975]. The group activity coefficient Γ_k is found from an expression similar to equation 2-22 and we arrive at the following expression for the residual activity coefficient.

$$\ln\gamma_i^R = q_i\left[1 - \sum_k\left(\theta_k\frac{\beta_{ik}}{s_k} - e_{ki}\ln\frac{\beta_{ik}}{s_k}\right)\right] \tag{4-9}$$

Along with the following definitions:

$$r_i = \sum_k \nu_k^{(i)} R_k \tag{4-10}$$

$$q_i = \sum_k \nu_k^{(i)} Q_k \tag{4-11}$$

$$e_{ki} = \frac{\nu_k^{(i)} Q_k}{q_i} \tag{4-12}$$

$$\beta_{ik} = \sum e_{mi}\tau_{mk} \tag{4-13}$$

$$\theta = \frac{\sum x_i q_i e_{ki}}{\sum_j x_j q_j} \tag{4-14}$$

$$s_k = \sum_m \theta_m \tau_{mk} \tag{4-15}$$

$$\tau_{mk} = \exp\frac{(u_{mk} - u_{km})}{T} = \exp\left(\frac{-a_{mk}}{T}\right) \tag{4-16}$$

Where *i* identifies species and *j* is a dummy index running over all species, *k* identifies subgroups and *m* is a dummy index running over all subgroups. R$_k$ and Q$_k$ are relative volume and surface areas respectively. The volume and surface area parameters r_i and q_i are in fact the van der Waals volume and surface areas calculated by Bondi [1969]. τ_{mk} is the group interaction parameter and u_{mk} is a measure of energy of interaction between groups' m and n. The parameters a_{mn}(2 parameters per binary mixture of groups) are parameters which have been evaluated over the years from experimental phase equilibrium data; a_{mk} has units of degrees Kelvin and $a_{mk} \neq a_{km}$.

Equations (4-1) to (4-16) are from the original UNIFAC model and will henceforth be referred to as "the original UNIFAC"

4.4 LIMITATIONS OF THE ORIGINAL UNIFAC

In spite of many successful applications of the UNIFAC model, it does have its limitations. Sandler [1993] outlined these limitations as follows:

- Due to solution-of-groups assumption, UNIFAC does not distinguish between isomers
- The activity coefficient approach as opposed to the equations of state approach limit UNIFAC to applications below 10-15 atmospheres in pressure.
- The temperature range is limited to temperatures between approximately 275-475 K
- It has been found that UNIFAC with parameters bases on vapour-liquid equilibrium data (UNIFAC-VLE) does not yield quantitative prediction of liquid-liquid equilibrium (this will be discussed in more detail later on) and has led to the development of a UNIFAC-LLE model. This indicates a fundamental deficiency of the solution-of-groups approach – activity coefficients do not "know" what they are being used for, and so, in principle it should be possible to use the same model with the same parameters for all applications.
- Proximity effects occur when two or more strongly polar groups are situated on the same or adjacent carbon atoms e.g. the -OH group in an alcohol does not have the same effect as an –OH group in a glycol

In order to improve the performance of the original UNIFAC model in the prediction of vapour-liquid equilibrium, liquid-liquid equilibrium (LLE), infinite dilution-activity coefficients, and excess enthalpies as well as the residual terms of original UNIFAC, several adjustments to the original UNIFAC have been suggested over the years. These will be discussed in brief detail in the sections that follow.

4.5 Modified UNIFAC Equations

One can see from the original UNIFAC model equations, the group interaction parameters are assumed to be temperature independent. For this reason the original UNIFAC model does not yield quantitative predictions of the excess enthalpy and extrapolations to temperatures beyond 425K are to be avoided.

Here are some of the modifications available in literature:

1. Magnussen *et. al* [1981] developed parameters suitable for use in LLE prediction. The equations for this model are identical to the original equations, however the parameters have been attained by fitting liquid-liquid equilibrium experimental data to the model. This is of particular importance to us and warrants further discussion later on in this chapter.

2. Larsen *et. al* [1987] made two modifications with respect to the original UNIFAC model. Firstly the combinatorial term was given as:

$$\ln \gamma_i^C = \ln\left(\frac{\varphi_i}{x_i}\right) + 1 - \frac{\varphi_i}{x_i} \qquad (4\text{-}17)$$

where

$$\varphi_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \qquad (4\text{-}18)$$

Secondly the interaction parameter τ_{mk} in the residual part of Equation (4-16) is defined as:

$$\tau_{mk} = \exp\left\{-\left[\frac{a_{mk} + a_{mk}\left(T - T_0\right) + a_{mk}\left(T \ln\frac{T_0}{T} + T - T_0\right)}{T}\right]\right\} \qquad (4\text{-}19)$$

Where T_0 is an arbitrary reference temperature of 298.15K.

3. Bastos *et. al* [1988] proposed a model modification most suited to determining infinite dilution activity coefficients. This model uses the combinatory term suggested by Kikic et. al [1980], and has the following form:

$$\ln \gamma_i^C = \ln\frac{\varphi i}{xi} + 1 - \frac{\varphi i}{xi} - \frac{z}{2}qi\left(\ln\frac{\varphi i}{\vartheta i} - \frac{\varphi i}{\vartheta i}\right) \qquad (4\text{-}20)$$

With

$$\varphi_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \qquad (4\text{-}21)$$

The residual part of this model has the same form as in the original UNIFAC, where the parameters have been obtained by fitting infinite dilution activity coefficient data.

4. Hooper *et. al* [1988] developed a model to correlate liquid-liquid equilibrium for water/hydrocarbon (and some hydrocarbon derivatives.) mixtures. The combinatorial part is identical to that of Larsen et. al [1987]and the interaction parameter in the residual part is given by

$$\tau_{mk} = \exp\left\{ -\left(\frac{a_{mk} \;+\; a_{mk}T \;+\; a_{mk}T^2}{T} \right) \right\} \qquad (4\text{-}22)$$

5. The original UNIFAC with temperature dependant interaction parameters was put forth by Hanson *et. al* [1992]. In this model the group interaction-parameters τ_{mk} in the residual part is given by

$$\tau_{mk} = \exp\left\{ -\left[\frac{a_{mk} + a_{mk}\left(T - T_0\right)}{T} \right] \right\} \qquad (4\text{-}23)$$

Where, again, T_0 is a reference temperature of 298.15K.

6. Gmehling *et. al* [1993] used the identical combinatorial term as Bastos *et. al* [1988] as indicated above with one difference, φ_i is defined as follows:

$$\varphi_i = \frac{x_i r_i^{3/4}}{\sum_j x_i r_i^{3/4}} \qquad (4\text{-}24)$$

and the interaction parameter is identical to that of Bastos *et. al* [1988].

4.5.1 UNIFAC-LLE (Liquid-Liquid Equilibrium) Model

In order to use activity coefficient models such as NRTL and UNIQUAC to calculate liquid-liquid equilibrium compositions, one must evaluate the model parameters from phase equilibrium data. As a minimum, it is necessary to have available experimental phase equilibrium data for all constituent binary pairs in the mixture (as in Chapter 2).

The number of different mixtures in chemical technology is extremely large and one cannot always find all the desired experimental information that one requires. It is therefore necessary to rely on some generalized method for prediction of the required information. Group-contribution methods for the prediction of liquid-phase activity coefficients are examples of such methods. The basic assumption of group-contribution methods for predicting activity coefficients is that the liquid solution can be treated as a solution of the groups that make up the components of the mixture. The size and shape of the groups and the interaction between the groups determine the properties of the liquid mixtures.

Tochigi and Kojima [1977] and Sugi and Katayama [1977] correlated a few liquid-liquid equilibrium data sets for mixtures with alcohols, ketones, water, and hydrocarbons using the ASOG (solution of groups) model. Their results showed a qualitative, but not quantitative agreement with experiment.

Fredenslund, Gmehling and Rasmussen [1977b] used the UNIFAC group interaction parameters for VLE (vapour-liquid equilibrium) to predict LLE (liquid-liquid equilibrium) for a large number of ternary systems. Their results also showed a qualitative agreement with experiment but still not a quantitative agreement.

Magnussen *et. al* [1980] performed similar calculations for 17 test systems using VLE parameters given by Skjold-Jϕrgensen *et. al.* [1979] and also showed that the results were, at best, in qualitative agreement with experiment.

The main reason for the above findings was that the UNIQUAC groups interaction parameters given by Skjold-Jϕrgensen *et. al* [1979], are wherever possible, based on VLE data often determined at temperatures far from those of liquid-liquid equilibrium.

Magnussen *et. al.* [1980] proposed that a database with both LLE and VLE data would lead to "average" parameters and such a database would predict both LLE and VLE fairly well. They also concluded that 75% of all LLE data available at the time were within 10 K of room temperature.

The above findings led to the development of a UNIFAC-LLE parameter table by Magnussen *et al* [1981]. These parameters are distinct from those in the VLE-UNIFAC matrix although, for a few group-group interactions the VLE-parameters of Skjold-Jϕrgensen *et. al* [1979] were used. UNIFAC-LLE group's interaction parameters are available for 32 different groups representing hydrocarbons, water, alcohols, organic acids, halogenated hydrocarbons, nitriles, etc.

The UNIFAC-LLE model is not applicable to:

- Components with normal boiling points below 300 K,
- Strong electrolytes
- Temperatures outside the range of 10-40°C. Extrapolating to outside this temperature range is not recommended since LLE interaction parameters are strongly temperature dependant.

Gupte and Danner [1987] comprehensively tested the UNIFAC-LLE model by using a database compiled by the Technical University of Denmark. This database contained data for 1130 binary, 1011 ternary and 28 quaternary systems and they arrived at the following conclusions:

- The UNIFAC model was found to yield the same quality of predictions for systems not used in the development of the parameters as for those used in the development (this emphasized the success of the group-contribution method for LLE).
- The UNIFAC-LLE model was found to yield quantitative estimations of phase compositions.
- The representation of distribution ratios and selectivities is not always good.
- For Type I and II systems (Chapter 2.4.2), no incorrect prediction of phases was found.
- For TYPE III systems, 2 out of 8 systems were incorrectly predicted for phases.
- The errors for non-isothermal were significantly larger than those for isothermal systems.

4.6 THE PROGRAM

Due to the fact that the UNIFAC model was used for "narrowing" our solvent selection we do not require that it predict fully the VLE of the systems under question, or that it predict the number of phases or determine quantitatively the equilibrium of these systems. In essence we require that it simply compare various common solvents to each other before experimenting on the entire number of available solvents. For these reasons we have used the parameters of Fredenslund and Sorensen given by Sandler [1993]. The Volume and Surface parameters R and Q are given in Appendix C-2 and the set of interaction parameters is given in the Appendix C-3, in Tables C-1 and C-2 respectively.

The program for calculation of activity coefficients was written in the Matlab programming language and has distinct advantages and disadvantages.

Disadvantages:

- The program is not user friendly
- The user has to enter the number of all 106 subgroups including zeros for those subgroups not present in the molecule into a parameter matrix since Matlab does not return a blank return as a zero value
- The activity coefficients calculated are for one set of mole fractions.
- The program does not predict LLE comprehensively.

Advantages:

- Calculates activity coefficients for a user-defined number of components. This is extremely useful when dealing with large numbers of molecules.
- One may add on to the solvent database as one sees fit. This may prove useful to future users.
- The program may be easily altered for the inclusion of a temperature dependence according to the equations given in Chapter 4.4
- If one seeks to predict LLE, the parameters matrix a_{mk} may be replaced by that given by Magnussen et. al [1981]
- Although the program is used for the prediction of activity coefficients at infinite dilution, one may use it to calculate the activity coefficients at any given composition.

4.6.1 Basic Algorithm of The Program

1. Input the number of chemicals in use (excluding the solvent).
2. Identify chemical (number i.e. 1, 2 etc.) for which selectivity profile is required.
3. Input number of each subgroup in the molecule (including zeros for groups not present.
4. Create stoichiometric matrix for solutes (i.e. for chemicals not including the solvents).
5. Input mole fractions of mixture.
6. Create matrix for q_i and r_i from solute matrix and the R_k and Q_k matrices.

7. Create component matrix from solute matrix and solvent data base matrix starting with the first solvent (one solvent at a time).
8. Calculate

$$\sum_i x_i r_i$$

And

$$\sum_i x_i q_i$$

9. Calculate e_{mk}
10. Calculate β_{ik}
11. Calculate denominator of θ_i terms.
12. Calculate numerator of θ_i terms.
13. Determine θ_i matrix
14. Calculate S_k
15. Calculate J_i
16. Calculate L_i
17. Create a $(1*(n+1))$ matrix of ones, where n is the number of components excluding the solvent
18. Calculate $Q_{(\mathrm{new})}$ where:

$$Q_{(new)} = q * Q_{(old)}$$

19. Calculate ln γ_i^C
20. Calculate ln γ_i^R
21. Calculate selectivity
22. Display selectivity profile.
23. End if solvent database is complete else return to step 7.

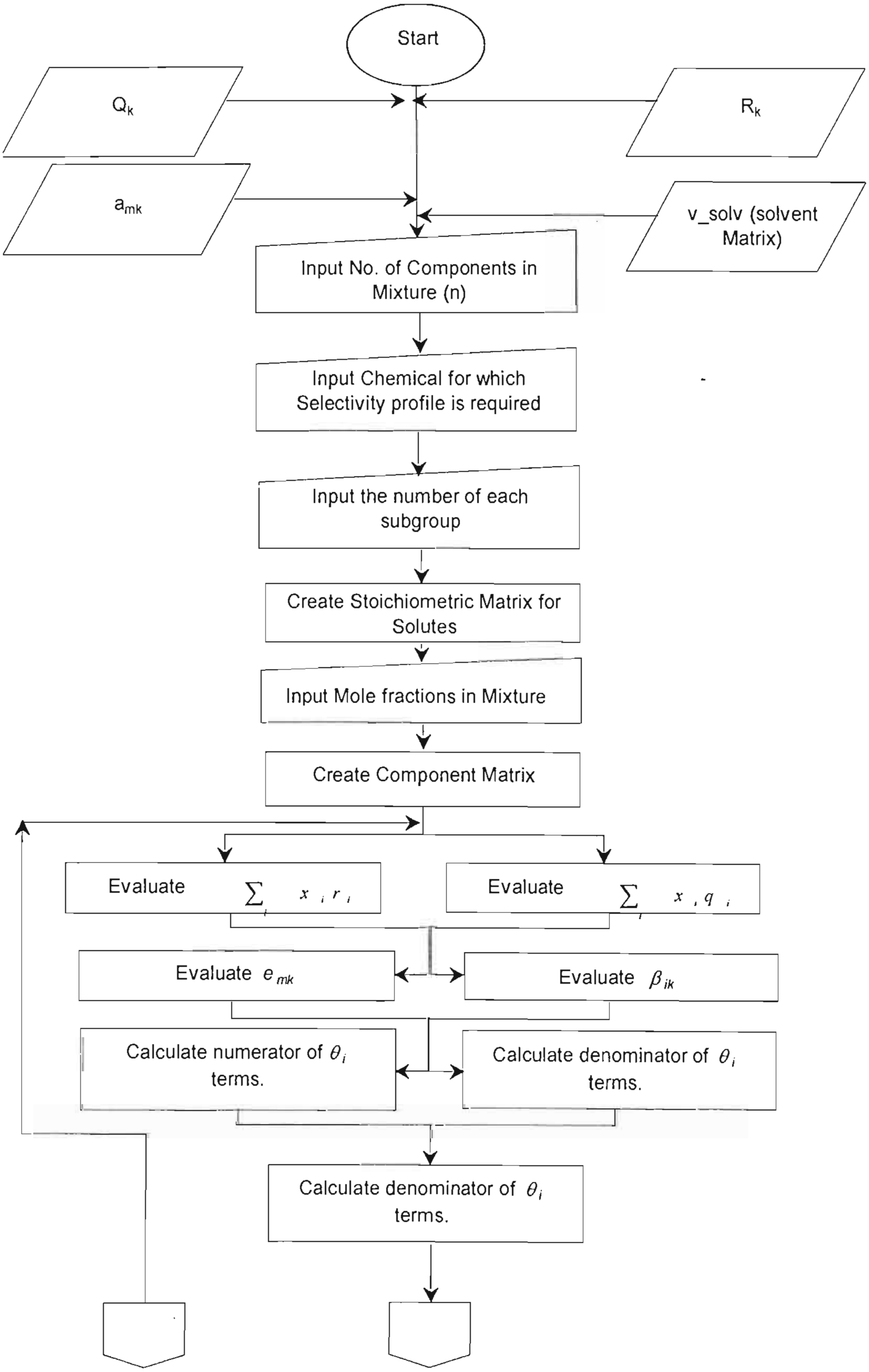


Figure 4-1: Flow diagram for Matlab Program

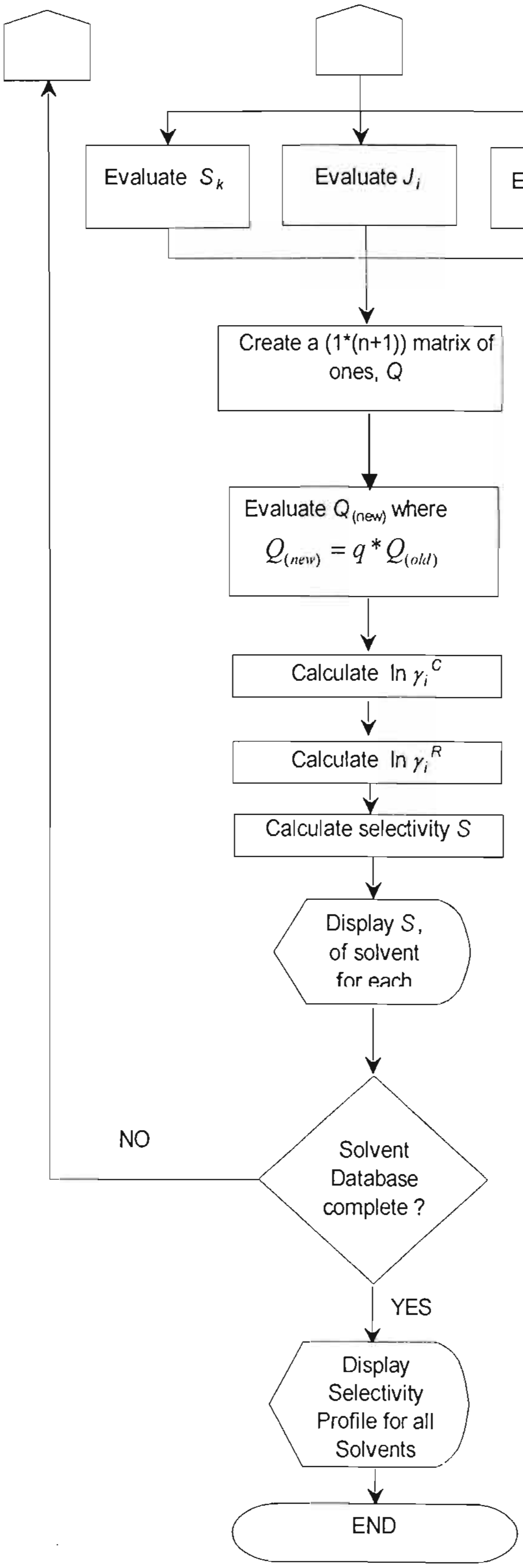


Figure 4-1(*contd.*): Flow diagram for Matlab program.

4.7 THE SOLVENT DATABASE

The solvent data base that was compiled contains 28 solvents, either used in industry or available in literature. Below is a table listing the names of the solvents as well as their use in industry and the reference thereof.

Solvent	Use in Industry	Reference
1) N-Formylmorpholine	BTX Aromatics Extraction	Lo, Baird and Hanson [1983]
2) Dimethyl Sulfoxide (DMSO)	BTX Aromatics Extraction	Lo, Baird and Hanson [1983]
3) Triethylene glycol	BTX Aromatics Extraction	Lo, Baird and Hanson [1983]
4) Ethylene glycol	Arosolvan Process	Lo, Baird and Hanson [1983]
5) Diethylene glycol	Arosolvan Process	Lo, Baird and Hanson [1983]
6) Triethylene glycol	Arosolvan Process	Lo, Baird and Hanson [1983]
7) Phenol	Phenol Extraction Process	Kenny and McCluer [1941]
8) N-Methyl-2-pyrollidone	Arosolvan Process Benzene Extraction	Lo, Baird and Hanson [1983] Lo, Baird and Hanson [1983]
9) furfural	Lube oil Manufacturing	Kemp et. al. [1948]
10) propane	Separation of Heavy petroleum Fractions Lube oil Extraction	Lo, Baird and Hanson [1983] Lo, Baird and Hanson [1983]
11) butane	Separation of Heavy petroleum Fractions	Lo, Baird and Hanson [1983]
12) pentane	Separation of Heavy petroleum Fractions	Lo, Baird and Hanson [1983]
13) benzene	Caprolactam extraction (Raschig Process)	Lo, Baird and Hanson [1983]
14) water	Caprolactam extraction (Raschig Process) Arosolvant Process Udex Process Union Carbide Tetra Process	Lo, Baird and Hanson [1983] Lo, Baird and Hanson [1983] Lo, Baird and Hanson [1983] Lo, Baird and Hanson [1983]
15) Toluene	Caprolactam extraction (Raschig Process)	Lo, Baird and Hanson [1983]

Table 4-1: Solvents used in solvent database

16) Ethyl acetate	Acetic Acid Extraction	Goring [1883]
17) Butyl acetate	Erythromycin Extraction	Kostereva et. al. [[1971]
18) Lactic acid	Erythromycin Extraction	Kostereva et. al. [[1971]
19) *n*-butanol	Bacitracin Extraction	Miescher [1974]
20) trichloroethylene	Decaffeination Caprolactam extraction	Lo, Baird and Hanson [1983]
21) Ethylene Chloride	Extraction of Flavours and Aroma	Lo, Baird and Hanson [1983]
22) Ethanol	Extraction of Flavours and Aroma	Lo, Baird and Hanson [1983]
23) Methanol	Extraction of Flavours and Aroma	Lo, Baird and Hanson [1983]
24) Chloroform	Caprolactam extraction	Lo, Baird and Hanson [1983]
25) Methylene Chloride	Caprolactam extraction	Lo, Baird and Hanson [1983]
26) Nitrobenzene	Caprolactam extraction	Lo, Baird and Hanson [1983]
27) Dichloroethylene	Caprolactam extraction	Lo, Baird and Hanson [1983]
28) Glycerol	Extraction of aromatics from non-aromatics	Naidoo and Letcher [2001]

Table 4-1(cont.): Solvents used in solvent database

4.8 RESULTS

The program was able to successfully predict the relative selectivities of the 28 solvents that make up the solvent database. Here we will present the output of the program for the binary pair of *n*-hexane + toluene at 298.2 K. The program requires the input of the subgroups that make up each molecule.

The program outputs a bar graph in the form of a selectivity profile. Figure 4-2 represents the selectivity of the solvent for *n*-hexane in the system the system *n*-hexane + toluene + solvent.

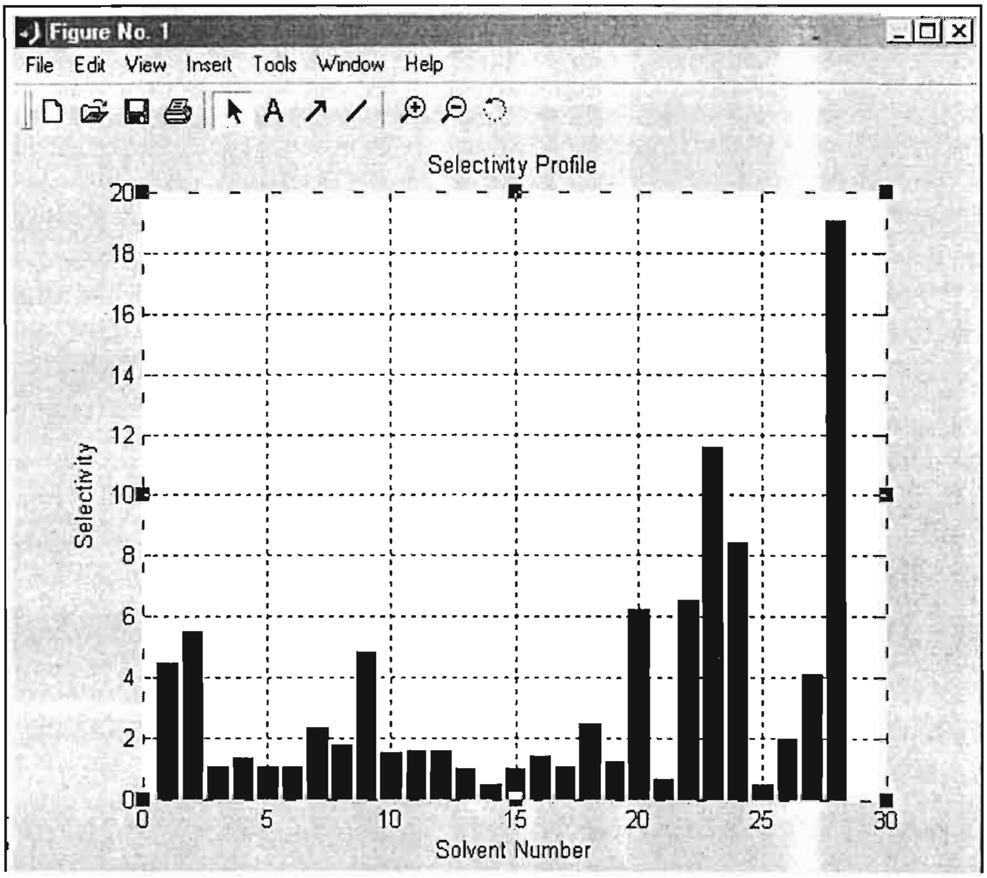


Figure 4-2: Selectivity profile of the system *n*-hexane + toluene + solvent where the solvent selectivity is that of toluene

The selectivity of the solvent is calculated as a ratio of the infinite-dilution activity coefficients: S is defined as:

$$S_i = \frac{\gamma_i^\infty}{\gamma_j^\infty} \tag{4-25}$$

Where S_i the selectivity of component *i*. The condition of infinite dilution is satisfied when $x_i \leq 1*10^{-5}$. This must be defined when the program prompts the user for the mole fractions of the solution.

From the selectivity profile one can deduce that the best possible solvents for use in the separation of *n*-hexane and toluene would be numbers 23, 24 and 28, which according to the solvent database corresponds to methanol , Chloroform and glycerol respectively. It can be seen that the selectivity using glycerol (according to the program) is the highest and is an interesting result comparing to the results presented in Chapter 2 on LLE.

We may also use the program to determine the selectivities of the solvents in the database, for a mixture of greater than 2 components. It should be noted however, that the component for which the user wishes to view the selectivity profile must be chosen initially.

Take, for instance, a mixture of benzene, *n*-hexane, and pentane yields the following profile for the selectivity of benzene:

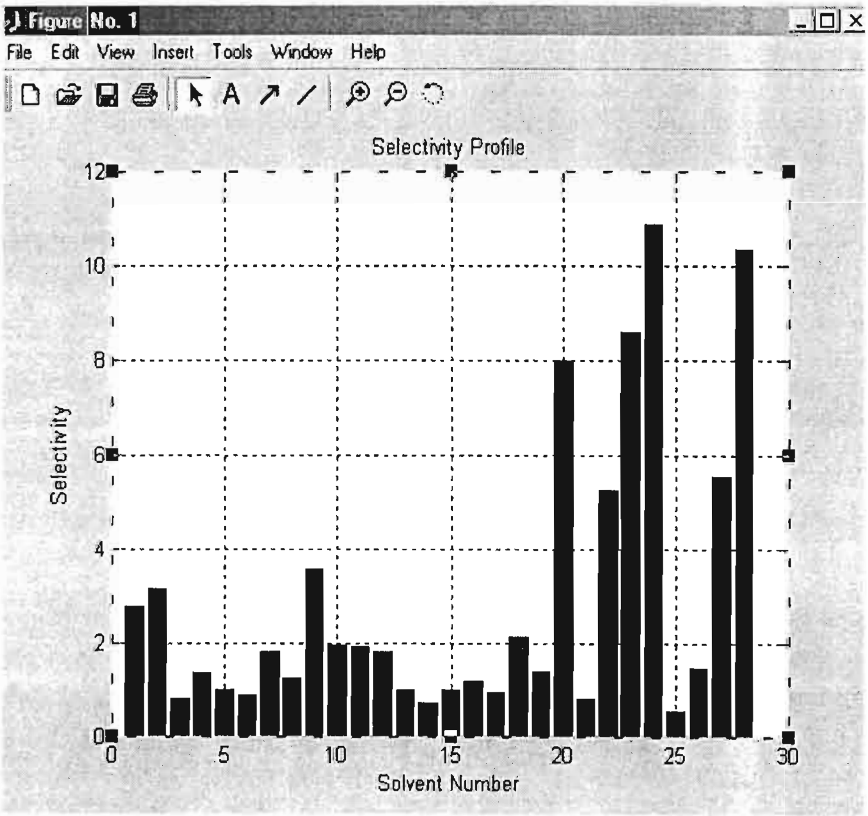


Figure 4-3: Selectivity profile of the system *n*-hexane + pentane + benzene + solvent where the solvent selectivity is that of benzene

Here the best results are obtained from solvents 20, 23, 24 and 28. Very similar to those results obtained for toluene previously.

The program may be used to calculate activity coefficients for an infinite number of components in a mixture as well.

4.9 DISCUSSION

The program written contains 28 solvents, which were found in literature or commonly used in industry. The program was written to compare the relative selectivities of the solvents in the database to each other for a user-defined number of chemicals in a mixture. These values for the selectivityies yield good qualitative results and should not be used on a quantitative basis.

The program is not very user-friendly; since the user was required to define the number of every possible subgroup contained in a molecule, including zeros for those subgroups that are not present. This is required in order to enable the program to build a suitable stoichiometric matrix for the solutes being used.

The results obtained from an input of *n*-hexane and toluene as the mixture solutes showed that the best aromatic selectivities were exhibited by methanol, chloroform and glycerol. This is a promising result and is further motivation for the future study of employing glycerol as an aromatic-*n*-alkane separation solvent.

The program was written using the original UNIFAC model as the basis of the calculation. This model has been modified many times over time and it should be noted that one would obtain far more quantitatively accurate results if a more suitable modified UNIFAC model were to replace the orginal one in the program.

CHAPTER
FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The aim of this thesis was to investigate the effectiveness of mixed solvents in the separation of aromatic compounds from aliphatic compounds, such as those used in the well known Arosolvan Process (Lo *et. al* [1983]), as well as to provide much needed thermodynamic data for systems containing such solvents. The effectiveness of these solvents for the separation of aliphatic and aromatic compounds was investigated in liquid-liquid extraction as well as extractive distillation. The determination of the effectiveness of the solvents was based on the selectivities for LLE and separation factors for extractive distillation. Both selectivity and separation factors are a measure of the solvents affinity for the component to be separated from the liquid mixture. The third part of this thesis dealt with the development of a computer program using the UNIFAC method to predict the separation factor of a solvent in a given mixture, thus reducing the time spent on experimental work to narrow down a choice of solvents.

The first part of this study involved the determination of the liquid-liquid equilibria of the mixed solvents with an aromatic and *n*-alkane solutes. A test system of *n*-hexane + toluene + NMP at 298.2 K was used (Letcher et al [1998]) to check the ability of the equipment and technique used to capably reproduce experimental measurements The results obtained showed a maximum deviation of ≤ 0.004 mass fraction in the binodal curve and a deviation of ≤ 0.005 mass fraction in the tie-lines obtained.

The solvents investigated in this part of the work were chosen on their structural and physical similarities to those used in the Arosolvan process (Lo *et. al* [1983]); *viz.* monoethyleneglycol (MEG) or water mixed with N-methyl-2-pyrollidone (NMP).
The solvents used were:

- NMP + 10% (W/W) Glycerol
- NMP + 30% (W/W) Glycerol
- NMP + 50% (W/W) Glycerol
- NMP + 10% (W/W) MEG
- NMP + 30% (W/W) MEG

- NMP + 5% (W/W) Diethylene glycol (DEG)
- NMP + 10% (W/W) DEG
- NMP + 10% (W/W) Triethylene glycol (TEG)
- NMP +5% (W/W) Water
- NMP +10% (W/W) Water

The solutes employed were *n*-hexane and toluene as the *n*-alkane and aromatic respectively.

The use of pure NMP as a solvent showed a poor selectivity for toluene and exhibited a poor range of concentrations over which separation could occur. The use of mixed solvents showed promising results in every case, with 50% Glycerol solvents and 10% water systems giving the best range of compositions over which separation could occur.

The best selectivities obtained were from the solvents 10% Glycerol, 10% TEG and 10% DEG, in ascending order. In all cases, the ratio of 9 parts NMP: 1 PART solvent i.e. (10% W/W solvent) proved to be most effective in terms of selectivities for the aromatic compound.

In short, NMP mixed with either a glycol, glycerol or water displayed a great increase in the effectiveness of the solvent for liquid-liquid extraction than NMP used as a solvent on its own.

In the second part of this study, the effectiveness of some of the solvents studied in the first part of this work were investigated for their use in extractive distillation. This was done by the determination of infinite dilution activity coefficients and thus separation factors of the solvents for given separations. The infinite dilution-activity coefficients (IDACs) of the {10% (W/W) solvent + NMP} solvents were determined and compared to the infinite dilution activity coefficients of the pure glycerol or glycol solvent. A gas-liquid chromatography technique was used for the determination of IDACs. A test system of a hexadecane solvent with pentane solvent was used. Our results showed a 0.11% deviation from literature. The following solvents were used:

- NMP
- Glycerol
- MEG
- TEG
- NMP + 10% Glycerol
- NMP + 10% MEG
- NMP+ 10% DEG
- NMP+ 10% TEG

IDACs were determined for the following solutes with each of the above solvents:

- Pentane
- Hexane
- Heptane
- Toluene
- Benzene

The separation factors for each *n*-alkane/aromatic mixture were then determined. The pure TEG solvent proved to have the best separation factors for each of the *n*-alkane/aromatic pairs, except for the heptane/benzene separation, for which the {NMP + 10% glycerol} solvent displayed the best separation factors. The mixed solvents did not show as promising results for extractive distillation applications as they did for liquid-liquid extraction, for the systems investigated.

When compared to the literature, the pure solvent systems did not show very good agreement, however, the values obtained from the literature showed a large spread of values for all the systems available (Tiegs et. al. [1986]). The systems were modelled using the original UNIFAC computational method and deviations fo up to 99% were observed. This was due to the fact that the original UNIFAC does not predict the behaviour of "unlike" molecules very well. This was also observed in thge work performed by Harris [2001]

In the third part of this work, a computer program was written using the original UNIFAC computational method to determine the activity coefficients of a mixture containing *n* components. The infinite dilution case could then be simulated by ensuring that the solvent mole fraction used was $\leq 1*10^{-5}$. The program was written with the purpose of assisting the user to narrow the list of possible experimental solvents being used for a given separation, thereby reducing the time spent on experimentation. A database of commonly used industrial solvents was used in the program in order to compare the effectiveness of each of the solvents on the desired separation. The program enables the user to compare the separation factors of each of the solvents in the database graphically for the separation concerned. The program was written using the original UNIFAC method and as a result did not work well for all types of molecules. This could be overcome by using a relevant modified UNIFAC method for the separation/s required. Although the program was written from an extractive distillation standpoint it can be modified to the liquid-liquid extraction case by changing the original UNIFAC model used to the liquid-liquid equilibrium model suggested by Magnusen *et al* [1981].

5.2 Recommendations

Due to the fact that the liquid-liquid Equilibria experiments showed promising results for the "mixed solvents" studied, it is suggested that they be investigated further with a wider range of alkanes and aromatics. This would help to determine whether or not they exhibit good aromatic selectivity for a larger range of aromatics.

It is also thought that the further investigation of glycerol as a solvent should be undertaken, as it has shown promising results. There is also need for proper liquid-liquid equilibrium experimental equipment. The design of a continuous measurement system that is cost-effective, easy to assemble and operate, would be a very useful tool in the rapid determination of liquid-liquid equilibria.

Although the results of the mixed solvents were not as promising for extractive distillation as they were for LLE, it is recommended that further investigation be performed on the use of mixed solvents in extractive distillation. Glycerol, especially, showed promising results as an additive to NMP as a solvent in both the LLE and extractive distillation. Not only would further in-depth investigation provide better insight into the use of mixed solvents, but would also serve to expand the limited data available for such systems.

A larger range of *n*-alkanes and aromatics should be used to form a more general conclusion as to the effectiveness of mixed solvents for their application in extractive distillation. A further recommendation is to develop a computer aided data logging system for the determination of residence times in the gas-liquid chromatograph column. This could help reduce the human error factor in experimentation thereby producing more accurate results. It would also provide a database of work done for future reference.

The computer program written for this study will not work well for "unlike" molecules due to the limitations of the original UNIFAC method. It is suggested that the original UNIFAC be replaced with a relevant, modified UNIFAC method for the desired separation, thus providing better qualitative and quantitative results. The program could also be extended to include liquid-liquid equilibria prediction by using the LLE UNIFAC method presented by Magnusen *et al* [1981].

The program as it has been written for this work is not very user friendly and requires the input of each of the subgroups, as defined by the UNIFAC method, of the solutes in the mixture to be separated. This could be overcome by developing a graphical interface for the selection of each of the subgroups, in this way, prior knowledge of the molecules subgroups would not be necessary. Another possible way of overcoming this would be to develop a database of solutes from which the user will be able to choose, from the solute database, those components that make up the mixture concerned.

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APPENDICES

A-1. Representation of Ternary Liquid-liquid equilibria:

An equilateral triangle may be use for representing the compositions of a ternary mixture. The sum of the perpendiculars from any point within the triangle to the three sides equals the altitude (Atkins [1986]).

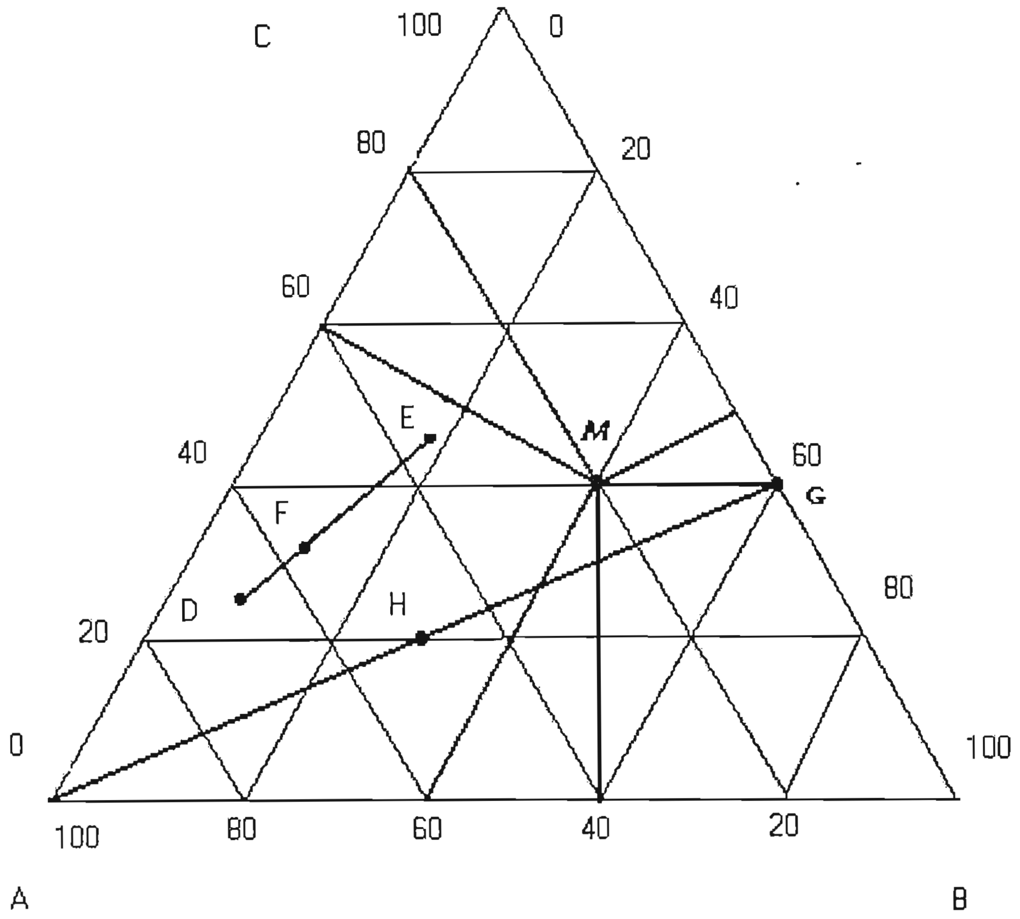


Figure A-1: Triangular Coordinates for the representation of ternary mixtures

The length of the altitude is allowed to represent 100 percent composition, and the length of the perpendiculars from any point within the triangle to the respective side gives the percentage of that component (see Figure A-1.). Alternatively the composition can be found by taking the distance between the sides of the triangle and lines drawn through point M parallel to the sides of the triangle (Treybal [1946]). The Apices of the triangle represent the pure components *A*, *B* and *C*.

Each side on the triangle represents a binary mixture indicated by the name of the side. . *i.e.* side *AB* represents a mixture of *A* and *B*, and thus any point on a side gives a binary mixture of the two components.
So, point *G* is a mixture of 60% B and 40% *C*.

Any point within the triangle represents a ternary mixture e.g. *M* is a mixture of composition 20% *A*, 40% *B* and 40% *C*. It is important to note that points outside the triangle represent imaginary mixtures and are for theoretical, mathematical and constructional purposes only. There are several other characteristics of such plots are significant. For example, if a mixture of composition *D* is added to a mixture of composition *E*, the resulting mixture is of composition *F*, which lies on the straight line *DE*.

A-2: Refractive Index Calibration Charts

Figure A-2: Refractive Index Calibration Chart for NMP + *n*-hexane (X_1) + toluene(X_2) at 298 K and 1 atm

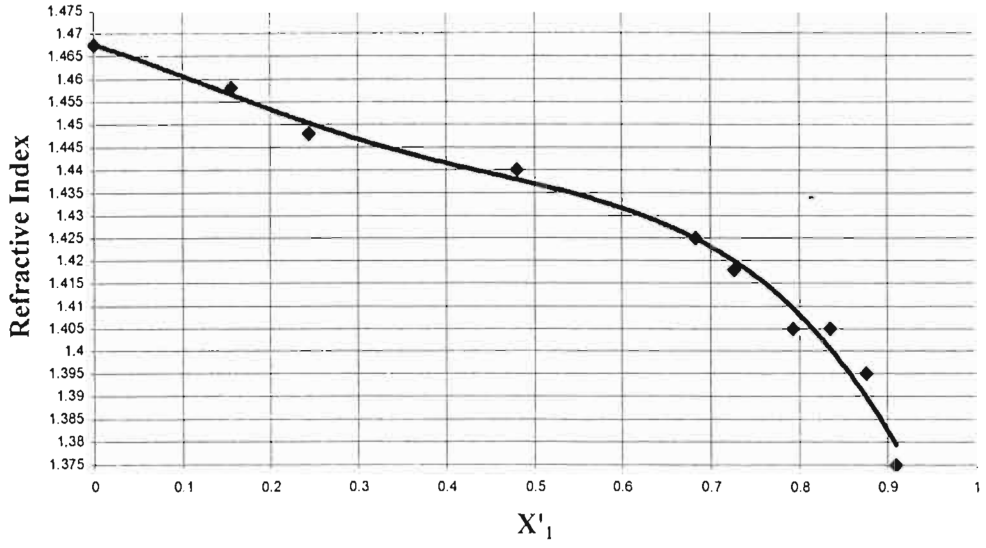


Figure A-3: Refractive Index Calibration Chart for (10%(w/w) Glycerol + NMP} + *n*-hexane(X_1) + toluene(X_2) at 298 K and 1 atm

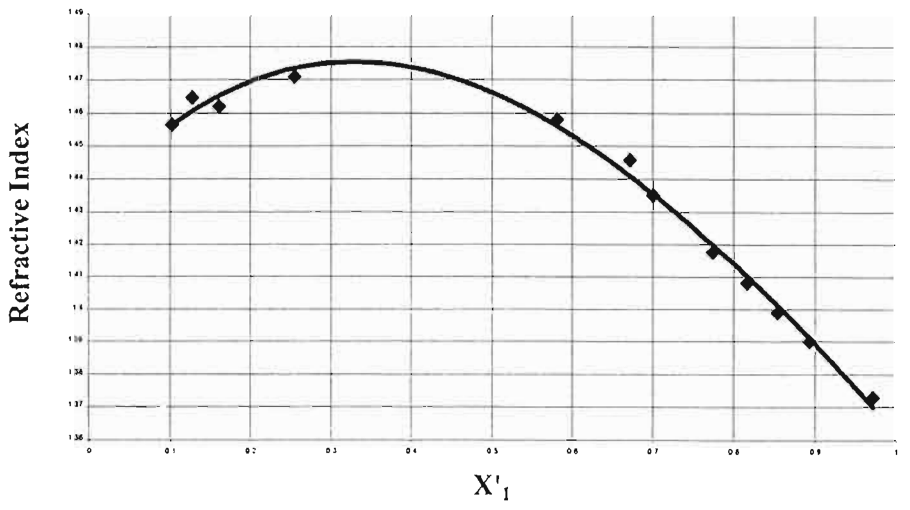


Figure A-4: Refractive Index Calibration Chart for {30%(w/w)Glycerol + NMP}+ n-hexane(X_1) + toluene(X_2) at 298 K and 1 atm

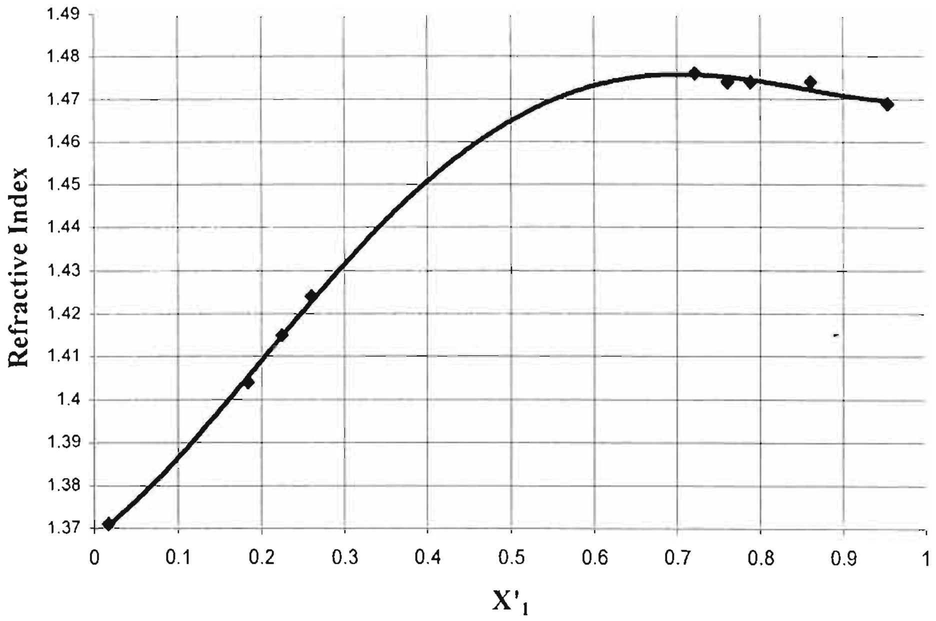


Figure A-5: Refractive Index Calibration Chart for {50% (w/w) Glycerol + NMP} + n-hexane(X_1) + toluene(X_2) at 298 K and 1 atm

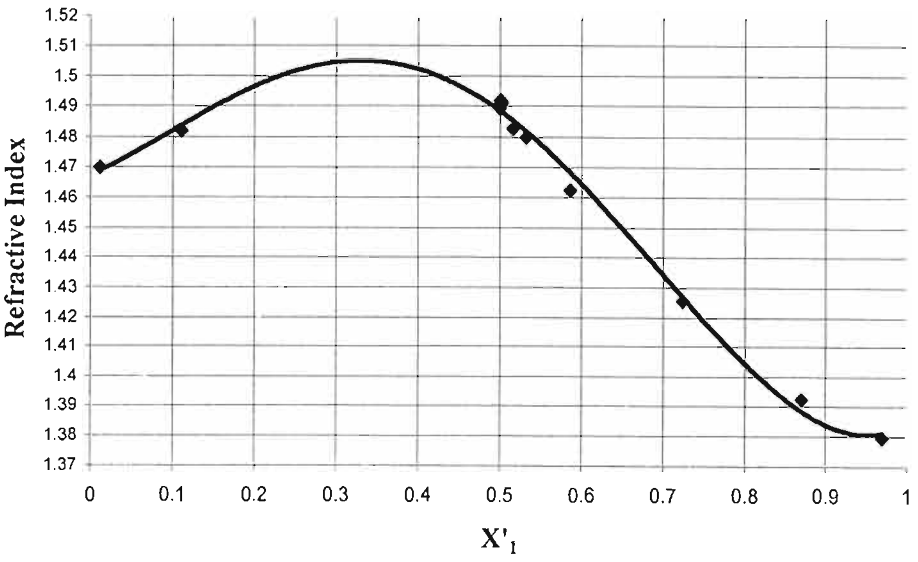


Figure A-6: Refractive Index Calibration Chart for {10% (w/w) MEG + NMP} + *n*-hexane(X_1) + toluene(X_2) at 298 K and 1 atm

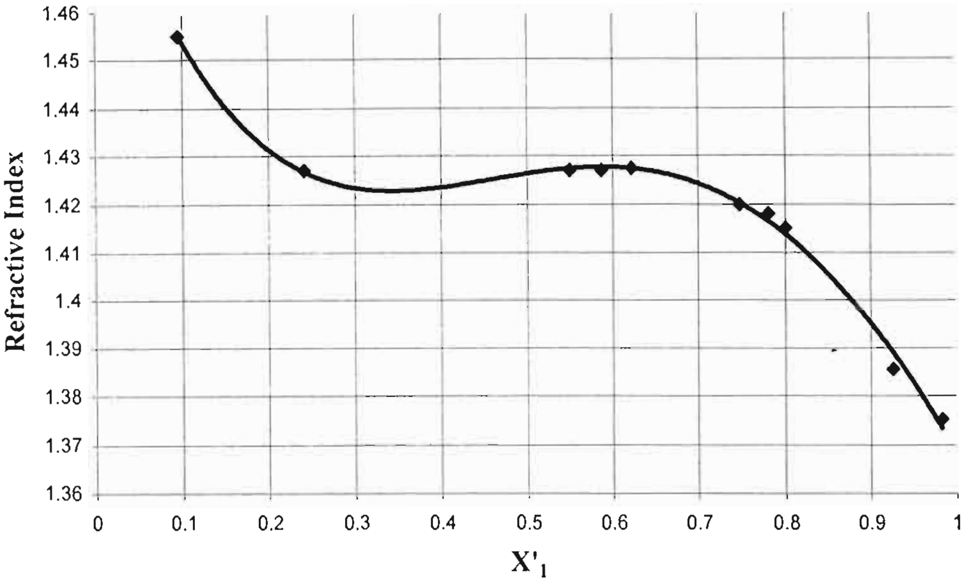


Figure A-7: Refractive Index Calibration Chart for {30% (w/w) MEG + NMP} + *n*-hexane(X_1) + toluene(X_2) at 298 K and 1 atm

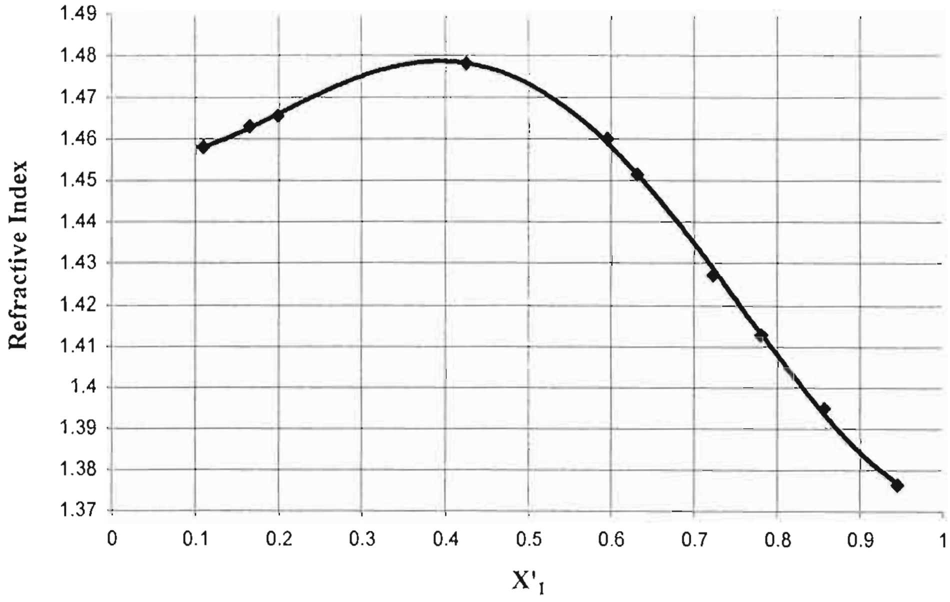


Figure A-8: Refractive Index Calibration Chart for {NMP + 5% DEG} + *n*-hexane(X_1) + toluene(X_2) at 298K and 1 atm

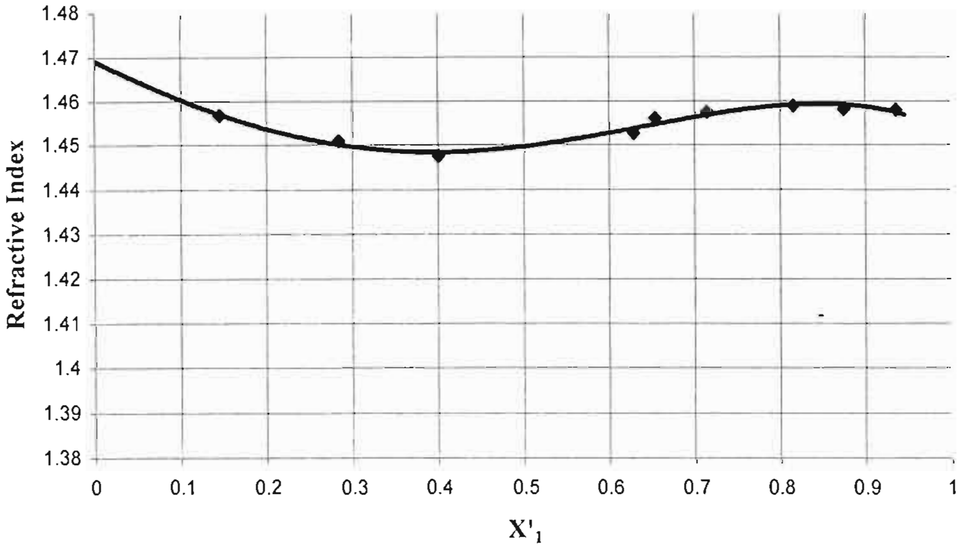


Figure A-9: Refractive Index Calibration Chart for {NMP + 10% (w/w) DEG} + *n*-hexane(X_1) + toluene(X_2) at 298 K and 1 atm

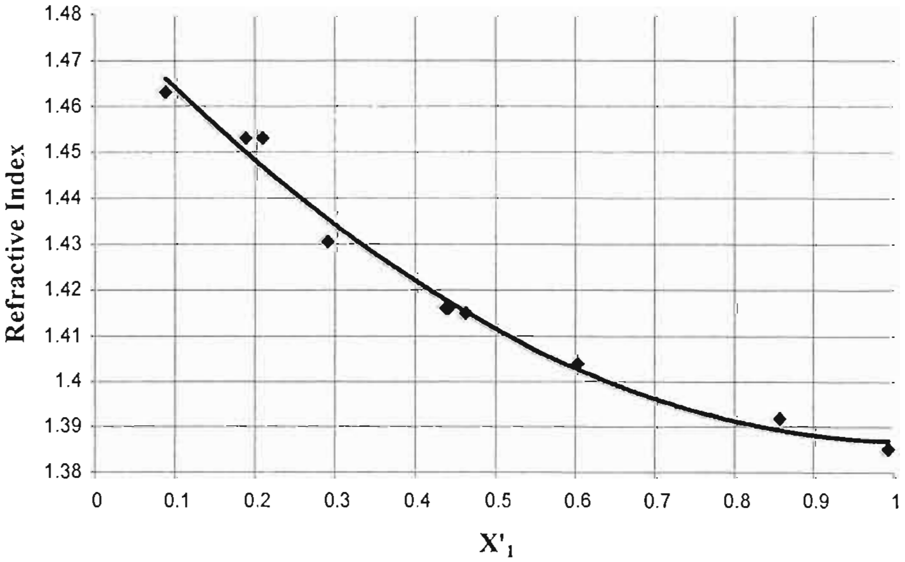


Figure A-10: Refractive Index Calibration Chart for {NMP + 10% (w/w) TEG} + n-hexane(X_1) + toluene(X_2) at 298 K and 1 atm

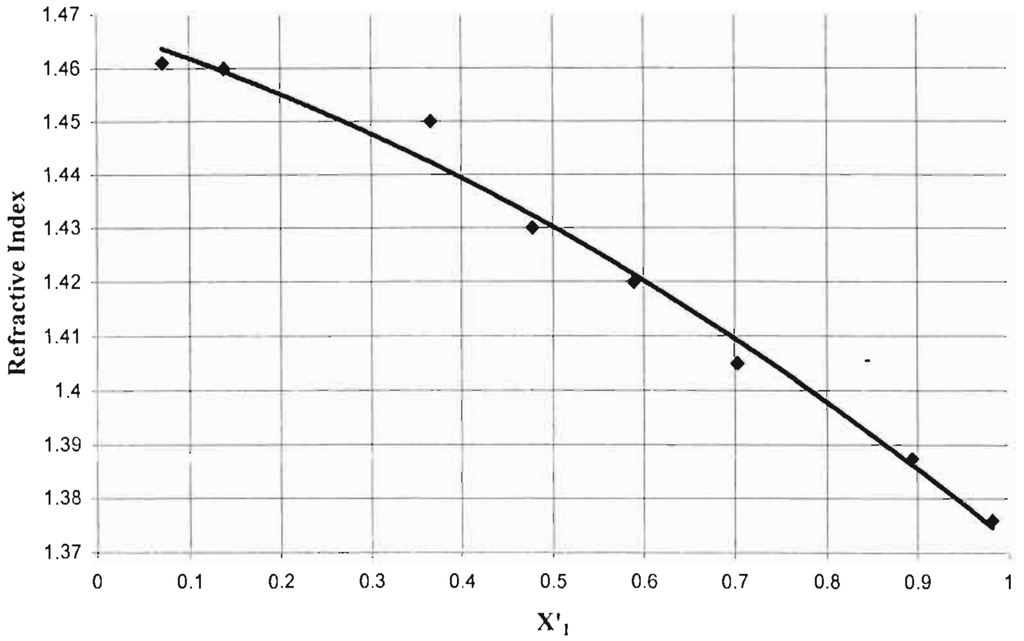


Figure A-11: Refractive Index Calibration Chart For the system {5% Water + NMP} + n-hexane(X_1) + toluene(X_2) at 298 K and 1 atm

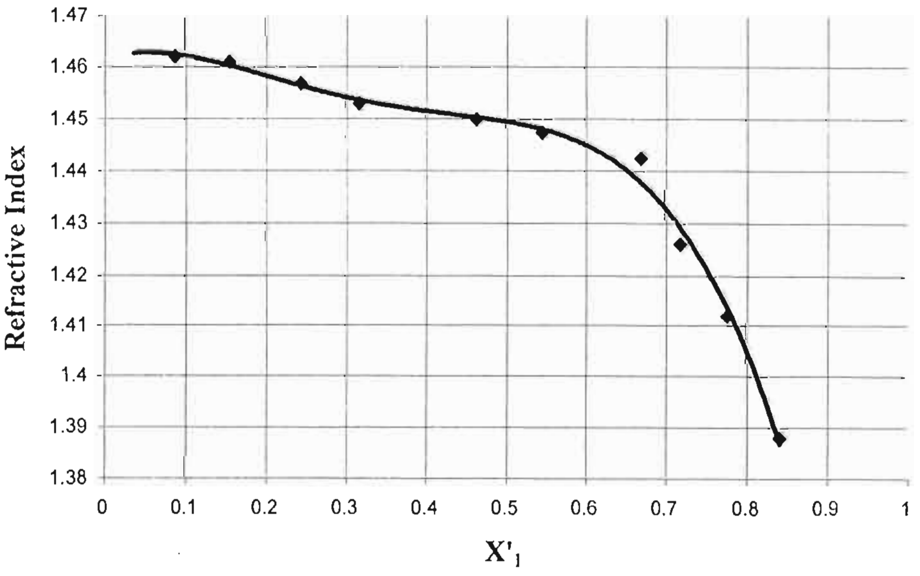
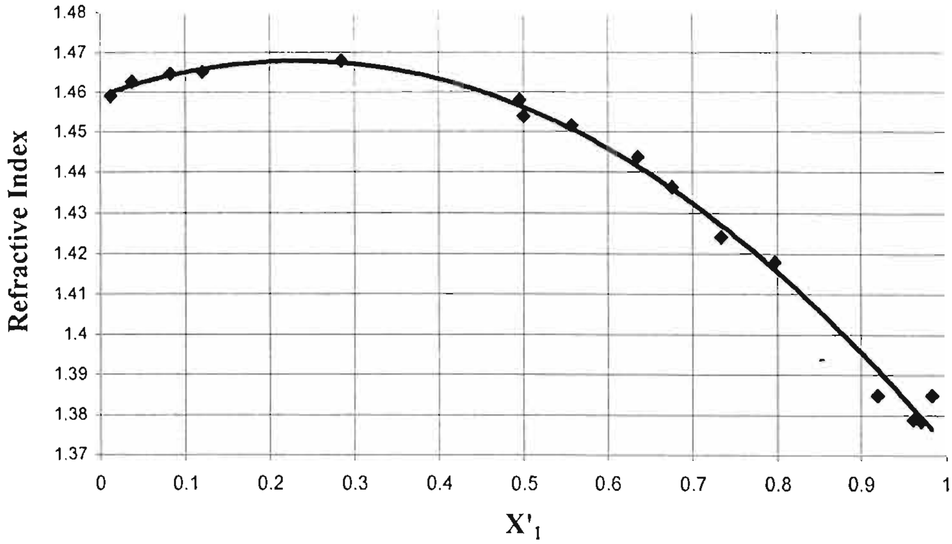


Figure A-12: Refractive Index Calibration Chart for { NMP + 10% water} + *n*-hexane(X_1) + toluene(X_2) at 298 K and 1 atm



A-3. Thermodynamics of Equilibrium:

A-3-1. Conditions of Equilibrium

In a heterogeneous systems comprising c components and ϕ phases the conditions for thermodynamic equilibrium may be written as follows:

$$\begin{aligned} T_{(1)} &= T_{(2)} = \dots = T_{(\phi)}, \\ P_{(1)} &= P_{(2)} = \dots = P_{(\phi)}, \\ \mu_{(1)} &= \mu_{(2)} = \dots = \mu_{(\phi)}, \quad i = 1, \dots, c \end{aligned} \tag{A-1}$$

Where μ_i is the chemical potential of component i, which is related to the total Gibbs, free energy $G_{(\alpha)}$ of any phase α by:

$$\mu_{i(\alpha)} = \left(\frac{\partial G_{(\alpha)}}{\partial n_{i(\alpha)}} \right)_{T,P,n_{j(\alpha)}} \tag{A-2}$$

Which means that the criterion for equilibrium requires that the temperature, pressure and chemical potential of each component are uniform throughout the system. Alternatively, a thermodynamic equivalent and sometimes more useful criteria for equilibrium is represented by:

$$d\left(\sum_{\alpha=1}^{\phi} G_{(\alpha)} \right)_{T,P} = 0 \tag{A-3}$$

meaning that at a constant temperature and pressure, the total Gibbs energy of the entire system is at a minimum.

A-3-2. Activities and Activity coefficients

If we apply the conditions of Equation (A-1) to liquid-liquid system, the problem of relating the equilibrium compositions of the liquid phases is reduced to that of determining the composition dependence of the chemical potential. At this stage it is necessary to resort to a physical model, since thermodynamics alone cannot provide a solution to this problem. It is useful at this juncture to introduce the concept of an ideal solution for which the chemical potential of every component is related to its mole fraction as follows:

$$\mu_i = \mu_i^{\bullet}(T, P) + RT \ln x_i \tag{A-4}$$

The quantity $\mu_i^{\bullet}(T,P)$ is the standard chemical potential of pure I in the same state of aggregation and at the same temperature and pressure as the solution. The form of Equation

(A-4) can be retained for a real solution by a quantity a_i known as the activity and which is identical to the product of the activity coefficient, γ_i, and the mole fraction x_i. Therefore:

$$\mu_i = \mu_i^{\bullet}(T,P) + RT \ln a_i = \mu_i^{\bullet}(T,P) + RT \ln \gamma_i x_i \tag{A-5}$$

The definition of the activity is completed by using the following convention for liquid mixtures whose pure components are liquids at the pressure and temperature of the solution.

$$\lim_{x_1 \to 1} \left({}^{a_i}\!/\!{}_{x_i} \right) = \lim_{x_1 \to 1} \gamma_i = 1 \tag{A-6}$$

Under this convention the quantity $\mu_i^{\bullet}(T,P)$ has the same meaning as in Equation (A-4). In general, a_i and γ_i are functions of temperature, pressure and composition.

Using Equations (A-1) and (A-5), it is easily shown that the condition for equilibrium between two liquid phases (L' and L") is also that:

$$a_i' = a_i'', \qquad i = 1, \ldots, c \tag{A-7}$$

Not only is the chemical potential of each component uniform throughout the system but so is the activity of each component.

A-3-3. The Gibbs-Duhem Equation

Although thermodynamics does not allow prediction of the composition dependence of the chemical potential, a relationship between the activity coefficients of a given phase can be obtained from the Gibbs-Duhem equation. This equation relates the intensive variables that characterize the state of the phase, namely the temperature, pressure, and chemical potential

$$S\, dT - V\, dP + \sum_{i=1}^{c} x_i\, d\mu_i = 0 \tag{A-8}$$

If both P and T are held constant then we get:

$$\sum_{i=1}^{c} x_i\, d\mu_i = 0 \tag{A-9}$$

If we apply this relationship to Equation (A-5) we arrive at:

$$\sum_{i=1}^{c} x_i\, d(\ln \gamma_i) = 0 \tag{A-10}$$

It is therefore a necessary thermodynamic condition that the activity coefficients of a phase are related in this way. Furthermore, any empirical or theoretical relations representing the composition dependence of the activity coefficients must be solutions of this equation. It should be noted that in a binary mixture it is not possible to vary the composition whilst keeping both T and P constant. This is a consequence of the phase rule, but usually the corrections require for variations in T or P are small and are often neglected. The phase rule was first derived using the Gibbs-Duhem equation which must apply to each of the ϕ phases in a multi-phase system. If the temperature, pressure and chemical potentials are uniform throughout the system, there are $c + 2$ variables and therefore $c + 2 - \phi$ degrees of freedom as stated by:

$$f = c + 2 - \phi \tag{A-11}$$

Where f is the number of degrees of freedom.

B-1. Constants used

The Vapour pressures used in the calculation of infinite dilution activity coefficients were calculated from the Antoine Equation (3-32). Table B-1 gives the constants *A, B, C* used for the calculation of the vapour pressures of the compounds indicated.

Solute	A	B	C
n-pentane	6.85296	1064.84	232.012
n-hexane	6.87601	1171.17	224.408
n-heptane	6.89677	1264.9	216.544
toluene	6.95464	1344.8	219.482
benzene	6.90565	1211.033	220.79
water	8.10765	1750.286	235
DECHEMA Data Base CD [1999)]			

Table B-1:Antoine equation constants for calculation of the solutes' and water vapour pressures

The constants required for the calculation of virial coefficients β_{ij} are given in Table B-2.

	I	Tc	Vc	n'
Compound	eV	K	$cm^3.mol^{-1}$	
helium	24.59	5.25	57.4	1
n-pentane	10.35	469.7	304	5
n-hexane	10.13	507.5	370	6
n-heptane	9.92	540.3	432	7
toluene	8.82	591.8	316	7
benzene	9.246	562.2	259	6

Table B-2: Ionisation potentials, critical temperatures, critical volumes and n' for all the solutes and helium

C-1. Code for UNIFAC Program

The following is the basic code of the program written for Chapter 4. It does not contain any of the matrices used in the program due to the poor readability that would result from displaying them as program code. The list of values used for the a_{mk}, R_k and Q_k matrices are tabulated in the preceding sections.

```
%Program for narrowing solvent choice based on UNIFAC calculations



%                         By Rolandra D. Naidoo
%                        Student No. : 941332914
%                 For MSc Degree in Chemical Engineering
%                     Thermodynamics Research Group
%                         University of Natal
%                               Durban




              size_v_solv = size(v_solv);
    b = size_v_solv(1,1);



    size_qk = size(Qk);
m = size_qk(1,2);

disp('When entering no. of groups please enter in the following order
');
disp('CH3     CH2     CH     C     CH2=CH CH=CH    CH2=C  CH=C    C=C    ACH
AC');


no_of_groups = size(Qk);


T = input('Please Input your Temperature in K  :');

n = input('How many chemicals do you have excluding the solvent ?  ');
```

```
a = input('Which component selectivity; 1,2...etc, would you like to
have shown graphically against the solvents  ');



% this loop is to create the stoichiometric matrix for the solutes


i = 1;
while i <= n;
   %v = v(n+1,amk_number);
   v(i,:) = input('Input the number of each subgroups you have ');
i = i + 1;
end




X =input('Please enter your mole fractions for each set of data');


j = 1;
for j = 1:b
   v(i,:)=v_solv(j,:);
   q = v*Qk';
   r = v*Rk';n
   size_v = size(v);
   no_comps = size_v(1,1);
   sum_qi_xi  = zeros(1,1);
sum_ri_xi  = zeros(1,1);



%summing over all components%


for k =1:no_comps
   qi(:,k) = X(:,k).*q(k,1);
   sum_qi_xi = sum_qi_xi + qi(:,k);


   ri(:,k) = X(:,k).*r(k,1);
   sum_ri_xi = sum_ri_xi + ri(:,k);
end


for l = 1:no_comps
   e_mk(:,l) =(v(l,:)'.*Qk')/q(l,1);
end
```

```
   %calculation of interaction parameters
   tau_mk = exp(-amk/T);

   beta_ik = e_mk'*tau_mk;


   %calculate theta_ik

   %denominator 1st%

   for jj = 1:n+1
      theta_den(:,jj) = X(:,jj)*q(jj,1);
   end

   theta_num = theta_den*e_mk';

for kk = 1:m
   theta(:,kk) = theta_num(:,kk)./sum_qi_xi;
end
sk = theta*tau_mk;

% J
     for ll = 1:n+1
      J(:,ll) = r(ll,1)/sum_ri_xi(:,1);
   end



%L
     for jjj = 1:n+1
      L(:,jjj) = q(jjj,1)/sum_qi_xi(:,1);
   end



Q = ones(1,n+1);

   for kkk = 1:n+1

      Q(:,kkk)=q(kkk,1)*Q(:,kkk);
   end
```

```
  %combinatorial gamma
  ln_gammaC = ones(1,n+1) - J + log(J)-5.*Q.*(ones(1,n+1)-J./L +
log(J./L));


  %the residual term is a bit more difficult to compute because it
involves summing over groups and components
  %therefore it is broken up into it's individual terms



  %First term is Q
  t1 = Q;

  %second term
  t2 = Q.*((theta./sk)*beta_ik');

  %third term

  t3 = ones(1,no_comps);


  for i = 1:no_comps
     sigma_t3(:,i) = (log( ones(1,1)*beta_ik(i,:)./sk))*e_mk(:,i);
  end


  t3 = Q.*sigma_t3;

  ln_gammaR = t1 -t2 + t3;
  ln_gamma = ln_gammaC + ln_gammaR;
  activity_coeff = exp(ln_gamma)

  for me =1:n
     selectivity(me,1)
=activity_coeff(1,me)./activity_coeff(1,no_comps);
  end
  selectivity
```

```
  bar(j,selectivity(a,1),'b*:');
    hold on
  ylabel('Selectivity');
  xlabel('Solvent Number');
  title('Selectivity Profile');
  axis on
  grid on

  nxt_pg =input('Press Enter to go to Next Solvent values');
clc
  end
```

C-2. Volume and Surface Parameters for UNIFAC

Table C-1: UNIQUAC and UNIFAC volume and surface parameters R and Q

Main group	Subgroup	No.	*R*	*Q*	Example assignments
1	CH_3	1	0.9011	0.8480	
CH_2	CH_2	2	0.6744	0.5400	*n*-Hexane: 4 CH_2, 2 CH_3
	CH	3	0.4469	0.2280	Isobutane: 1 CH, 3 CH_3
	C	4	0.2195	0.0000	Neopentane: 1 C, 4 CH_3
2	CH_2=CH	5	1.3454	1.1760	1-Hexene: 1 CH_2=CH, 3 CH_2, 1 CH_3
C=C	CH=CH	6	1.1167	0.8670	2-Hexene: 1 CH=CH, 2 CH_3, 2 CH_2
	CH_2=C	7	1.1173	0.9880	
	CH=C	8	0.8886	0.6760	
	C=C	9	0.6605	0.4850	
3	ACH	10	0.5313	0.4000	Benzene: 6 ACH
ACH	AC	11	0.3652	0.1200	
4	$ACCH_3$	12	1.2663	0.9680	Toluene: 5 ACH, 1 $ACCH_3$
$ACCH_2$	$ACCH_2$	13	1.0396	0.6600	Ethylbenzene: 5 ACH, 1 $ACCH_2$, 1 CH_3
	ACCH	14	0.8121	0.3480	
5 OH	OH	15	1.0000	1.2000	*n*-Propanol: 1 OH, 1 CH_3, 2 CH_2
6 CH_3OH	CH_3OH	16	1.4311	1.4320	Methanol
7 Water	H_2O	17	0.9200	1.400	Water
8 ACOH	ACOH	18	0.8952	0.6800	Phenol: 1 ACOH, 5 ACH
9	CH_3CO	19	1.6724	1.4880	Dimethylketone: 1 CH_3CO, 1 CH_3
CH_2CO	CH_2CO	20	1.4457	1.1800	Diethylketone: 1 CH_2CO, 2 CH_3, 1 CH_2
10 CHO	CHO	21	0.9980	0.9480	Ethanal : 1 CHO, 1 CH_3
11	CH_3COO	22	1.9031	1.7280	Methyl acetate: 1 CH_3COO, 1 CH_3
CCOO		23	1.6764	1.4200	Methyl propionate: 1 CH_2COO, 2 CH_3
12 HCOO	HCOO	24	1.2420	1.1880	Methyl formate: 1 HCOO, 1CH_3
13	CH_3O	25	1.1450	1.0880	
CH_2O	CH_2O	26	0.9183	0.7800	Ethyl ether: 1 CH_2O, 1 CH_3, 1 CH_2
	CO-O	27	0.6908	0.4680	
	FCH_2O	28	0.9183	1.1000	Tetrahydrofuran: 1 FCH_2O, 3CH_2
14	CH_3NH_2	29	1.5959	1.5440	
CNH_2	CH_2NH_2	30	1.3692	1.2360	Propyl amine: 1 CH_2NH_2, 1 CH_3, 1 CH_2
	$CHNH_2$	31	1.1417	0.9240	

Table C-1(cont.): UNIQUAC and UNIFAC volume and surface parameters R and Q

15	CH_3NH	32	1.4337	1.2440	
CNH	CH_2NH	33	1.2070	0.9360	Diethyl amine: 1 CH_2NH, 2 CH_3, 1 CH_2
	CHNH	34	0.9795	0.6240	
16	CH_3N	35	1.1865	0.9400	
$(C)_3N$	CH_2N	36	0.9597	0.6320	Triethylamine: 1 CH_2N, 2 CH_2, 3 CH_3
17 $ACNH_2$	$ACNH_2$	37	1.0600	0.8160	Aniline: 1 $ACNH_2$, 5 ACH
18	C_5H_5N	38	2.9993	2.1130	
Pyridine	C_5H_4N	39	2.8332	1.8330	Methyl pyridine: 1 C_5H_4N, 1 CH_3
	C_5H_3N	40	2.6670	1.5530	
19	CH_3CN	41	1.8701	1.7240	
CCN	CH_2CN	42	1.6434	1.4160	Propionnitrile: 1 CH_2CN, 1 CH_3
20	COOH	43	1.3013	1.2240	Acetic acid: 1 COOH, 1 CH_3
COOH	HCOOH	44	1.5280	1.5320	Formic acid
21	CH_2Cl	45	1.4654	1.2640	Chloroethane: 1 CH_2Cl, 1 CH_3
CCl	CHCl	46	1.2380	0.9520	
	CCl	47	1.0060	0.7240	
22	CH_2Cl_2	48	2.2564	1.9880	
CCl_2	$CHCl_2$	49	2.0606	1.6840	1,1-Dichloroethane: 1 $CHCl_2$, 1 CH_3
	CCl_2	50	1.8016	1.4480	
23	$CHCl_3$	51	2.8700	2.4100	
CCl_3	CCl_3	52	2.6401	2.1840	1,1,1-Trichloroethane: 1 CCl_3, 1 CH_3
24 CCl_4	CCl_4	53	3.3900	2.9100	Chloroform
25 ACCl	ACCl	54	1.1562	0.8440	Chlorbenzene: 1 ACCl, 5 ACH
26 CNO_2	CH_3NO_2	55	2.0086	1.8680	Nitromethane
	CH_2NO_2	56	1.7818	1.5600	Nitroethane: 1 CH_2NO_2, 1 CH_3
	$CHNO_2$	57	1.5544	1.2480	
27 $ACNO_2$	$ACNO_2$	58	1.4199	1.1040	Nitrobenzene: 1$ACNO_2$, 5 ACH
28 CS_2	CS_2	59	2.0570	1.6500	Carbon disulfide
29	CH_3SH	60	1.8770	1.6760	Methanethiol
CH_3SH	CH_2SH	61	1.6510	1.3680	Ethanethiol: 1 CH_2SH, 1 CH_3
30 Furfural	Furfural	62	3.1680	2.4810	Furfural
31 DOH	$(CH_2OH)_2$	63	2.4088	2.2480	Ethylene glycol
32 I	I	64	1.2640	0.9920	Iodomethane: 1 I, 1 CH_3

Table C-1(cont.): UNIQUAC and UNIFAC volume and surface parameters R and Q

Main group	Subgroup	No.	*R*	*Q*	Example assignments
33 Br	Br	65	0.9492	0.8320	Bromomethane: 1 Br, 1 CH_3
34 C≡C	CH≡C	66	1.2920	1.0880	1-Hexyne: 1 CH≡C, 1 CH_3, 3 CH_2
	C≡C	67	1.0613	0.7840	2-Hexyne: 1 C≡C, 2 CH_3. 2 CH_2
35 Me_2SO	Me_2SO	68	2.8266	2.4720	Dimethyl sulfoxide
36 ACRY	ACRY	69	2.3144	2.0520	Acrylonitrile
37 ClCC	Cl(C=C)	70	0.7910	0.7240	Trichloroethylene: 3 Cl(C=C), 1 CH=C
38 ACF	ACF	71	0.6948	0.5240	Hexafluorobenzene: 6 ACF
39 DMF	DMF-1	72	3.0856	2.7360	Dimethyl formamide
	DMF-2	73	2.6322	2.1200	Diethyl formamide: 1 DMF-2, 2 CH_3
40 CF_2	CF_3	74	1.4060	1.3800	
	CF_2	75	1.0105	0.9200	Perfluorohexane: 4 CF_2, 2 CF_3
	CF	76	0.6150	0.4600	
41 COO	COO	77	1.3800	1.2000	Butylacetate: 1 COO, 2 CH_3, 3 CH_2
42 SiH_2	SiH_3	78	1.6035	1.2632	Methylsilane: 1 SiH_3, 1 CH_3
	SiH_2	79	1.4443	1.0063	
	SiH	80	1.2853	0.7494	
	Si	81	1.0470	0.4099	Hexamethyldisiloxane: 1 Si, 1 SiO, 6 CH_3
43 SiO	SiH_2O	82	1.4838	1.0621	
	SiHO	83	1.3030	0.7639	
	SiO	84	1.1044	0.4657	Hexamethyldisiloxane: 1 Si, 1 SiO, 6 CH_3
44 NMP	NMP	85	3.9810	3.2000	N-methylpyrrolidone
45 CClF	CCl_3F	86	3.0356	2.644	Trichlorofluoromethane: 1CCl_3F
	CCl_2F	87	2.2287	1.916	Tetrachloro-1,2-difluoroethane: 2 CCl_2F
	$HCCl_2F$	88	2.4060	2.116	Dichlorofluoromethane: 1 $HCCl_2F$
	HCClF	89	1.6493	1.416	1-Chloro-1,2,2,2-tetrafluoroethane: 1 CF_3, 1 HCClF
	$CClF_2$	90	1.8174	1.648	1,2-Dichlorotetrafluoroethane: 2 $CClF_2$
	$HCClF_2$	91	1.9670	1.828	Chlorodifluoromethane: 1 $HCClF_2$
	$CClF_3$	92	2.1721	2.100	Chlorotrifluoromethane: 1 $CClF_3$
	CCl_2F_2	93	2.6243	2.376	Dichlorodifluoromethane: 1 CCl_2F_2

Table C-1(cont.): UNIQUAC and UNIFAC volume and surface parameters R and Q

46 CON	$CONH_2$ $CONHCH_3$ $CONHCH_2$ $CON(CH_3)_2$ $CONCH_3CH_2$ $CON(CH_2)_2$	94 95 96 97 98 99	1.4515 2.1905 1.9637 2.8589 2.6322 2.4054	1.248 1.796 1.488 2.428 2.120 1.812	Acetamide: 1 CH_3, 1 $CONH_2$ N-Methylacetamide: 1 CH_3, 1 $CONHCH_3$ N-Ethylacetamide: 2 CH_3, 1 $CONHCH_2$ N,N-Dimethylacetamide: 1 CH_3, 1 $CON(CH_3)_2$ N,N-Methylethylacetamide: 2 CH_3, 1 $CONCH_3CH_2$ N,N-Diethylacetamide: 3 CH_3, 1 $CON(CH_2)_2$
47 OCCOH	$C_2H_5O_2$ $C_2H_4O_2$	100 101	2.1226 1.8952	1.904 1.592	2-Ethoxyethanol: 1 CH_3, 1 CH_2, 1 $C_2H_5O_2$ 2-Ethoxy-1-propanol: 2 CH_3, 1 CH_2, 1 $C_2H_4O_2$
48 CH_2S	CH_3S CH_2S CHS	102 103 104	1.6130 1.3863 1.1589	1.368 1.060 0.748	Dimethylsulfide: 1 CH_3, 1 CH_3S Diethylsulfide: 2 CH_3, 1 CH_2, 1 CH_2S Diisopropylsulfide: 4 CH_3, 1 CH, 1 CHS
49 Morpho-line	MORPH	105	3.4740	2.796	Morpholine: 1 MORPH
50 Thiophene	C_4H_4S C_4H_3S C_4H_2S	106 107 108	2.8569 2.6908 2.5247	2.140 1.860 1.580	Thiophene: 1 C_4H_4S 2-Methylthiophene: 1 CH_3, 1 C_4H_3S 2,3-Dimethylthiophene: 2 CH_3, 1 C_4H_2S

C-3. Interaction Parameters for UNIFAC

Table C-2.: Values of a_{mn} for the UNIFAC method

	1	2	3	4	5	6	7	8	9	10
1. CH2	.0000	86.02	61.13	76.50	986.5	697.2	1318.0	1333.0	476.4	677.0
2. C=C	-35.36	.0000	38.81	74.15	524.1	787.6	270.6	526.1	182.6	448.8
3. ACH	-11.12	3.446	.0000	167.0	636.1	637.4	903.8	1329.0	25.77	347.3
4. ACCH2	-69.70	-113.6	-146.8	.0000	803.2	603.3	5695.0	884.9	-52.10	586.6
5. OH	156.4	457.0	89.60	25.82	.0000	-137.1	353.5	-259.7	84.00	-203.6
6. CH3OH	16.51	-12.52	-50.00	-44.50	249.1	.0000	-181.0	-101.7	23.39	306.4
7. H2O	300.0	496.1	362.3	377.6	-229.1	289.6	.0000	324.5	-195.4	-116.0
8. ACOH	275.8	217.5	25.34	244.2	-451.6	-265.2	-601.8	.0000	-356.1	-271.1
9. CH2CO	26.76	42.92	140.1	365.8	164.5	108.7	472.5	-133.1	.0000	-37.36
10. CHO	505.7	56.30	23.39	106.0	529.0	-340.2	480.8	-155.6	128.0	.00
11. CCOO	114.8	132.1	85.84	-170.0	245.4	249.6	200.8	-36.72	372.2	185.1
12. HCOO	329.3	110.4	18.12	428.0	139.4	227.8	n.a.	n.a.	n385.4	-236.5
13. CH2O	83.36	26.51	52.13	65.69	237.7	238.4	-314.7	n.a.	191.1	-7.83
14. CNH2	-30.48	1.163	-44.85	296.4	-242.8	-481.7	-330.4	n.a.	n.a.	n.a.
15. CNH	65.33	-28.70	-22.31	223.0	-150.0	-370.3	-448.2	n.a.	394.6	n.a.
16. (C)3N	-83.98	-25.38	-223.9	109.9	28.6	-406.8	-598.8	n.a.	225.3	n.a.
17. ACNH2	1139.0	2000.0	247.5	762.8	-17.40	-118.1	-341.6	-253.1	-450.3	n.a.
18. Pyridine	-101.6	-47.63	31.87	49.80	-132.3	-378.2	-332.9	-341.6	29.10	n.a.
19. CCN	24.82	-40.62	-22.97	-138.4	185.4	162.6	242.8	n.a.	-287.5	n.a.
20. COOH	315.3	1264.0	62.32	89.86	-151.0	339.8	-66.17	-11.00	-297.8	-165.5
21. CCl	91.46	40.25	4.680	122.9	562.2	529.0	698.2	n.a.	286.3	-47.51
22. CCl2	34.01	-23.50	121.3	140.8	527.6	669.9	708.7	n.a.	82.86	190.6
23. CCl3	36.70	51.06	288.5	69.90	742.1	649.1	826.8	n.a.	552.1	242.8
24. CCl4	-78.45	160.9	-4.700	134.7	856.3	709.6	1201.0	10000.0	372.0	n.a.
25. ACCl	106.8	70.32	-97.27	402.5	325.7	612.8	-274.5	622.3	518.4	n.a.
26. CNO2	-32.69	-1.996	10.38	-97.05	261.6	252.6	417.9	n.a.	-142.6	n.a.
27. ACNO2	5541.0	n.a.	1824.0	-127.8	561.6	n.a.	360.7	n.a.	-101.5	n.a.
28. CS2	-52.65	16.62	21.50	40.68	609.8	914.2	1081.0	1421.0	303.7	n.a.
29. CH3SH	-7.481	n.a.	28.41	19.56	461.6	448.6	n.a.	n.a.	160.6	n.a.
30. Furfural	-25.31	82.64	157.3	128.8	521.6	n.a.	23.48	n.a.	317.5	n.a.
31. DOH	140.0	n.a.	221.4	150.6	267.6	240.8	-137.4	838.4	135.4	n.a.

Table C-2(cont.): Values of a_{mn} for UNIFAC method

	1	2	3	4	5	6	7	8	9	10
32. I	128.0	n.a.	58.68	26.41	501.3	431.3	n.a.	n.a.	138.0	245.9
33. Br	-31.52	174.6	-154.2	1112.0	524.9	494.7	n.a.	n.a.	-142.6	n.a.
34. C—C	-72.88	41.38	n.a.	n.a.	68.95	n.a.	n.a.	n.a.	443.6	n.a.
35. Me2SO	50.49	64.07	-2.504	-143.2	-25.87	695.0	-240.0	n.a.	110.4	n.a.
36. ACRY	-165.9	573.0	-123.6	397.4	389.3	218.8	386.6	n.a.	n.a.	354.0
37. ClC=C	47.41	124.2	395.8	419.1	738.9	528.0	n.a.	n.a.	-40.90	183.8
38. ACF	-5.132	-131.7	-237.2	-157.3	649.7	645.9	n.a.	n.a.	n.a.	n.a.
39. DMF	-31.95	249.0	-133.9	-240.2	64.16	172.2	-287.1	n.a.	97.04	13.89
40. CF2	147.3	62.40	140.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
41. COO	529.0	1397.0	317.6	615.8	88.63	171.0	284.4	-167.3	123.4	577.5
42. SiH2	-34.36	n.a.	787.9	191.6	1913.0	n.a.	180.2	n.a.	992.4	n.a.
43. SiO	110.2	n.a.	234.4	221.8	84.85	n.a.	n.a.	n.a.	n.a.	n.a.
44. NMP	13.89	16.11	-23.88	6.214	796.9	n.a.	832.2	-234.7	n.a.	n.a.
45. CClF	30.74	n.a.	167.9	n.a.	794.4	762.7	n.a.	n.a.	n.a.	n.a.
46. CON	27.97	9.755	n.a.	n.a.	394.8	n.a.	-509.3	n.a.	n.a.	n.a.
47. OCCOH	-11.92	132.4	-86.88	-19.45	517.5	n.a.	-205.7	n.a.	156.4	n.a.
48. CH2S	39.93	543.6	n.a.	n.a.	n.a.	420.0	n.a.	n.a.	n.a.	n.a.
49. Morpholine	-23.61	161.1	142.9	274.1	61.20	-89.24	-384.3	n.a.	n.a.	n.a.
50. Thiophene	-8.479	n.a.	23.93	2.845	682.5	597.8	n.a.	810.5	278.8	n.a.

Table C-2(cont): Values of a_{mn} for UNIFAC method

	11	12	13	14	15	16	17	18	19	20
1. CH2	232.1	507.0	251.5	391.5	255.7	206.6	920.7	287.8	597.0	663.5
2. C=C	37.85	333.5	214.5	240.9	163.9	61.11	749.3	280.5	336.9	318.9
3. ACH	5.994	287.1	32.14	161.7	122.8	90.49	648.2	-4.449	212.5	537.4
4. ACCH2	5688.0	197.8	213.1	19.02	-49.29	23.50	664.2	52.80	6096.0	872.3
5. OH	101.1	267.8	28.06	8.6420	42.70	-323.0	-52.39	170.0	6.712	199.0
6. CH3OH	-10.72	179.7	-128.6	359.3	-20.98	53.90	489.7	580.5	53.28	-202.0
7. H2O	72.87	n.a.	540.5	48.89	168.0	304.0	243.2	459.0	112.6	-14.09
8. ACOH	-449.4	n.a.	n.a.	n.a.	n.a.	n.a.	119.9	-305.5	n.a.	408.9
9. CH2CO	-213.7	-190.4	-103.6	n.a.	-174.2	-169.0	6201.0	7.341	481.7	669.4
10. CHO	-110.3	766.0	304.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	497.5
11. CCOO	.0000	-241.8	-235.7	n.a.	-73.50	-196.7	475.5	n.a.	494.6	660.2
12. HCOO	1167.0	.0000	n.a.	n.a.	n.a.	n.a.	n.a.	-233.4	-47.25	-268.1
13. CH2O	461.3	n.a.	.0000	-78.36	251.5	5422.3	n.a.	213.2	-18.51	664.6
14. CNH2	n.a.	n.a.	222.1	.0000	-107.2	-41.11	-200.7	n.a.	358.9	n.a.
15. CNH	136.0	n.a.	-56.08	127.4	.0000	-189.2	n.a.	n.a.	147.1	n.a.
16. (C)3N	2889.0	n.a.	-194.1	38.89	865.9	.0000	n.a.	n.a.	n.a.	n.a.
17. ACNH2	-294.8	n.a.	n.a.	-15.07	n.a.	n.a.	.0000	89.70	-281.6	-396.0
18. Pyridine	n.a.	554.4	-156.1	n.a.	n.a.	n.a.	117.4	.0000	-169.7	-153.7
19. CCN	-266.6	99.37	38.81	-157.3	-108.5	n.a.	777.4	134.3	.0000	n.a.
20. COOH	-256.3	193.9	-338.5	n.a.	n.a.	n.a.	493.8	-313.5	n.a.	.0000
21. CCl	35.38	n.a.	225.4	131.2	n.a.	n.a.	429.7	n.a.	54.32	519.1
22. CCl2	-132.9	n.a.	-197.7	n.a.	n.a.	-141.4	n.a.	587.3	258.6	543.3
23. CCl3	176.5	235.6	-20.93	n.a.	n.a.	-293.7	n.a.	18.98	74.04	504.2
24. CCl4	129.5	351.9	113.9	261.1	91.13	316.9	898.2	368.5	492.0	631.0
25. ACCl	-171.1	383.3	-25.15	108.5	102.2	2951.0	334.9	n.a.	363.5	993.4
26. CNO2	129.3	n.a.	-94.49	n.a.	n.a.	n.a.	n.a.	n.a.	.2827	n.a.
27. ACNO2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	134.9	2475.0	n.a.	n.a.
28. CS2	243.8	n.a	112.4	n.a.	n.a.	n.a.	n.a.	n.a.	335.7	n.a.
29. CH3SH	n.a.	201.5	63.71	106.7	n.a.	n.a.	n.a.	n.a.	161.0	n.a.
30. Furfural	146.3	n.a.	-87.31	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	570.6
31. DOH	152.0	n.a.	9.207	n.a.	n.a.	n.a.	192.3	n.a	169.6	n.a.

Table C-2(cont.): Values of a_{mn} for UNIFAC method

	11	12	13	14	15	16	17	18	19	20
32. I	21.92	n.a.	476.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	616.6
33. Br	24.37	n.a.	736.4	n.a.	n.a.	n.a.	n.a.	-42.71	136.9	5256.0
34. C---C	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	329.1	n.a.
35. Me2SO	41.57	n.a.	-93.51	n.a.	n.a.	-257.2	n.a.	n.a.	n.a.	-180.2
36. ACRY	175.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-42.31	n.a.
37. ClC=C	611.3	134.5	-217.9	n.a.	n.a.	n.a.	n.a.	281.6	335.2	898.2
38. ACF	n.a.	n.a.	167.1	n.a.	-198.8	116.5	n.a.	159.8	n.a.	n.a.
39. DMF	-82.12	-116.7	-158.2	49.70	n.a.	-185.2	343.7	n.a.	150.6	-97.77
40. CF2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
41. COO	-234.9	65.37	-247.8	n.a.	284.5	n.a.	-22.10	n.a.	-61.60	1179.0
42. SiH2	n.a.	n.a.	448.5	961.8	1464.0	n.a.	n.a.	n.a.	n.a.	2450.0
43. SiO	n.a.	n.a.	n.a.	-125.2	1604.0	n.a.	n.a.	n.a.	n.a.	2496.0
44. NMP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
45. CClF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
46. CON	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-70.25
47. OCCOH	-3.444	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	119.2	n.a.
48. CH2S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
49. Morpholine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
50. Thiophene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	221.4	n.a.	n.a.

Table C-2(cont): Values of a_{mn} for UNIFAC method

22	23	24	25	26	28	27	29	30
53.76	24.90	104.3	11.44	661.5	153.6	543.0	184.4	354.6
58.55	-13.99	-109.7	100.1	357.5	76.30	n.a.	n.a.	262.9
-144.4	-231.9	3.000	187.0	168.0	52.07	194.9	-10.43	-64.69
-111.0	-80.25	-141.3	-211.0	3629.0	-9.451	4448.0	393.6	48.49
65.28	-98.12	143.1	123.5	256.5	488.9	157.1	147.5	-120.5
-102.5	-139.4	-44.76	-28.25	75.14	-31.09	n.a.	17.50	n.a.
370.4	353.7	497.5	133.9	220.6	887.1	399.5	n.a.	188.0
n.a.	n.a.	1827.0	6915.0	n.a.	8484.0	n.a.	n.a.	n.a.
-130.3	-354.6	-39.20	-119.8	137.5	216.1	548.5	-46.28	-163.7
67.52	-483.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.n.a.	n.a.
108.9	-209.7	54.57	442.4	-81.13	183.0	n.a.	n.a.	202.3
n.a.	-126.2	179.7	24.28	n.a.	n.a.	n.a.	103.9	n.a.
137.8	-154.3	47.67	134.8	95.18	140.9	n.a.	-8.538	170.1
n.a.	n.a.	-99.81	30.05	n.a.	n.a.	n.a.	-70.14	n.a.
n.a.	n.a.	71.23	-18.93	n.a.	n.a.	n.a.	n.a.	n.a.
-73.85	-352.9	-262.0	-181.9	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	n.a.	882.0	617.5	n.a.	n.a.	-139.3	n.a.	n.a.
-351.6	-114.7	-205.3	n.a.	n.a.	n.a.	2845.0	n.a.	n.a.
-152.7	-15.62	-54.86	-4.6240	-.5150	230.9	n.a.	.4604	n.a.
-44.70	39.63	183.4	-79.08	n.a.	n.a.	n.a.	n.a.	-208.9
108.3	249.2	62.42	153.0	32.73	450.1	86.20	59.02	n.a.
.0000	.0000	56.33	223.1	108.9	n.a.	n.a.	n.a.	n.a.
.0000	.0000	-30.10	192.1	n.a.	116.6	n.a.	n.a.	-64.38
17.97	51.90	.0000	-75.97	490.9	132.2	534.7	n.a.	546.7
-8.309	-.2266	248.4	.0000	132.7	n.a.	2213.0	n.a.	n.a.
-9.639	n.a.	-34.68	132.9	.0000	320.2	533.2	n.a.	n.a.
n.a.	n.a.	514.6	-123.1	-85.12	n.a.	.0000	n.a.	n.a.
n.a.	-26.06	-60.71	n.a.	277.8	.0000	n.a.	n.a.	n.a.
n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	.0000	n.a.
n.a.	48.48	-133.2	n.a.	n.a.	n.a.	n.a.	n.a.	.0000
n.a.	n.a.	n.a.	n.a.	481.3	n.a.	n.a.	n.a.	n.a.

Table C-2(cont.): Values of a_{mn} for UNIFAC method

	21	22	23	24	25	26	28	27	29	30
32. I	n.a.	-40.82	21.76	48.49	n.a.	64.28	-27.45	2448.0	n.a.	n.a.
33. Br	-262.3	-174.5	n.a.	77.55	-185.3	125.3	n.a.	4288.0	n.a.	n.a.
34. C--C	n.a.	n.a.	n.a.	n.a.	n.a.	174.4	n.a.	n.a.	n.a.	n.a.
35. Me2SO	n.a.	-215.0	-343.6	-58.43	n.a.	n.a.	n.a.	n.a.	85.70	n.a.
36. ACRY	n.a.	n.a.	n.a.	-85.15	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
37. ClC=C	383.2	301.9	-149.8	-134.2	n.a.	379.4	167.9	n.a.	n.a.	82.64
38. ACF	n.a.	n.a.	n.a.	-124.6	n.a.	n.a.	n.a	n.a.	n.a.	n.a.
39. DMF	n.a.	n.a.	n.a.	-186.7	n.a.	223.6	n.a.	n.a.	-71.00	n.a.
40. CF2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
41. COO	182.2	305.4	-193.0	335.7	1107.0	-124.7	885.5	n.a.	n.a.	-64.28
42. SiH2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
43. SiO	n.a.	n.a.	n.a.	70.81	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
44. NMP	n.a.	n.a.	-196.2	n.a.	n.a.	n.a.	n.a.	n.a.	-274.1	n.a.
45. CClF	n.a.	n.a.	n.a.	n.a.	n.a.	844.0	n.a.	n.a.	n.a.	n.a.
46. CON	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
47. OCCOH	n.a.	-194.7	n.a.	3.163	7.082	n.a.	n.a.	n.a.	n.a.	n.a.
48. CH2S	n.a.	n.a.	-363.1	-11.30	n.a.	n.a.	n.a.	n.a.	6.971	n.a.
49. Morpholine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
50. Thiophene	n.a.	n.a.	n.a.	-79.34	n.a.	176.3	n.a.	n.a.	n.a.	n.a.

Table C-2(cont.): Values of a_{mn} for UNIFAC method

	31	32	33	34	35	36	37	38	39	40
1. CH2	3025.0	335.8	479.5	298.9	526.5	689.0	-4.189	125.8	485.3	-2..859
2. C=C	n.a.	.n.a.	183.8	31.14	179.0	-52.87	-66.46	359.3	-70.45	449.4
3. ACH	210.4	113.3	261.3	n.a.	169.9	383.9	-259.1	389.3	245.6	22.67
4. ACCH2	4975.0	259.0	210.0	n.a.	4284.0	-119.2	-282.5	101.4	5629.0	n.a.
5. OH	-318.9	313.5	202.1	727.8	-202.1	74.27	225.8	44.78	-143.9	n.a.
6. CH3OH	-119.2	212.1	106.3	n.a.	-399.3	-5.224	33.47	-48.25	-172.4	n.a.
7. H2O	12.72	n.a.	n.a.	n.a.	-139.0	160.8	n.a.	n.a.	319.0	n.a.
8. ACOH	-687.1	n.a.	n.a.	n.a.	n.a.	n.a.n.a.	n.a.	n.a.	n.a.	n.a.
9. CH2CO	71.46	53.59	245.2	-246.6	-44.58	n.a.	-34.57	n.a.	-61.70	n.a.
10. CHO	n.a.	117.0	n.a.	n.a.	n.a.	-339.2	172.4	n.a.	-268.8	n.a.
11. CCOO	-101.7	148.3	18.88	n.a.	52.08	-28.61	-275.2	n.a.	85.33	n.a.
12. HCOO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-11.40	n.a.	308.9	n.a.
13. CH2O	-20.11	-149.5	-202.3	n.a.	128.8	n.a.	240.2	-273.9	254.8	n.a.
14. CNH2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-164.0	n.a.
15. CNH	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	570.9	n.a.	n.a.
16. (C)3N	n.a.	n.a.	n.a.	n.a.	243.1	n.a.	n.a.	-196.3	22.05	n.a.
17. ACNH2	.1004	n.a.	n.a.	n.a.n.a.	n.a.	n.a.	n.a.	n.a.	-334.4	n.a.
18. Pyridine	n.a.	n.a.	-60.78	n.a.	n.a.	n.a.	160.7	-158.8	n.a.	n.a.
19. CCN	177.5	n.a.	-62.17	-203.0	n.a.	81.57	-55.77	n.a.	-151.5	n.a.
20. COOH	n.a.	228.4	-95.00	n.a.	-463.6	n.a.	-11.16	n.a.	-228.0	n.a.
21. CCl	n.a.	n.a.	344.4	n.a.	n.a.	n.a.	-168.2	n.a.	n.a.	n.a.
22. CCl2	n.a.	177.6	315.9	n.a.	215.0	n.a.	-91.80	n.a.	n.a.	n.a.
23. CCl3	n.a.	86.40	n.a.	n.a.	363.7	n.a.	111.2	n.a.	n.a.	n.a.
24. CCl4	n.a.	247.8	146.6	n.a.	337.7	369.5	187.1	215.2	498.6	n.a.
25. ACCl	n.a.	n.a.	593.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
26. CNO2	139.8	304.3	10.17	-27.70	n.a.	n.a.	10.76	n.a.	-223.1	n.a.
27. ACNO2	n.a.	2990.0	-124.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28. CS2	n.a.	292.7	n.a.	n.a.	n.a.	n.a.	-47.37	n.a.	n.a.	n.a.
29. CH3SH	n.a.	n.a.	n.a.	n.a.	31.66	n.a.	n.a.	n.a.	78.92	n.a.
30. Furfural	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	262.9	n.a.	n.a.	n.a.
31. DOH	.0000	n.a.	n.a.	n.a.	-417.2	n.a.	n.a.	n.a.	302.2	n.a.

Table C-2(cont.): Values of a_{mn} for UNIFAC method

	31	32	33	34	35	36	37	38	39	40
32. I	n.a.	.0000	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
33. Br	n.a.	n.a.	.0000	n.a.	32.90	n.a.	n.a.	n.a.	n.a.	n.a.
34. C---C	n.a.	n.a.	n.a.	.0000	n.a.	n.a.	2073.0	n.a.	-119.8	n.a.
35. Me2SO	535.8	n.a.	-111.2	n.a.	.0000	n.a.	n.a.	n n.a.	-97.71	n.a.
36. ACRY	n.a.	n.a.	n.a.	n.a.	n.a.	.0000	-208.8	n.a.	-8.804	n.a.
37. ClC=C	n.a.	n.a.	n.a.	631.5	n.a.	837.2	.0000	n.a.	255.0	n.a.
38. ACF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	.0000	n.a.	-117.2
39. DMF	-191.7	n.a.	n.a.	6.699	136.6	5.150	-137.7	n.a.	.0000	-5.579
40. CF2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	185.6	55.80	.0000
41. COO	-264.3	288.1	627.7	n.a.	-29.34	-53.91	-198.0	n.a.	-28.65	n.a.
42. SiH2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
43. SiO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
44. NMP	262.0	n.a.	n.a.	n.a.	n.a.	n.a.	-66.31	n.a.	n.a.	n.a.
45. CClF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-32.17
46. CON	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
47. OCCOH	515.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
48. CH2S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	148.9	n.a.	n.a.	n.a.
49. Morpholine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a
50. Thiophene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table C-2(cont): Values of a_{mn} for UNIFAC method

	41	42	43	44	45	46	47	48	49	50
1. CH2	387.1	-450.4	252.7	220.3	-5.869	390.9	553.3	187.0	216.1	92.99
2. C=C	48.33	n.a.	n.a.	86.46	n.a.	200.2	268.1	-617.0	62.56	n.a.
3. ACH	103.5	-432.3	238.9	30.04	-88.11	n.a.	333.3	n.a.	-59.58	-39.16
4. ACCH2	69.26	683.3	355.5	46.38	n.a.	n.a.	421.9	n.a.	-203.6	184.9
5. OH	190.3	-817.7	202.7	-504.2	72.96	-382.7	-248.3	n.a.	104.7	57.65
6. CH3OH	165.7	n.a.	n.a.	n.a.	-52.10	n.a.	n.a.	37.63	-59.40	-46.01
7. H2O	-197.5	-363.8	n.a.	452.2	n.a.	835.6	139.6	n.a.	407.9	n.a.
8. ACOH	-494.2	n.a.	n.a.	-659.0	n.a.	n.a.	n.a.	n.a.	n.a.	1005.0
9. CH2CO	-18.80	-588.9	n.a.	n.a.	n.a.	n.a.	37.54	n.a.	n.a.	-162.6
10. CHO	-275.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
11. CCOO	560.2	n.a.	n.a.	n.a.	n.a.	n.a.	151.8	n.a.	n.a.	n.a.
12. HCOO	-70.24	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
13. CH2O	417.0	1338.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
14. CNH2	n.a.	-664.4	275.9	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
15. CNH	-38.77	448.1	-1327.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
16. (C)3N	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
17. ACNH2	-89.42	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
18. Pyridine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-136.6
19. CCN	120.3	n.a.	n.a.	n.a.	n.a.	n.a.	16.23	n.a.	n.a.	n.a.
20. COOH	-337.0	169.3	127.2	n.a.	n.a.	-322.3	n.a.	n.a.	n.a.	n.a.
21. CCl	63.67	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
22. CCl2	-96.87	n.a.	n.a.	n.a.	n.a.	n.a.	361.1	n.a.	n.a.	n.a.
23. CCl3	255.8	n.a.	n.a.	-35.68	n.a.	n.a.	n.a.	565.9	n.a.	n.a.
24. CCl4	256.5	n.a.	233.1	n.a.	n.a.	n.a.	423.1	63.95	n.a.	108.5
25. ACCl	-145.1	n.a.	n.a.	n.a.	n.a.	n.a.	434.1	n.a.	n.a.	n.a.
26. CNO2	248.4	n.a.	n.a.	n.a.	-218.9	n.a.	n.a.	n.a.	n.a.	-4.565
27. ACNO2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28. CS2	469.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
29. CH3SH	n.a.	n.a.	n.a.	1004.0	n.a.	n.a.	n.a.	-18.27	n.a.	n.a.
30. Furfural	43.37	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
31. DOH	347.8	n.a.	n.a.	-262.0	n.a.	n.a.	-353.5	n.a.	n.a.	n.a.

Table C-2 (concl.): Values of a_{mn} for UNIFAC method

	41	42	43	44	45	46	47	48	49	50
32. I	68.55	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
33. Br	-195.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
34. C---C	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
35. Me2SO	153.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
36. ACRY	423.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
37. ClC=C	730.8	n.a.	n.a.	26.35	n.a.	n.a.	n.a.	2429.0	n.a.	n.a.
38. ACF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
39. DMF	72.31	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
40. CF2	n.a.	n.a.	n.a.	n.a.	111.8	n.a.	n.a.	n.a.	n.a.	n.a.
41. COO	.0000	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
42. SiH2	n.a.	.0000	-21.660	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
43. SiO	n.a.	745.3	.0000	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
44. NMP	n.a.	n.a.	n.a.	.0000	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
45. CClF	n.a.	n.a.	n.a.	n.a.	.0000	n.a.	n.a.	n.a.	n.a.	n.a.
46. CON	n.a.	n.a.	n.a.	n.a.	n.a.	.0000	n.a.	n.a.	n.a.	n.a.
47. OCCOH	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	.0000	n.a.	n.a.	n.a.
48. CH2S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	.0000	n.a.	n.a.
49. Morpholine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	.0000	n.a.
50. Thiophene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	.0000