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LIQUID-LIQUID EQUILIBRIA RELATED TO THE SEPARATION OF ORGANIC ACIDS

Nokukhanya Mavis Xhakaza

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Submitted in fulfilment of the requirements of the Masters Degree in Technology: Department of Chemistry in the Faculty of Applied Sciences at the Durban University of Technology

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Abstract

The thesis involves a study of the thermodynamics of ternary liquid mixtures involving carboxylic acids with sulfolane, hydrocarbons and acetonitrile. Carboxylic acids are an important group of polar compounds with many industrial and commercial uses and applications. In South Africa, these carboxylic acids together with many other oxygenates and hydrocarbons are manufactured by SASOL using the Fischer–Tropsch process. The separation of these acids from hydrocarbons is a commercially viable option, and is an important reason for this study. This work focuses on the use of sulfolane in effecting separation by solvent extraction and not by the more common and energy intensive method of distillation. Sulfolane was chosen because of its high polarity and good solvent extraction properties.

The first part of this study involves the determination of excess molar volumes (V_m^E) of binary mixtures of sulfolane (1) + carboxylic acids (2) at different temperatures of 303.15 K and 308.15 K, where carboxylic acids refer to acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid respectively. The densities of the binary systems of sulfolane (1) + carboxylic acids (2) were measured at T = 303.15 K and 308.15 K. The excess molar volumes were calculated from the experimental densities at each temperature. The V_m^E were negative for the entire mole fractions for all the binary systems. It was found that the V_m^E in the systems studied increase with an increase in temperature, and also V_m^E decreases with an increase in the carbon chain length of the carboxylic acid. The V_m^E data results were correlated using Redlich-Kister equation.

The second part was the study of the binodal or solubility curves and tie line data for the ternary systems of [sulfolane (1) + carboxylic acids (2) + hydrocarbons (3)] and [acetonitrile (1) + carboxylic acids (2) + hydrocarbon (3)].

Hydrocarbons refer to pentane, hexane, dodecane and hexadecane. The binodal curve experimental data was determined by the cloud point technique. Liquid-liquid equilibrium (LLE) phase diagrams were constructed using the mole fractions and refractive indices (n_D). Tie line data were obtained for the sulfolane-rich and hydrocarbon-rich phases as well as the acetonitrile-rich and hydrocarbon-rich phases respectively. The tie lines in both cases were skewed towards the hydrocarbon-rich phases indicating that relative mutual solubility of carboxylic acids is higher in the hydrocarbon-rich phase than in the solvent-rich phase. Selectivity values were calculated from the tie-lines to determine the extraction capabilities of solvents sulfolane and acetonitrile. Selectivity values in all cases were greater than one, meaning that both sulfolane and acetonitrile can be used to separate carboxylic acids from hydrocarbons. Binodal curve data were correlated by the Hlavatý, beta (β) and logγ equations; average standard deviation error for Hlavatý was 0.012, for beta (β), 0.023 and for logγ, 0.021. The NRTL and UNIQUAC models were used to correlate the experimental tie-lines. The calculated values based on the NRTL equation were found to be better than those based on UNIQUAC equation; the average root-mean square deviation, (rmsd), between the phase composition obtained from experiment and that from calculation was 0.061 for the NRTL model, as compared to 0.358 for UNIQUAC model for the ternary systems involving sulfolane. For ternary systems of acetonitrile, the NRTL equation was better than the UNIQUAC with the rsmd of 0.003 and 0.287for UNIQUAC equation.

Declaration

The work described herein was performed under the supervision of Professor G. G. Redhi at Durban University of Technology, Durban, KZN, South Africa.

I hereby certify that this research is the result of my own investigation, which has not been accepted in substance for any degree, and is not being concurrently submitted for any other degree. Where use of the work of others, it has been duly acknowledge in the text.

.... Date:....................................

Nokukhanya Mavis Xhakaza

I hereby certify that the above statement is correct.

.... Date:...

Professor G. G. Redhi

Dedication

To my family

Acknowledgements

I would like to thank the Almighty God for giving me life and strength to undertake this project. I would like to record my appreciation and gratitude to Professor G.G. Redhi my Supervisor for this project at the Durban University of Technology, who had faith in me and for his valuable support, guidance and suggestions, from the start of this research till the end of the project.

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Finally I would thank my family, my husband Nkanyiso Xhakaza, my children, Amandla Skhambane Xhakaza and Ayanda Mhlophekazi Xhakaza for their patience, endless love and support while most of the family time was used during this research.

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ρ	density
ν	frequency
V_m^E	excess molar volume
T	temperature
K	Kelvin
x_1	mole fraction of sulfolane or acetonitrile
x_2	mole fraction of carboxylic acid
x_3	mole fraction of hydrocarbons
M_1	molar mass of 1st component
M_2	molar mass of 2nd component
M_3	molar mass of 3rd component
ω	selectivity
x_1'	mole fraction of acetonitrile or sulfolane in sulfolane or acetonitrile-rich layer
x_2'	mole fraction of carboxylic acid in sulfolane or acetonitrile-rich layer
x_1''	mole fraction of acetonitrile or sulfolane in hydrocarbon-rich layer
x_2''	mole fraction of carboxylic acid in hydrocarbon-rich layer
n_D	refractive index

NRTL	non-random two liquid model
UNIQUAC	universal quasichemical model
R	pure component volume parameter
Q	pure component surface parameter
V_{mi}	molar volume
A_i	polynomial coefficient
n	number of experimental points
N	polynomial degree
α	NRTL nonrandomness parameter
exp	experimental
calc	calculated
$(g_{ij} - g_{jj})$, $(g_{ji} - g_{ii})$	NRTL binary interaction parameters
$(\Delta u_{ij}, \Delta u_{ij})$	UNIQUAC binary interaction parameters
σ	standard deviation
δ	root mean square deviation between calculated and experimental property

Publications

1. **Xhakaza, N. M**., Redhi, G. G.; Liquid-liquid equilibria for mixtures of (sulfolane + a carboxylic acid + pentane) at 303.15 K: *In Preparation*

2. **Xhakaza, N. M**., Redhi, G. G.; Liquid-liquid equilibria for mixtures of Sulfolane + a carboxylic acid + hexane at 303.15 K: *In Preparation*

3. **Xhakaza, N. M**., Redhi, G. G**.**; Phase equilibria for liquid mixtures of (Acetonitrile + a carboxylic Acid + dodecane) at 303.15 K: *Submitted*

4. **Xhakaza, N. M**., Redhi, G. G.; Phase equilibria for liquid mixtures of (Sulfolane + a carboxylic acid + hexadecane at 303.15 K: *In Preparation*

CHAPTER 1

INTRODUCTION

1.1 Extraction or Separation processes in Chemical Industries

Separation processes are of great importance in refineries, chemical, petrochemical, gas processing and pharmaceutical industries. The reactor can be regarded as the heart of a chemical plant and in most cases, 60-80 percent of the total cost is taken up by the separation step. This step involves one or more thermal separation processes such as distillation, extraction, absorption, crystallization, adsorption, membrane processes, etc., which are used to obtain the products at the required purity (Letcher, 2004).

In various separation processes, concentration differences between two different streams or different phases are employed to carry out the separation. For extractive distillation, extraction and absorption processes, highly polar solvents are required. Selective solvents (entrainers) have the task of altering the partition coefficients in a way that high separation factors and selectivities for the different phase equilibria viz, vapour-liquid equilibrium (VLE), liquid-liquid equilibrium (LLE), gas-liquid equilibrium (GLE), are achieved, resulting in a separation of compounds. As the total cost of these separation processes is strongly influenced by the selectivity of the solvent, the search for new and better solvents is important and has been a priority for many decades (Letcher, 2004).

The separation or the removal of organic residues from waste streams released from industries has been important from the points of view of pollution control and recovery of useful materials. The disposal of waste waters containing most widely used industrial organic acids such as acetic acid, propanoic acid has been recognized as a significant expense to the industry and environment (Kumar *et al*., 2008).

1.2 Carboxylic acids in South African Industries

In South Africa, Sasol is involved in the production of crude oil from coal using a series of processes. One of the processes is the Fischer-Tropsch Conversion, which is the heart of the Sasol synfuel process and where its major technological efforts have been concentrated. The original Fischer-Tropsch process licensed in 1950 was a combination of German fixed bed and the American fluid-bed Fischer-Tropsch, a circulating fluidised bed reactor. After years of research to make the process economically viable, Sasol licensed its own design in 1972 as the Sasol Synthol Process (Hodge, 2000).

Since then, the process has been further improved with the most recent innovations leading to the development of the Sasol Advanced Synthol Reactor which is more cost-effective than previous models. In the Fischer-Tropsch process, the synthesis feed gas is sent into the reactor and the hydrogen and carbon monoxide react under pressure in the presence of a catalyst to form a range of hydrocarbons in the C_1-C_{20} range (Hodge, 2000).

In the Product Recovery Process, the C_1-C_{20} hydrocarbons emerging from the Fischer-Tropic reactor are cooled in stages to separate the various chemicals streams, the C_1-C_6 stream which contains carboxylic acids, ketones and alcohols; the C_2-C_3 stream which contains ethylene and propylene; the C_4-C_{20} stream which consists of liquid fuels and alpha olefins, and the C_1 stream consisting of pipeline gas (Hodge, 2000).

Polar products from Fischer-Tropsch synthesis such as short-chain alcohols, carbonyl compounds and carboxylic acids on condensation dissolve in the water formed in the Fischer-Tropsch process to form an aqueous product phase. Recovery of the organic compounds from this aqueous product phase involves complex separations (Reiner, *et al*., 2007). The efficient separation of carboxylic acids from aqueous solutions is an important concept in the chemical and fermentation industries where many solvents have been tried and tested to improve such recovery (Arce, *et al*., 1995; Fahim, *et al*., 1997).

1.3 Research Objectives

Many investigators have published the liquid-liquid equilibria (LLE) of ternary and quaternary systems involving sulfolane viz; (sulfolane + p-xylene + cyclohexane), (sulfolane + p-xylene + n-hexane), (sulfolane + toluene + n-hexane) at T = 308.15 K and 323.15 K (Rappel, *et al*., 2002); (sulfolane + benzene + n-hexane), (sulfolane + N-formylmorpholine + benzene + n-hexane) at T = 298.15 to 318.15 K (Mahmoudi, *et al*., 2010). However the experimental LLE results involving sulfolane, carboxylic acids and hydrocarbons at 303.15 K have not been reported. The carboxylic acids investigated in this study are: acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid; the hydrocarbons used are pentane, n-hexane, hexadecane and dodecane respectively.

For the design of separation equipment and to test theories of solutions, there is a constant need for thermodynamics excess property data. Excess properties provide information about the molecular interactions and macroscopic behaviour of fluids mixtures and can be used to test and improve thermodynamic models for calculating and predicting fluid phase equilibria (Letcher and Redhi, 2001).

The first part of this research work is to measure the excess thermodynamic properties, namely excess molar volumes of binary systems containing (sulfolane + carboxylic acids) in order to gain the information of the molecular interactions between the carboxylic acids and sulfolane.

Excess properties provide information about the molecular properties of fluid mixtures which in turn can be used to improve current models for liquid mixtures. Experimental data analysis of various liquid mixtures may ultimately be instrumental in the generation of new hypothesis relating to better understanding of the mechanism of liquid mixing.

The second part of the research involves the use of the polar industrial solvents, namely sulfolane and acetonitrile as potential solvent extractors in the separation of mixtures of carboxylic acids and hydrocarbons at ambient temperatures (this involves the addition of an excess quantity of a hydrocarbon to a ternary mixtures of sulfolane + carboxylic acid + hydrocarbon to give achieve a two layered separation).

In chemical industries liquid-liquid extraction plays an important and cost effective role as a separation process. Ternary liquid-liquid equilibrium data are also important for a proper understanding of the solvent extraction process as well as experimental designs.

Solvent extraction is initiated by adding a polar solvent as a separating agent in a liquid-liquid extraction process. A mixture of polar solvent, organic acid and hydrocarbon would then be expected to separate into two liquid phases, a hydrocarbon-rich phase and a solvent-rich phase and finally separation of the acids from hydrocarbons would be effected after separation of these two phases.

Liquid-liquid extraction is a major industrial process in the chemical industry, that depends on the physical and chemical properties of a solvent to effect the separation of complex liquid mixtures, such as in the recovery of valuable products, and the removal of contaminants in effluents streams (Letcher and Reddy, 2003). Selectivity of the solvent is important in characterising the solvent, and assessing the feasibility of utilising the solvent in LLE (Letcher and Reddy, 2005).

1.4 SULFOLANE

Sulfolane is also known as tetramethylene sulfone and its systematic name is 2, 3, 4, 5-tetrahydrothiophene1, 1 dioxide.

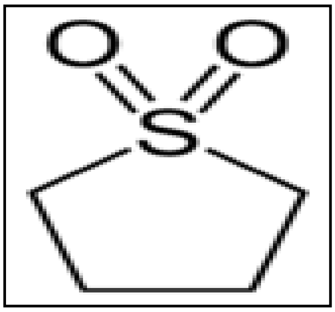

Figure 1.1 Structure of sulfolane

Sulfolane is a highly polar, very stable, water soluble compound with solvent power for many organic materials.

It is a colourless liquid commonly used in the chemical industry as an extractive distillation solvent or reaction solvent. It was originally developed by Shell Oil Company in the 1960s as a solvent to purify butadiene.

Sulfolane has been widely used in the chemical industry for the extraction of aromatics (Wheeler, 1986). Sulfolane offers good thermal, hydrolytic stability, high density, high boiling point and a good selectivity and meets the requirements as solvent for extraction (Im *et al*., 2006).

1.4.1 CHEMICAL PROPERTIES OF SULFOLANE

It is classified as a sulfone, which is a group of organosulfur compounds containing a sulfonyl functional group. The sulfonyl group is a sulphur atom double-bonded to two oxygen atoms as shown in Figure 1.1. It is synthesized by hydrogenating sulfolene, the product of a reaction between butadiene and sulphur dioxide. The sulphur-oxygen double bond is highly polar allowing for its high solubility in water while the four carbon ring provides non polar stability. These properties allow it to be miscible in both water and hydrocarbons, resulting in its widespread use as a solvent for purifying hydrocarbons. Sulfolane is a high boiling solvent with excellent extraction properties and is widely used in the extraction of aromatics from refinery process streams (Changsheng et al., 2004).

1.4.2 Uses of Sulfolane

Sulfolane has been widely used in the petrochemical industry for the extraction of aromatic hydrocarbons. Petrochemical industries uses sulfolane as the solvent for the recovery of high purity aromatics, such as benzene, toluene and xylene from refinery process streams (Bailes, 1977).

1.5 Acetonitrile

Acetonitrile is a colourless liquid with the formula CH_3CN which has a -CN functional group; the carbon atom and the nitrogen are triple bonded together. It is used as a polar aprotic solvent in synthetic chemistry and as a medium polarity solvent in High Performance Liquid Chromatography (HPLC). Acetonitrile is a by-product in the manufacture of acrylonitrile.

1.5.1 Uses of acetonitrile

Its low viscosity and low chemical reactivity makes it a popular choice in high performance liquid chromatography.

Acetonitrile is used in battery application because of its relatively high dielectric constant and ability to dissolve electrolytes.

Industrially it is used as a solvent in the purification of butadiene and in the manufacture of pharmaceuticals and photographic films (European Chemicals Bureau, 2002).

1.6 Hydrocarbons

Hydrocarbons are the principal constituents of petroleum and natural gas and serve as fuels, lubricants and raw materials for the production of plastics, fibres, rubbers, solvents, explosives and industrial chemicals.

The two major categories are aliphatic with the carbon atoms in a straight chain or a branched chain, or in a non-aromatic ring.

Aliphatic hydrocarbons may be saturated alkanes where carbon atoms are singly bonded or unsaturated where carbon atoms are joined by a double or triple bond. Natural substances e.g. natural gas, petroleum and asphalt are complex mixtures of hydrocarbons. Hydrocarbons are also used as fuels, and burn with air to form carbon dioxide and water. Crude oil is processed through several stages to form desirable hydrocarbons, which are used in fuel and other commercial products.

1.7 AREA OF RESEARCH COVERED IN THIS STUDY

In the first part of this research the excess molar volumes of the binary mixtures, i.e. sulfolane + a carboxylic acid were determined at two temperatures (T) of 303.15 K and 308.15 K. The carboxylic acids refer to acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid respectively.

The excess molar volumes were measured in order to understand the magnitude and the effect of molecular interaction of liquids during mixing processes.

The second part of this research, is to investigate extraction capabilities of sulfolane and acetonitrile in the separation of carboxylic acids from hydrocarbons at T = 303.15 K.

Liquid-liquid equilibria (LLE) data at T = 303.15 K were obtained for the following systems:

(a) Sulfolane + acetic acid / propanoic acid / butanoic acid / 2-methylpropanoic acid / pentanoic acid / 3-methylbutanoic acid + pentane at T = 303.15 K.
(b) Sulfolane + acetic acid / propanoic acid / butanoic acid / 2-methylpropanoic acid / pentanoic acid / 3-methylbutanoic acid + hexane at T = 303.15 K.
(c) Sulfolane + acetic acid / propanoic acid / butanoic acid / 2-methylpropanoic acid / pentanoic acid / 3-methylbutanoic acid + hexadecane at T = 303.15 K.
(d) Acetonitrile + acetic acid / propanoic acid / butanoic acid / 2-methylpropanoic acid / pentanoic acid / 3-methylbutanoic acid + dodecane at T = 303.15 K.

In this work, the suitability of sulfolane or acetonitrile as an extraction solvent for the separation of (carboxylic acids and hydrocarbon) mixtures using liquid- liquid equilibrium was investigated.

The effect of carbon on the phase equilibria of the ternary mixtures (sulfolane or acetonitrile + a carboxylic acid + hydrocarbon) when increasing the carbon chain length of the carboxylic acid was also investigated. The Redlich-Kister smoothing equations were applied to the excess molar volumes data and the ternary liquid-liquid binodal data. The Universal quasi-chemical (UNIQUAC) and the Non-Random Two Liquid models (NRTL) theories of liquid mixtures were applied to correlate the experimental tie-line data (Renon and Prausnitz 1968).

The aim of this work was to obtain good liquid-liquid equilibrium data for the ternary mixtures mentioned so that the use of sulfolane or acetonitrile in the separation of carboxylic acids from hydrocarbons could be established.

The chemical formula and the names of the hydrocarbons, carboxylic acids, sulfolane and acetonitrile used in this study are shown in Table 1.1

Table 1.1 Chemical formulas of carboxylic acids, hydrocarbons and solvents used in this study.

Chemical formula	Name
CH_3COOH	acetic acid
CH_3CH_2COOH	propanoic acid
$CH_3CH_2CH_2COOH$	butanoic acid
$(CH_3)_2CHCOOH$	2-methylpropanoic acid
$CH_3CH_2CH_2CH_2COOH$	pentanoic acid
$(CH_3)_2CHCH_2COOH$	3-methylbutanoic acid
CH_3CN	acetonitrile
$C_4H_8SO_2$	sulfolane
$CH_3CH_2CH_2CH_2CH_2CH_3$	hexane
$CH_3CH_2CH_2CH_2CH_3$	pentane
$C_{12}H_{26}$	dodecane
$C_{16}H_{34}$	hexadecane

1.8 LITERATURE REVIEW

Liquid-liquid equilibria (LLE) is one of the most important methods used to separate liquid mixtures. Many experimental data have been published for typical mixtures. Thermodynamic data for mixtures containing industrially important compounds, sulfolane and acetonitrile have been reported previously, and will be now reviewed.

Letcher and Whitehead (1996) determined the activity coefficient for hydrocarbons such as alkenes, alkynes and cycloalkanes in sulfolane, in order to predict phase separation using the correlation models such as NRTL or UNIQUAC for three component systems involving sulfolane, an aromatic and a hydrocarbon using gas liquid chromatography. They reported that alkynes are completely miscible in sulfolane over the whole concentration range while the alkenes and cycloalkanes are only partially miscible. The activity coefficient for solute in sulfolane increases with increasing carbon number of alkenes or cycloalkanes.

Yu and Li (1998) reported the excess molar volumes of sulfolane in binary mixtures with six aromatic hydrocarbons, namely toluene, *m*-xylene, *p*-xylene, ethylbenzene and 1, 2, 4-trimethyl benzene over the entire composition range at T = 298.15 K. Their results showed that the V_m^E were negative over the entire mole fraction range for all binary mixtures. This was caused by two opposing effects:

(a) expansion in volume due to mutual loss of dipolar association and the difference in size and shape of the component molecules and

(b) contraction in volume, resulting from dipole-induced dipole and dipole-dipole interactions, as well as donor-acceptor interactions between unlike molecules. The latter effect is dominant in the binary sulfolane + aromatic hydrocarbon mixtures. The introduction of the methyl or ethyl group in the ring increased the donor- acceptor interaction.

Kao and Lin (1999) investigated the LLE of (alkanes, C_{10} / C_{12} / C_{14} + 1.4-diisopropylbenzene + sulfolane) at T = 323.15 K, 348.15 K and 373.15 K. The addition of 1.4-diisopropylbenzene to sulfolane was found to increase the solubility of alkenes in the order of n-decane > n-dodecane > n-tetradecane and the relative mutual solubility of 1.4-diisopropylbenzene is higher in (n-decane + sulfolane) than in (n-dodecane + sulfolane) or (n-tetradecane + sulfolane) mixtures.

Letcher *et al.,* (2000) determined the excess molar volumes and excess molar enthalpies for the mixtures (sulfolane + [1-hexyne, 1-heptyne, 1-octyne]) at a temperature of 303.15 K. Their results were compared in an attempt to investigate the interactions between the highly polar sulfolane molecule and the terminal proton of the alkynes. The excess molar volumes for all the mixtures of (sulfolane + 1-alkyne) obtained, were negative and slightly asymmetrical in form. The negative values for $\mathrm{V_m^E}$ were probably a result of both molecular packing and intermolecular interactions. The $\mathrm{H_m^E}$ results reported were positive as a result of two endothermic effects (due to the dissociation of sulfolane and the dissociation of the 1-alkyne on mixing) and the exothermic effect (due to the association of the sulfolane and the 1-alkyne).

Yu *et al*., (2001) studied the boiling points for five binary systems of sulfolane with aromatic hydrocarbons at 101.33 kPa. From their experimental work it was evident that the introduction of a methyl group in the benzene ring will increase the activity coefficient of the aromatic hydrocarbon and decrease the activity coefficient of sulfolane in the system of (sulfolane + aromatic hydrocarbon) at infinite dilution.

Letcher and Redhi (2001) studied the phase equilibria for liquid mixtures of (benzonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + water) at T = 298.15 K. They reported that the relative mutual solubility of each of the carboxylic acids is higher in the benzonitrile layer than in the aqueous layer.

The mutual solubility of the components is increased as the carbon chain length is decreased. They concluded that the benzonitrile is a good component for the separation of mixtures of (water and pentanoic acid) or (water and 3-methylbutanoic acid).

Letcher and Redhi (2002) reported the excess molar enthalpies ($\mathrm{H_m^E}$) and excess molar volumes ($\mathrm{V_m^E}$) of six liquid mixtures viz; (benzonitrile + [acetic acid / propanoic acid / butanoic acid / 2-methylpropanoic acid / pentanoic acid and 3-methylbutanoic acid]) over the whole composition range at T = 298.15 K. The $\mathrm{H_m^E}$ values for the mixtures under investigation were positive over the whole composition range, and the magnitude decreases in the order: 3-methylbutanoic acid > 2-methylpropanoic acid > pentanoic acid > butanoic acid > propanoic acid > acetic acid. Their results have shown that the $\mathrm{V_m^E}$ were all negative for all the six systems over the entire composition range at T = 298.15 K. The excess molar volumes were most negative in the case of 2-methylpropanoic acid and the magnitude decreases in the following order: 2-methylpropanoic acid > 3-methylbutanoic acid > butanoic acid > propanoic acid > pentanoic acid > acetic acid.

It was also found that the position of the minima for $\mathrm{V_m^E}$ (benzonitrile + acetic acid) shifted slowly to the benzonitrile-rich mole fraction region of the scale, as the methylation of acetic acid increase. This could be due to free volume effects which are primarily due to the difference in the size between components of the mixtures. The NRTL and UNIQUAC models fitted with standard deviations were within the experimental error. The NRTL model fitted the data slightly better than the UNIQUAC model.

Rappel *et al.,* (2002) presented the liquid-liquid equilibria for the ternary systems: (sulfolane + *p*-xylene + *n*-hexane) and (sulfolane + toluene + *n*-hexane) at 308.15 K and 323.15 K. Tie-line data were correlated by Hand and Othmer-Tobias methods with correlation coefficients near unity. Parameters for NRTL and UNIQUAC activity coefficient models were estimated. The square mean root deviations (rmsd) obtained when comparing the calculated and the experimental two-phase compositions were found to be < 1.61% for NRTL and < 2.1% for UNIQUAC model. The NRTL model fits slightly better the liquid-liquid equilibrium data studied.

Al-Dujaili *et al.,* (2006) measured the liquid-liquid equilibrium for five pseudo-ternary systems: [sulfolane + 1-alkanol (C_1 to C_5) + octane + toluene] at 293.15 K. Two components were kept the same (octane and toluene), a pseudo-component was made up of a mixture of sulfolane with a small amount of a 1-alkanol (methanol + ethanol, + propanol, + 1-butanol, or + 1-pentanol). It was observed that the selectivity of (sulfolane + 5% methanol) was higher than that of the pure sulfolane but decreases as the chain length of 1-alkanol increases.

Im *et al.,* (2006), investigated the LLE for the binary systems of sulfolane with branched cycloalkanes over a temperature range of 300 K to 460 K. The branched cycloalkanes studied were methylcyclopentane,methylcyclohexane and ethylcyclohexane. The binary LLE were correlated using the NRTL and UNIQUAC models, and using the temperature dependent parameters. Both models correlated with good accuracy.

Kinart *et al.,* (2007), studied the thermodynamic and physicochemical properties of binary mixtures of sulfolane with ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol systems at 303.15 K. Densities and relative permittivities were measured as a function of composition. Their conclusion was that the specific interaction between sulfolane and glycols increases as the glycol carbon chain increases, and also molecular size differences between solvent molecules also play a significant part.

Mohsen-Nia and Paikar (2007) reported the LLE of ternary and quaternary systems containing *n*-hexane, toluene, *m*-xylene, propanol, sulfolane and water at T = 303.15 K. Their conclusion was that for extraction of toluene and m-xylene from n-hexane the mixed- solvent (solvent + propanol) has a lower selectivity factor and higher distribution coefficient than the pure solvent sulfolane at T= 303.15 K.

Kinart *et al.,* (2008), measured the densities, viscosities and relative permittivities at T = 303.15 K for the binary mixtures of (sulfolane + 2-methoxyethanol or 2-ethoxyethanol, 2-propoxyethanol or 2-buthoxyethanol) as function of composition. From the experimental data, excess molar volumes, deviations in the viscosity and the deviations in the relative permittivity were calculated. The results showed that $\mathrm{V_m^E}$ for each binary system studied were negative over the complete composition range. The minima values for $\mathrm{V_m^E}$ became more negative as the alkyl chain length of alkoxyethanols is increased. Negative deviation in viscosity which regularly increase as the size of the alkoxyethanol increases was found to occur.

The LLE data for (sulfolane + benzene + n-hexane), (N-formylmorpholine + benzene + n-hexane), and (sulfolane + N-formylmorpholine + benzene + n-hexane) at temperatures ranging from 298.15 K to 318.15 K was measured by Jafar and Mohammad (2009). The experimental distribution coefficients and selectivity factors were presented to evaluate the efficiency of the solvents for extraction of benzene from n-hexane. From their experimental findings, it was observed that the effect of temperature on the extraction of benzene from n-hexane indicated that increasing the temperature, decreases the selectivity for all solvents. Binary interaction parameters for the UNIQUAC model were fitted to the experimental values in order to minimize the rmsd. The results of the rmsd values obtained by comparing the calculated and the experimental two-phase compositions was 0.0163 mole fraction for (N-formylmorpholine + benzene + n-hexane) system and 0.0120 mole fraction for (sulfolane + benzene + n-hexane) system. Their conclusion was that at lower temperatures, all the solvents are more selective for extraction of benzene.

CHAPTER 2

EXCESS MOLAR VOLUMES

2.1 INTRODUCTION

A thorough knowledge of thermodynamic and transport properties of multi-component systems is essential in many industrial applications such as design calculation, heat transfer, mass transfer, fluid flow, etc (Wang *et al*., 2004). Excess molar volume is an important thermodynamic quantity used in chemical engineering for the design of plant and separation equipment (Sandler *et al.,* 1989*).* Excess molar volumes provide information about the nature of molecular interactions and macroscopic behaviour of fluid mixtures which in turn can be used to improve theoretical models of liquid mixtures. These properties have been used extensively to understand how the molecules interact within a mixture.

Excess molar volumes are more informative and easier to handle when expressed relative to some kind of ideal behaviour (McGlashan, 1979; Walas*,* 1985*;* Letcher, 1975). The excess molar volumes, V_m^E, is defined as:

$$V_m^E = V_{mixture} - \sum x_i V_i^0 \tag{2.1}$$

where x_i is the mole fraction of component, i, whilst $V_{mixture}$ and V_i^0 are the molar volumes of the mixture, and pure component, i, respectively.

For a binary mixture,

$$V_m^E = V_{mixture} - (x_i V_i^0 + x_2 V_2^0) \qquad (2.2)$$

The change in volume on mixing two liquids 1 and 2, especially two polar liquids can attribute to a number of processes (Letcher, 1975):

(a) The breakdown of 1-1 and 2-2 intermolecular interactions which have a positive effect on the volume.
(b) The formation of 1-2 intermolecular interactions which results in diminution of the volume of the mixture.
(c) Packing effects caused by a difference in the size and shape of the component species which may have a positive or negative effect on the particular species involved.
(d) Formation of new chemical species (Redhi, 2003).

It was also reported that there is no volume change upon mixing two liquids to form a thermodynamically ideal solution at constant temperature and pressure, but a volume change may occur when two real liquids are mixed (Battino, 1971).

2.2 Methods for the measurements of excess molar volumes

The excess molar volumes, V_m^E, upon mixing two liquids may be measured either directly or indirectly.

2.2.1 Direct Determination

In the direct determination, the volume change that occurs when different liquids are mixed is measured. Direct methods of measurements of V_m^E include batch dilatometry and continuous dilation dilatometry (Handa, and Benson, 1979). Batch dilatometers are characterised by one composition per loading at a single temperature whilst continuous dilution dilatometers are characterised by a number of compositions per loading at a single temperature (Handa and Benson, 1979; Nevines, 1997; Redhi, 2003).

2.2.2 Batch dilatometry

The dilatometer is filled with known masses of pure liquids, which are separated by mercury. The height of the mercury in the calibrated graduated column is noted. The liquids are mixed by rotating the dilatometer, and the volume change is indicated by the change in the height of mercury in the calibrated capillary. The V_m^E is determined from the volume change and the masses of the components. It was reported that a precision of 0.003 cm^3/ mol in V_m^E could be achieved over the temperature range of 280 to 350K using this technique (Prausnitz *et al*., 1986). A disadvantage of this technique is that it is difficult to fill the dilatometer. A major source of error in this method is in the determination of the composition as it is necessary to weigh the dilatometer as it contains mercury. This results in large errors in the measured mass (Keyes and Hildebrand, 1917; Nevines, 1997; Redhi, 2003).

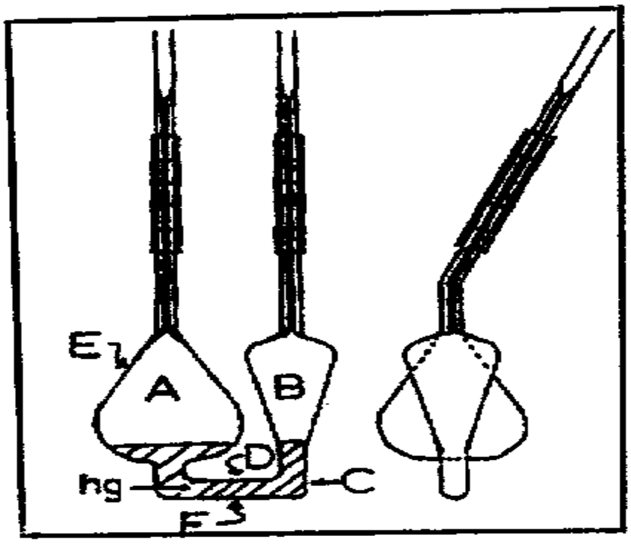

Figure 2.1 The Keyes and Hildebrand Dilatometer (1917)

2.2.3 Continuous dilatometer

This technique is less time consuming than the batch technique and more data are generated per loading. The mode of operation involves the successive addition of one liquid into the reservoir which contains the other liquid, and detecting the volume change that accompanies the addition. One of the earliest dilatometers of this type was designed by Geffcken, Kruis and Solana (1937). This dilatometer has been used and modified by many workers (McLure and Swinton, 1965; Watson *et al.,* 1965; Pflug and Benson, 1968; Pasfield, 1965; Beath *et al.*, 1969).

The mixing chamber C is initially loaded with pure component A and mercury as shown in Figure 2.2. The stopcock S leads to reservoir R where pure component B is confined over mercury. The change in mercury level upon mixing in the calibrated capillary D is read with respect to a reference mark F. The entire apparatus is thermostatted and provision is made for stirring the contents of C. When S is opened, mercury from C forces some of the component B into C via the connecting tube E. S is now closed and mixing begins. The change in the level begins, and the change in the level of mercury in capillary D is noted.

Successive increments of B are then added in a similar fashion in order to directly determine V_m^E as a function of composition at one temperature.

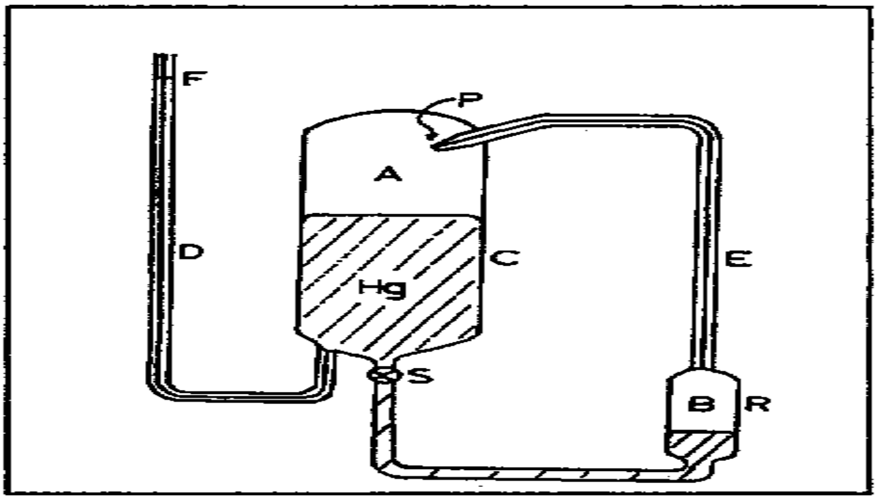

Figure 2.2 Continuous Dilatometer of Geffcken, Kruis and Solana (1937).

2.2.4 The Kumaran and McGlashan Dilatometer

A more recent design of a dilatometer was developed by Kumaran and McGlashan (1977), shown in Figure 2.3.

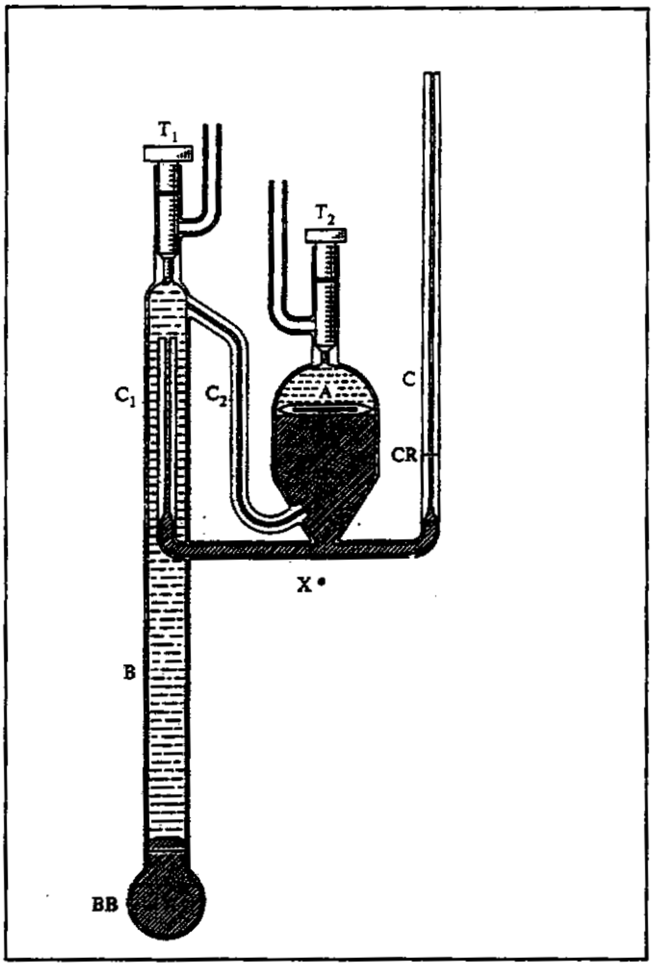

Figure 2.3 The Kumaran and McGlashan dilatometer (1977)

A typical measurement is made by filling the burette B with one of the pure liquids and the bulb A with the other pure liquid (diluent). The dilatometer is tilted by anticlockwise rotation of its frame so that some mercury flowed from C1 into B. This displaced mercury in turn forces an equal volume of the diluent liquid through C2 into bulb A. After mixing, the change in volume is registered as a change in the level of the mercury in the calibrated capillary C. The difference in the heights of the mercury meniscus in C, and of the reference mark CR was determined with the aid of a cathetometer. Corrections for the changes in pressure arising from changes in mercury levels during measurements had to be made when determining the excess molar volume (Kumaran and McGlashan, 1977).

2.3 Indirect determination

Indirect measurements involve measuring the density of the pure solvents as well as the density of the mixture, and calculating V_m^E from these values using a pycnometer or densitometer (Battino 1971; Letcher 1975; Handa and Benson 1979; Kumaran and McGlashan 1977; Govender 1996; Redhi 2003). There are many different methods used to determine densities of liquids these; include pycnometry, magnetic float and mechanical oscillating densitometers.

Density is defined as:

$$\rho = m/v \qquad (2.3)$$

where m is the mass of the substance, and v is the volume.

The V_m^E, for a binary mixture is determined from density measurements using the following equation:

$$V_m^E = (x_1M_1+x_2M_2)/\rho - [(x_1M_1 / \rho_1) + (x_1M_2 / \rho_2)] \qquad (2.4)$$

where x_1 and x_2 are the mole fractions, of components 1 and 2 respectively, M_1 and M_2 are molar masses of pure components 1 and 2 respectively,

$\rho_1$and ρ_2 are the densities of the pure species 1 and 2 respectively, and ρ is the density of the mixture.

2.3.1 Pycnometry

One of the earliest pycnometers was used by Wood and Bruisie (1943). This pycnometer is illustrated in Figure 2.4. The single arm pycnometer is capable of accuracy of up to one in hundred thousand. This apparatus consisted of a bulb of capacity of 11 cm^3, a 1 mm internal diameter precision base capillary with eleven lines lightly etched all around the stem and spaced 1 mm apart. A hypodermic syringe and cannula is used to fill the pycnometer during measurement. In the process of determining densities by pycnometer, it is important to accurately determine the composition of the mixture.

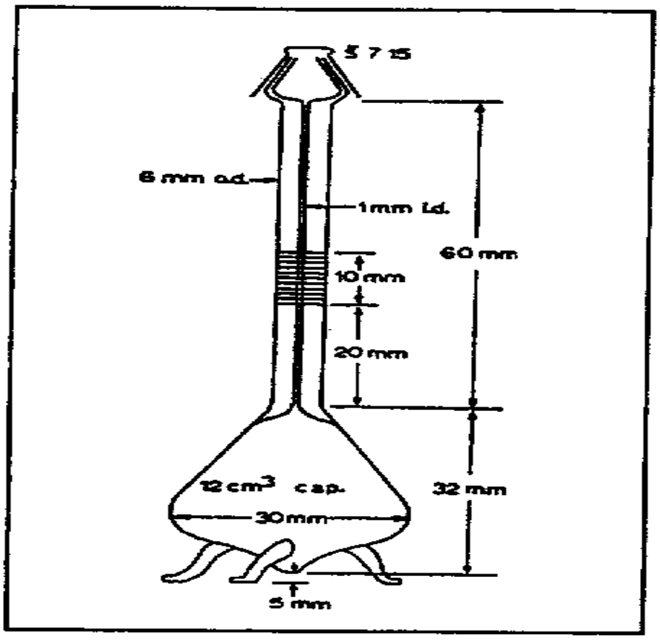

Figure 2.4 Single-arm Pycnometer of Wood and Bruisie (1943)

The magnetic float densitometer designed by Franks and Smith (1967) and the mechanical oscillating densitometer by Handa and Benson (1979) were designed to give greater accuracy in density measurements. The latter is coupled with digital output displays is widely used in the chemical industry and research laboratories to measure densities of liquid and liquid mixtures.

The development of highly accurate vibrating tube densitometer has made it possible to determine V_m^E with acceptable accuracy from density measurements.

EXPERIMENTAL SECTION

2.4 EXPERIMENTAL APPARATUS AND TECHNIQUE

2.4.1 Experimental Apparatus

In this work the Anton Paar DMA 38 vibrating tube densitometer was used to measure the densities of mixtures at different temperatures.

2.4.2 The Vibrating Tube Densitometer Anton Paar DMA 38

The density determination is based on the measurements of the oscillation of a vibrating U-shaped sample tube which is filled with the liquid sample mixture being measured. The relationship between the period τ and the density ρ of the mixture is given by:

$$\rho = A + B\,\tau^2 \tag{2.5}$$

where A and B are the instrument constants for each individual oscillator and can be determined by two calibration measurements with samples of known density, deionised water and dry air.

Figure 2.5   DMA 38 Densitometer

2.4.3 Method of operation of the DMA 38 Densitometer

The density measurements are based on the electromagnetically induced oscillation of the glass U-tube. One complete back and forth movement of a vibration is a period τ, its duration is the period of oscillation. The number of oscillations per second is the frequency ν. Each glass tube vibrates at a characteristic or natural frequency, this changes when the tube is filled with substance. As the frequency is the function of mass, when the mass increases the frequency decreases or period of oscillation increases

$$\nu = \frac{1}{\tau} \tag{2.6}$$

A magnet is fixed to the measurement tube which is made to oscillate by a transmitter. A sensor measures the period of oscillation.

The period of oscillation is obtained from the equation:

$$\tau = 2\pi \sqrt{\rho Vc + mc/K} \tag{2.7}$$

where ρ *is* the density of the sample in measurements, V_c is the volume of sample or capacity of the tube, m_c is the mass of the measured tube, K is the measurement tube constant. It follows that

$$\rho = (K\tau^2) / (4\pi^2 V_c) - m_c / V_c \tag{2.8}$$

The density and the period oscillation τ are related as follows:

$$\rho = A\,\tau^2 + B \tag{2.9}$$

$$A = K\tau^2 / 4\pi^2 V_c \quad \text{and} \tag{2.10}$$

$$B = m_c / V_c \tag{2.11}$$

where A and B are constants, which are determined by the elasticity, structure and mass of the measurement tube. In this work the density was given as the output from the DMA 38 densitometer.

2.4.4 Materials

A summary of the chemicals, their suppliers and purities used in this research is given below:

Table 2.1 Chemicals used, the suppliers and stated mass % purities.

Component	Supplier	Mass % Purity
Acetic acid	Riedel de Haën	99.8%
Propanoic acid	Fluka	>99.9%
Butanoic acid	Fluka	99.5%
2-Methylpropanoic acid	Fluka	99.5%
Pentanoic acid	Fluka	99.0%
3-Methylbutanoic acid	Fluka	>98.5%
Sulfolane	Fluka	>99.5%

Table 2.2 Densities, ρ, of pure components at various temperatures.

	$\rho/(g.cm^3)$		
Carboxylic acid	**Literature**[a]	**Experimental**	
	298.15 K	**303.15 K**	**313.15 K**
Acetic acid	1.0439	1.0403	1.0360
Propanoic acid	0.9881	0.9814	0.9786
Butanoic acid	0.9532	0.9452	0.9434
2-Methylpropanoic acid	0.9428	0.9409	0.9335
Pentanoic acid	0.9345	0.9305	0.9266
3-Methylbutanoic acid	0.9173	0.9129	0.9113
Sulfolane	1.2640	1.2612	1.2570

[a] Riddick *et al*. (1986)

2.4.5 Preparation of binary mixtures for density measurements

The water content of the pure solvents were determined using the Karl Fischer method and the moisture content was found to be less than 0.001 percent in each case. All the chemicals were kept under 0.4 nm molecular sieves to remove any traces of water. The binary mixtures were made up in an air-tight glass stoppered 10 ml vial. Mixtures with compositions spanning the entire mole-fraction range were prepared by mass using an OHAUS analytical balance with a precision of 0.0001 g. The mixtures were shaken to ensure complete homogeneity of the two components. The mixtures were then degassed for 30 minutes by means of an ultrasonic bath to prevent formation of air bubbles in the U-tube of the densitometer.

2.4.6 Experimental procedure for the DMA 38 instrument

The densities of the pure compounds and binary mixtures were measured using the Anton Paar DMA 38 vibrating U-Tube densitometer, which consists of a built-in thermostat controller capable of maintaining the temperature precisely to ± 0.01 K, and measuring density to ±0.001 $g.cm^{-3}$. The densitometer was calibrated by measuring the density of ultrapure water supplied by SH Calibration Service GmbH Graz, and air dried at the same temperature.

Prior to each run, the cell of the U-tube was flushed with absolute ethanol, and dried with air. The sample mixtures were injected into the U-tube slowly ensuring so that there were no air bubbles trapped in the U-tube. The syringe was left in place during each measurement. Each measuring cycle was allowed to continue until a constant measurement value was obtained.

Between measurements, deionised water, pure solvents and air were measured to monitor the operation of the densitometer.

The densities of all the mixtures as well as their pure solvents were measured at T = 298.15 K, 303.15 K and 308.15 K.

The excess molar volumes were calculated according to equation 2.3 using the density value obtained from the DMA 38 for the corresponding mole fraction composition of the mixtures that were prepared over the entire mole fraction range, at each temperature.

2.4.7 Specifications of the DMA 38 instrument:

Accuracy : 1×10^{-3} g.cm^{-3}

Minimum Sample Volume : 1 cm^{3}

Density Range : 0 - 3 g.cm^{-3}

Temperature Range : 15 - 40 ^{0}C

Pressure Range : 10 bar (145 psi)

2.4.8 Validation of the experimental technique

The experimental technique was validated by use of the DMA 38 Densitometer by the determination of the excess molar volumes for the test system (toluene + cyclohexane) at T = 298.15 K and comparing it with literature values (Oswal and Maisura, 2004) as shown in Figure 2.7. The difference between experimental and literature values were within the experimental error.

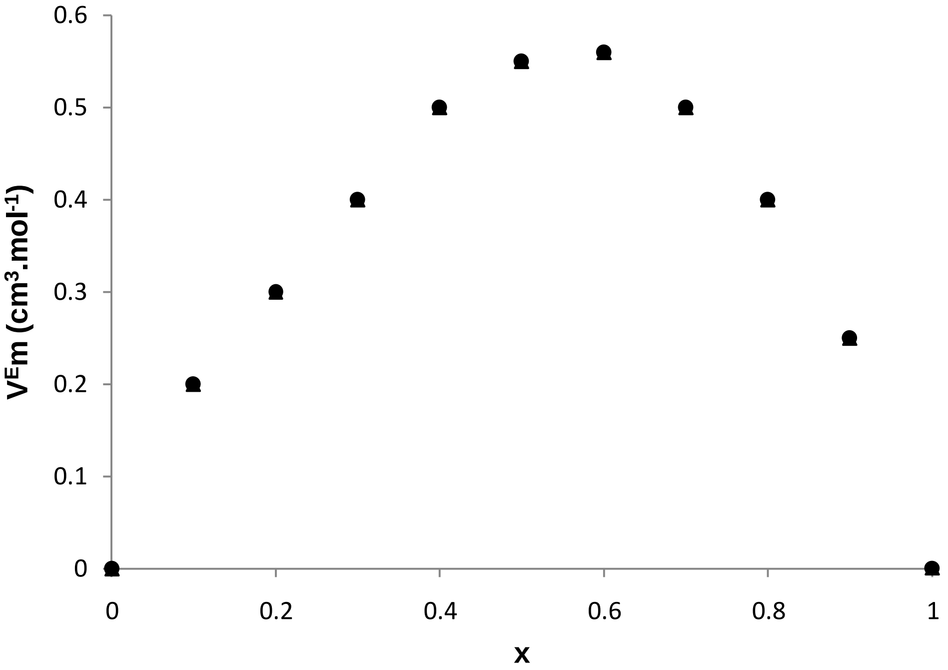

Figure 2.6 **Validation of the experimental technique: Comparison of the V_m^E from this work with the literature results (Oswal and Maisura, 2004) for the mixtures of toluene + cyclohexane at T = 298.15 K, ●, literature results, ▲, this work.**

2.4.9 Binary Systems studied in this work

Excess molar volumes for the following binary mixtures were determined over the entire composition range at various temperatures:

(i) [Sulfolane + carboxylic acids] at $T = 303.15$ K,

(ii) [Sulfolane + carboxylic acids] at $T = 308.15$ K,

where carboxylic acids refers to acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid.

2.5 RESULTS OF EXCESS MOLAR VOLUMES

The excess molar volumes for each system at different temperature were calculated from the experimental density values of mole fraction and density using this equation 2.4:

$$V_m^E = (x_1M_1+x_2M_2)/\rho - [(x_1 M_1 / \rho_1) - (x_2 M_2 / \rho_2)] \qquad (2.12)$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are molar masses of pure components, ρ_1 and ρ_2 are the densities of the pure species (1 and 2) and ρ is the density of the mixture at 303.15 K.

The Redlich-Kister polynomial smoothing function:

$$\delta V_m^E = x(1-x)\sum_{r=0}^{N} A_r(1-2x)^r \qquad (2.13)$$

was fitted to the experimental data by the method of unweighted least squares, where x denotes the mole fraction of sulfolane, A_r are the polynomial coefficients, N is the polynomial degree and $r = 0, 1, 2$ or 3.

The parameters A_0, A_1, A_2, A_3 and the deviations were calculated from the equation below:

The standard deviation, σ is given by:

$$\sigma = [\sum(V_m^E{}_{(expt)} - V_m^E{}_{(calc)})^2 / (n - a)]^{1/2} \qquad (2.14)$$

where n is the number of experimental points and a is the number of fitting coefficients.

The experimental results for excess molar volumes, V_m^E for binary mixtures are presented in the following order:

2.5.1 Sulfolane + carboxylic acids at T = 303.15 K
2.5.2 Sulfolane + carboxylic acids at T = 308.15 K

Carboxylic acids refers to acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid.

2.5.1 Excess Molar Volume data for mixtures of sulfolane (1) + a carboxylic acid (2) at T = 303.15 K.

Table 2.3 **Excess molar volumes for the system: Sulfolane (1) + a carboxylic acids (2) and the deviations, δV_m^E calculated from equations 2.11 and 2.12 at 303.15 K as function of mole fraction of sulfolane.**

x_1	V_m^E ($cm^3.mol^{-1}$)	δV_m^E ($cm^3.mol^{-1}$)
Sulfolane (1) acetic acid (2) at 303.15 K		
0.0550	-0.090	0.118
0.0888	-0.280	0.051
0.1061	-0.408	-0.018
0.1251	-0.520	-0.067
0.2088	-0.741	-0.051
0.2992	-0.870	-0.006
0.3448	-0.899	0.023
0.3963	-0.970	-0.004
0.4504	-0.978	0.013
0.4940	-0.991	0.009
0.5455	-0.973	0.024
0.5934	-0.968	0.018
0.6456	-0.990	-0.025
0.6860	-0.951	-0.011
0.7538	-0.917	-0.041
0.7832	-0.850	-0.013
0.8416	-0.691	0.034
0.9009	-0.548	-0.003
0.9574	-0.237	0.044

Table 2.3 continued

x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^3.mol^{-1})
Sulfolane (1) + propanoic acid (2) at 303.15 K		
0.0491	-0.100	-0.011
0.0809	-0.140	0.017
0.1454	-0.301	0.014
0.1765	-0.420	-0.022
0.2138	-0.482	0.018
0.2620	-0.659	-0.038
0.3061	-0.729	0.008
0.3510	-0.829	0.015
0.4359	-0.978	0.003
0.4801	-1.050	-0.027
0.5379	-1.011	0.027
0.5865	-0.998	0.013
0.7493	-0.720	-0.035
0.7955	-0.550	-0.008
0.8289	-0.422	0.011
0.8533	-0.331	0.022
0.8860	-0.254	-0.004
0.9406	-0.101	0.003

Table 2.3 continued

x_1	V_m^E ($cm^3.mol^{-1}$)	δV_m^E ($cm^3.mol^{-1}$)
Sulfolane (1) + butanoic acid (2) at 303.15 K		
0.0308	-0.318	-0.127
0.0567	-0.396	-0.072
0.0897	-0.457	0.009
0.1216	-0.539	0.034
0.1665	-0.609	0.069
0.1979	-0.656	0.078
0.2463	-0.798	-0.029
0.2868	-0.824	-0.042
0.3246	-0.822	-0.061
0.3792	-0.751	-0.013
0.4261	-0.693	0.006
0.4648	-0.624	0.032
0.5384	-0.563	0.014
0.5869	-0.523	0.005
0.6354	-0.482	-0.007
0.6681	-0.441	0.003
0.8010	-0.332	-0.014
0.8425	-0.273	-0.001
0.9161	-0.164	0.009

Table 2.3 continued

x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^3.mol^{-1})
	Sulfolane (1) + 2-methylpropanoic acid (2) at 303.15 K	
0.0510	-0.529	-0.069
0.1102	-0.801	0.063
0.1602	-1.101	0.003
0.1992	-1.211	0.032
0.2468	-1.402	-0.069
0.3003	-1.362	0.011
0.4052	-1.302	-0.002
0.5226	-1.068	-0.002
0.5813	-0.904	0.026
0.6233	-0.815	0.012
0.6475	-0.753	0.019
0.6966	-0.712	-0.041
0.7067	-0.658	-0.021
0.7210	-0.603	0.006
0.7424	-0.561	0.001
0.7822	-0.482	0.009
0.8688	-0.321	-0.003
0.9020	-0.232	0.019

Table 2.3 continued

x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^3.mol^{-1})
Sulfolane (1) + pentanoic acid (2) at 303.15 K		
0.0431	-0.193	0.107
0.0862	-0.495	0.093
0.1558	-1.071	-0.065
0.1876	-1.254	-0.065
0.2094	-1.353	-0.076
0.2930	-1.591	-0.064
0.3308	-1.701	0.038
0.3855	-1.825	0.041
0.4392	-1.899	0.033
0.4965	-1.949	0.021
0.5377	-1.924	-0.019
0.5923	-1.821	-0.021
0.6474	-1.725	0.026
0.6856	-1.612	-0.021
0.7390	-1.431	-0.016
0.7851	-1.225	-0.023
0.8433	-0.904	0.049
0.8992	-0.706	-0.054
0.9468	-0.315	0.048

Table 2.3 continued

x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^3.mol^{-1})
	Sulfolane (1) + 3-methylbutanoic acid (2) at 303.15 K	
0.0400	-0.092	0.236
0.0775	-0.501	0.092
0.1377	-0.897	0.044
0.2041	-1.251	-0.038
0.2537	-1.474	-0.118
0.3240	-1.573	-0.096
0.3612	-1.591	-0.081
0.4233	-1.581	-0.044
0.4782	-1.501	0.039
0.5453	-1.417	0.125
0.5790	-1.332	0.181
0.6389	-1.213	0.272
0.6877	-1.056	0.396
0.7257	-0.955	-0.541
0.7701	-0.846	-0.491
0.8340	-0.682	-0.491
0.8788	-0.524	0.486
0.9161	-0.408	0.381
0.9593	-0.249	0.195

Table 2.4 Coefficient, A_r, and standard deviation σ for the Redlich-Kister Equation of the system: [Sulfolane (1) + a carboxylic acid (2)] at 303.15 K using equations 2.13 and 2.14.

Carboxylic Acid	A_0	A_1	A_2	A_3	σ
Acetic	-4.469	-4.461	-2.196	1.015	0.034
Propanoic	-4.132	0.736	2.895	-1.079	0.020
Butanoic	-2.653	-2.305	-0.641	-0.465	0.024
2-Methylpropanoic	-3.999	0.039	-1.715	1.799	0.023
Pentanoic	-6.143	-0.366	-4.497	2.302	0.014
3-Methylbutanoic	-7.715	-0.749	0.601	0.912	0.042

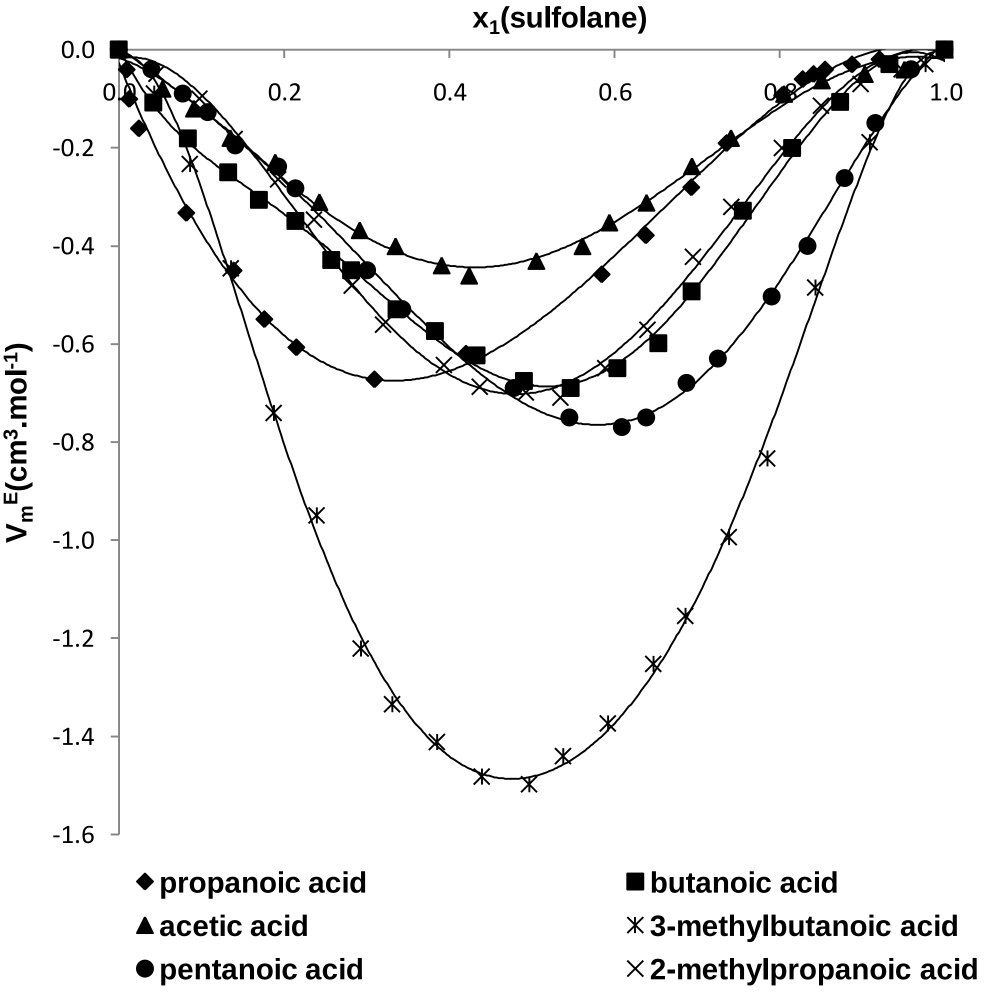

Figure 2.7 Excess molar volumes for the systems: [Sulfolane (1) + a Carboxylic acid (2)] at T = 303.15 K, plotted as a function of mole fraction x_1.

2.5.2 Excess Molar Volume data for mixtures of sulfolane (1) + a carboxylic acid (2) at T = 308.15 K.

Table 2.5 **Excess molar volumes for the system: [Sulfolane (1) + a carboxylic acids (2)] and the deviations, δV_m^E calculated from equation 2.11 and 2.12 at 308.15 K as function of mole fraction of sulfolane.**

x_1	V_m^E ($cm^3.mol^{-1}$)	δV_m^E ($cm^3.mol^{-1}$)
Sulfolane (1) + acetic acid (2) at 308.15 K		
0.0092	-0.042	0.004
0.0126	-0.106	-0.042
0.0242	-0.161	-0.048
0.0813	-0.332	-0.007
0.1387	-0.455	0.033
0.1761	-0.552	0.002
0.2146	-0.607	-0.001
0.3094	-0.672	-0.006
0.4202	-0.632	0.004
0.5844	-0.458	-0.015
0.6381	-0.378	-0.013
0.6927	-0.281	-0.003
0.7356	-0.191	0.017
0.8027	-0.092	0.015
0.8281	-0.062	0.013
0.8409	-0.051	0.008
0.8546	-0.043	0.003
0.8877	-0.033	-0.018
0.9207	-0.025	-0.029

Table 2.5 continued

x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^3.mol^{-1})
Sulfolane (1) + propanoic acid (2) at 308.15 K		
0.0421	-0.108	-0.101
0.0838	-0.181	-0.022
0.1330	-0.251	-0.008
0.1702	-0.307	-0.005
0.2142	-0.354	0.024
0.2577	-0.428	0.014
0.2816	-0.456	0.029
0.3362	-0.538	-0.018
0.3827	-0.574	-0.011
0.4335	-0.624	-0.015
0.4909	-0.676	0.011
0.5472	-0.692	-0.008
0.6042	-0.651	-0.009
0.6534	-0.599	-0.023
0.6939	-0.493	0.013
0.7556	-0.328	0.044
0.8155	-0.201	0.019
0.8732	-0.106	-0.018
0.9329	-0.034	-0.035

Table 2.5 continued

x_1	V_m^E ($cm^3.mol^{-1}$)	δV_m^E ($cm^3.mol^{-1}$)
Sulfolane (1) + butanoic acid (2) at 308.15 K		
0.0525	-0.081	-0.026
0.0906	-0.125	-0.014
0.1347	-0.182	-0.009
0.1895	-0.231	0.022
0.2426	-0.311	0.013
0.2915	-0.367	0.008
0.3348	-0.402	0.011
0.3904	-0.442	-0.003
0.4241	-0.465	-0.018
0.5050	-0.431	-0.008
0.5612	-0.402	-0.016
0.5940	-0.352	0.003
0.6389	-0.311	-0.003
0.6934	-0.237	0.009
0.7410	-0.183	0.009
0.8052	-0.092	0.025
0.8512	-0.062	0.007
0.9026	-0.054	-0.021
0.9508	-0.042	-0.034

Table 2.5 continued

x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^3.mol^{-1})
	Sulfolane (1) + 2-methylpropanoic acid (2) at 308.15 K	
0.0461	-0.049	-0.031
0.0982	-0.101	-0.013
0.1401	-0.182	-0.015
0.1932	-0.265	0.019
0.2363	-0.347	0.034
0.2819	-0.481	-0.002
0.3202	-0.564	-0.009
0.3942	-0.643	0.011
0.4374	-0.688	-0.001
0.4930	-0.706	-0.002
0.5349	-0.711	-0.029
0.5887	-0.652	-0.019
0.6402	-0.572	0.027
0.6954	-0.423	0.032
0.7417	-0.321	0.017
0.8029	-0.201	0.008
0.8503	-0.114	-0.024
0.8979	-0.072	-0.042
0.9481	-0.043	-0.041

Table 2.5 continued

x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^3.mol^{-1})
Sulfolane (1) + pentanoic acid (2) at 308.15 K		
0.0400	-0.040	0.009
0.0775	-0.091	0.004
0.1077	-0.128	0.014
0.1409	-0.196	-0.019
0.1934	-0.239	0.016
0.2140	-0.282	0.006
0.3012	-0.450	-0.011
0.3433	-0.529	-0.017
0.4782	-0.690	0.020
0.5453	-0.752	0.009
0.6090	-0.774	-0.010
0.6389	-0.751	-0.006
0.6877	-0.681	0.002
0.7257	-0.633	-0.010
0.7901	-0.504	-0.018
0.8340	-0.401	-0.002
0.8788	-0.263	0.030
0.9161	-0.155	0.024
0.9593	-0.041	0.030

Table 2.5 continued

x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^3.mol^{-1})
Sulfolane (1) + 3-methylbutanoic acid (2) at 308.15 K		
0.0431	-0.090	0.018
0.0862	-0.233	0.031
0.1358	-0.445	0.033
0.1876	-0.741	-0.022
0.2394	-0.950	0.001
0.2930	-1.220	-0.056
0.3308	-1.334	-0.044
0.3855	-1.412	0.015
0.4392	-1.482	0.022
0.4965	-1.498	0.050
0.5377	-1.440	0.026
0.5923	-1.374	0.006
0.6474	-1.252	-0.018
0.6856	-1.154	-0.055
0.7390	-0.994	-0.079
0.7851	-0.833	0.032
0.8433	-0.485	0.076
0.9092	-0.189	0.025
0.9768	-0.030	-0.018

Table 2.6 Coefficient, A_r, and standard deviations σ for the Redlich-Kister Equation of the system: [Sulfolane (1) + a carboxylic acid (2)] at 308.15 K calculated using equations 2.13 and 2.14.

Carboxylic Acid	A_0	A_1	A_2	A_3	σ
Acetic	-2.238	-2.296	0.155	-0.529	0.024
Propanoic	-2.753	0.229	2.353	-1.966	0.032
Butanoic	-1.696	-0.952	1.347	0.526	0.017
2-Methylpropanoic	-2.788	-0.475	3.198	0.225	0.021
Pentanoic	-2.923	1.701	-1.733	-1.771	0.031
3-Methylbutanoic	-6.076	-0.772	4.12	0.955	0.042

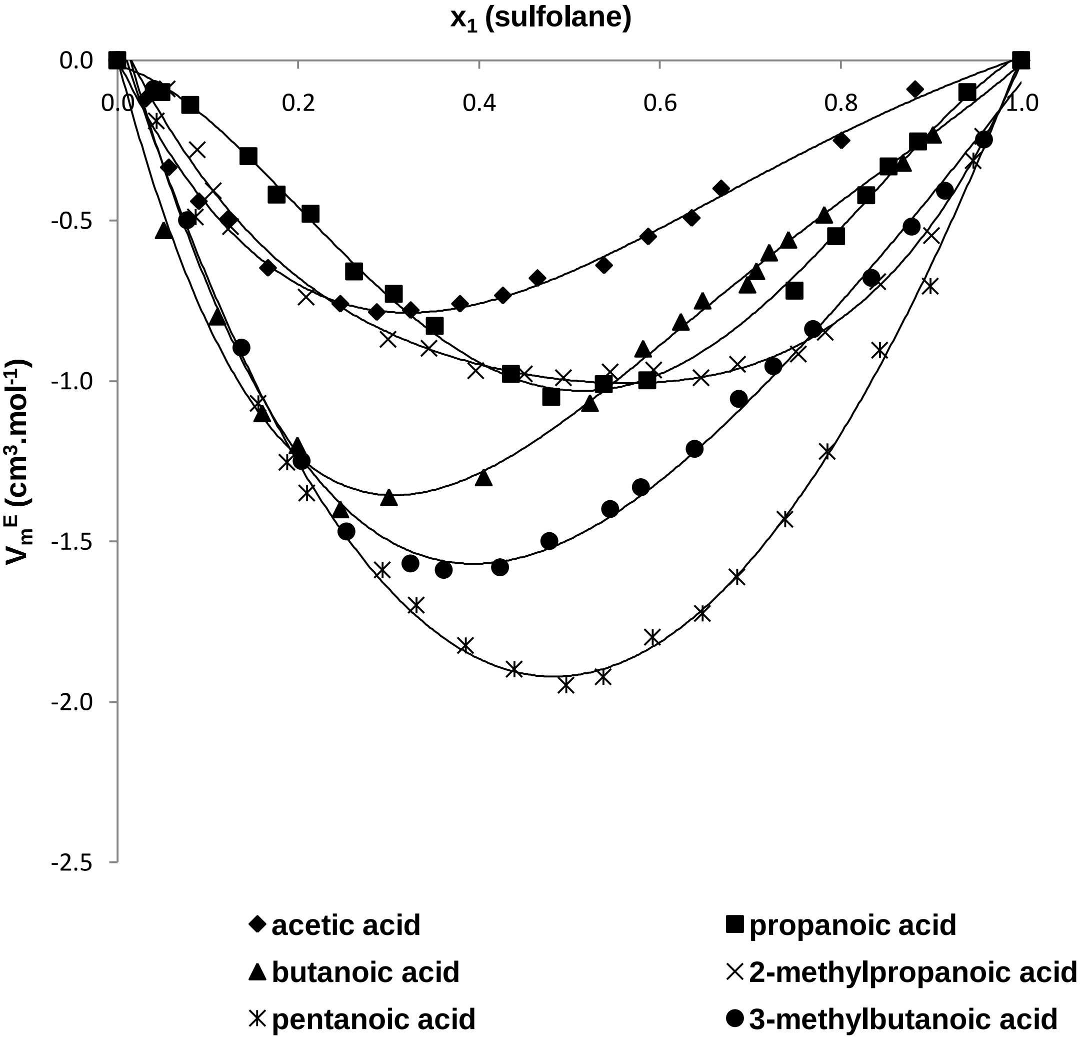

Figure 2.8 **Excess molar volumes for the systems: [Sulfolane (1) + a Carboxylic acid (2)] at T = 308.15 K, plotted as a function of mole fraction x_1.**

2.6 DISCUSSION OF EXCESS MOLAR VOLUMES

2.6.1 Binary mixtures of sulfolane (1) + a carboxylic acid (2)

It has been reported that excess molar volumes values of the binary mixtures result from the chemical, physical and structural characteristics of liquids (Tresczanowica *et al*., 1981). The excess molar volumes shown in Table 2.3, and Table 2.5 are negative over the entire mole fraction range for all binary mixtures at both temperatures. The values of V_m^E for system of sulfolane (1) + carboxylic acids (2) were plotted in Figure 2.7 at 303.15 K and Figure 2.8 at 313.15 K. The graphs are parabolic, nearly symmetrical, composition dependent with increase in absolute values with an increase in temperatures.

These can be explained in terms of two opposing effects (Verma *et al*., 1990):

(a) The difference in size and shape of the component molecules and mutual loss of dipolar association leads to expansion in volume.
(b) The physical interaction between unlike molecules such as donor-acceptor, dipole to dipole interactions, results to contraction in volume. The experimental results suggest that the latter effect is dominant in the binary (sulfolane + carboxylic acid) mixtures.

Sulfolane undergoes self-association according to a hydrogen bonding scheme similar to self-association in pyridine and quinoline. Kalra *et al.,* (1993) have proposed that there are intermolecular interactions between quinoline and aromatic hydrocarbon molecules through weak hydrogen bonding.

The excess molar volumes for the binary mixtures of sulfolane (1) + a carboxylic acid at T = 303.15 K and 308.15 K were investigated to determine the interaction of components involved, as well as the effect of increasing both the temperature and the carbon chain length of the carboxylic acids.

The presentation of the results is shown in the Figures 2.7 and 2.9. At T = 303.15 K the magnitude of the area of the excess molar volumes increases in the following order: acetic acid < propanoic acid < 2-methylpropanoic acid < butanoic acid < pentanoic acid < 3-methylbutanoic acid. At T = 308.15 K the magnitude of the area of the excess molar volumes increases in the following order: acetic acid < propanoic acid < butanoic acid < 2-methylpropanoic acid < pentanoic acid < 3-methylbutanoic acid.

A negative $\mathrm{V_m^E}$ could be due to an association of the species involved bringing the molecules closer together, resulting in a contraction in volume, or it could be due to the packing effect of the molecules where they become closely packed (Letcher and Redhi, 2002). Packing effects could also contribute either positively or negatively to excess molar volumes (Redhi, 2003). The negative excess molar volumes obtained are most likely due to strong association between molecules leading to diminution in volume. The negative values suggest strong interaction between sulfolane and a carboxylic acid. A similar effect was observed by Changseng *et al.,* (2004) in the study of excess molar volumes of binary mixtures of sulfolane + *p*-xylene or ethylbenzene at T = 303.15 K to 353.15 K, where the negative values of excess molar volumes suggested strong interaction between sulfolane and aromatic hydrocarbons. The variation in $\mathrm{V_m^E}$ of these mixtures will be due to the variation in magnitude of the interaction energy in these mixtures.

The negative values for $\mathrm{V_m^E}$ may be explained as follows:

The dimerization constants, K_d values tend to increase as the length of the alkyl group of the carboxylic acid increases (Affsprung *et al.,* 1968) (Apelblat and Kohler, 1976). The increase in dimerization causes the $\mathrm{V_m^E}$ values to decrease further resulting in excess molar volumes becoming more negative. This is observed from butanoic acid to 3-methylbutanoic acid at both temperatures. It is also found that the position of minima for V_m^E for [sulfolane (1) + pentanoic acid (2)] mixture and [sulfolane (1) + 3-methylbutanoic acid (2)] mixture shifts slowly to the sulfolane rich region of mole fraction scale as the methylation of acetic acid increases. These are explained by hindrance caused by the additional methyl groups. A similar trend was observed by Letcher and Redhi (2001) in their study for the mixtures of (butanenitrile + carboxylic acids) at T = 298.15 K, where the magnitude decreases in the following order: propanoic acid > acetic acid > 3-methylbutanoic acid > 2-methylpropanoic acid > pentanoic acid > butanoic acid.

The introduction of a methyl group from the acetic acid to the 3-methylbutanoic acid would increase the electron density, hence 3-methylbutanoic acid would have a highest electron donor capacity compared to the other carboxylic acids and resulting in a weaker bonding between the hydrogen atom associated with the carbon and the sulphur atom in the sulfolane. The larger the carboxylic acid, the weaker the interaction between sulfolane and carboxylic acid (Changseng *et al.,* 2004). Therefore the V_m^E values are more negative and obey the following sequence; 3-methylbutanoic acid > pentanoic acid > 2-methylpropanoic acid > butanoic acid > propanoic acid > acetic acid in both temperatures of 303.15 and 313.15 K.

Table 2.7 $\mathbf{V_m^E}$ **at equimolar concentrations for the binary mixtures of (sulfolane + a carboxylic acid) with the most negative** $\mathbf{V_m^E}$ **at each temperature.**

Temperature/ K	Carboxylic acid	V_m^E / ($cm^3.mol^{-1}$)
303.15	3-methylbutanoic acid	-1.498
308.15	3-methylbutanoic acid	-1.949

The excess molar volumes are most negative in the case of 3-methylbutanoic acid at T = 303.15 K and 308.15 K respectively. According to Figures 2.7 and 2.8, it is observed that an increase in the carbon chain causes the excess molar volumes to be more negative leading to the increase in the packing effect and a large degree of volume contraction. The V_m^E increases with an increase in temperature.

Table 2.8 V_m^E **(cm^3.mol^{-1}) at equimolar concentrations for the binary mixtures of (sulfolane + a carboxylic acid) at various temperatures.**

	Temperature/ K	
Carboxylic acid	**303.15 K**	**308.15 K**
Acetic acid	-0.461	-0.786
Propanoic acid	-0.652	-1.053
Butanoic acid	-0.672	-1.362
2-Methylpropanoic acid	-1.711	-0.971
Pentanoic acid	-0.772	-1.591
3-Methylbutanoic acid	-1.498	-1.949

The V_m^E at equimolar concentrations of binary mixtures of the (sulfolane + carboxylic acid) tend to be slightly more negative at high temperature, T = 308.15 K as presented in Table 2.8. As the temperature increases the kinetic energy of molecules also increases. As seen in Figures 2.7 and 2.8 the excess molar volumes are negative and increases when temperature increases. It can be summarized that excess values may be affected by three factors. The first factor is the specific forces between molecules, such as hydrogen bonds, charge transfer complexes, breaking of the hydrogen bonds and complexes bringing negative excess values (Changsheng, *et al*., 2006).

The second factor is the physical intermolecular forces, including electrostatic forces between charged particles and between a permanent dipole and an induced dipole, and forces of attraction and repulsion between non polar molecules.

Third factor is the structural characteristics of the components arising from geometrical fitting of one component into another structure due to the differences in shape and size of the components and free volume. In this study the negative V_m^E values indicate that interactions between molecules are stronger than interactions between molecules in the pure liquids and that associative force dominate the behaviour of the solution (Rena *et al*., 2006).

The same behaviour was observed in the study of para anisaldehyde with ethylbenzene at 303.15, 313.15 and 323.15 K (Bakrasan and Kubendran, 2009). Therefore in this system contraction in volume is considered to occur, making the mixture more compressible than the ideal mixture which is shown by the negative excess molar volumes values at both temperatures.

CHAPTER 3

LIQUID-LIQUID EQUILIBRIUM

3.1 Introduction

Phase separation involves the transfer of substances from one phase to another. When two phases are brought into contact, they tend to exchange their constituents until the composition of each phase attains a constant value and when this state is reached, the phases are said to be in macroscopic equilibrium. The equilibrium composition of two phases are usually different from one another and this difference makes it possible to separate mixtures by distillation, extraction and other phase contacting processes (Prausnitz *et al.,* 1986).

The equilibrium phase composition depends on several properties such as temperature, pressure, chemical nature and concentrations of the substances in the mixture. Phase equilibrium thermodynamics seek to establish the relations among these properties which prevail when two or more phases reach a state of equilibrium.

3.2 Liquid-Liquid Extraction

This is a process for separating two components in solution by their distribution between two immiscible liquid phases, after the addition of a third component. The liquid which is added to the solution to bring about extraction is called the solvent or the entrainer. This solvent takes up part of the components of the original solution and forms an immiscible layer with the remaining solution. The solvent layer is called the extract, and the other layer composed of the remainder of the original solution plus some of the solvent is called the raffinate (Peters, 1984).

Liquid-liquid extraction has been applied extensively in the separation of hydrocarbons in the petroleum industry**.**

3.3 Uses of liquid-liquid extraction

It is used primarily when distillation is impractical or too costly to use. In other cases the components to be separated may be heat sensitive like antibiotics, or relatively non-volatile like mineral salts. Liquid-liquid extraction processes have been employed in the chemical industry, e.g. the recovery of acetic acid from water using ethyl ether or ethyl acetate (Brown,1963*)*, and in the separation of aromatics from aliphatics where tertaethylene glycol is used as a solvent. Other extraction solvents used include sulfolane, N-methyl-2-pyrrolidone, quinoline and dimethyl sulfoxide.

3.4 USEFUL PROPERTIES OF SOLVENTS

3.4.1 Selectivity

Selectivity or relative separation, ω, of a solvent is a measure of the ability of a solvent to separate a mixture into its individual components (Perry and Green,1997). It is also defined as the ratio of the mole fraction of two components in one phase, divided by the ratio of the mole fractions of the same two components in the other phase, and is given by:

$$\omega = (x_2/x_3)_{phase1} \;/\; (x_2/x_3)_{phase2} \qquad (3.1)$$

where x_2 and x_3 refer to the mole fractions of the components to be separated.

The separation power of a liquid system is governed by the deviation of the selectivity value from unity. For an effective separation of components between two liquid phases, ω must be greater or less than unity, whereas for $\omega = 1$, no separation is possible i.e. the composition of both phases is identical.

3.4.2 Distribution Coefficient

Distribution coefficient is defined as the mole fraction of solute in the extract phase divided by the mole fraction of the same solute in the raffinate phase, at equilibrium (Perry and Green, 1997).

$$K = x_{23} / x_{21} \tag{3.2}$$

Where x_{23} is the mole fraction of component 2 in the phase that is rich in component 3 and x_{21} is the mole fraction of component 2 in the phase that is rich in component 1. The distribution coefficient, K, for a chosen solute should preferably be high so that a low ratio of extraction solvent to feed solvent may be utilized for an effective liquid-liquid separation**.**

3.4.3 Recoverability

The extraction solvent should be easy to recover from the extract stream as well as the raffinate stream after the extraction process.

3.4.4 Capacity

Capacity refers to the maximum loading of solute per mole fraction of solvent in the extraction solvent rich phase (Perry and Green, 1997) and is an indication of the magnitude of the two phase envelope that will form for a particular system. The formation of the two phase mixture is crucial to the usage of liquid-liquid extraction processes. For a system in which only one of the binary pairs is immiscible, capacity data is deduced from a plait point in a ternary diagram.

3.4.5 Solvent

A low solubility of the extraction solvent in one of the components is desirable (Perry and Green, 1997). A low solubility of feed solvent in the extract leads to a high relative separation and generally to low solute recovery costs. A ternary phase diagram with a large two phase region implies a high mutual insolubility of the three components in the ternary mixture.

3.4.6 Density

The differences in densities between two liquid phases in equilibrium affects the rates that can be achieved in extraction equipment as well as the coalescence rates (Perry and Green, 1997). There should be a large difference in the densities of the liquid phases to ensure a rapid disengagement of phase (Rawat *et al.,* 1972).

3.4.7 Viscosity

Liquids which possess the highest solvent power, yield solutions of lowest viscosity and the fluidity of a solution is an indirect measure of the solvent power of the solvent (Rawat *et al.,* 1972).

3.4.8 Interfacial Tension

A good extraction solvent should have a high interfacial tension, as this will promote rapid coascelence and ensures the rapid disengagement of the two phases (Lo *et al.,* 1982).

3.4.9 Toxicity

Low toxicity from solvent vapour inhalation or skin contact is essential as with modern industrial processes where workplace conditions must conform with high standards.

3.4.10 Chemical Characteristics

Extraction solvents should have a the following characteristics: high boiling point, low melting point, density range from 1.0 to 1.3 g/cm^3, high thermal and chemical stability. It should be non corrosive, low latent heat and specific heat**.**

3.4.11 Availability and Cost

A good solvent must be easy available and if not commercially available, it may represent a large initial cost for charging the system and a heavy continuing expense for replacing inevitable losses.

3.5 TERNARY PHASE EQUILIBRIA

3.5.1 Phase Rule

This involves a three component system. According to Gibbs, the phase rule is a general relation between the variance F (no. of degrees of freedom), the number of components C, and the number of phases P at equilibrium**.**

$$F = C - P + 2 \qquad (3.1)$$

For a three component system at constant temperature and pressure the phase rule becomes,

$$F = 5 - P \qquad (3.2)$$

where F is the number of degrees of freedom i.e. the smallest number of independent variables required to completely describe the state of the system.

3.5.2 Triangular phase diagrams

Phase diagrams for ternary systems are usually represented using a triangular phase diagram as shown in Figure 3.1

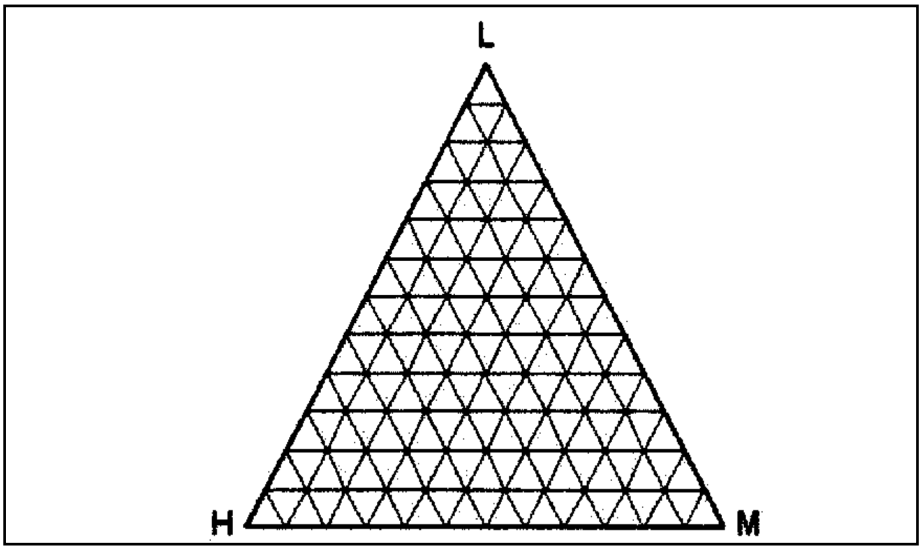

Figure 3.1 Ternary Phase phase diagram representation.

The graph in Figure 3.1 shows an example of a ternary phase diagram and the relationship among the concentrations of the components.

Features of the ternary phase diagram are:

- Any point within the triangle represents the overall composition of a ternary system at a fixed temperature and pressure.
- By convention, the lightest component (L) is located at the apex or top of the triangle. The heavy (H) and medium (M) components are placed at the left and right hand corner, respectively.

- Every corner represents a pure condition. Hence, at the top we have 100 percent L, and at left 100 percent H and at right 100 percent M, respectively.
- Each side of the triangle represents all possible binary combinations of the three components.
- On any of those sides, the fraction of the third component is zero (0%).
- Moving from one side 0% to the 100% or pure condition, the composition of the given component is increasing gradually and proportionally.
- In this work axes have been labelled in terms of mole fractions.

In a triangular ternary phase diagram, compositions of mixtures that are completely miscible are separated from compositions of mixtures that are not completely miscible, by the binodal curve (Atkins,1986) as shown in Figure 3.2. An important feature of the phase diagram are the tie-lines which link the compositions of the phases in equilibrium. The tie-lines are used to determine the distribution of a solute between two phases.

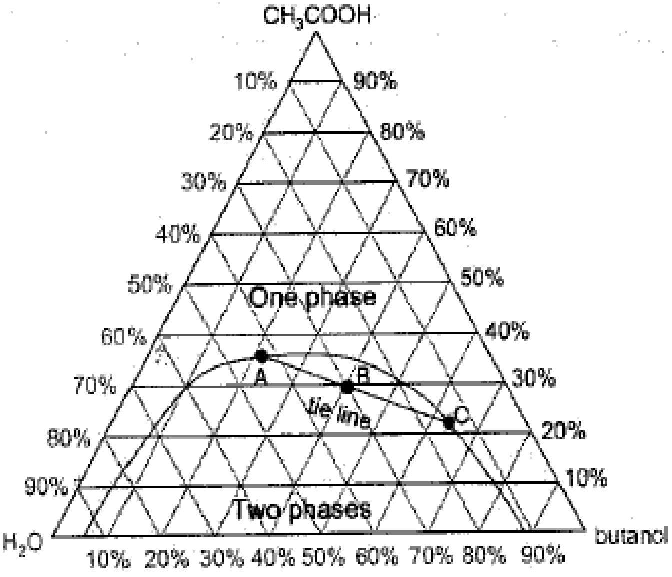

Figure 3.2 Representation of a tie-line in a triangular phase diagram.

In the case of a (water + acetic acid + butanol) system illustrated in Figure 3.2, where three components are mixed to give an overall system composition that falls in the two phase region, the system will separate into two phases, a phase rich in water and another phase rich in butanol. The compositions of the phases that form are given by the intersection of a tie line with phase boundary. The tie-line contains the point describing the overall system composition. When the solution is stirred, the transition from one region to another can be observed by the appearence or disappearence of cloudiness or turbidity in the solution.The turbidity results from the scattering of light by the large number of very small oily droplets of the second phase that are produced when the system is stirred.

3.5.3 Diagrams showing different ternary systems

Ternary liquid-liquid equlibrium systems are categorized according to the types of binary systems that make up the ternary system (Novak *et al*., 1987). In any ternary system there are three binary systems. Triangular diagrams are commonly used to depict liquid-liquid equilibra, and in ternary mixtures many different kinds of diagrams can occur. The Figure 3.3 below shows schematics of six common kinds of isothermal-isobaric diagrams, with the diagrams (a) to (f) arranged according to the number of two-phase regions. Many ternaries display the simple behaviour shown in Figure 3.3(a) to (f) in which only one binary undergoes liquid-liquid equilibrium and the third component is completely miscible in both phases. The resulting triangular diagram contains one single-phase region and one two-phase region, and the two phase boundary must contain plait point. The plait point corresponds to a tie line of zero length.

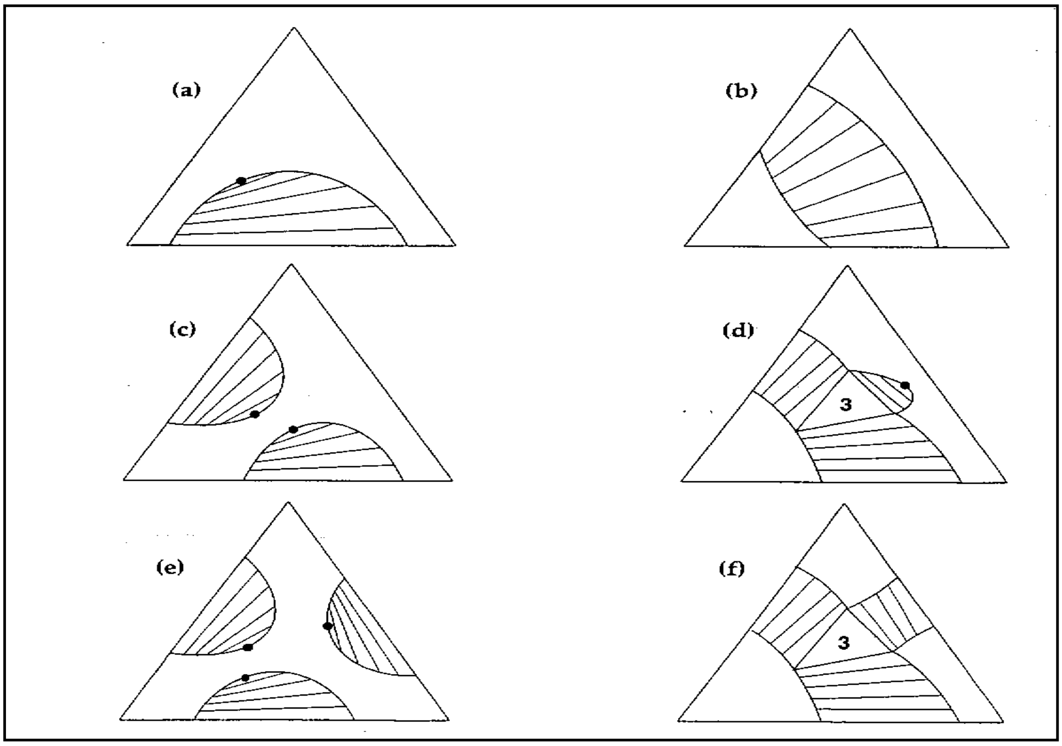

Figure 3.3 Six common types of isothermal-isobaric triangular diagrams for ternary mixtures that exhibit liquid- liquid equilibria (Walas, 1985).

When two of the binaries can exhibit LLE, the resulting ternary diagram usually takes one of the forms shown in (b), (c), or (d) of Figure 3.3. Of these, the simplest appears in Figure 3.3 (b). This diagram contains two single-phase regions separated by one two-phase region that extends from one immiscible binary to the other. In Figure 3.3 (c) the two immiscible binaries give rise to two different two-phase regions separated by one single-phase region. Each two-phase boundary contains a consulate point, and at states between the two-phase regions, the ternary is completely miscible. This behaviour is common, in some cases, mixtures at states between the two-phase regions are not micsible, but instead split into three phases. This possibility appears in Figure 3.3(d).

The composition of the three phases form the vertices of a triangle, and each side of the triangle is bounded by a two-phase region. Neither the vertices nor the sides of the three-phase triangle contain consulate points, but since only two of the binaries exhibit liquid-liquid equilibrium, the third two-phases region must end at a plait point. If all three binaries exhibit liquid-liquid equilibrium, the resulting ternary diagram usually appears as in either (e) or (f). In (e) a one-phase region separates the three two-phase regions, and each two-phase boundary contains a plait point. If a three-phase region separates the two-phase regions, then a diagram like that in (f), is obtained (Walas, 1985).

3.6 EXPERIMENTAL TECHNIQUES

3.6.1 Introduction

The measurements of phase equilibria involves the experimental determination of pressure, temperature, phase compositions and phase amounts. It is not simple to obtain the experimental data of high accuracy. Care must be taken to assure that equilibrium really exists (Walas, 1985).

3.6.1.1 Determination of binodal curve in a ternary sytem

The binodal curve defines the heterogeneous region and can be used to determine the composition of the conjugate phases when other properties of the system studied are known (Noval *et al*.,1987). The usual or classical method of determining the tie-lines and the binodal curve is to make a lot of mixtures of unlimited miscibility, let them reach equlibrium, analyse each of the layers by gas liquid chromatography (GLC) and then mark the concentrations of the liquids in equilibrium. Joining all the experimental points relating to a system in equilibrium gives the tie-lines and joining all the points gives the binodal curve on a ternary graph. Mixtures with compositions lying below the binodal curve will separate into two phases, while all other mixtures form homogeneous solutions.

In this work, the titration method, adapted from that of Briggs and Comings (1943), and modified by Letcher *et al*.(1989) was used. The titration method was developed for the situation when one of the three components is a non-volatile liquid hence difficult to analyse by GLC. The binodal curve was first determined followed by an analysis using the refractive index in order to determine the tie-lines.

A number of mixtures of three substances with unlimited miscibility are prepared, then the third component is added to a known amount of each of the mixture from a microburette until the appearance of turbidity occurs. This gives the first two points in the phase diagram that lie along the horizontal axis, the starting points for the arc. The points defining the arc will be determined by starting from the two-phase region and adding the second component until the disappearance of turbidity occurs in the mixture.The tie-lines are then determined by choosing a point from the two-phase region and determining the compositions of the two phases formed.

3.7 DETERMINATION OF TIE-LINES BY TITRATION METHOD IN A BINODAL CURVE

If properties similar to refractive index, density and the shape of the binodal curve are known in the equilibrium phase, determination of the corresponding position on the binodal curve can be obtained and thus the tie-lines can be found. Otherwise it is sufficient to determine the concentration of only one of the components in both phases, which yield their composition (Redhi, 2003).

3.7.1 Different methods for the determination of tie-lines

3.7.1.1 Karl- Fischer Titration

The tie-lines can also be obtained using the Karl-Fischer method, provided one of the components is water (Skoog *et al*.,1991). In this method the Karl-Fischer reagent is used to titrate against the water in each phase. In this way the aqueous content of each phase can be determined and these are located on the binodal curve and the corresponding tie-lines drawn. There are several variations of the basic technique depending on the solubility of the material, the state in which water is retained and the physical state of the sample.

3.7.1.2 Method based on Mass Balance and the Lever Rule

This method permits the determination of the tie-lines without analysis (Novak *et al*.,1987). A heterogenous mixture is prepared with a composition corresponding to a point N as shown in Figure 3.4. Both co-existing phases are then separated in a thermostatted separating funnel and weighed. Assuming that the turbid phase, richer in substance (1) is present in twice the amount of the turbid phase richer in substance (3), a scale is prepared to assist in the evaluation (here in a ratio of 1:2). Point O is placed over point N and the scale is turned until a position is found such that the same numerical value is obtained on both branches at points intersecting the binodal curve. Care should be taken that the binodal curve is plotted in mass fractions as the masses of both phases are compared in the experiment.

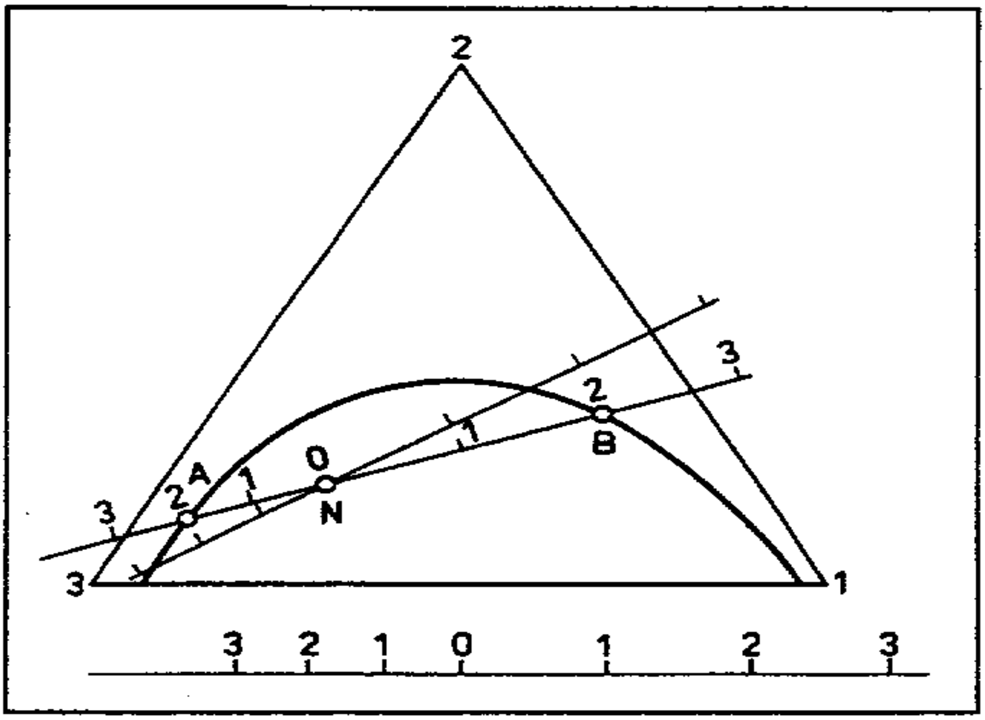

Figure 3.4 Application of lever rule for determination of the compositions of the equilibrium phases (tie-lines) when the binodal curve is known (Novak et al., 1987).

3.8 DETERMINATION OF THE PLAIT POINT IN A TERNARY SYSTEMS

3.8.1 The Coolidge Method

In this method the plait point is found geometrically by extrapolating the experimental tie-lines. Coolidge recommends constructing two triangles on each tie-line (Figure 3.5) whose sides are parallel with those of the concentration triangle (Washburn,1928). A smooth curve connecting the apixes of the triangle passes through the binodal curve in the plait point K.

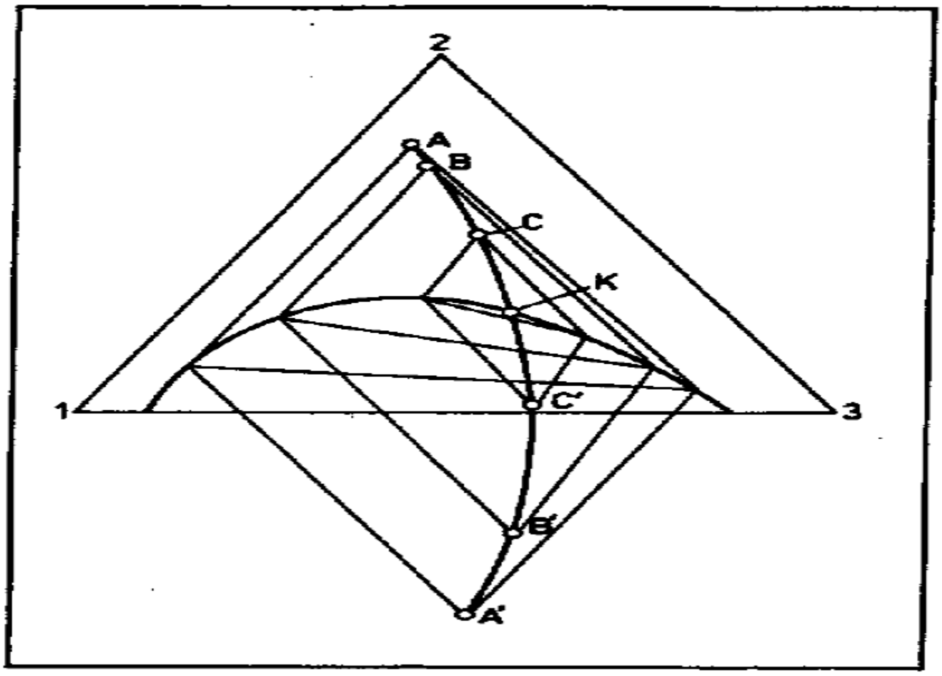

Figure 3.5 **Determination of the critical point by the Coolidge Method (Washburn, 1928).**

In non-symmetrical systems, the curve obtained intersects the binodal curve at a small angle, and determination of the intercept is quite imprecise. It is then preferable to construct isosceles triangles above and below the tie-lines with arms equal to between 60 and 75 percent of the length of the tie-line (depending on the size of the triangle).

3.9 EXPERIMENTAL SECTION

3.9.1 Chemicals used

The carboxylic acids, namely acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid and all the solvents, sulfolane, acetonitrile, hexane, pentane, dodecane and hexadecane were all stored under 0.4 nm molecular sieves before use. The water content was found to be less than 0.01 mass percent for all the chemicals.

A summary of the chemicals, their suppliers and purities used in this work is given below.

Table 3.1 Chemicals used, the suppliers and mass % purities

Compound	Supplier	Mass % purity
Acetic acid	Riedel de Haën	>98.9
Propanoic acid	Fluka	>99.9
Butanoic acid	Fluka	99.5
2-Methylpropanoic acid	Fluka	99.5
Pentanoic acid	Fluka	99.0
3-Methylbutanoic acid	Fluka	>98.5
Sulfolane	Fluka	>99.5
Acetonitrile	HiperSolv	99.5
Hexane	HiperSolv BDH	97.8
Pentane	Fluka	99.0
Dodecane	Fluka	>99.0
Hexadecane	Fluka	>99.5

3.9.2 Procedure

In this study, the titration method, adapted from that of Briggs and Comings (1943) and described by (Letcher *et al.,* 1989) was used to determine the ternary liquid-liquid equilibrium. The binodal curve data is first obtained and the tie-lines are then determined. The points on the binodal curves were obtained in the following manner: a binary mixture of two miscible components, that it is (sulfolane + carboxylic acid) or (acetonitrile + carboxylic acid) were prepared accurately by weighing using the OHAUS analytical balance accurate to within ±10^{-4} g. The mixtures were then left to equilibrate in a water bath maintained at 303.15 K ± 0.01 K for at least one hour.

The third component, either pentane, hexane, hexadecane or dodecane, was then added dropwise from a weighed gas tight syringe until the mixture turned cloudy or turbid. The syringe was again weighed to determine the mass of either pentane, hexane, hexadecane or dodecane added. To ensure the maintenance of only one phase for refractive index measurements, a measured drop of carboxylic acid was added in each case. The refractive index of the clear mixture was then measured using the Bellingham and Stanley RFM 90 Refractometer set at 303.15 K ± 0.01 K for all the ternary systems. The standard calibration curve for each system was obtained by relating the refractive index of each mixture on the co-existence curve, to a composition which was determined by dropping a perpendicular from the co-existence curve to the sulfolane or the acetonitrile mole fraction axis (Letcher *et al*., 1986).

For the tie-line determination, a known amount of the hydrocarbon was added to each mixture, well shaken, and the mixture was left to equilibrate in a controlled water bath at 303.15 K ± 0.01 K at least 24 hours to allow phase separation of the sulfolane-rich layer and the hydrocarbon-rich layer and to ensure equilibrium. Samples of the separated phases were then withdrawn using warmed, gas tight syringes and analyzed immediately using the refractive index method. The refractive indices of the two phases were then related to compositions on the binodal curve by linear interpolation of the refractive indices against the mole fraction of sulfolane or acetonitrile as indicated in Figure 3.6. Each tie-line was checked to ensure that the line joining the two points representing the compositions of the solutions at equilibrium, passed through the composition of the overall mixture (Redhi, 2003).

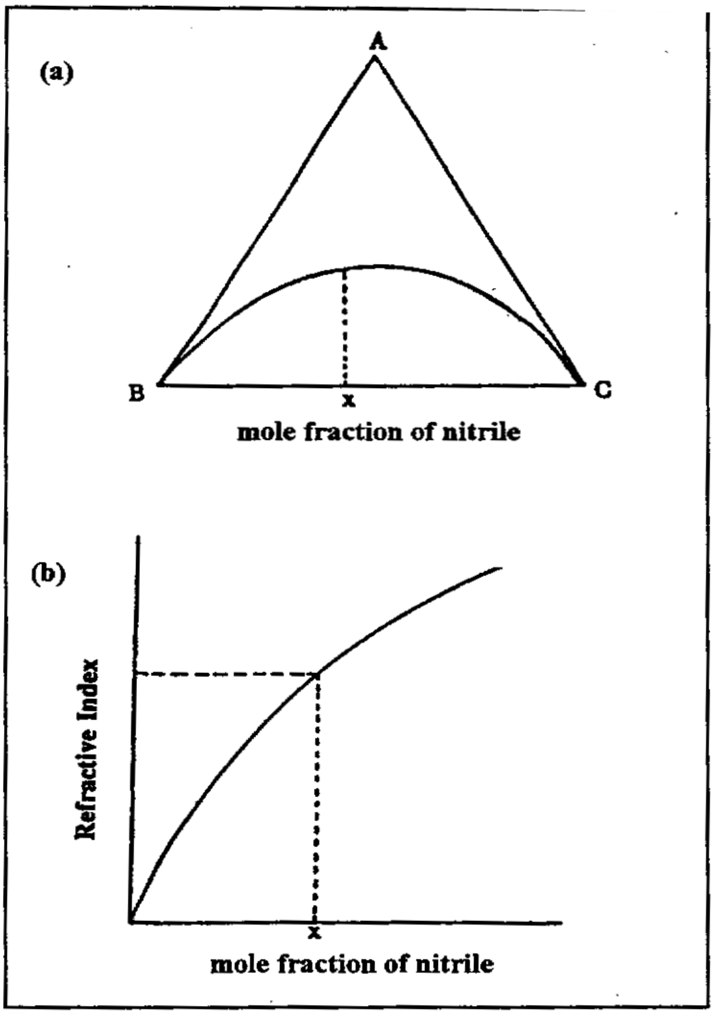

Figure 3.6 **The refractive index method for drawing tie-lines using (a) binodal curve and (b) the calibration curve (Redhi, 2003).**

3.10 FITTING MATHEMATICAL EQUATIONS TO THE BINODAL CURVE DATA

All design methods for separations require quantitative estimates of liquid phase equilibria and the liquid phase activity must be known. In other cases where the equilibrium data is not available, predictive models have been developed in chemical process designs.

For a ternary liquid mixture with only one pair of immiscible liquids, the use of Hlavatý has been until recently the only successful method in fitting an equation to the binodal curve (Hlavatý, 1972). Three equations have been fitted to the ternary data for each system following the work of Hlavatý. The coefficient A*i* relate to a modified Hlavatý equation:

$$x_2 = A_1 x_A \ell n x_A + A_2 x_B \ell n x_B + A_3 x_A x_B \qquad (3.5)$$

Unfortunately the independent variables are highly correlated and slight changes in the binodal curve data produces large changes in the magnitude of the coefficients A_1, A_2 and A_3.

The β-density function equation proposed by Letcher *et al*. (1989), does not suffer from this disadvantage. The coefficient B_i relate to β-function equation:

$$x_2 = \beta_i (1-x_A)^{B2} x_A^{B3} \qquad (3.6)$$

The logarithmic-gamma equation is another equation proposed by (Letcher *et al*., 1986) which does not suffer the disadvantage of being highly correlative. The coeffiecient C_i, relate to the log γ equation:

$$x_2 = C_i (- \ell n x_A)^{C2} x_A^{C3} \qquad (3.7)$$

where $x_A = (x_1 + 0.5\, x_2 – x_2 – x_1{}^0) / (x_{11}{}^0 – x_1{}^0)$ and

$$x_B = (x_{11}{}^0 - x_1 -0.5x_2) / (x_{11}{}^0 – x_1{}^0)$$

and in the case of ternary system (sulfolane + carboxlic acid + hydrocarbon) for example, x_1 refers to mole fraction of sulfolane, x_2 refers to mole fraction of carboxylic acid and x_{11}^0 and x_1^0 are the values of x_1 on the binodal curve which cuts the x_2 at zero. These equations (3.5 to 3.7) have been fitted to the binodal curves with the standard deviations σ, defined as:

$$\sigma = [\sum [x_2(\text{calc}) - x_2(\text{exp})]^2 / (n-3)]^{1/2} \tag{3.8}$$

where n is the number of data points and 3 is the number of estimated coefficients (Sen and Srivastava, 1990) which is defined as the square root of the variance of the estimated coefficients.

Thermodynamics models such as the non-random two liquid equation, NRTL (Renon and Pransnitz, 1968) and the universal quasichemical UNIQUAC (Abrams and Pransnitz, 1975) equations have been used to correlate the experimental tie-line data for the LLE systems. The equations and algorithms used in the calculation of the compositions of the liquid phases follows the method used by Walas (1985). The data is correlated using a computer software programme that minimized the objective F(P). The objective function is used to minimize the difference between the experimental and the calculated concentrations as:

$$\begin{aligned} F(P) = \sum_{i=1}^{n} [x_{li}^{'exp} - x_{li}^{'calc}(P,T)]^2 + [x_{2i}^{'exp} - x_{2i}^{'calc}(P,T)]^2 \\ + [x_{li}^{''exp} - x_{li}^{''calc}(P,T)]^2 + [x_{2i}^{''exp} - x_{2i}^{''calc}(P,T)]^2 \end{aligned} \tag{3.9}$$

where P is set of parameters vector, n is the number of experimental points, $x_{li}^{'exp}$, $x_{2i}^{'exp}$ and $x_{li}^{'calc}(P,T)$, $x_{2i}^{'calc}(P,T)$ are experimental and calculated mole fractions of one phase, and $x_{li}^{''exp}$, $x_{2i}^{''exp}$ and $x_{li}^{''calc}(P,T)$, $x_{2i}^{''calc}(P,T)$ are the experimental and calculated mole fractions of the second phase.

The pure component structural parameters R (volume parameter) and Q (surface parameter) in the NRTL and UNIQUAC equations are obtained from the tables of modified UNIFAC published by Gmehling *et al.* (1993).

The model correlation parameters are calculated as, ($g_{ij} – g_{jj}$), ($g_{ij} – g_{ii}$), and (Δu_{ij}, Δu_{jj}) for the NRTL and UNIQUAC together with the root mean square deviations (rmsd) values and can be taken as a measure of the precision of the correlations.

$$rmsd = \left(\sum_i \sum_l \sum_m \left[x_{ilm}^{exp} - x_{ilm}^{calc} \right]^2 / 6k\right)^{1/2} \qquad (3.10)$$

where x is the mole fraction, k is the number of tie-lines, and the subscripts i, ℓ and m designate the component, phase and tie-line respectively.

CHAPTER 4

4.1 EXPERIMENTAL RESULTS

The experimental liquid-liquid equilibrium data are presented in the following order:

4.1.4 [Sulfolane (1) + a carboxylic acid (2) + pentane (3)] at 303.15 K.
4.1.5 [Sulfolane (1) + a carboxylic acid (2) + hexane (3)] at 303.15 K.
4.1.6 [Sulfolane (1) + a carboxylic acid (2) + hexadecane (3)] at 303.15 K
4.1.7 [Acetonitrile (1) + a carboxylic acid (2) + dodecane (3)] at 303.15 K.

Where carboxylic acid refers to acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid.

4.1.1 Liquid-liquid equilibria for mixtures of [sulfolane (1) + a carboxylic acid (2) + pentane (3)] at 303.15 K.

Table 4.1 Physical properties of pure components at 303.15K; Refractive Indices n_D.

	n_D	
Component	**exp**	**lit[a]**
Acetic acid	1.3716	1.3698
Propanoic acid	1.3829	1.3843
Butanoic acid	1.3947	1.3955
2-Methylpropanoic acid	1.3893	1.3917
Pentanoic acid	1.4047	1.4060
3-Methylbutanoic acid	1.3997	1.4022
Sulfolane	1.4823	1.4816
Pentane	1.3523	1.3547

[a] Riddick *et al*. (1986)

Table 4.2 Physical Properties of Pure Components at 303.15 K for NRTL and UNIQUAC Structural Parameters; Molar Volumes, V_{mi}, Volume and Surface Parameters, R and Q.

Component	**V_{mi} ($cm^3.mol^{-1}$)** [a]	**R**	**Q**
Acetic acid	57.72	2.202[c]	2.072[c]
Propanoic acid	75.48	2.877[c]	2.612[c]
Butanoic acid	93.21	3.551[b]	3.152[b]
2-Methylpropanoic acid	93.64	3.550[b]	3.148[b]
Pentanoic acid	109.76	4.226[b]	3.692[b]
3-Methylbutanoic acid	111.87	4.225[b]	3.688[b]
Sulfolane	95.28	4.038[e]	3.200[e]
Pentane	116.92	3.825[d]	3.316[d]

[a] Riddick *et al.* (1986)

[b] Gmehling *et al.* (1993)

[c] Santiago *et al*. (2010)

[d] Huang *et al*, (2010)

[e] Mahmoudi *et al.* (2010)

Table 4.3 **Calibration Curve Data at 303.15 K for the systems: [Sulfolane (1) + a Carboxylic acid (2) + Pentane(3)], Equilibrium Mole Fraction, x_1 and Refractive Index, n_D.**

x_1	n_D	x_1	n_D
	Acetic Acid		
0.0000	1.3523	0.5203	1.4722
0.0100	1.3676	0.6211	1.4757
0.0201	1.3852	0.6990	1.4768
0.0457	1.3988	0.7732	1.4811
0.1043	1.4139	0.8821	1.4817
0.1773	1.4319	0.9398	1.4819
0.2600	1.4490	0.9941	1.4820
0.3700	1.4607	1.0000	1.4823
	Propanoic Acid		
0.0000	1.3523	0.4682	1.4672
0.0110	1.3643	0.5900	1.4731
0.0397	1.3813	0.8012	1.4766
0.0511	1.3876	0.8741	1.4793
0.1413	1.4200	0.9418	1.4813
0.2503	1.4407	0.9952	1.4814
0.3400	1.4526	1.0000	1.4823
	Butanoic Acid		
0.0000	1.3523	0.6108	1.4633
0.0200	1.3743	0.7227	1.4728
0.0344	1.3822	0.8105	1.4761
0.1186	1.4134	0.9101	1.4789
0.1958	1.4289	0.9512	1.4797
0.3401	1.4407	0.9981	1.4801
0.4956	1.4530	1.0000	1.4823

Table 4.3 continued

x_1	n_D	x_1	n_D
	2-Methylpropanoic Acid		
0.0000	1.3523	0.5700	1.4688
0.0100	1.3709	0.6532	1.4720
0.0201	1.3799	0.7421	1.4750
0.0330	1.3954	0.8712	1.4793
0.0508	1.4039	0.9300	1.4804
0.1433	1.4422	0.9961	1.4805
0.3743	1.4590	1.0000	1.4823
0.4255	1.4620		
	Pentanoic Acid		
0.0000	1.3523	0.6506	1.4567
0.0164	1.3702	0.7600	1.4658
0.0612	1.3850	0.8000	1.4720
0.1399	1.4012	0.8904	1.4781
0.2435	1.4225	0.9300	1.4788
0.3472	1.4340	0.9972	1.4805
0.5426	1.4498	1.0000	1.4823
	3-Methylbutanoic Acid		
0.0000	1.3523	0.5476	1.4572
0.0081	1.3673	0.6276	1.4645
0.0258	1.3851	0.7177	1.4724
0.0655	1.3981	0.8709	1.4776
0.1239	1.4105	0.9377	1.4795
0.2911	1.4380	0.9987	1.4802
0.4155	1.4477	1.0000	1.4823

Table 4.4 Compositions of Points on the Binodal Curve at 303.15 K for the systems: [Sulfolane (1) + a Carboxylic acid (2) + Pentane (3)], Equilibrium Mole Fraction, x_1 and x_2.

x_1	x_2	x_1	x_2
	Acetic Acid		
0.0058	0.0000	0.2600	0.6701
0.0070	0.0600	0.3700	0.5700
0.0080	0.1400	0.5203	0.4422
0.0090	0.2130	0.6211	0.3501
0.0100	0.3608	0.6990	0.2398
0.0201	0.5573	0.7732	0.2109
0.0457	0.7151	0.8821	0.1122
0.1043	0.7499	0.9398	0.0562
0.1773	0.7181	0.9941	0.0000
	Propanoic Acid		
0.0058	0.0000	0.3400	0.4900
0.0060	0.0650	0.4682	0.4000
0.0110	0.1610	0.5900	0.3010
0.0150	0.2800	0.8312	0.1236
0.0397	0.4122	0.9041	0.0698
0.0511	0.5055	0.9418	0.0355
0.1413	0.5523	0.9941	0.0000
0.2503	0.5399		
	Butanoic Acid		
0.0058	0.0000	0.3401	0.4832
0.0060	0.0050	0.4956	0.3937
0.0070	0.1880	0.6108	0.3190
0.0080	0.2801	0.7227	0.2400
0.0100	0.3000	0.8105	0.1700
0.0200	0.2101	0.9101	0.0810
0.0344	0.4017	0.9512	0.0450
0.1186	0.4731	0.9952	0.0000
0.1958	0.5195		

Table 4.4 continued

x_1	x_2	x_1	x_2
2-Methylpropanoic Acid			
0.0058	0.0000	0.4255	0.4853
0.0100	0.1100	0.5700	0.3621
0.0201	0.3133	0.6532	0.2983
0.0330	0.4508	0.7721	0.2001
0.0508	0.5300	0.8912	0.0922
0.1433	0.6010	0.9300	0.0500
0.3743	0.5400	0.9961	0.0000
Pentanoic Acid			
0.0058	0.0000	0.5426	0.3459
0.0060	0.0084	0.6506	0.2615
0.0163	0.1650	0.7600	0.1804
0.0164	0.2916	0.8000	0.1533
0.0612	0.4620	0.8504	0.1002
0.1399	0.4921	0.9300	0.0501
0.2435	0.4953	0.9972	0.0000
0.3472	0.4489		
3-Methylbutanoic Acid			
0.0058	0.0000	0.4155	0.5201
0.0121	0.0600	0.5476	0.4087
0.0165	0.1650	0.6276	0.3307
0.0220	0.2750	0.7477	0.2275
0.0258	0.4622	0.8709	0.1003
0.0655	0.5964	0.9577	0.0200
0.1039	0.6122	0.9987	0.0000
0.2911	0.5992		

Table 4.5 Compositions of the Conjugate Solutions, x_1', x_2' and x_1'', x_2'', at 303.15 K, Refractive Index, n_D.

Pentane-rich phase			Sulfolane-rich phase		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) + Acetic Acid (2) + Pentane (3)					
0.0086	0.2700	1.3767	0.9770	0.0200	1.4161
0.0088	0.3701	1.3784	0.9562	0.0400	1.4344
0.0147	0.4600	1.4600	0.8993	0.0902	1.4607
0.0236	0.5601	1.5601	0.8761	0.1114	1.4705
0.0300	0.6150	1.6150	0.8601	0.1222	1.4758
Sulfolane (1) + Propanoic Acid (2) + Pentane (3)					
0.0110	0.1100	1.3667	0.9708	0.0100	1.4249
0.0133	0.2671	1.3645	0.9677	0.0160	1.4312
0.0256	0.4238	1.3585	0.9502	0.0280	1.4460
0.0399	0.4686	1.3560	0.8903	0.0690	1.4474
0.0511	0.5002	1.3546	0.7871	0.1501	1.4637
Sulfolane (1) + Butanoic Acid (2) + Pentane (3)					
0.0069	0.1334	1.4421	0.9723	0.0152	1.4199
0.0074	0.2888	1.4456	0.9561	0.0252	1.4478
0.0251	0.3550	1.4590	0.9328	0.0491	1.4599
0.0485	0.4235	1.4657	0.8968	0.0848	1.4685
0.0660	0.4519	1.4701	0.8460	0.1350	1.4732

Table 4.5 continued

Pentane-rich phase			Sulfolane-rich phase		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) + 2-Methylpropanoic Acid (2) + Pentane (3)					
0.0180	0.1540	1.3741	0.9502	0.0319	1.4454
0.0221	0.2258	1.4498	0.9497	0.0392	1.4629
0.0400	0.4398	1.4600	0.9388	0.0489	1.4681
0.0260	0.3604	1.4615	0.9255	0.0508	1.4684
0.0606	0.5230	1.4769	0.9184	0.0685	1.4776
Sulfolane (1) + Pentanoic Acid (2) + Pentane (3)					
0.0088	0.1400	1.3811	0.9493	0.0279	1.4551
0.0084	0.2369	1.4554	0.9380	0.0343	1.4565
0.0521	0.4108	1.4611	0.9304	0.0439	1.4609
0.0630	0.4683	1.4649	0.9205	0.0491	1.4650
0.0244	0.2830	1.4749	0.9195	0.0525	1.4750
Sulfolane (1) + 3-Methylbutanoic Acid (2) + Pentane (3)					
0.0296	0.4700	1.3756	0.9745	0.0955	1.4515
0.0108	0.1687	1.3739	0.9693	0.0150	1.4565
0.0100	0.2402	1.3683	0.9690	0.0308	1.4621
0.0099	0.2770	1.3653	0.9401	0.0430	1.4648
0.0315	0.3780	1.3560	0.9196	0.0598	1.4688

Table 4.6 Representative selectivity values of sulfolane for the separation of carboxylic acids from pentane at 303.13 K using $\omega = (x_2/x_3)_{phase1} / (x_2/x_3)_{phase2}$

Carboxylic acid	Selectivity (ω)
Acetic acid	11.2
Propanoic acid	2.5
Butanoic acid	1.2
2-Methylpropanoic acid	33.8
Pentanoic acid	19.8
3-Methylbutanoic acid	20.0

Table 4.7 Coefficients A_i, B_i and C_i for Hlavaty, β and $\log\gamma$ at 303.15 K

Hlavatý	**β**	**$\log\gamma$**
	Sulfolane (1) + Acetic Acid (2) + Pentane (3)	
$A_1 = 0.891$	$B_1 = 3.155$	$C_1 = 2.797$
$A_2 = 1.278$	$B_2 = 1.152$	$C_2 = 1.114$
$A_3 = 5.833$	$B_3 = 1.137$	$C_3 = 1.527$
$\sigma = 0.027$	$\sigma = 0.041$	$\sigma = 0.039$
	Sulfolane (1) + Propanoic Acid (2) + Pentane (3)	
$A_1 = 0.102$	$B_1 = 2.667$	$C_1 = 2.295$
$A_2 = 0.812$	$B_2 = 1.274$	$C_2 = 1.224$
$A_3 = 3.403$	$B_3 = 1.078$	$C_3 = 1.501$
$\sigma = 0.016$	$\sigma = 0.016$	$\sigma = 0.014$
	Sulfolane (1) + Butanoic Acid (2) + Pentane (3)	
$A_1 = -0.255$	$B_1 = 2.134$	$C_1 = 1.713$
$A_2 = 0.111$	$B_2 = 1.024$	$C_2 = 0.955$
$A_3 = 1.816$	$B_3 = 1.011$	$C_3 = 1.273$
$\sigma = 0.008$	$\sigma = 0.017$	$\sigma = 0.008$
	Sulfolane (1) + 2-Methylpropanoic Acid (2) + Pentane (3)	
$A_1 = 0.399$	$B_1 = 3.114$	$C_1 = 2.771$
$A_2 = 0.747$	$B_2 = 1.243$	$C_2 = 1.203$
$A_3 = 3.966$	$B_3 = 1.157$	$C_3 = 1.597$
$\sigma = 0.012$	$\sigma = 0.012$	$\sigma = 0.011$
	Sulfolane (1) + Pentanoic Acid (2) + Pentane (3)	
$A_1 = 0.731$	$B_1 = 4.388$	$C_1 = 3.741$
$A_2 = 0.968$	$B_2 = 1.443$	$C_2 = 1.388$
$A_3 = 4.884$	$B_3 = 1.312$	$C_3 = 1.798$
$\sigma = 0.007$	$\sigma = 0.012$	$\sigma = 0.016$
	Sulfolane (1) + 3-Methylbutanoic Acid (2) + Pentane (3)	
$A_1 = 0.148$	$B_1 = 0.812$	$C_1 = 0.811$
$A_2 = 0.125$	$B_2 = 0.913$	$C_2 = 0.612$
$A_3 = 0.402$	$B_3 = 0.755$	$C_3 = 1.239$
$\sigma = 0.004$	$\sigma = 0.005$	$\sigma = 0.005$

Table 4.8 Values of the Parameters for the NRTL and UNIQUAC Equations and the calculated Root Mean Square Deviation (rmsd[b]), determined from ternary liquid-liquid equilibra for the system of [Sulfolane (1) + Carboxylic acids (2) + Pentane (3)].

	Parameters/ (J.mol^{-1})			
Component	**NRTL**[a]		**UNIQUAC**	
i-j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ij}
Sulfolane (1) + Acetic acid (2) + Pentane (3)				
	(0.006)		(0.378)	
1-2-2-1	3265.22	6245.89	1.71	0.07
1-3-3-1	7855.99	7616.44	-0.25	-0.71
2-3-3-2	22541.45	-3617.86	-0.56	1.31
Sulfolane (1) + Propanoic acid (2) + Pentane (3)				
	(0.102)		(0.358)	
1-2-2-1	1971.08	2656.65	1.70	0.11
1-3-3-1	2010.07	2098.16	-0.25	-0.71
2-3-3-2	71.19	73.86	1.56	1.31
Sulfolane (1) + Butanoic acid (2) + Pentane (3)				
	(0.092)		(0.353)	
1-2-2-1	1275.96	2836.04	-0.44	0.01
1-3-3-1	2276.59	2301.27	0.01	-0.01
2-3-3-2	414.35	-322.12	2.12	-2.12

[a] Calculated with $\alpha_{ij} = 0.2$

[b] The rmsd are given in parenthesis

Table 4.8 continued

	Parameters/ (J.mol^{-1})			
Component	**NRTL**[a]		**UNIQUAC**	
i-j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ij}
	Sulfolane (1) + 2-Methylpropanoic acid (2) + Pentane (3)			
	(0.096)		(0.344)	
1-2-2-1	2115.81	2603.69	-1.11	-0.04
1-3-3-1	2062.25	2189.82	0.63	-0.21
2-3-3-2	202.83	10.06	1.02	-0.70
	Sulfolane (1) + Pentanoic acid (2) + Pentane (3)			
	(0.032)		(0.354)	
1-2-2-1	2003.13	1942.09	-1.11	-0.28
1-3-3-1	15630.78	5862.69	0.51	-0.02
2-3-3-2	893.75	-435.26	-1.11	-0.26
	Sulfolane (1) + 3-Methylbutanoic acid (2) + Pentane (3)			
	(0.106)		(0.372)	
1-2-2-1	1896.47	2507.01	-0.55	-1.48
1-3-3-1	2124.05	2278.38	-0.01	0.31
2-3-3-2	-570.54	1160.24	1.81	-0.16

[a] Calculated with α_{ij} = 0.2

[b] The rmsd are given in parenthesis

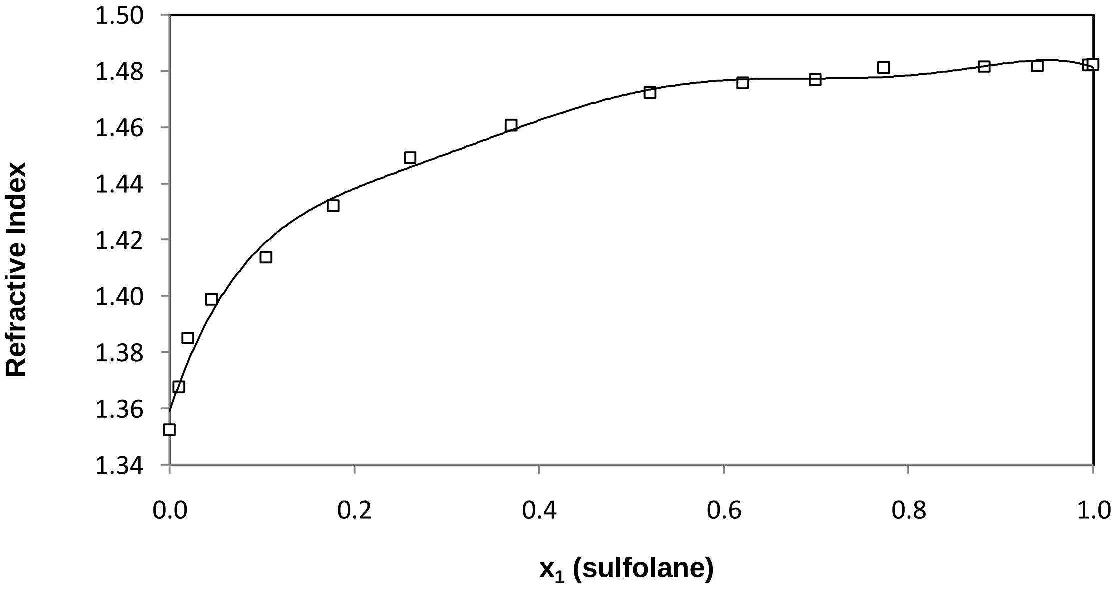

Figure 4.1 Calibration curve for (sulfolane + acetic acid + pentane) system at 303.15 K.

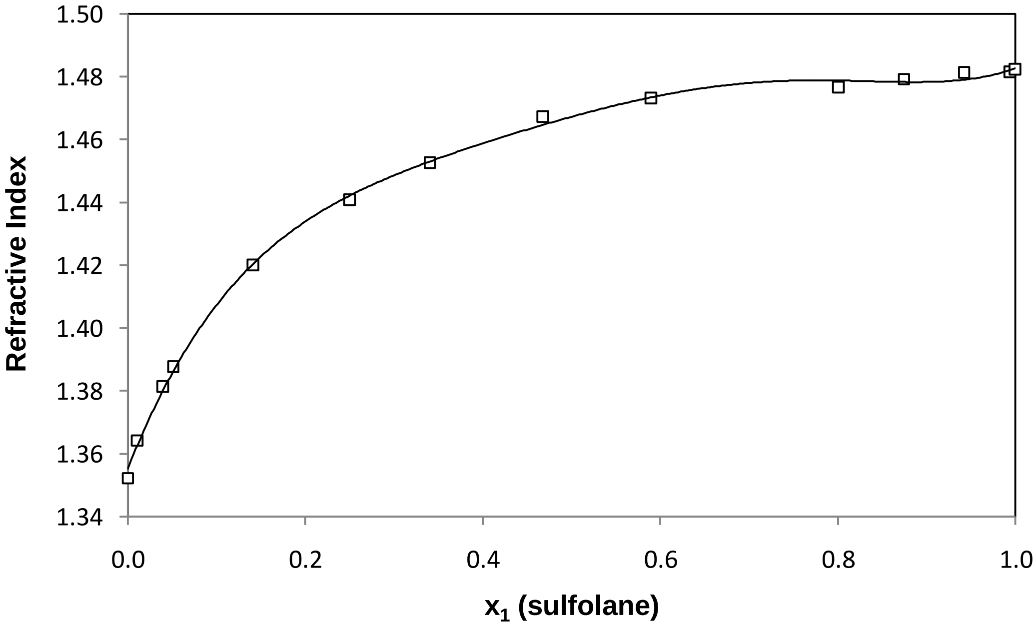

Figure 4.2 Calibration curve for (sulfolane + propanoic acid +pentane) system at 303.15 K.

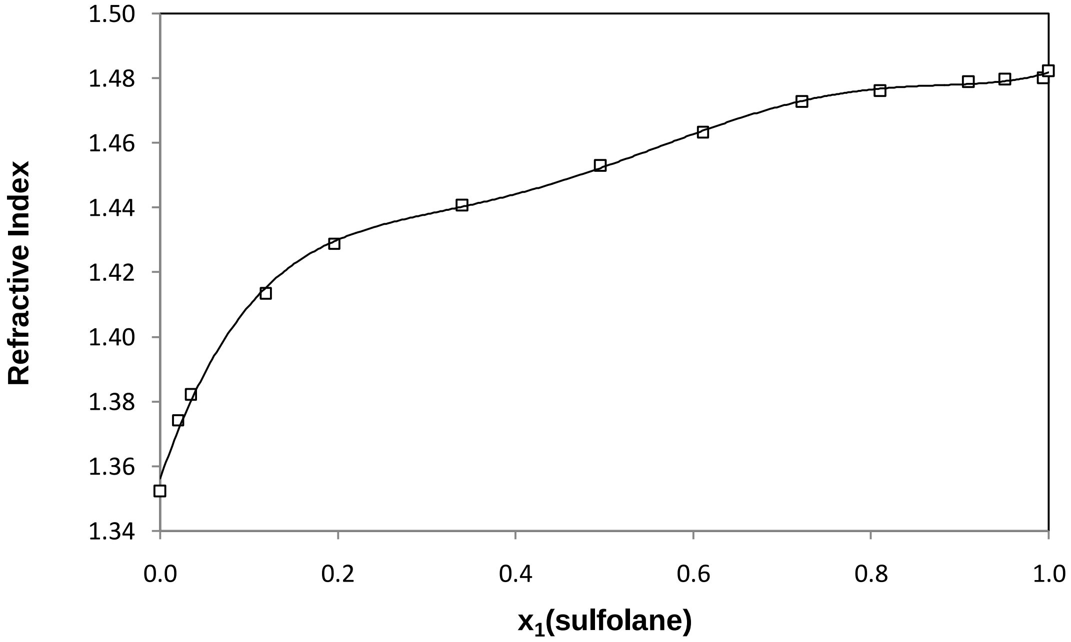

Figure 4.3 **Calibration curve for (sulfolane + butanoic acid + pentane) system at 303.15 K.**

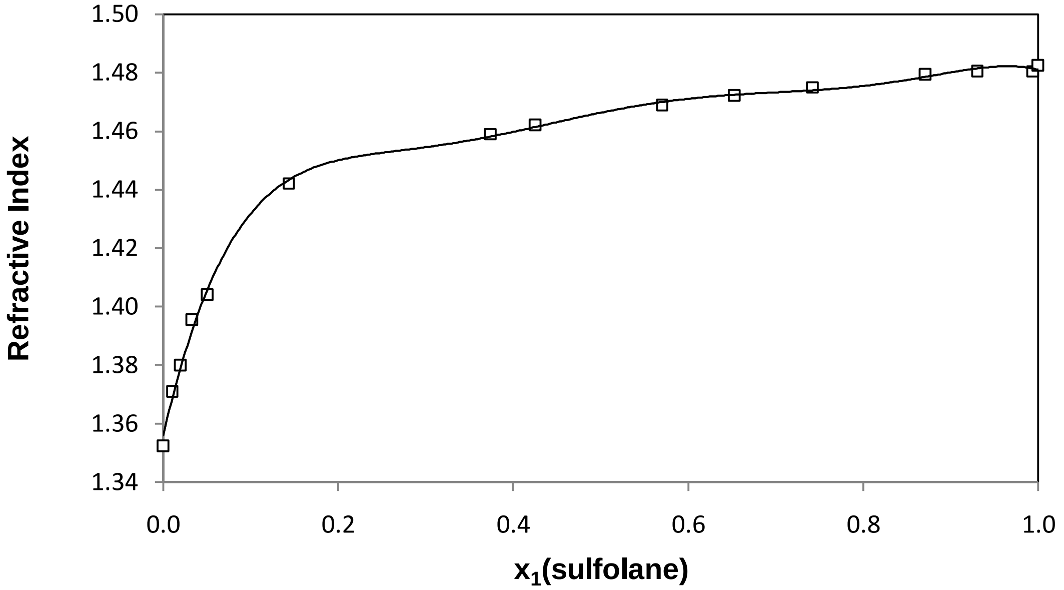

Figure 4.4 **Calibration curve for (sulfolane + 2-methylpropanoic acid + pentane system) at 303.15 K.**

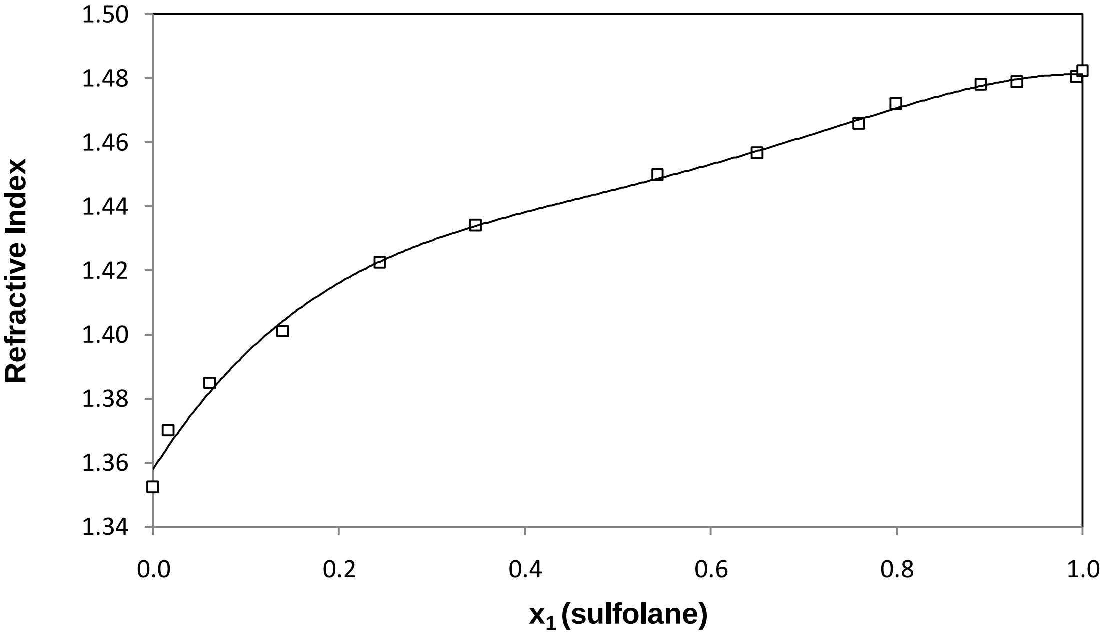

Figure 4.5 Calibration curve for (sulfolane + pentanoic acid + pentane) system at 303.15 K.

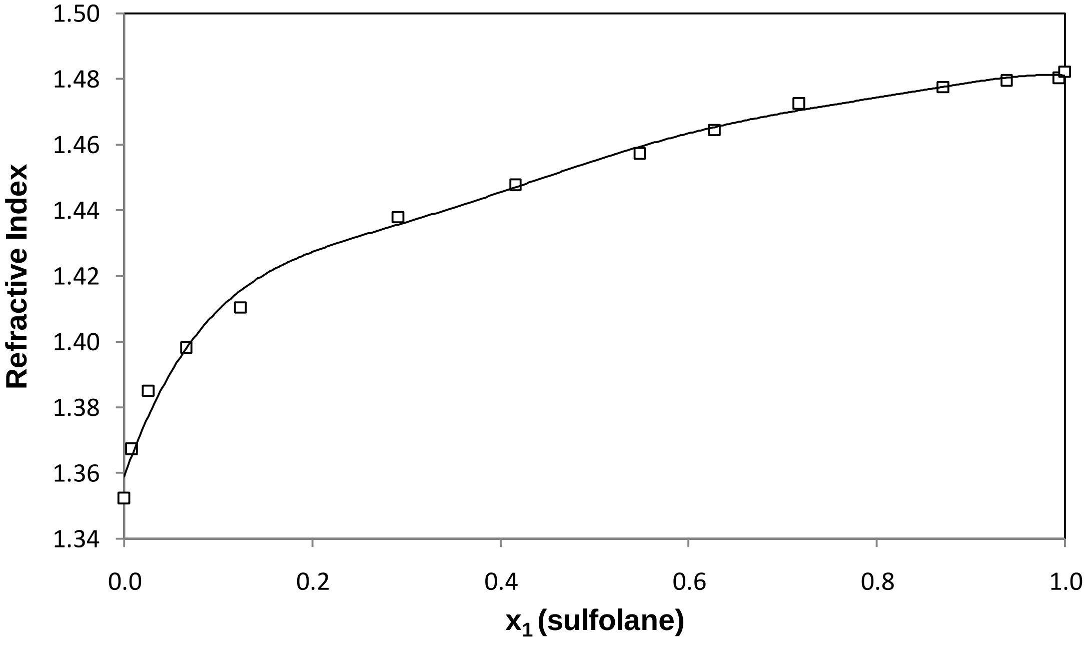

Figure 4.6 Calibration curve for (sulfolane + 3-methylbutanoic acid + pentane system) at 303.15 K.

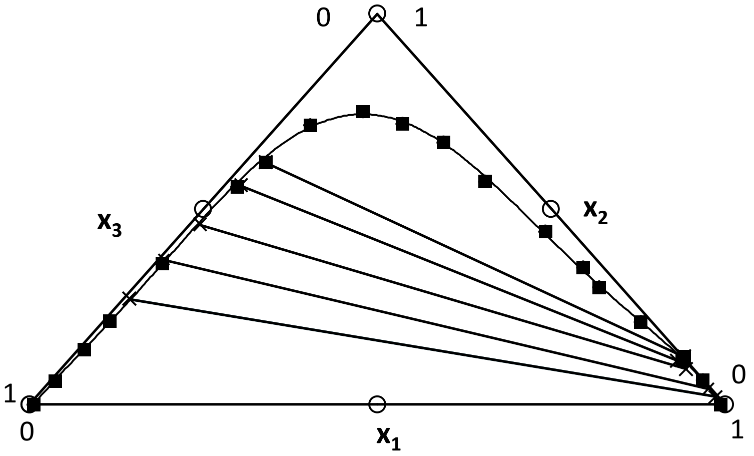

Figure 4.7 **Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + acetic acid (2) + pentane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.**

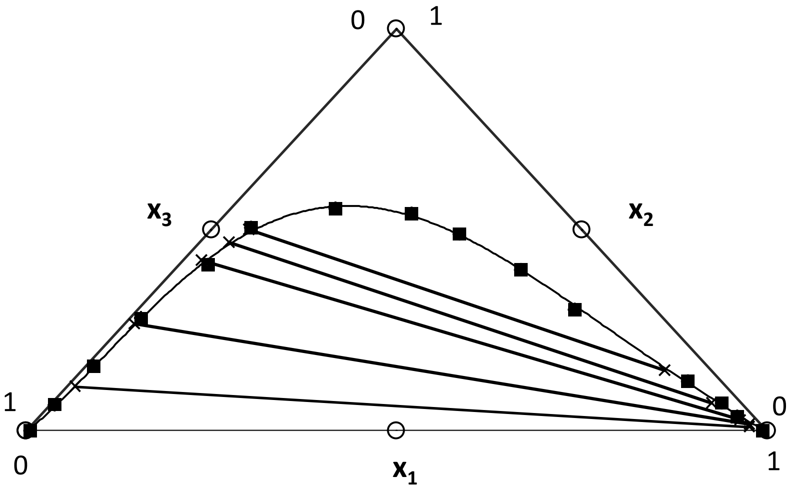

Figure 4.8 **Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + propanoic acid (2) + pentane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.**

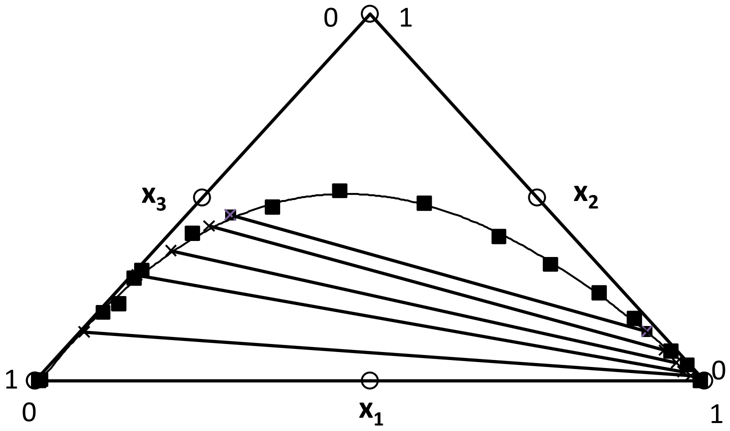

Figure 4.9 **Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + butanoic acid (2) + pentane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.**

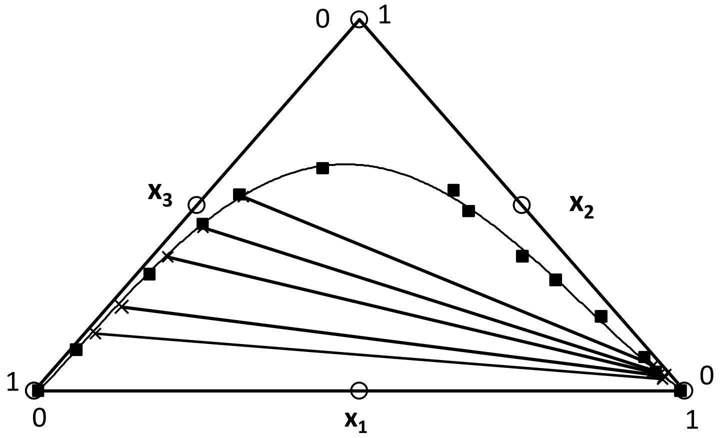

Figure 4.10 **Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + 2-methylpropanoic acid (2) + pentane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.**

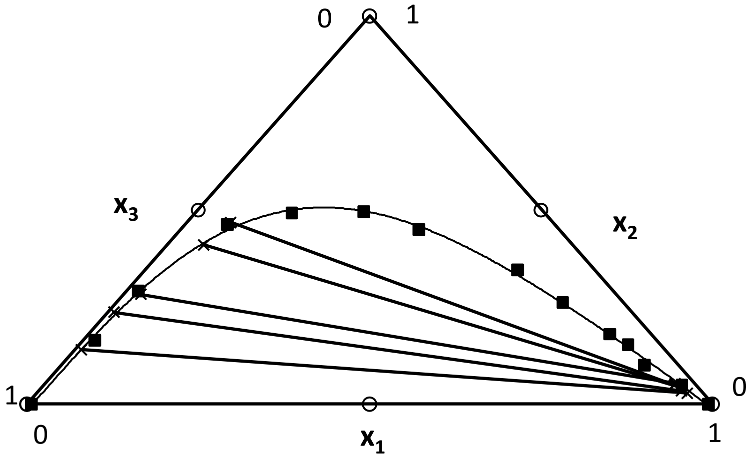

Figure 4.11 Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + pentanoic acid (2) + pentane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

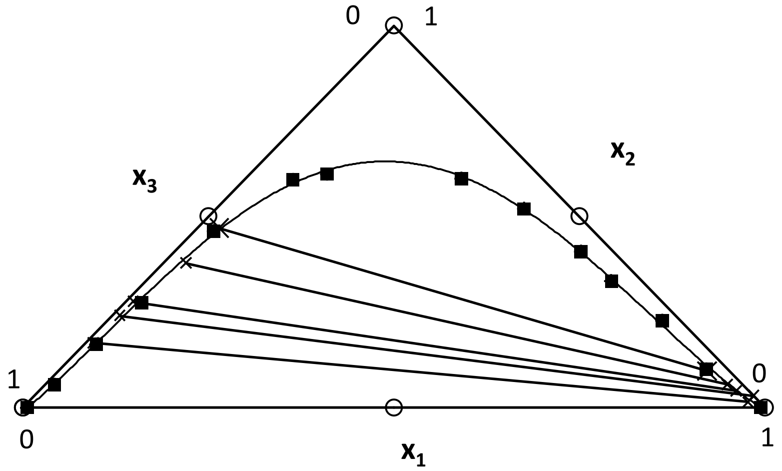

Figure 4.12 Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + 3-methylbutanoic acid (2) + pentane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

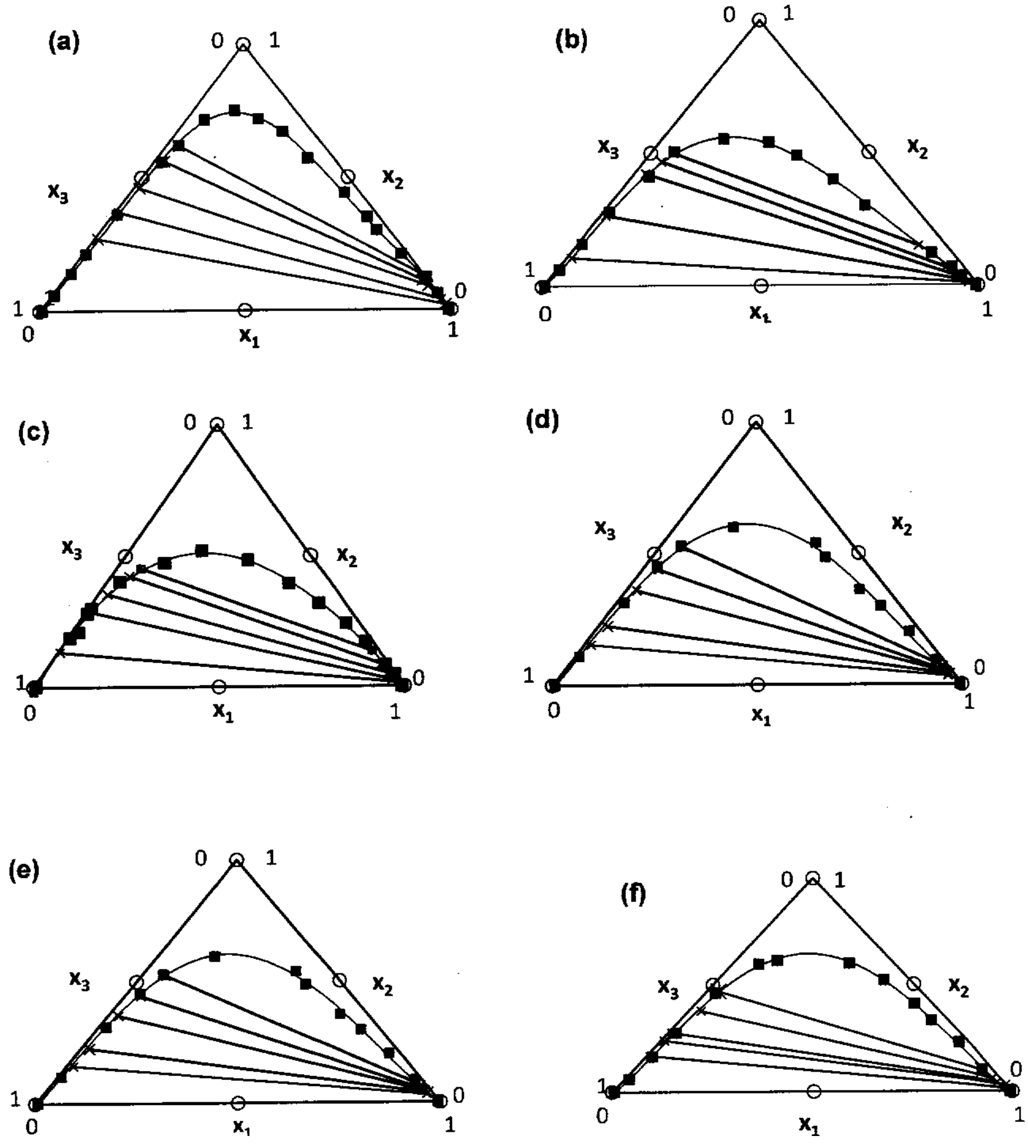

Figure 4.13 Summary of liquid-liquid equilibrium data for the following systems at 303.15 K: (a) sulfolane (1) + acetic acid (2) + pentane (3); (b) sulfolane (1) + propanoic acid (2) + pentane (3); (c) sulfolane (1) + butanoic acid (2) + pentane (3); (d) sulfolane (1) + 2-methylpropanoic acid (2) + pentane (3); (e) sulfolane (1) + pentanoic acid (2) + pentane (3); (f) sulfolane (1) + 3-methylbutanoic acid (2) + pentane (3). Key: (×) experimental tie-lines; (■) experimental points.

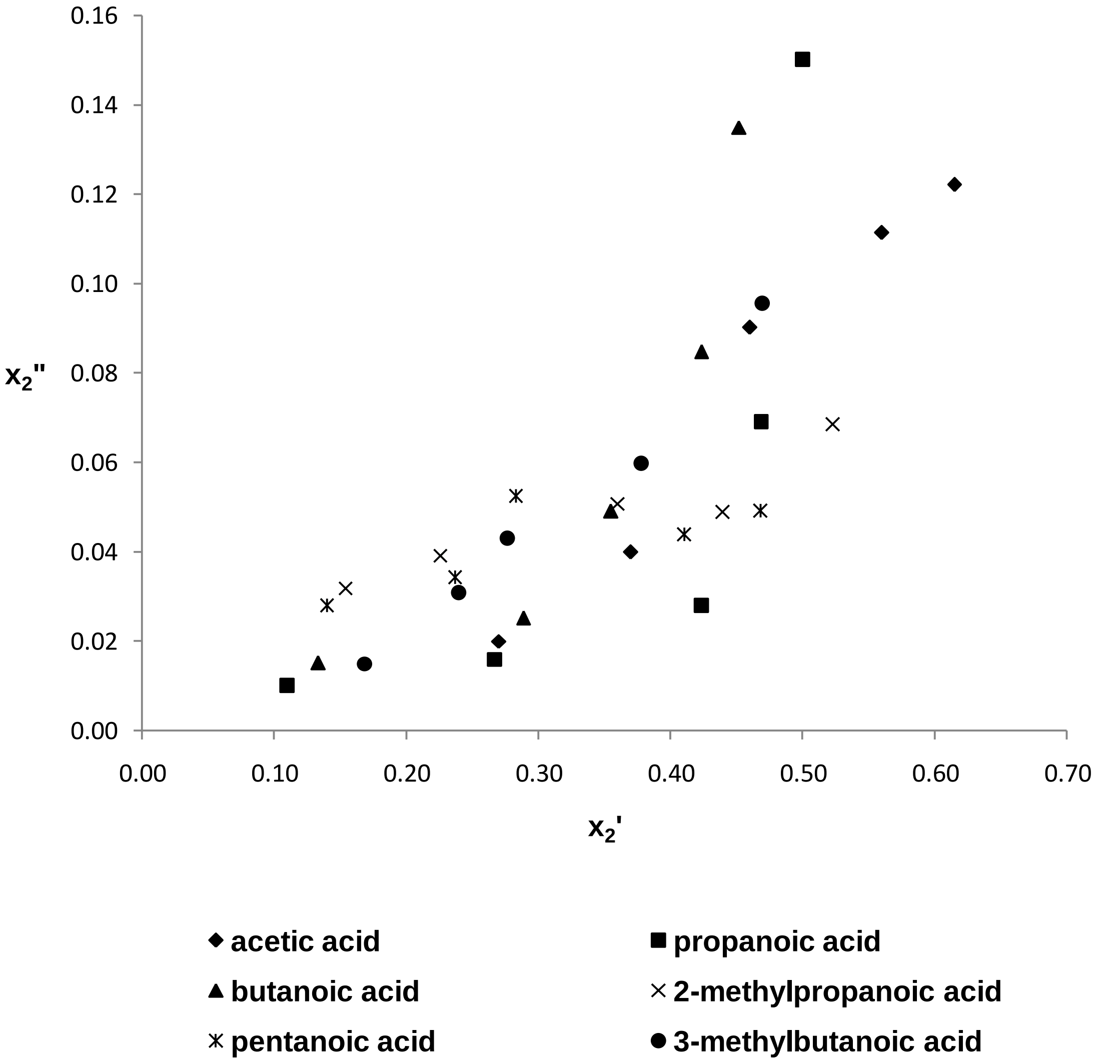

Figure 4.14 A plot of x_2" against x_2' showing the relative solubilities of the carboxylic acids in the sulfolane-rich and the pentane-rich layers at 303.15 K.

4.1.2 Liquid-liquid equilibria for mixtures of [sulfolane (1) + a carboxylic acid (2) + hexane (3)] at 303.15K

Table 4.9 Physical properties of pure components at 303.15 K; Refractive Indices n_D.

	n_D	
Component	**exp**	**lit**[a]
Acetic acid	1.3716	1.3698
Propanoic acid	1.3829	1.3843
Butanoic acid	1.3947	1.3955
2-Methylpropanoic acid	1.3893	1.3917
Pentanoic acid	1.4047	1.4060
3-Methylbutanoic acid	1.3997	1.4022
Sulfolane	1.4823	1.4816
Hexane	1.3706	1.3722

[a] Riddick *et al. (*1986)

Table 4.10 Physical Properties of Pure Components at 303.15 K for NRTL and UNIQUAC Structural Parameters; Molar Volumes, V_{mi}, Volume and Surface Parameters, R and Q.

Component	V_{mi} ($cm^3.mol^{-1}$) [a]	R	Q
Acetic acid	57.72	2.202[c]	2.072[c]
Propanoic acid	75.48	2.877[c]	2.612[c]
Butanoic acid	93.21	3.551[b]	3.152[b]
2-Methylpropanoic acid	93.64	3.550[b]	3.148[b]
Pentanoic acid	109.76	4.226[b]	3.692[b]
3-Methylbutanoic acid	111.87	4.225[b]	3.688[b]
Sulfolane	95.28	4.038[d]	3.200[d]
Hexane	132.38	4.499[d]	3.856[d]

[a] Riddick *et al.* (1986)

[b] Gmehling *et al.* (1993)

[c] Santiago *et al*. (2010)

[d] Mahmoudi *et al.* (2010)

Table 4.11 Calibration Curve Data at 303.15 K for the systems: [Sulfolane (1) + a Carboxylic acid (2) + Hexane (3)], Equilibrium Mole Fraction, x_1 and Refractive Index, n_D.

x_1	n_D	x_1	n_D
Acetic Acid			
0.0000	1.3706	0.4464	1.4373
0.0042	1.3710	0.5574	1.4473
0.0057	1.3718	0.6600	1.4591
0.0198	1.3722	0.8204	1.4680
0.0431	1.3790	0.8996	1.4762
0.1063	1.3857	0.9407	1.4789
0.1811	1.3999	0.9957	1.4798
0.2637	1.4133	1.0000	1.4823
Propanoic Acid			
0.0000	1.3706	0.5364	1.4421
0.0042	1.3756	0.7418	1.4636
0.0373	1.3803	0.8431	1.4715
0.1140	1.3894	0.9107	1.4760
0.2083	1.4034	0.9460	1.4786
0.3196	1.4203	0.9957	1.4792
0.5277	1.4405	1.0000	1.4823

Table 4.11 continued

x_1	n_D	x_1	n_D
	Butanoic Acid		
0.0000	1.3706	0.6617	1.4553
0.0042	1.3728	0.7670	1.4637
0.0060	1.3765	0.8545	1.4723
0.0300	1.3794	0.9060	1.4772
0.0511	1.3821	0.9507	1.4788
0.1418	1.3998	0.9724	1.4790
0.2337	1.4097	0.9957	1.4794
0.3392	1.4225	1.0000	1.4823
0.5438	1.4436		
	2-Methylpropanoic Acid		
0.0000	1.3706	0.3325	1.4199
0.0042	1.3895	0.5364	1.4449
0.0057	1.3911	0.6692	1.4569
0.0064	1.3954	0.7712	1.4639
0.0074	1.3967	0.8789	1.4752
0.0250	1.3985	0.9275	1.4791
0.0502	1.3991	0.9957	1.4811
0.1105	1.4069	1.0000	1.4823
0.2250	1.4133		

Table 4.11 continued

x_1	n_D	x_1	n_D
	Pentanoic Acid		
0.0000	1.3706	0.5200	1.4446
0.0042	1.3731	0.6102	1.4524
0.0044	1.3787	0.7768	1.4666
0.0155	1.3823	0.8730	1.4743
0.0584	1.3986	0.9245	1.4777
0.1543	1.4137	0.9470	1.4787
0.3174	1.4282	0.9957	1.4816
0.4148	1.4373	1.0000	1.4823
	3-Methylbutanoic Acid		
0.0000	1.3706	0.3335	1.4215
0.0042	1.3999	0.4857	1.4451
0.0055	1.4000	0.6319	1.4561
0.0060	1.4010	0.7267	1.4650
0.0100	1.4017	0.8237	1.4736
0.0262	1.4022	0.9014	1.4773
0.0629	1.4055	0.9381	1.4793
0.1493	1.4099	0.9957	1.4811
0.2443	1.4139	1.0000	1.4823

Table 4.12 **Compositions of Points on the Binodal Curve at 303.15 K for the systems: [Sulfolane (1) + a Carboxylic acid (2) + Hexane (3)], Equilibrium Mole Fraction, x_1 and x_2.**

x_1	x_2	x_1	x_2
Acetic Acid			
0.0042	0.0000	0.1811	0.7512
0.0203	0.1050	0.2637	0.6917
0.0090	0.2100	0.4464	0.5102
0.0131	0.2900	0.5574	0.4143
0.0147	0.4212	0.6800	0.2893
0.0150	0.5500	0.8204	0.1613
0.0198	0.6683	0.8996	0.0811
0.0431	0.7799	0.9407	0.0416
0.1063	0.7989	0.9957	0.0000
Propanoic Acid			
0.0042	0.0000	0.3196	0.5719
0.0150	0.0700	0.5277	0.4224
0.0200	0.2100	0.5364	0.4134
0.0250	0.2820	0.7418	0.2158
0.0300	0.3750	0.8431	0.1265
0.0373	0.4647	0.9107	0.0635
0.1140	0.5793	0.9460	0.0358
0.2083	0.6019	0.9957	0.0000
Butanoic Acid			
0.0042	0.0000	0.6617	0.2981
0.0180	0.2112	0.7670	0.2039
0.0300	0.3702	0.8745	0.1060
0.0511	0.5271	0.9260	0.0520
0.1418	0.6067	0.9507	0.0253
0.2337	0.6199	0.9724	0.0122
0.3392	0.5349	0.9957	0.0000
0.5438	0.3840		

Table 4.12 continued

x_1	x_2	x_1	x_2
2-Methylpropanoic Acid			
0.0042	0.0000	0.2499	0.5903
0.0185	0.0550	0.3325	0.5400
0.0257	0.2566	0.5364	0.3978
0.0304	0.3711	0.6692	0.2947
0.0374	0.4211	0.7712	0.2037
0.0403	0.5033	0.8789	0.1032
0.0502	0.5346	0.9275	0.0546
0.1105	0.6024	0.9705	0.0232
0.2100	0.6010	0.9957	0.0000
Pentanoic Acid			
0.0042	0.0000	0.5200	0.3829
0.0044	0.1000	0.6102	0.3096
0.0155	0.2696	0.7768	0.1750
0.0584	0.4577	0.8730	0.0873
0.1543	0.5357	0.9245	0.0457
0.3174	0.4948	0.9470	0.0010
0.4148	0.4420	0.9957	0.0000
(f) 3-Methylbutanoic Acid			
0.0042	0.0000	0.3335	0.5285
0.0055	0.0060	0.4857	0.4522
0.0060	0.1200	0.6319	0.3245
0.0100	0.1900	0.7267	0.2420
0.0262	0.3807	0.8237	0.1605
0.0629	0.5138	0.9014	0.0848
0.1493	0.5910	0.9381	0.0425
0.2443	0.5715	0.9957	0.0000

Table 4.13 Compositions of the Conjugate Solutions, x_1', x_2' and x_1'', x_2'', at 303.15 K, Refractive Index, n_D.

Hexane-rich phase			Sulfolane-rich phase		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) + Acetic Acid (2) + Hexane (3)					
0.0192	0.1300	1.3997	0.9729	0.0100	1.4597
0.0199	0.3080	1.3947	0.9680	0.0182	1.4490
0.0154	0.4000	1.3867	0.9562	0.0254	1.4381
0.0142	0.5101	1.3789	0.9453	0.0382	1.4022
0.0169	0.6800	1.3772	0.8832	0.0985	1.3889
Sulfolane (1) + Propanoic Acid (2) + Hexane (3)					
0.0202	0.1000	1.4288	0.9736	0.0109	1.4653
0.0220	0.2000	1.4255	0.9593	0.0199	1.4557
0.0270	0.2990	1.4133	0.9548	0.0260	1.4486
0.0280	0.3650	1.4089	0.9412	0.0363	1.4321
0.0450	0.4800	1.4052	0.9352	0.0388	1.4234
Sulfolane (1) + Butanoic Acid (2) + Hexane (3)					
0.0099	0.0900	1.4384	0.9799	0.0046	1.4732
0.0148	0.2200	1.4267	0.9648	0.0095	1.4622
0.0178	0.2700	1.4172	0.9608	0.0227	1.4569
0.0190	0.3700	1.4051	0.9569	0.0328	1.4475
0.0328	0.4760	1.4033	0.9315	0.0482	1.4461

Table 4.13 continued

Hexane-rich phase			Sulfolane-rich phase		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) +2-Methylpropanoic Acid (2) + Hexane (3)					
0.0120	0.1300	1.4128	0.9790	0.0122	1.4705
0.0198	0.1700	1.4051	0.9622	0.0290	1.4665
0.0188	0.2300	1.4020	0.9435	0.0436	1.4607
0.0409	0.4310	1.3915	0.9095	0.0745	1.4527
0.0699	0.5438	1.3898	0.8961	0.0900	1.4503
Sulfolane (1) + Pentanoic Acid (2) + Hexane (3)					
0.0216	0.1376	1.4700	0.9692	0.0180	1.4367
0.0271	0.2408	1.4622	0.9510	0.0285	1.4245
0.0290	0.2990	1.4565	0.9318	0.0480	1.4178
0.0396	0.3500	1.4501	0.9200	0.0610	1.4089
0.0410	0.3930	1.4497	0.8891	0.0800	1.4055
Sulfolane (1) + 3-Methylbutanoic Acid (2) + Hexane (3)					
0.0081	0.1700	1.4634	0.9752	0.0104	1.4693
0.0096	0.2200	1.4590	0.9636	0.0235	1.4642
0.0180	0.2700	1.4198	0.9562	0.0290	1.4586
0.0299	0.4300	1.4174	0.9400	0.0468	1.4523
0.1070	0.5542	1.4133	0.9020	0.0792	1.4513

Table 4.14 Representative selectivity values of sulfolane for the separation of carboxylic acids from hexane at 303.15 K, using $\omega = (x_2/x_3)_{phase1} / (x_2/x_3)_{phase2}$

Carboxylic acid	Selectivity (ω)
Acetic acid	2.64
Propanoic acid	3.56
Butanoic acid	3.11
2-Methylpropanoic acid	9.24
Pentanoic acid	5.49
3-Methylbutanoic acid	4.42

Table 4.15 Coefficients A_i, B_i and C_i for Hlavaty, β and logγ at 303.15 K

Hlavatý	**β**	**logγ**
Sulfolane (1) + Acetic Acid (2) + Hexane (3)		
$A_1 = -0.1766$	$B_1 = 0.812$	$C_1 = 0.811$
$A_2 = -0.185$	$B_2 = 0.913$	$C_2 = 0.612$
$A_3 = 0.412$	$B_3 = 0.755$	$C_3 = 1.239$
$\sigma = 0.004$	$\sigma = 0.005$	$\sigma = 0.005$
Sulfolane (1) + Propanoic Acid (2) + Hexane (3)		
$A_1 = 0.067$	$B_1 = 1.989$	$C_1 = 1.592$
$A_2 = 0.738$	$B_2 = 1.139$	$C_2 = 1.055$
$A_3 = 3.516$	$B_3 = 0.755$	$C_3 = 1.067$
$\sigma = 0.012$	$\sigma = 0.041$	$\sigma = 0.052$
Sulfolane (1) + Butanoic Acid (2) + Hexane (3)		
$A_1 = -0.039$	$B_1 = 3.629$	$C_1 = 3.299$
$A_2 = 0.706$	$B_2 = 1.395$	$C_2 = 1.366$
$A_3 = 3.516$	$B_3 = 1.139$	$C_3 = 1.662$
$\sigma = 0.013$	$\sigma = 0.015$	$\sigma = 0.018$
Sulfolane (1) + 2-Methylpropanoic Acid (2) + Hexane (3)		
$A_1 = -0.064$	$B_1 = 1.666$	$C_1 = 1.365$
$A_2 = 0.603$	$B_2 = 1.011$	$C_2 = 0.944$
$A_3 = 3.12$	$B_3 = 0.652$	$C_3 = 0.919$
$\sigma = 0.013$	$\sigma = 0.039$	$\sigma = 0.050$
Sulfolane (1) + Pentanoic Acid (2) + Hexane (3)		
$A_1 = 0.209$	$B_1 = 3.333$	$C_1 = 2.953$
$A_2 = 0.718$	$B_2 = 1.398$	$C_2 = 1.355$
$A_3 = 3.348$	$B_3 = 1.253$	$C_3 = 1.754$
$\sigma = 0.014$	$\sigma = 0.016$	$\sigma = 0.014$
Sulfolane (1) + 3-Methylbutanoic Acid (2) + Hexane (3)		
$A_1= 0.287$	$B_1= 3.406$	C1=2.386
$A_2= 0.531$	$B_2= 1.232$	C2=1.141
$A_3= 3.449$	$B_3= 1.145$	C3=1.471
$\sigma = 0.007$	$\sigma = 0.007$	σ=0.012

Table 4.16 Values of the Parameters for the NRTL Equation and the calculated Root Mean Square Deviation, rmsd[b], determined from ternary liquid-liquid equilibria for the system of [Sulfolane(1) + Carboxylic acids(2) + Hexane(3)].

	Parameters/(J.mol^{-1})			
Component	**NRTL[a]**		**UNIQUAC**	
i-j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ij}
	Sulfolane (1) + Acetic acid (2) + Hexane (3)			
	(0.126)		(0.404)	
1-2-2-1	2064.19	2496.19	-0.11	-0.19
1-3-3-1	1883.89	1973.08	-0.13	0.18
2-3-3-2	-164.43	327.81	-0.28	0.69
	Sulfolane (1) + Propanoic acid (2) + Hexane (3)			
	(0.002)		(0.395)	
1-2-2-1	4265.81	4778.75	1.67	-5.47
1-3-3-1	6041.02	6964.16	0.95	2.47
2-3-3-2	2318.60	-209.88	-4.46	4.57
	Sulfolane (1) + Butanoic acid (2) + Hexane (3)			
	(0.002)		(0.391)	
1-2-2-1	2656.46	4354.86	-0.59	-0.01
1-3-3-1	5710.69	8862.74	1.04	-0.01
2-3-3-2	-339.65	1959.40	0.20	0.89

[a] Calculated with $\alpha_{ij} = 0.2$

[b] The rmsd are given in parenthesis

Table 4.16 continued

Component	Parameters/(J.mol^{-1})			
	NRTL[a]		UNIQUAC	
i-j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ij}
Sulfolane (1) + 2-Methylpropanoic acid (2) + Hexane (3)				
	(0.105)		(0.364)	
1-2-2-1	2101.36	2615.15	1.31	-0.47
1-3-3-1	1907.32	2007.15	0.80	0.34
2-3-3-2	100.55	-8.68	-2.91	3.01
Sulfolane (1) + Pentanoic acid (2) + Hexane (3)				
	(0.003)		(0.360)	
1-2-2-1	117.95	4981.98	1.45	-5.41
1-3-3-1	5852.11	7389.77	0.74	1.18
2-3-3-2	-3562.14	255.05	-2.59	3.33
Sulfolane (1) + 3-Methylbutanoic acid (2) + Hexane (3)				
	(0.002)		(0.334)	
1-2-2-1	5007.39	1249.69	1.47	5.51
1-3-3-1	6231.03	14811.89	1.29	-2.31
2-3-3-2	-2984.79	3105.79	-2.31	2.73

[a] Calculated with $\alpha_{ij} = 0.2$

[b] The rmsd are given in parenthesis

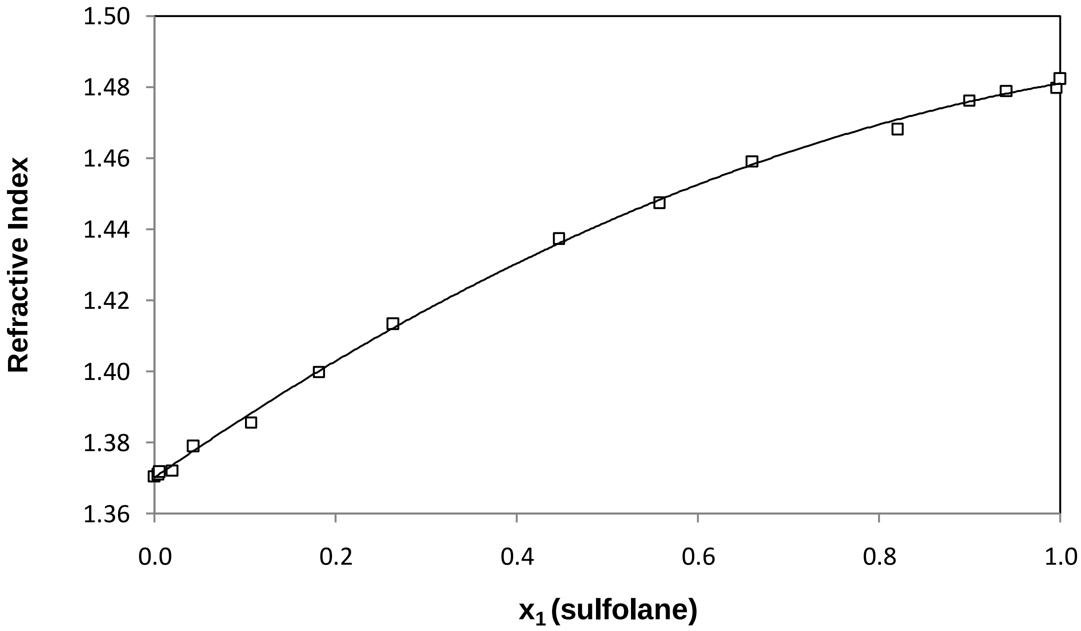

Figure 4.15 Calibration curve for (sulfolane + acetic acid + hexane) system at 303.15 K.

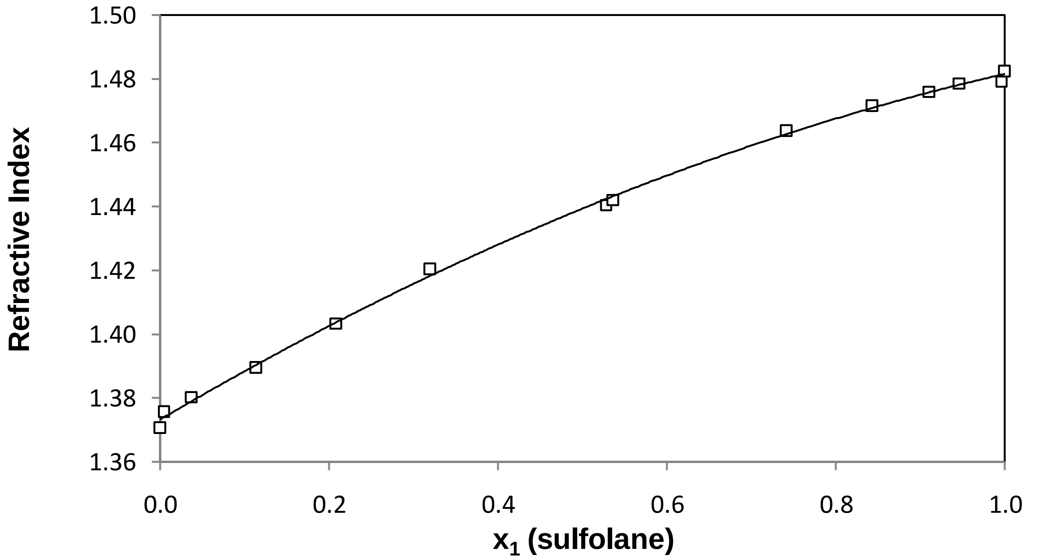

Figure 4.16 Calibration curve for (sulfolane + propanoic acid + hexane) system at 303.15 K.

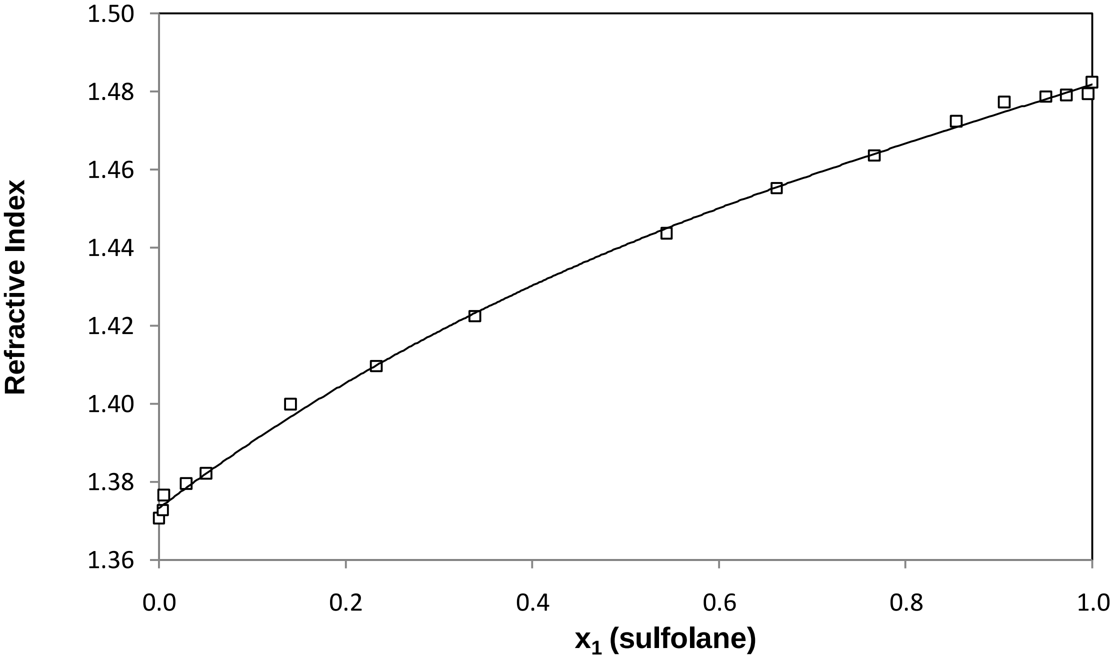

Figure 4.17 Calibration curve for (sulfolane + butanoic acid + hexane) system at 303.15 K.

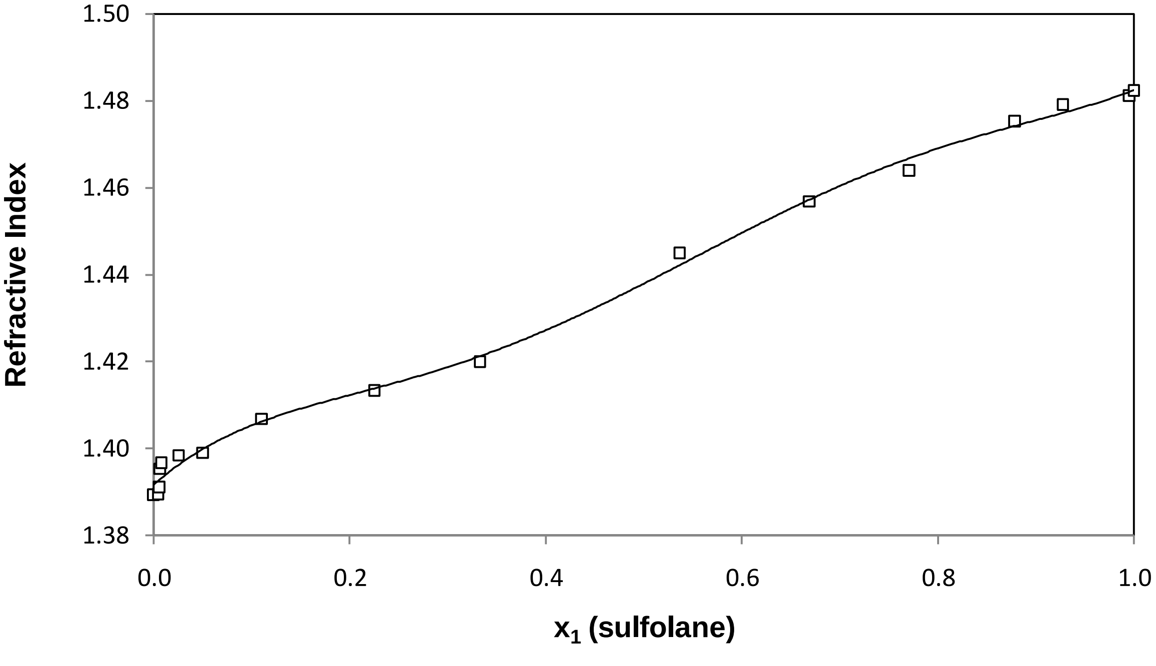

Figure 4.18 Calibration curve for (sulfolane + 2-methylpropanoic acid + hexane) system at 303.15 K.

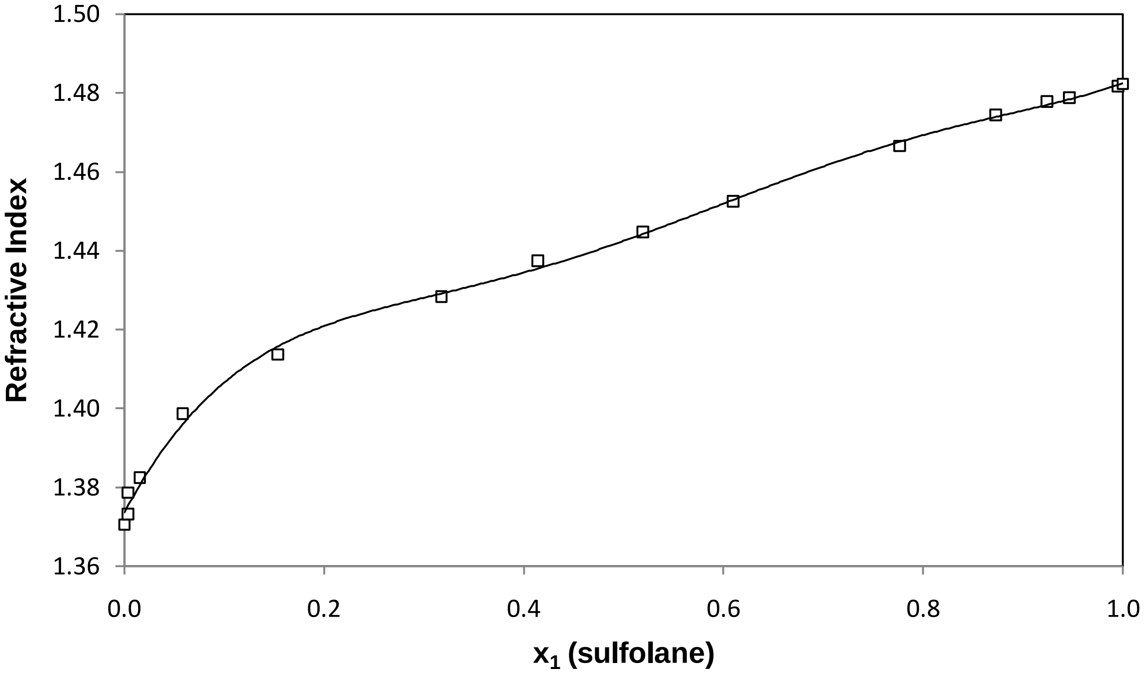

Figure 4.19 **Calibration curve for (sulfolane + pentanoic acid + hexane) system at 303.15 K.**

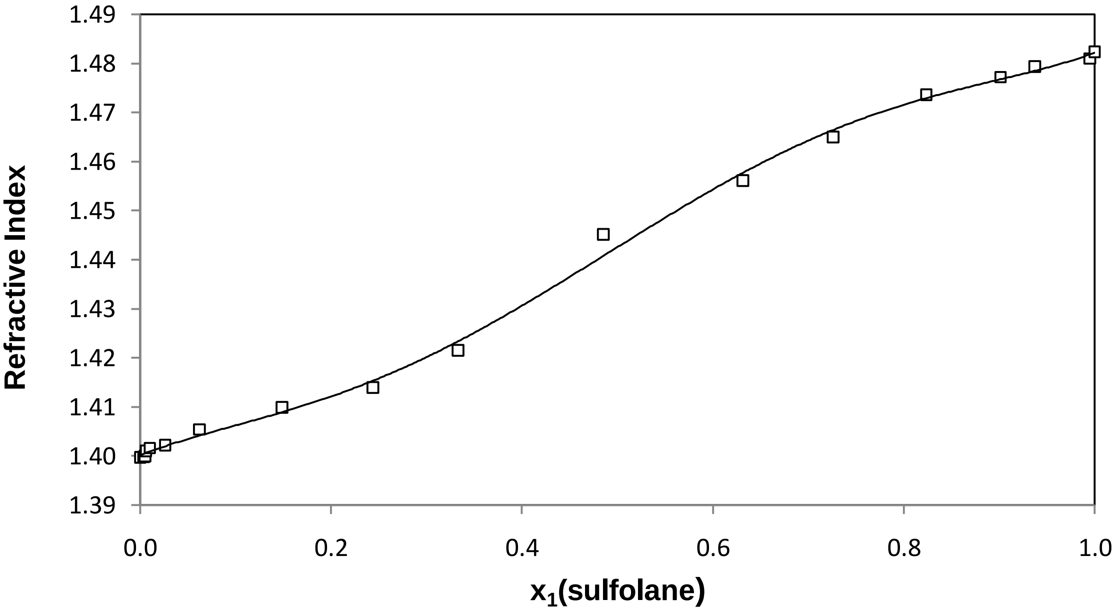

Figure 4.20 **Calibration curve for (sulfolane + 3-methylbutanoic acid + hexane) system at 303.15 K.**

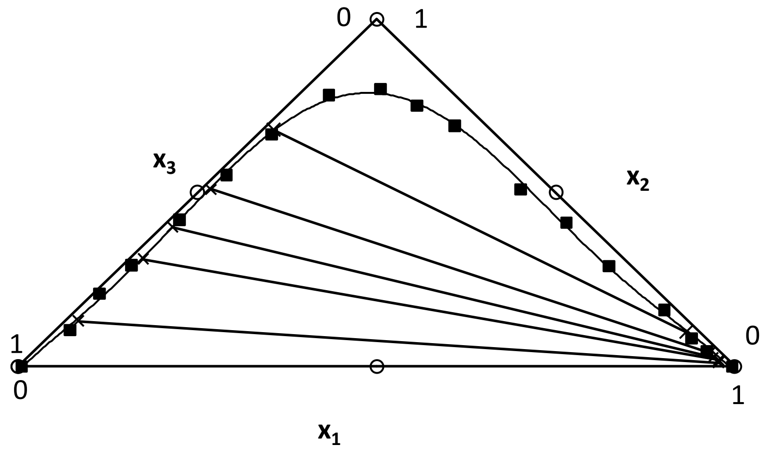

Figure 4.21 Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + acetic acid (2) + hexane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

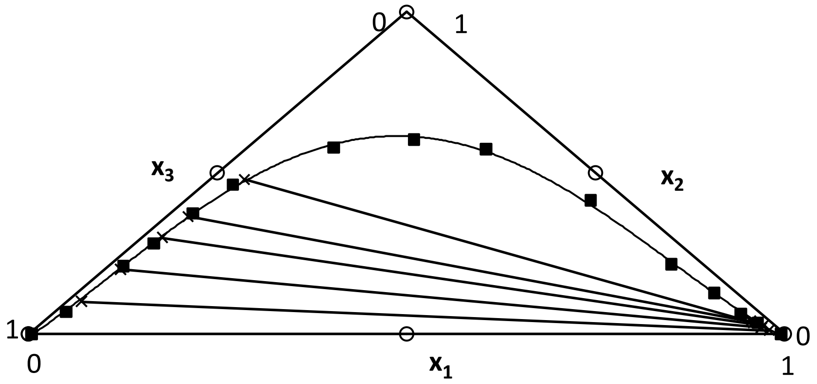

Figure 4.22 Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + propanoic acid (2) + hexane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

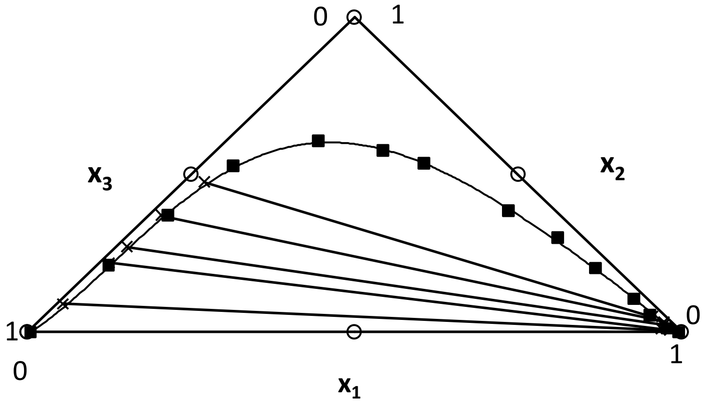

Figure 4.23 Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + butanoic acid (2) + hexane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

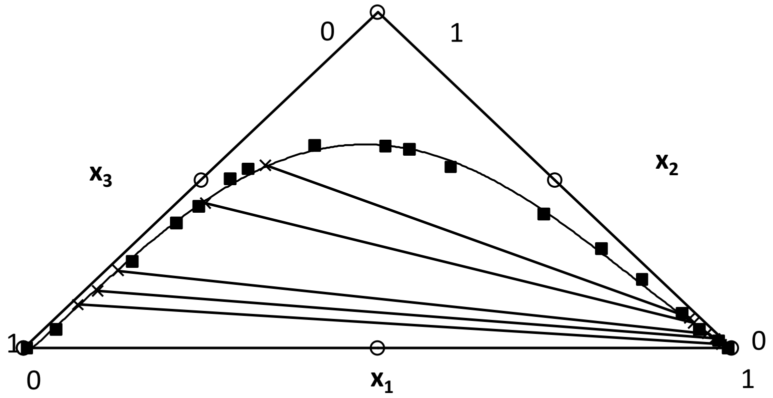

Figure 4.24 Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + 2-methylpropanoic acid (2) + hexane] (3) at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

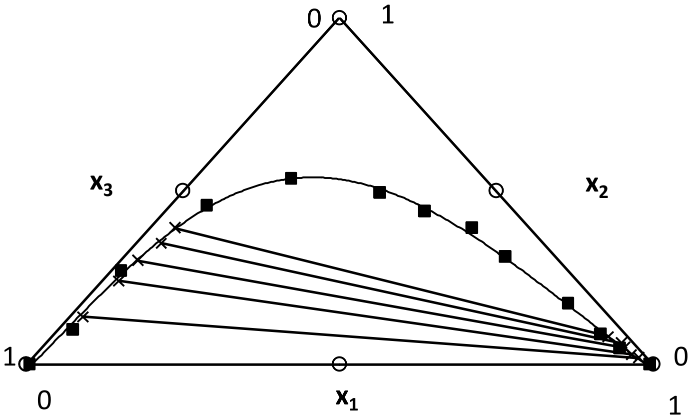

Figure 4.25 Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + pentanoic acid (2) + hexane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

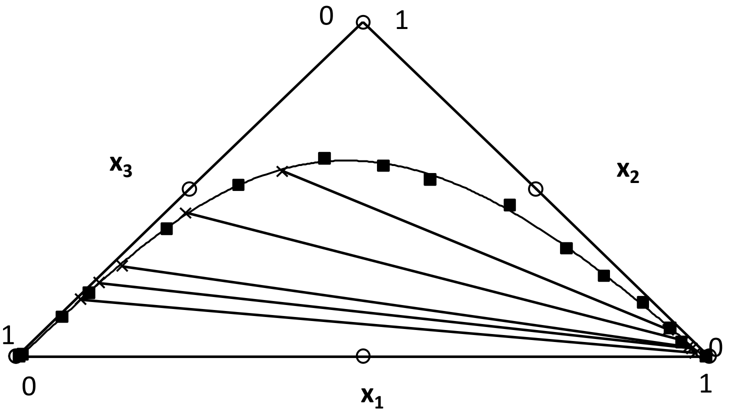

Figure 4.26 Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + 3-methylbutanoic acid (2) + hexane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

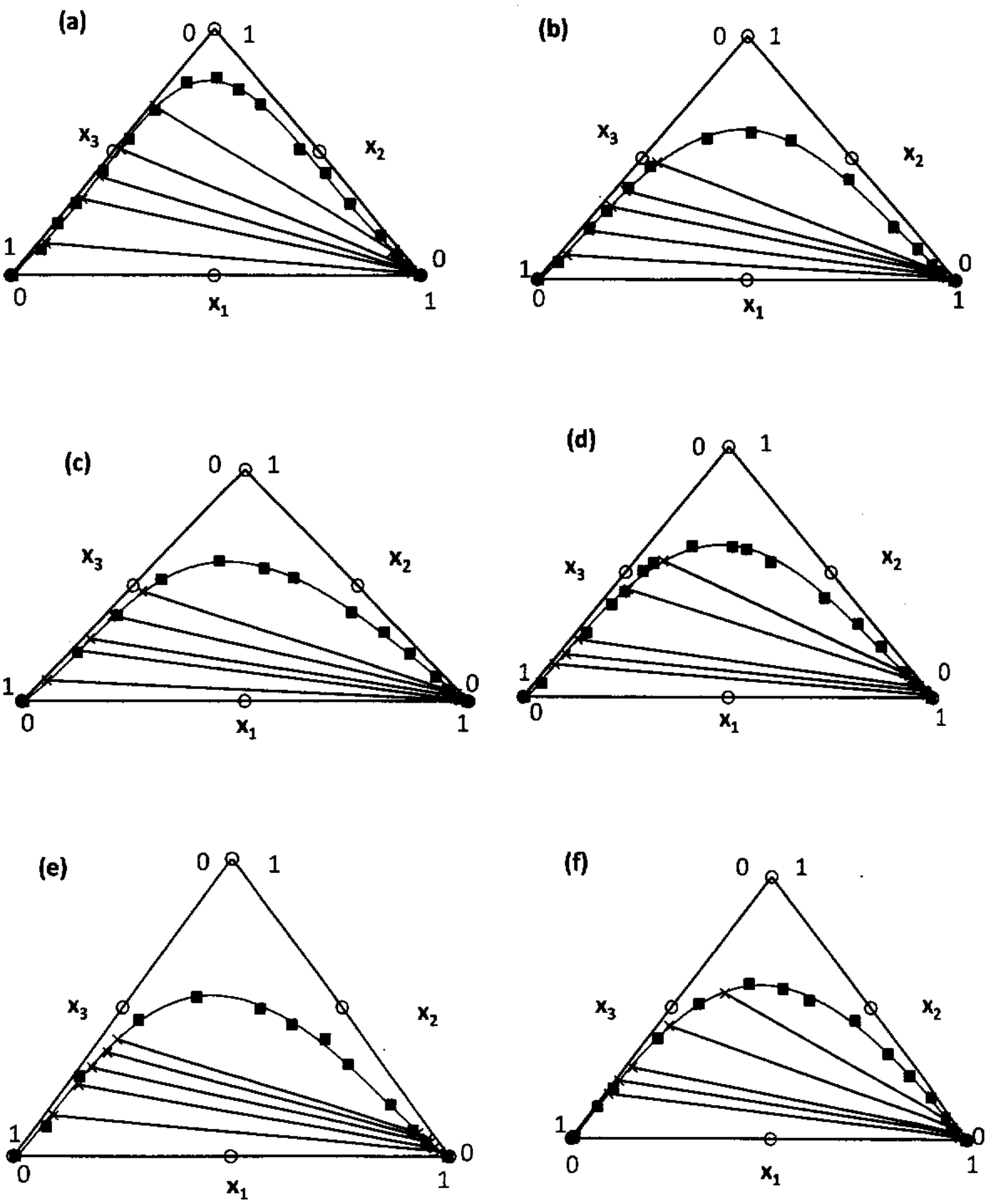

Figure 4.27 Summary of liquid-liquid equilibrium data for the following systems at 303.15 K: (a) sulfolane (1) + acetic acid (2) + hexane (3); (b) sulfolane (1) + propanoic acid (2) + hexane (3); (c) sulfolane (1) + butanoic acid (2) + hexane (3); (d) sulfolane (1) + 2-methylpropanoic acid (2) + hexane (3); (e) sulfolane (1) + pentanoic acid (2) + hexane (3); (f) sulfolane (1) + 3-methylbutanoic acid (2) + hexane (3). Key: (×) experimental tie-lines; (■) experimental points.

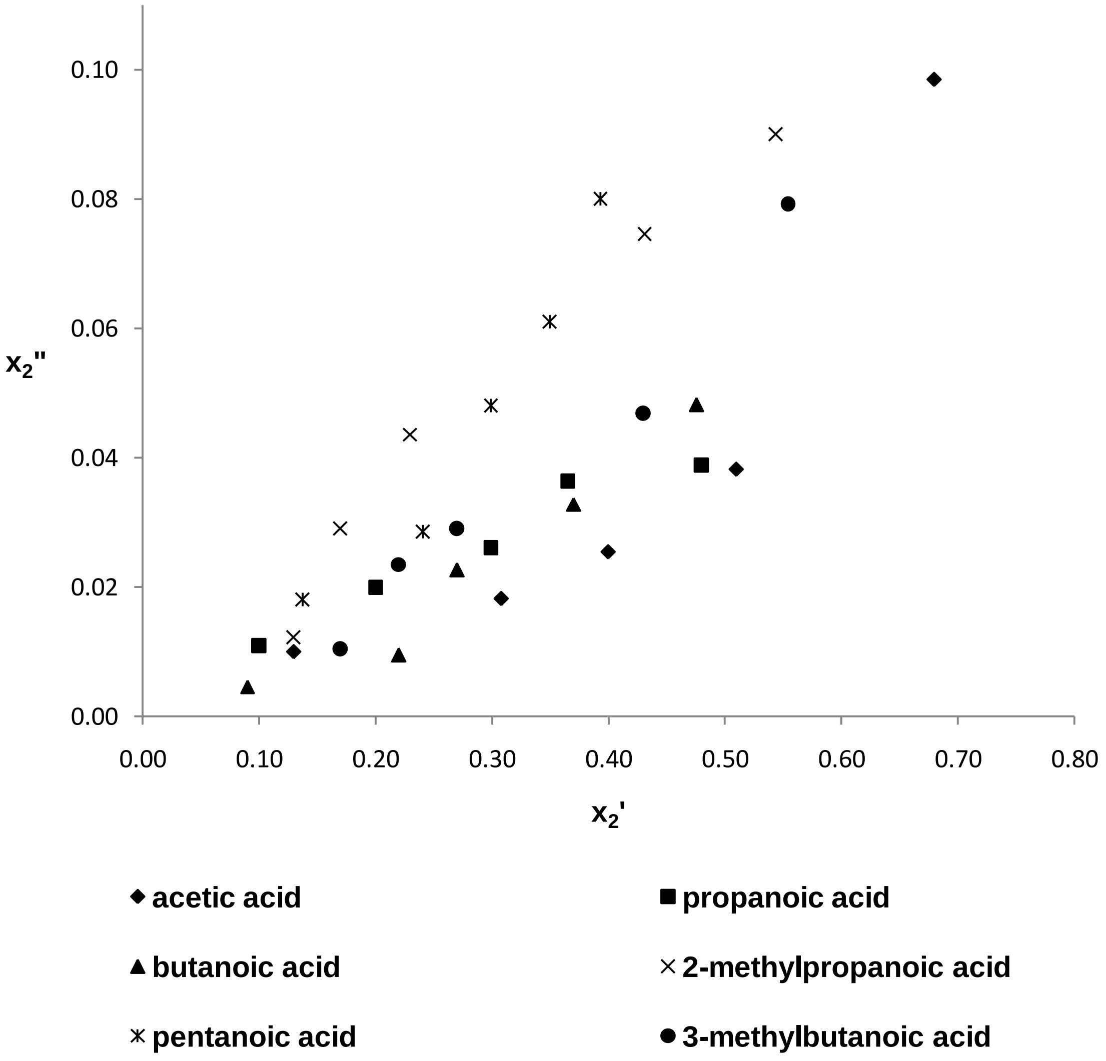

Figure 4.28 **A plot of x_2'' against x_2' showing the relative solubilities of the carboxylic acids in the sulfolane-rich and hexane-rich layers at 303.15 K.**

4.1.3 Liquid-liquid equilibria for mixtures of [sulfolane (1) + a carboxylic acids (2) + hexadecane (3)] at 303.15 K

Table 4.17 Physical properties of pure components at 303.15 K; Refractive Indices n_D.

	n_D	
Component	**exp**	**lit[a]**
Acetic acid	1.3716	1.3698
Propanoic acid	1.3829	1.3843
Butanoic acid	1.3947	1.3955
2-Methylpropanoic acid	1.3893	1.3917
Pentanoic acid	1.4047	1.4060
3-Methylbutanoic acid	1.3997	1.4022
Sulfolane	1.4823	1.4816
Hexadecane	1.4311	1.4340

[a] Riddick *et al.* (1986)

Table 4.18 Physical Properties of Pure Components at 303.15 K for NRTL and UNIQUAC Structural Parameters; Molar Volumes, V_{mi}, Volume and Surface Parameters, R and Q.

Component	V_{mi} ($cm^3.mol^{-1}$) [a]	R	Q
Acetic acid	57.72	2.202[c]	2.072[c]
Propanoic acid	75.48	2.877[c]	2.612[c]
Butanoic acid	93.21	3.551[b]	3.152[b]
2-Methylpropanoic acid	93.64	3.550[b]	3.148[b]
Pentanoic acid	109.76	4.226[b]	3.692[b]
3-Methylbutanoic acid	111.87	4.225[b]	3.688[b]
Sulfolane	95.28	4.038[d]	3.200[d]
Hexadecane	294.84	11.244[c]	9.256[c]

[a] Riddick *et al.* (1986)

[b] Gmehling *et al.* (1993)

[c] Santiago *et al*. (2010)

[d] Mahmoudi *et al.* (2010)

Table 4.19 **Calibration Curve Data at 303.15 K for the systems: [Sulfolane (1) + a Carboxylic acid (2) + Hexadecane (3)], Equilibrium Mole Fraction, x_1 and Refractive Index, n_D.**

x_1	n_D	x_1	n_D
Acetic Acid			
0.0000	1.4311	0.1244	1.4412
0.0030	1.4314	0.1955	1.4432
0.0080	1.4319	0.2726	1.4457
0.0110	1.4322	0.4605	1.4499
0.0130	1.4328	0.5749	1.4556
0.0140	1.4336	0.7140	1.4630
0.0150	1.4341	0.8322	1.4720
0.0156	1.4353	0.9077	1.4780
0.0157	1.4360	0.9530	1.4790
0.0315	1.4365	0.9950	1.4815
0.0618	1.4398	1.0000	1.4823
Propanoic Acid			
0.0000	1.4311	0.1638	1.4401
0.0030	1.4313	0.3431	1.4431
0.0100	1.4314	0.5230	1.4478
0.0120	1.4315	0.6260	1.4560
0.0130	1.4316	0.7328	1.4650
0.0140	1.4317	0.8437	1.4742
0.0150	1.4318	0.9209	1.4780
0.0190	1.4320	0.9475	1.4806
0.0261	1.4321	0.9950	1.4814
0.0653	1.4322	1.0000	1.4823
0.1419	1.4367		
Butanoic Acid			
0.0000	1.4311	0.2893	1.4427
0.0030	1.4313	0.3912	1.4437
0.0100	1.4314	0.6119	1.4501
0.0120	1.4316	0.6997	1.4573
0.0130	1.4322	0.7960	1.4649
0.0140	1.4332	0.9163	1.4766
0.0150	1.4341	0.9449	1.4793
0.0160	1.4355	0.9609	1.4802
0.0765	1.4370	0.9950	1.4816
0.1889	1.4412	1.0000	1.4823

Table 4.19 continued

x_1	n_D	x_1	n_D
	2-Methylpropanoic Acid		
0.0000	1.4311	0.2724	1.4420
0.0030	1.4312	0.3813	1.4465
0.0100	1.4314	0.5900	1.4511
0.0120	1.4319	0.6914	1.4574
0.0130	1.4322	0.8015	1.4668
0.0140	1.4332	0.8891	1.4739
0.0150	1.4338	0.9369	1.4782
0.0764	1.4367	0.9950	1.4811
0.1809	1.4397	1.0000	1.4823
	Pentanoic Acid		
0.0000	1.4311	0.2957	1.4398
0.0030	1.4312	0.4133	1.4415
0.0122	1.4313	0.6256	1.4547
0.0167	1.4314	0.7249	1.4625
0.0169	1.4315	0.8085	1.4691
0.0233	1.4316	0.9048	1.4761
0.0264	1.4317	0.9363	1.4789
0.0273	1.4319	0.9950	1.4810
0.0925	1.4336	1.0000	1.4823
0.1812	1.4340		
	3-Methylbutanoic Acid		
0.0000	1.4311	0.2451	1.4394
0.0030	1.4312	0.3889	1.4456
0.0122	1.4313	0.5664	1.4501
0.0162	1.4314	0.7009	1.4597
0.0169	1.4315	0.7951	1.4672
0.0230	1.4316	0.8636	1.4749
0.0264	1.4319	0.9445	1.4792
0.0325	1.4320	0.9950	1.4816
0.0749	1.4323	1.0000	1.4823
0.1617	1.4367		

Table 4.20 Compositions of Points on the Binodal Curve at 303.15 K for the systems: [Sulfolane (1) + a Carboxylic acid (2) + Hexadecane (3)], Equilibrium Mole Fraction, x_1 and x_2.

x_1	x_2	x_1	x_2
		Acetic Acid	
0.0030	0.0000	0.1044	0.8410
0.0090	0.0540	0.1955	0.7697
0.0095	0.1200	0.2926	0.6859
0.0110	0.7310	0.4905	0.4913
0.0130	0.6700	0.5749	0.4022
0.0140	0.5522	0.7040	0.2745
0.0150	0.4388	0.8242	0.1565
0.0156	0.3711	0.8974	0.0771
0.0157	0.8211	0.9329	0.0442
0.0415	0.8419	0.9950	0.0010
0.0618	0.9234		
		Propanoic Acid	
0.0030	0.0000	0.1419	0.7926
0.0100	0.0301	0.3431	0.6352
0.0120	0.2012	0.5230	0.4618
0.0130	0.3705	0.6260	0.3592
0.0140	0.4990	0.7328	0.2442
0.0150	0.5501	0.8237	0.1539
0.0190	0.6700	0.9209	0.0647
0.0261	0.7100	0.9475	0.0318
0.0653	0.7835	0.9950	0.0000
		Butanoic Acid	
0.0030	0.0000	0.1889	0.7064
0.0130	0.0650	0.2893	0.6615
0.0142	0.1500	0.3912	0.5774
0.0153	0.2331	0.6019	0.3737
0.0160	0.3001	0.6897	0.2794
0.0165	0.4101	0.7860	0.1902
0.0176	0.5422	0.9063	0.0645
0.0299	0.5762	0.9349	0.0401
0.0765	0.7017	0.9950	0.0061

Table 4.20 continued

x_1	x_2	x_1	x_2
	2-Methylpropanoic Acid		
0.0030	0.0000	0.2724	0.6800
0.0100	0.0650	0.3813	0.6008
0.0120	0.1550	0.5700	0.4005
0.0130	0.2331	0.6614	0.3019
0.0140	0.3001	0.7815	0.1894
0.0150	0.4101	0.8791	0.0985
0.0764	0.7243	0.9269	0.0493
0.1809	0.7317	0.9950	0.0000
	Pentanoic Acid		
0.0030	0.0000	0.2957	0.6247
0.0122	0.0620	0.4133	0.5492
0.0167	0.1531	0.6256	0.3611
0.0169	0.2433	0.7249	0.2648
0.0233	0.3201	0.8085	0.1763
0.0264	0.4201	0.9048	0.0827
0.0273	0.5666	0.9363	0.0467
0.0925	0.6983	0.9950	0.0000
0.1812	0.6997		
	3-Methylbutanoic Acid		
0.0030	0.0000	0.2451	0.6716
0.0122	0.0620	0.3889	0.5749
0.0162	0.1531	0.5664	0.4206
0.0169	0.2433	0.7009	0.2867
0.0230	0.3201	0.7951	0.1915
0.0264	0.4201	0.9031	0.0937
0.0325	0.5704	0.9445	0.0442
0.0749	0.6957	0.9950	0.0012
0.1617	0.7172		

Table 4.21 **Compositions of the Conjugate Solutions, x_1', x_2 'and x_1", x_2", at 303.15 K, Refractive Index, n_D.**

Hexadecane-rich phase			Sulfolane-rich phase		
x_1'	x_2'	n_D	x_1"	x_2"	n_D
Sulfolane (1) + Acetic Acid (2) + Hexadecane (3)					
0.0266	0.7900	1.4349	0.8799	0.0931	1.4429
0.0200	0.6600	1.4573	0.8885	0.0799	1.4481
0.0131	0.5811	1.4596	0.9101	0.0628	1.4503
0.0121	0.3880	1.4619	0.9294	0.0430	1.4626
0.0118	0.2000	1.4717	0.9495	0.0312	1.4718
Sulfolane (1) + Propanoic Acid (2) + Hexadecane (3)					
0.0350	0.7300	1.4475	0.9509	0.0512	1.4640
0.0204	0.6410	1.4448	0.9444	0.0401	1.4503
0.0194	0.5852	1.4438	0.9399	0.0340	1.4374
0.0173	0.4300	1.4358	0.9360	0.0303	1.4325
0.0122	0.2609	1.4319	0.9348	0.0215	1.4312
Sulfolane (1) + Butanoic Acid (2) + Hexadecane (3)					
0.0340	0.5890	1.4590	0.9303	0.0590	1.4769
0.0255	0.4700	1.4508	0.9290	0.0480	1.4754
0.0234	0.3550	1.4506	0.9192	0.0380	1.4688
0.0223	0.2504	1.4484	0.9426	0.0240	1.4619
0.0203	0.1508	1.4457	0.9691	0.0203	1.4544

Table 4.21 continued

Hexadecane-rich phase			Sulfolane-rich phase		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) + 2-Methylpropanoic Acid (2) + Hexadecane (3)					
0.0400	0.6660	1.4529	0.8335	0.1330	1.4512
0.0277	0.4046	1.4547	0.8794	0.0833	1.4525
0.0211	0.2680	1.4603	0.8991	0.0680	1.4591
0.0133	0.1600	1.4685	0.9263	0.0373	1.4681
0.0110	0.0800	1.4742	0.9522	0.0238	1.4743
Sulfolane (1) + Pentanoic Acid (2) + Hexadecane (3)					
0.0185	0.5550	1.4409	0.8807	0.1038	1.4485
0.0188	0.4851	1.4517	0.8940	0.0850	1.4518
0.0190	0.3800	1.4549	0.9106	0.0690	1.4613
0.0200	0.2300	1.4570	0.9389	0.0441	1.4648
0.0220	0.1500	1.4600	0.9591	0.0266	1.4712
Sulfolane (1) + 3-Methylbutanoic Acid (2) + Hexadecane (3)					
0.0289	0.6000	1.4484	0.8857	0.0995	1.4435
0.0231	0.5500	1.4509	0.8987	0.0855	1.4460
0.0220	0.4800	1.4627	0.9140	0.0750	1.4530
0.0198	0.3700	1.4641	0.9485	0.0447	1.4630
0.0199	0.1800	1.4696	0.9602	0.0300	1.4680

Table 4.22 Representative selectivity values of sulfolane for the separation of carboxylic acids from hexadecane at 303.15 K, using $\omega = (x_2/x_3)_{phase1} / (x_2/x_3)_{phase2}$

Carboxylic acid	Selectivity (ω)
Acetic acid	2.48
Propanoic acid	1.34
Butanoic acid	2.92
2-Methylpropanoic acid	5.39
Pentanoic acid	6.67
3-Methylbutanoic acid	7.97

Table 4.23 Coefficients A_i, B_i and C_i for Hlavaty, β and $\log\gamma$ at 303.15 K

Hlavatý	β	$\log\gamma$
Sulfolane (1) + Acetic Acid (2) + Hexadecane (3)		
A_1 = 1.472	A_1 = 3.223	A_1 = 4.451
A_2 = 1.034	A_2 = 1.091	A_2 = 1.032
A_3 = 5.289	A_3 =1.547	A_3 = 1.062
σ = 0.018	σ = 0.026	σ = 0.014
Sulfolane (1) + Propanoic Acid (2) + Hexadecane (3)		
A_1 = 1.501	B_1 = 4.957	C_1 = 4.079
A_2 = 1.497	B_2 = 1.409	C_2 = 1.341
A_3 = 7.184	B_3 = 1.351	C_3 = 1.793
σ = 0.019	σ = 0.022	σ = 0.029
Sulfolane (1) + Butanoic Acid (2) + Hexadecane (3)		
A_1 = 1.205	B_1 = 3.777	C_1 = 3.238
A_2 = 1.312	B_2 = 1.402	C_2 = 1.348
A_3 = 6.311	B_3 = 1.255	C_3 = 1.734
σ = 0.010	σ = 0.050	σ = 0.053
Sulfolane (1) + 2-Methylpropanoic Acid (2) + Hexadecane (3)		
A_1 = 1.268	B_1 = 4.865	C_1 = 4.151
A_2 = 1.443	B_2 = 1.435	C_2 = 1.376
A_3 = 6.657	B_3 = 1.351	C_3 = 1.837
σ = 0.017	σ = 0.019	σ = 0.023
Sulfolane (1) + Pentanoic Acid (2) + Hexadecane (3)		
A_1 = 1.095	B_1 = 4.33	C_1 = 3.735
A_2 = 0.918	B_2 = 1.318	C_2 = 1.266
A_3 = 5.573	B_3 = 1.332	C_3 = 1.779
σ = 0.015	σ = 0.016	σ = 0.020
Sulfolane (1) + 3-Methylbutanoic Acid (2) + Hexadecane (3)		
A_1 = 1.064	B_1 = 3.857	C_1 = 3.384
A_2 = 0.919	B_2 = 1.232	C_2 = 1.188
A_3 = 5.525	B_3 = 1.284	C_3 = 1.707
σ = 0.014	σ = 0.016	σ = 0.017

Table 4.24 Values of the Parameters for the NRTL Equation and the calculated Root Mean Square Deviation, rmsd[b], determined from ternary liquid-liquid equilibria for the system of [Sulfolane (1) + Carboxylic acids (2) + Hexadecane (3)].

	Parameters/ (J.mol^{-1})			
Component	**NRTL**[a]		**UNIQUAC**	
i-j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ij}
Sulfolane (1) + Acetic acid (2) + Hexadecane (3)				
	(0.005)		(0.345)	
1-2-2-1	1910.05	9345.13	0.25	0.37
1-3-3-1	4665.57	8973.56	-0.15	0.09
2-3-3-2	-2864.16	5205.99	-9.61	7.51
Sulfolane (1) + Propanoic acid (2) + Hexadecane (3)				
	(0.120)		(0.329)	
1-2-2-1	1878.23	2189.94	-0.35	7.25
1-3-3-1	1956.25	2351.23	5.12	-0.65
2-3-3-2	146.76	-215.77	3.37	0.85
Sulfolane (1) + Butanoic acid (2) + Hexadecane (3)				
	(0.103)		(0.337)	
1-2-2-1	2073.70	2664.91	-0.90	1.91
1-3-3-1	1930.50	2036.82	4.76	-2.01
2-3-3-2	4.45	443.88	1.90	-1.76

[a] Calculated with $\alpha_{ij} = 0.2$

[b] The rmsd are given in parenthesis

Table 4.24 continued

	Parameters/ (J.mol^{-1})			
Component	**NRTL**[a]		**UNIQUAC**	
i-j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ij}
Sulfolane (1) + 2-Methylpropanoic acid (2) + Hexadecane (3)				
	(0.002)		(0.356)	
1-2-2-1	1701.19	7169.19	-0.17	0.92
1-3-3-1	10187.54	71525.18	2.17	-0.07
2-3-3-2	-514.32	2869.39	0.92	3.10
Sulfolane (1) + Pentanoic acid (2) + Hexadecane (3)				
	(0.074)		(0.350)	
1-2-2-1	3264.06	-772.66	-0.12	4.13
1-3-3-1	2653.10	2739.19	-3.16	2.09
2-3-3-2	2345.74	2561.70	-1.85	0.98
Sulfolane (1) + 3-Methylbutanoic acid (2) + Hexadecane (3)				
	(0.105)		(0.329)	
1-2-2-1	1980.91	2857.25	2.56	-0.12
1-3-3-1	1692.71	1880.56	3.11	-2.01
2-3-3-2	-96.62	84.66	-0.91	1.90

[a] Calculated with $\alpha_{ij} = 0.2$

[b] The rmsd are given in parenthesis

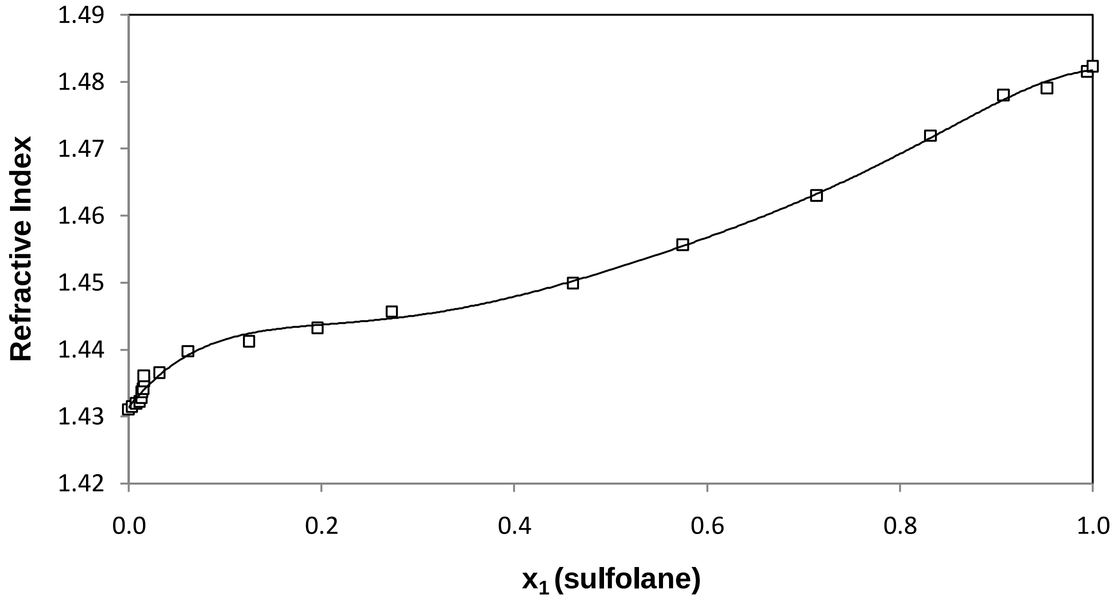

Figure 4.29 Calibration curve for (sulfolane + acetic acid + hexadecane) system at 303.15 K.

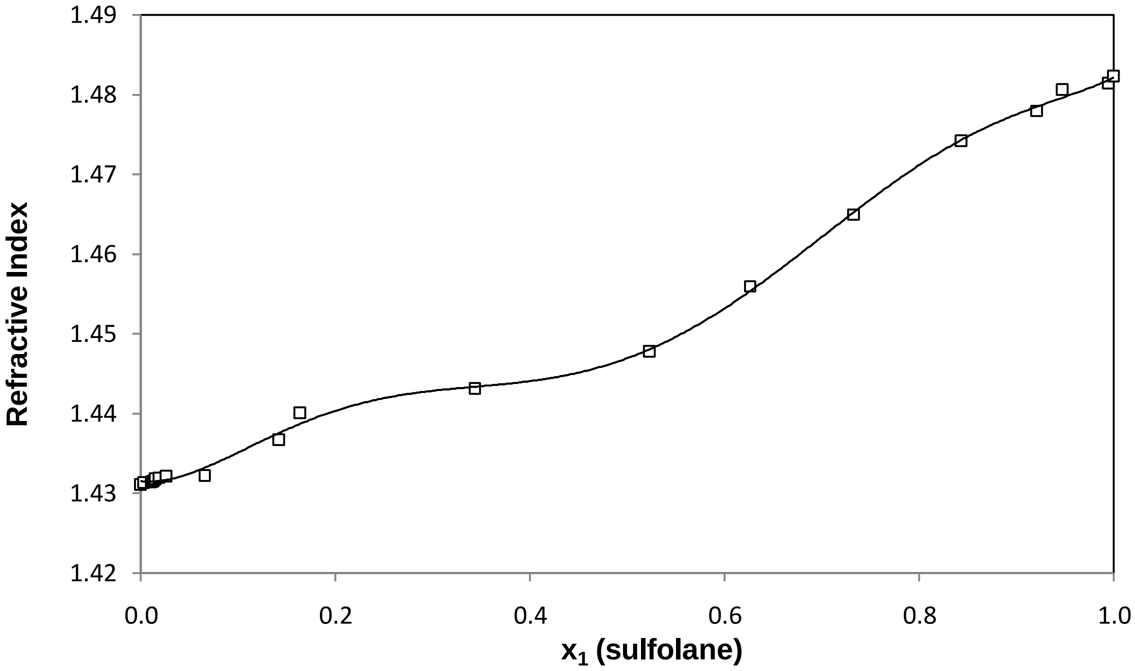

Figure 4.30 Calibration curve for (sulfolane + propanoic acid + hexadecane) system at 303.15 K.

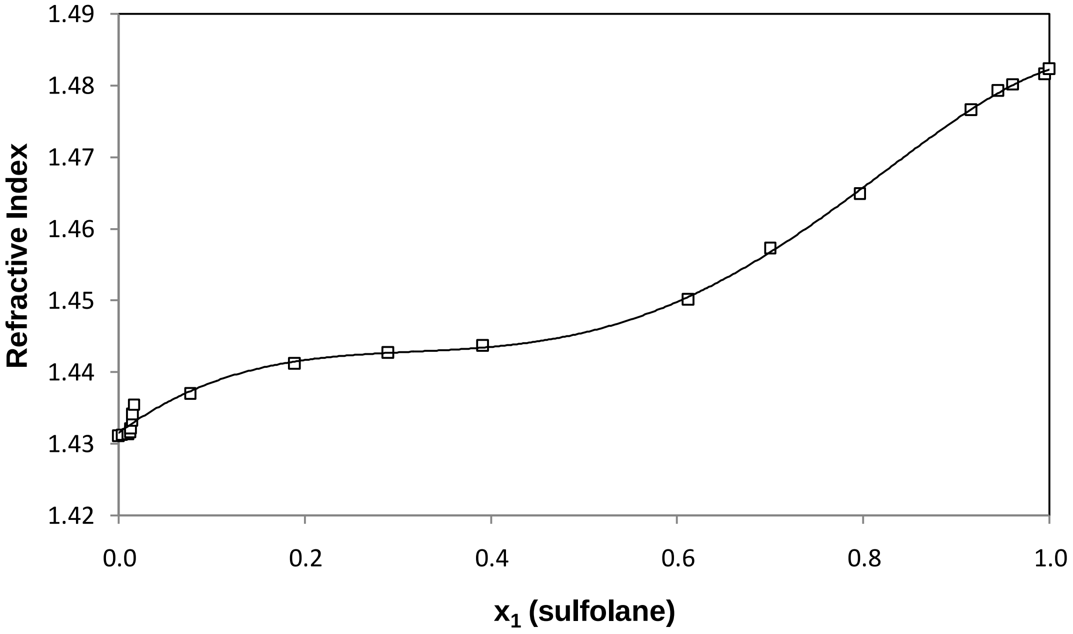

Figure 4.31 Calibration curve for (sulfolane + butanoic acid + hexadecane) system at 303.15 K.

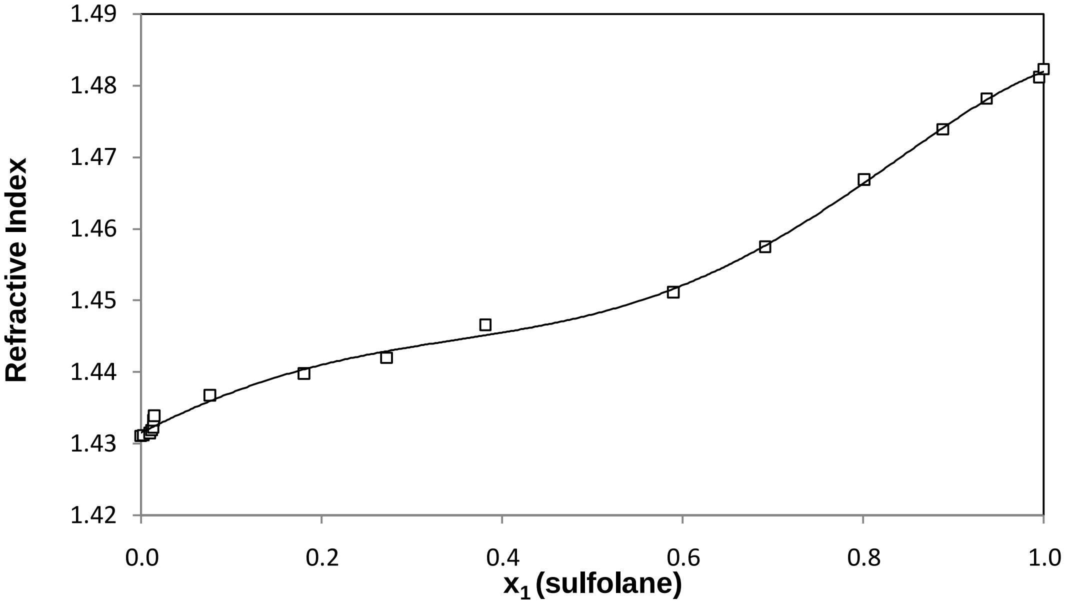

Figure 4.32 Calibration curve for (sulfolane + 2-methylpropanoic acid + hexadecane) system at 303.15 K.

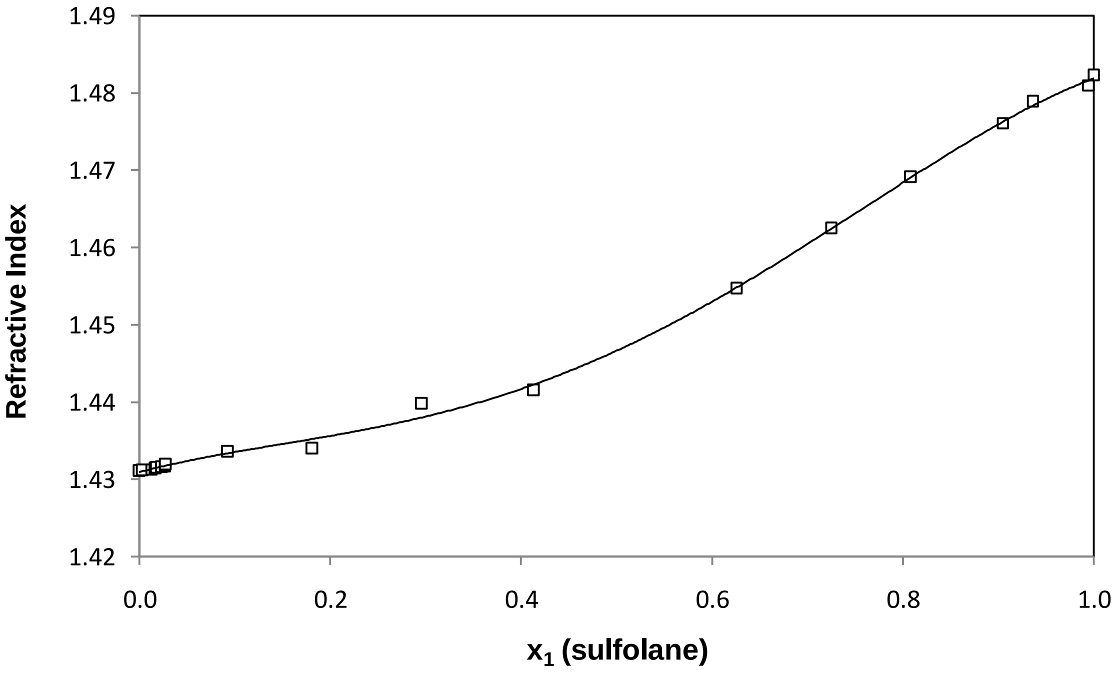

Figure 4.33 Calibration curve for (sulfolane + pentanoic acid + hexadecane) system at 303.15 K.

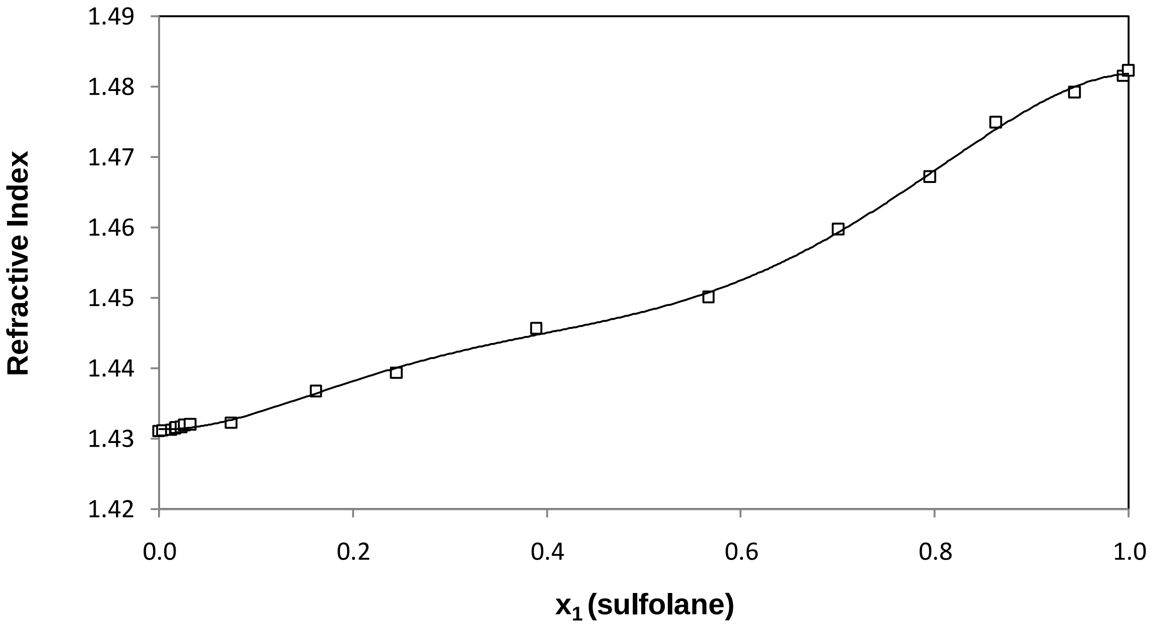

Figure 4.34 Calibration curve for (sulfolane + 3-methylbutanoic acid + hexadecane) system at 303.15 K.

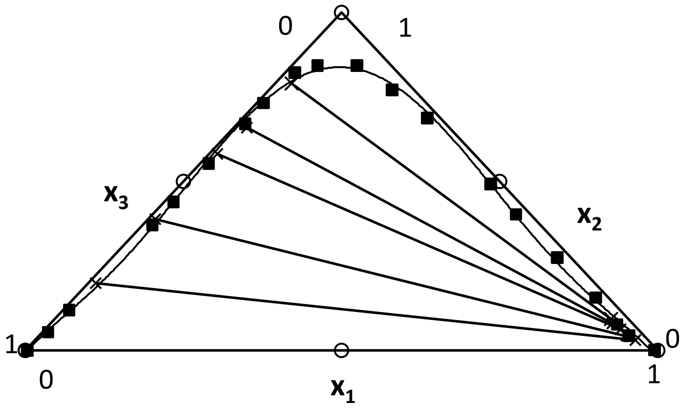

Figure 4.35 **Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + acetic acid (2) + hexadecane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.**

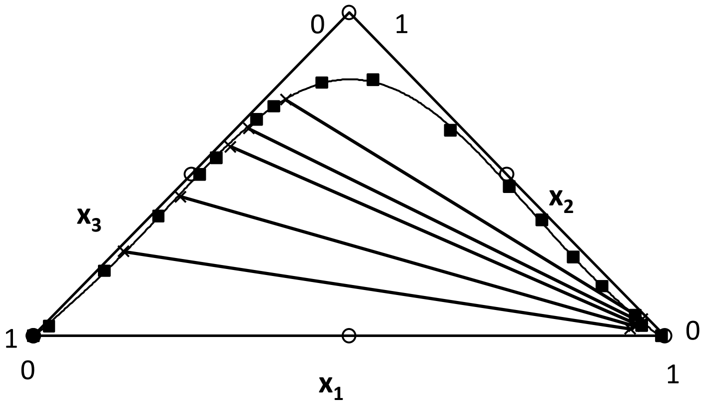

Figure 4.36 **Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + propanoic acid (2) + hexadecane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.**

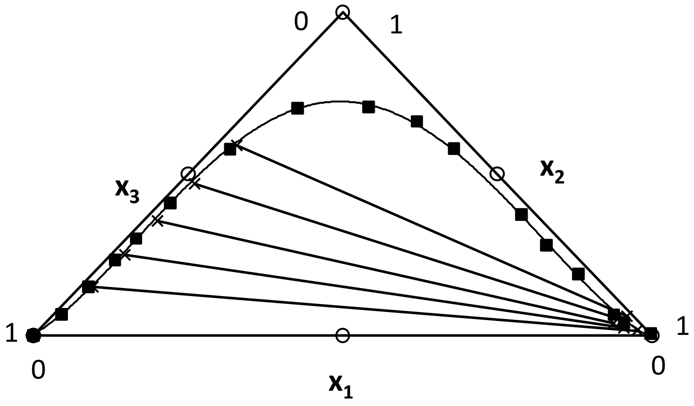

Figure 4.37 Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + butanoic acid (2) + hexadecane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

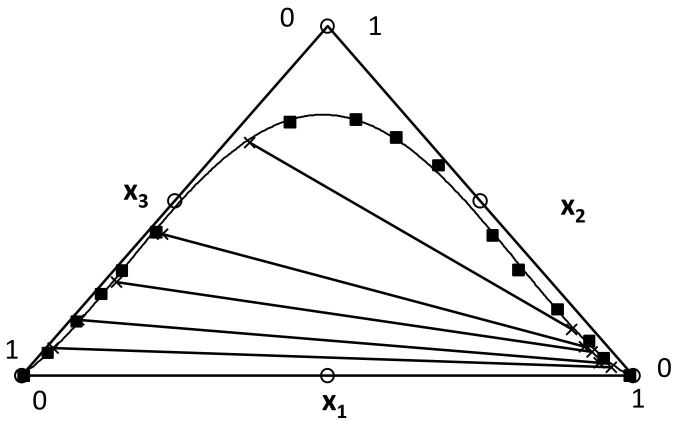

Figure 4.38 Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + 2-methylpropanoic acid (2) + hexadecane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

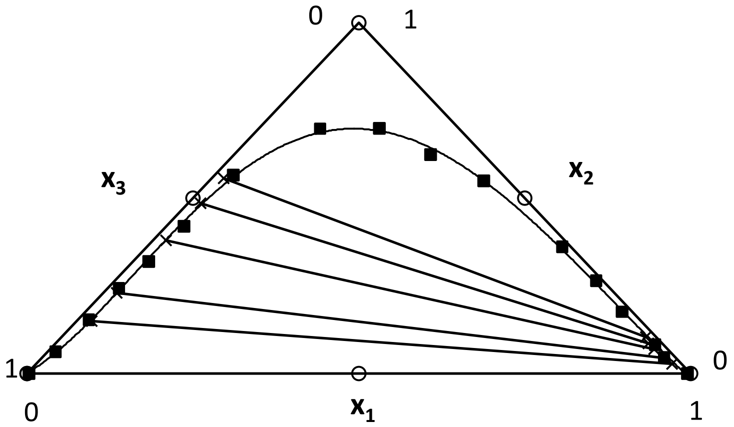

Figure 4.39 Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + pentanoic acid (2) + hexadecane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

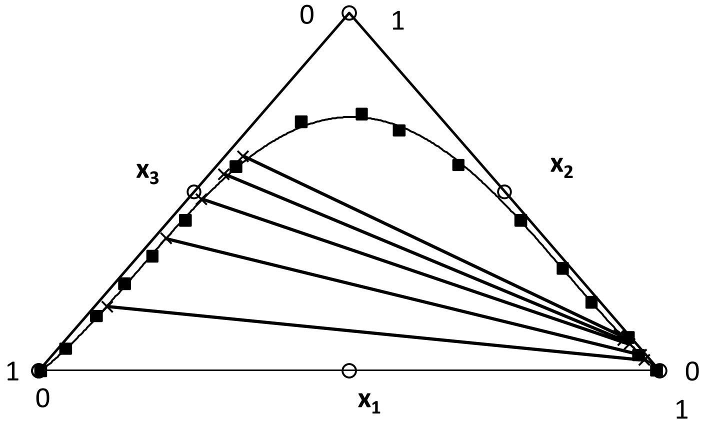

Figure 4.40 Binodal curve for the liquid-liquid equilibrium data for the system: [Sulfolane (1) + 3-methylbutanoic acid (2) + hexadecane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

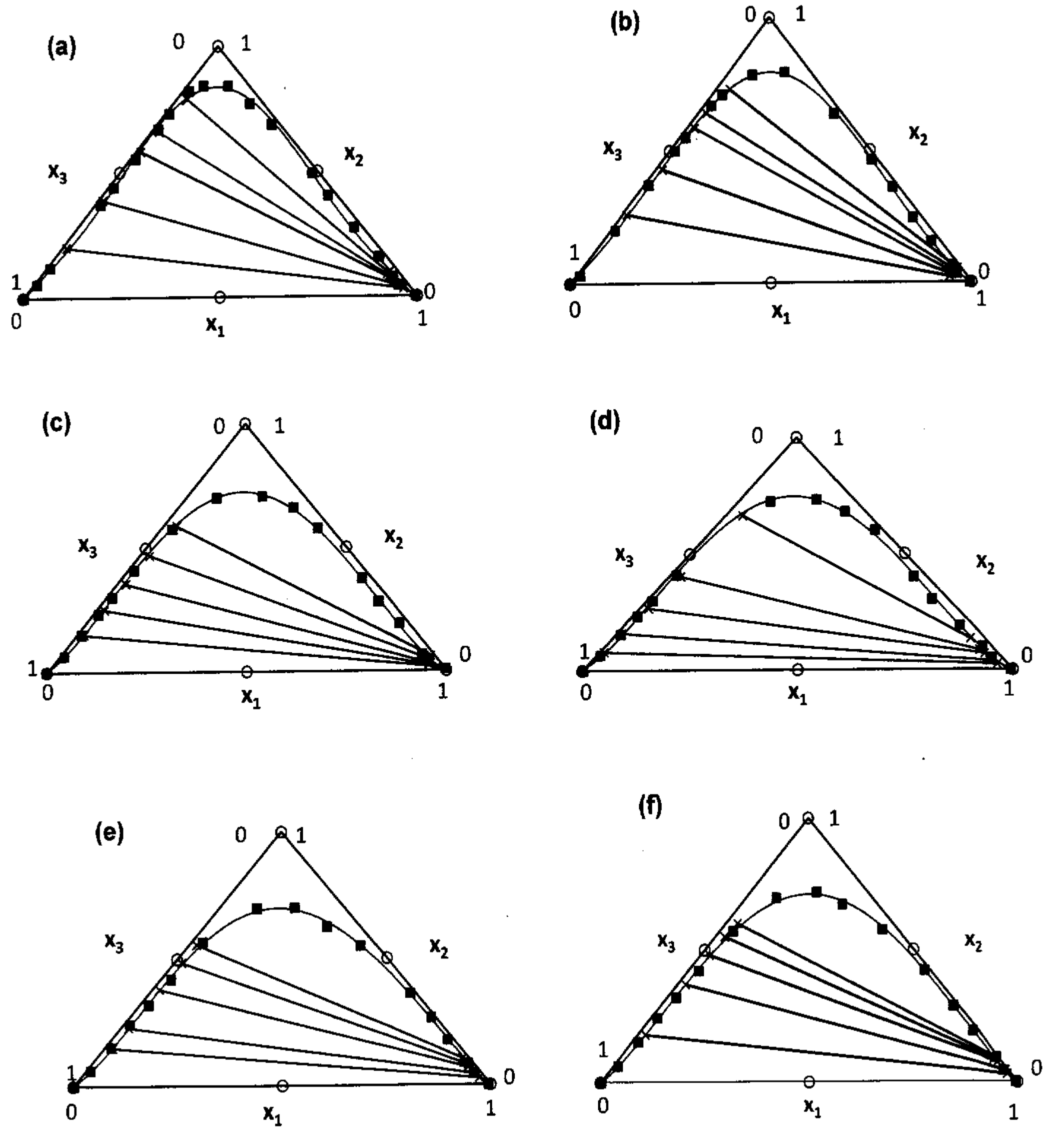

Figure 4.41 Summary of liquid-liquid equilibrium data for the following systems at 303.15 K: (a) sulfolane (1) + acetic acid (2) + hexadecane (3); (b) sulfolane (1) + propanoic acid (2) + hexadecane (3); (c) sulfolane (1) + butanoic acid (2) + hexadecane (3); (d) sulfolane (1) + 2-methylpropanoic acid (2) + hexadecane (3); (e) sulfolane (1) + pentanoic acid (2) + hexadecane (3); (f) sulfolane (1) + 3-methylbutanoic acid (2) + hexadecane (3). Key: (×) experimental tie-lines; (■) experimental points.

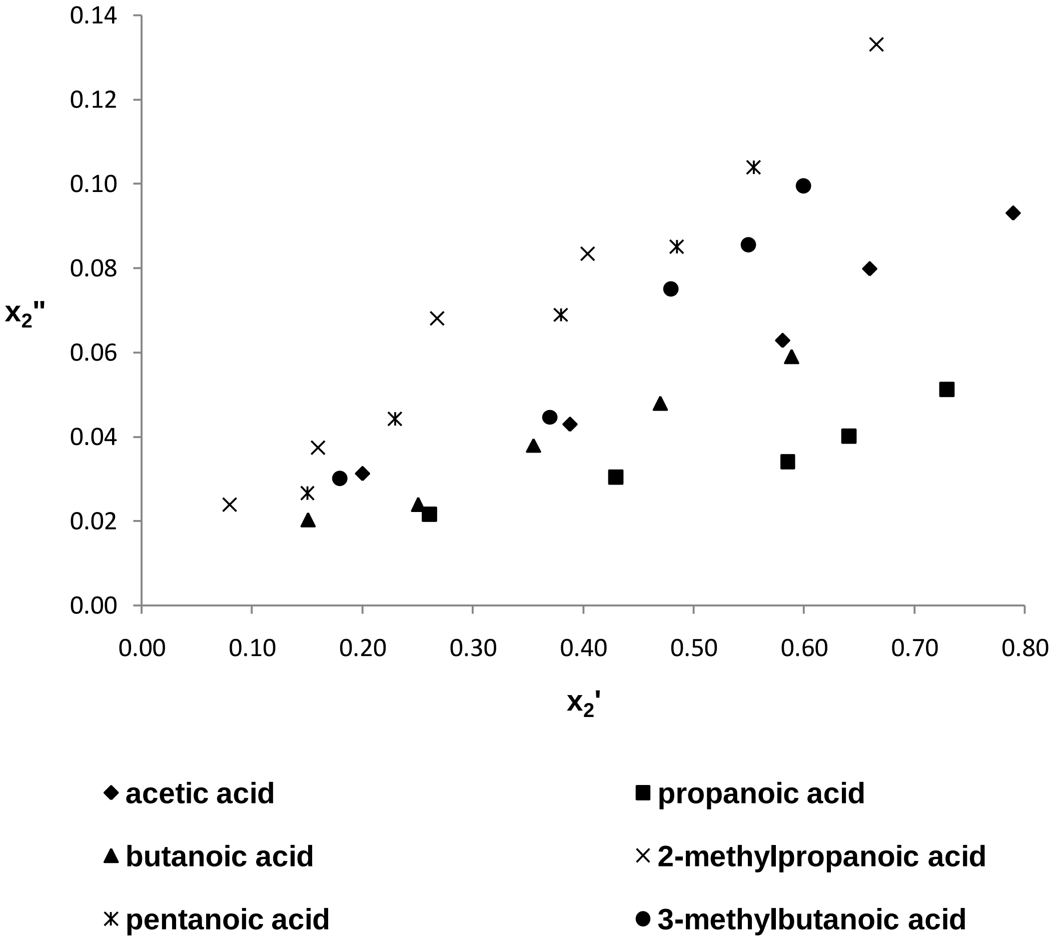

Figure 4.42 A plot of x_2'' against x_2' showing the relative solubilities of the carboxylic acids in the sulfolane-rich and hexadecane-rich layers at 303.15 K.

4.1.3 Liquid-liquid equilibria for mixtures of [acetonitrile (1) + a carboxylic acid (2) + dodecane (3)] at 303.15 K.

Table 4.25 Physical properties of pure components at 303.15 K; Refractive Indices n_D.

	n_D	
Component	**exp**	**lit**[a]
Acetic acid	1.3716	1.3698
Propanoic acid	1.3829	1.3843
Butanoic acid	1.3947	1.3955
2-Methylpropanoic acid	1.3893	1.3917
Pentanoic acid	1.4047	1.4060
3-Methylbutanoic acid	1.3997	1.4022
Acetonitrile	1.3396	1.3416
Dodecane	1.4181	1.4195

[a] Riddick *et al.* (1986)

Table 4.26 Physical Properties of Pure Components at 303.15 K for NRTL and UNIQUAC Structural Parameters; Molar Volumes, V_{mi}, Volume and Surface Parameters, R and Q.

Component	V_{mi} ($cm^3.mol^{-1}$)[a]	R	Q
Acetic acid	57.72	2.202[c]	2.072[c]
Propanoic acid	75.48	2.877[c]	2.612[c]
Butanoic acid	93.21	3.551[b]	3.152[b]
2-Methylpropanoic acid	93.64	3.550[b]	3.148[b]
Pentanoic acid	109.76	4.226[b]	3.692[b]
3-Methylbutanoic acid	111.87	4.225[b]	3.688[b]
Acetonitrile	52.87	1.870[b]	1.724[b]
Dodecane	229.49	8.546[c]	7.096[c]

[a] Riddick *et al.* (1986)

[b] Gmehling *et al.* (1993)

[c] Santiago *et al*. (2010)

Table 4.27 **Calibration Curve Data at 303.15 K for the systems: [Acetonitrile (1) + a Carboxylic acid (2) + Dodecane (3)], Equilibrium Mole Fraction, x_1 and Refractive Index, n_D.**

x_1	n_D	x_1	n_D
Acetic Acid			
0.0000	1.4181	0.3011	1.3630
0.0400	1.4173	0.3959	1.3611
0.0500	1.4170	0.5893	1.3590
0.0520	1.4164	0.6851	1.3534
0.0620	1.4155	0.7871	1.3491
0.0654	1.4129	0.8817	1.3454
0.0701	1.4099	0.9269	1.3410
0.1401	1.3954	0.9560	1.3402
0.1702	1.3844	1.0000	1.3396
0.2000	1.3789		
Propanoic Acid			
0.0000	1.4181	0.4643	1.3736
0.0400	1.4153	0.6678	1.3650
0.0510	1.4132	0.7608	1.3600
0.0600	1.4092	0.8402	1.3540
0.0700	1.4081	0.9178	1.3485
0.2062	1.3901	0.9560	1.3428
0.3509	1.3780	1.0000	1.3396
Butanoic Acid			
0.0000	1.4181	0.4972	1.3800
0.0400	1.4156	0.6985	1.3664
0.0450	1.4138	0.7968	1.3602
0.0500	1.4096	0.8696	1.3534
0.0600	1.4072	0.9241	1.3476
0.1344	1.4043	0.9545	1.3444
0.1777	1.4011	0.9560	1.3427
0.3541	1.3850	1.0000	1.3396

Table 4.27 continued

x_1	n_D	x_1	n_D
2-Methylpropanoic Acid			
0.0000	1.4181	0.7414	1.3647
0.0400	1.4163	0.7925	1.3587
0.0600	1.4132	0.8718	1.3524
0.0900	1.4067	0.9317	1.3468
0.1822	1.4011	0.9455	1.3445
0.3607	1.3863	0.9560	1.3425
0.4972	1.3798	1.0000	1.3396
Pentanoic Acid			
0.0000	1.4181	0.7327	1.3717
0.0400	1.4164	0.7988	1.3646
0.0500	1.4154	0.8719	1.3572
0.0600	1.4133	0.9252	1.3498
0.0800	1.4098	0.9426	1.3450
0.1798	1.4032	0.9560	1.3430
0.3516	1.3965	1.0000	1.3396
0.5099	1.3893		
3-Methylbutanoic Acid			
0.0000	1.4181	0.7144	1.3727
0.0400	1.4164	0.7687	1.3679
0.0500	1.4154	0.8962	1.3559
0.0600	1.4133	0.9522	1.3510
0.1255	1.4098	0.9535	1.3482
0.2661	1.3982	0.9560	1.3440
0.4548	1.3890	1.0000	1.3396
0.6224	1.3760		

Table 4.28 Compositions of Points on the Binodal Curve at 303.15 K for the systems: [Acetonitrile (1) + a Carboxylic acid (2) + Dodecane (3)], Equilibrium Mole Fraction, x_1 and x_2.

x_1	x_2	x_1	x_2
Acetic Acid			
0.0400	0.0000	0.3011	0.6645
0.0510	0.1501	0.3959	0.5713
0.0520	0.3100	0.5893	0.3711
0.0532	0.5203	0.6851	0.2787
0.0654	0.7011	0.7871	0.1766
0.0990	0.7111	0.8817	0.0830
0.1401	0.7121	0.9269	0.0361
0.1702	0.7701	0.9560	0.0000
0.2400	0.7260		
Propanoic Acid			
0.0400	0.0000	0.3509	0.5810
0.0420	0.0160	0.4643	0.4946
0.0510	0.1850	0.6678	0.3130
0.0540	0.2700	0.7608	0.2204
0.0600	0.4202	0.8402	0.1390
0.0700	0.5011	0.9178	0.0625
0.1240	0.5600	0.9560	0.0200
0.2062	0.5885		
Butanoic Acid			
0.0400	0.0000	0.3541	0.4911
0.0420	0.0500	0.4972	0.4251
0.0430	0.1200	0.6985	0.2662
0.0450	0.2766	0.7699	0.1868
0.0500	0.3411	0.8556	0.1155
0.0600	0.4200	0.9124	0.0554
0.1344	0.4811	0.9545	0.0262
0.1777	0.4860	0.9560	0.0125
0.2254	0.4900		

Table 4.28 continued

x_1	x_2	x_1	x_2
2-Methylpropanoic Acid			
0.0400	0.0000	0.7414	0.2325
0.0600	0.2211	0.7925	0.1793
0.0900	0.3511	0.8718	0.1044
0.1822	0.4407	0.9000	0.0523
0.3607	0.4723	0.9355	0.0296
0.4972	0.4289	0.9560	0.0120
Pentanoic Acid			
0.0400	0.0000	0.7327	0.2347
0.0500	0.0720	0.7988	0.1734
0.0600	0.2311	0.8719	0.1000
0.0800	0.3504	0.9252	0.0400
0.1798	0.4025	0.9342	0.0238
0.3516	0.4236	0.9549	0.0113
0.5099	0.3731	0.9560	0.0100
3-Methylbutanoic Acid			
0.0400	0.0000	0.6090	0.3352
0.0500	0.0726	0.7400	0.2205
0.0600	0.1633	0.8700	0.0903
0.1255	0.3153	0.9522	0.0339
0.2661	0.3509	0.9531	0.0224
0.4045	0.3506	0.9545	0.0111
0.5322	0.3501	0.9560	0.0100

Table 4.29 Compositions of the Conjugate Solutions, x_1', x_2 'and x_1", x_2", at 303.15 K, Refractive Index, n_D.

Dodecane-rich phase			Acetonitrile-rich phase		
x_1'	x_2 '	n_D	x_1"	x_2"	n_D
Acetonitrile (1) + Acetic Acid (2) + Dodecane (3)					
0.0459	0.0971	1.3567	0.3590	0.6100	1.3619
0.0457	0.0778	1.3557	0.4985	0.4710	1.3556
0.0419	0.0650	1.3521	0.6806	0.2830	1.3521
0.0400	0.0383	1.3488	0.7992	0.1648	1.3489
0.0397	0.0211	1.3417	0.9012	0.0600	1.3435
Acetonitrile (1) + Propanoic Acid (2) + Dodecane (3)					
0.0460	0.0800	1.3851	0.3930	0.5400	1.3856
0.0464	0.0648	1.3780	0.4624	0.4896	1.3782
0.0469	0.0534	1.3743	0.6792	0.2990	1.3718
0.0474	0.0408	1.3667	0.8058	0.1780	1.3621
0.0477	0.0300	1.3621	0.8754	0.0999	1.3565
Acetonitrile (1) + Butanoic Acid (2) + Dodecane (3)					
0.0393	0.0825	1.3867	0.3762	0.4800	1.3779
0.0371	0.0669	1.3815	0.5559	0.3800	1.3649
0.0412	0.0570	1.3745	0.7115	0.2470	1.3593
0.0435	0.0386	1.3723	0.7901	0.1780	1.3530
0.0482	0.0235	1.3656	0.8675	0.0998	1.3473

Table 4.29 continued

Dodecane-rich phase			Acetonitrile-rich phase		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Acetonitrile (1) + 2-Methylpropanoic Acid (2) + Dodecane (3)					
0.0805	0.0756	1.3903	0.5276	0.3997	1.3773
0.0459	0.0589	1.3867	0.6107	0.3401	1.3734
0.0452	0.0424	1.3815	0.7693	0.2103	1.3626
0.0419	0.0236	1.3745	0.8026	0.1750	1.3579
0.0395	0.0148	1.3723	0.8771	0.0990	1.3519
Acetonitrile (1) + Pentanoic Acid (2) + Dodecane (3)					
0.0158	0.0850	1.4101	0.6594	0.2900	1.4099
0.0382	0.0832	1.4037	0.4217	0.4100	1.3826
0.0398	0.0523	1.3986	0.7169	0.2400	1.3678
0.0424	0.0340	1.3932	0.8124	0.1600	1.3617
0.0487	0.0118	1.3856	0.8640	0.1000	1.3556
Acetonitrile (1) + 3-Methylbutanoic Acid (2) + Dodecane (3)					
0.0467	0.0890	1.3998	0.5400	0.3438	1.3795
0.0465	0.0741	1.3845	0.6891	0.2600	1.3768
0.0462	0.0637	1.3721	0.7731	0.1931	1.3656
0.0450	0.0506	1.3676	0.8401	0.1320	1.3592
0.0422	0.0365	1.3632	0.9100	0.0600	1.3534

Table 4.30 Representative selectivity values of acetonitrile for the separation of carboxylic acids from dodecane at 303.15 K, using $\omega = (x_2/x_3)_{phase1} / (x_2/x_3)_{phase2}$

Carboxylic acid	Selectivity (ω)
Acetic acid	126
Propanoic acid	166
Butanoic acid	92
2-Methylpropanoic acid	5
Pentanoic acid	112
3-Methylbutanoic acid	61

Table 4.31 Coefficients A_i, B_i and C_i for Hlavatý, β and $\log\gamma$ at 303.15K

Hlavatý	β	$\log\gamma$
Acetonitrile (1) + Acetic Acid (2) + Dodecane (3)		
$A_1 = 1.472$	$B_1 = 3.275$	$C_1 = 3.075$
$A_2 = 1.067$	$B_2 = 1.069$	$C_2 = 1.052$
$A_3 = 6.435$	$B_3 = 1.224$	$C_3 = 1.636$
$\sigma = 0.022$	$\sigma = 0.040$	$\sigma = 0.038$
Acetonitrile (1) + Propanoic Acid (2) + Dodecane (3)		
$A_1 = 0.425$	$B_1 = 1.940$	$C_1 = 1.746$
$A_2 = -0.096$	$B_2 = 0.768$	$C_2 = 0.741$
$A_3 = -2.875$	$B_3 = 1.035$	$C_3 = 1.272$
$\sigma = 0.012$	$\sigma = 0.032$	$\sigma = 0.029$
Acetonitrile (1) + Butanoic Acid (2) + Dodecane (3)		
$A_1 = 0.008$	$A_1 = 1.052$	$A_1 = 1.030$
$A_2 = -0.114$	$A_2 = 1.003$	$A_2 = 1.414$
$A_3 = 0.842$	$A_3 = 1.022$	$A_3 = 0.976$
$\sigma = 0.012$	$\sigma = 0.015$	$\sigma = 0.017$
Acetonitrile (1) + 2-Methylpropanoic Acid (2) + Dodecane (3)		
$A_1 = 0.031$	$B_1 = 1.503$	$C_1 = 1.457$
$A_2 = -0.373$	$B_2 = 0.817$	$C_2 = 0.809$
$A_3 = 1.472$	$B_3 = 0.892$	$C_3 = 1.224$
$\sigma = 0.011$	$\sigma = 0.016$	$\sigma = 0.016$
Acetonitrile (1) + Pentanoic Acid (2) + Dodecane (3)		
$A_1 = -0.133$	$A_1 = 0.781$	$A_1 = 1.295$
$A_2 = -0.124$	$A_2 = 1.212$	$A_2 = 0.922$
$A_3 = 0.452$	$A_3 = 1.005$	$A_3 = 0.843$
$\sigma = 0.002$	$\sigma = 0.041$	$\sigma = 0.005$
Acetonitrile (1) + 3-Methylbutanoic Acid (2) + Dodecane (3)		
$A_1 = -0.1766$	$B_1 = 0.812$	$C_1 = 0.811$
$A_2 = -0.185$	$B_2 = 0.913$	$C_2 = 0.612$
$A_3 = 0.412$	$B_3 = 0.755$	$C_3 = 1.239$
$\sigma = 0.004$	$\sigma = 0.005$	$\sigma = 0.005$

Table 4.32 Values of the Parameters for the NRTL Equation and the calculated Root Mean Square Deviation, rmsd[b], determined from ternary liquid-liquid equilibria for the system of [Acetonitrile (1) + Carboxylic acids (2) + Dodecane (3)].

Component	Parameters/ (J.mol^{-1})			
	NRTL[a]		UNIQUAC	
i-j	$g_{ij} – g_{jj}$	$g_{ji} – g_{ii}$	Δu_{ij}	Δu_{ij}
Acetonitrile (1) + Acetic acid (2) + Dodecane (3)				
	(0.003)		(0.277)	
1-2-2-1	2274.09	1539.79	-30.35	59.15
1-3-3-1	5364.93	5017.04	601.55	90.85
2-3-3-2	10592.40	1892.19	455.42	66.28
Acetonitrile (1) + Propanoic acid (2) + Dodecane (3)				
	(0.002)		(0.253)	
1-2-2-1	3016.61	946.99	-3.41	9.98
1-3-3-1	9005.87	3882.88	0.25	-0.15
2-3-3-2	3966.18	4159.47	2.64	3.01
Acetonitrile (1) + Butanoic acid (2) + Dodecane (3)				
	(0.002)		(0.269)	
1-2-2-1	-1090.18	9975.74	-5.26	-11.16
1-3-3-1	7839.07	4506.43	-0.81	-0.12
2-3-3-2	1932.45	6355.29	-7.62	10.61

[a] Calculated with $\alpha_{ij} = 0.2$

[b] The rmsd are given in parenthesis

Table 4.32 continued

	Parameters/ (J.mol^{-1})			
Component	**NRTL**[a]		**UNIQUAC**	
i-j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ij}
Acetonitrile (1) + 2-Methylpropanoic acid (2) + Dodecane (3)				
	(0.005)		(0.274)	
1-2-2-1	3015.67	-551.95	19.47	-9.67
1-3-3-1	2759.11	2543.72	-4.09	0.87
2-3-3-2	1652.48	3303.47	15.41	-22.62
Acetonitrile (1) + Pentanoic acid (2) + Dodecane (3)				
	(0.005)		(0.332)	
1-2-2-1	1583.92	21576.65	552.45	499.79
1-3-3-1	7446.23	5066.32	-98.68	568.69
2-3-3-2	325.18	9778.83	-1220.86	1320.69
Acetonitrile (1) + 3-Methylbutanoic acid (2) + Dodecane (3)				
	(0.003)		(0.319)	
1-2-2-1	3731.97	704.45	3.52	55.47
1-3-3-1	8791.02	4636.72	102.11	65.32
2-3-3-2	-386.62	7185.36	-251.12	-20.96

[a] Calculated with $\alpha_{ij} = 0.2$

[b] The rmsd are given in parenthesis

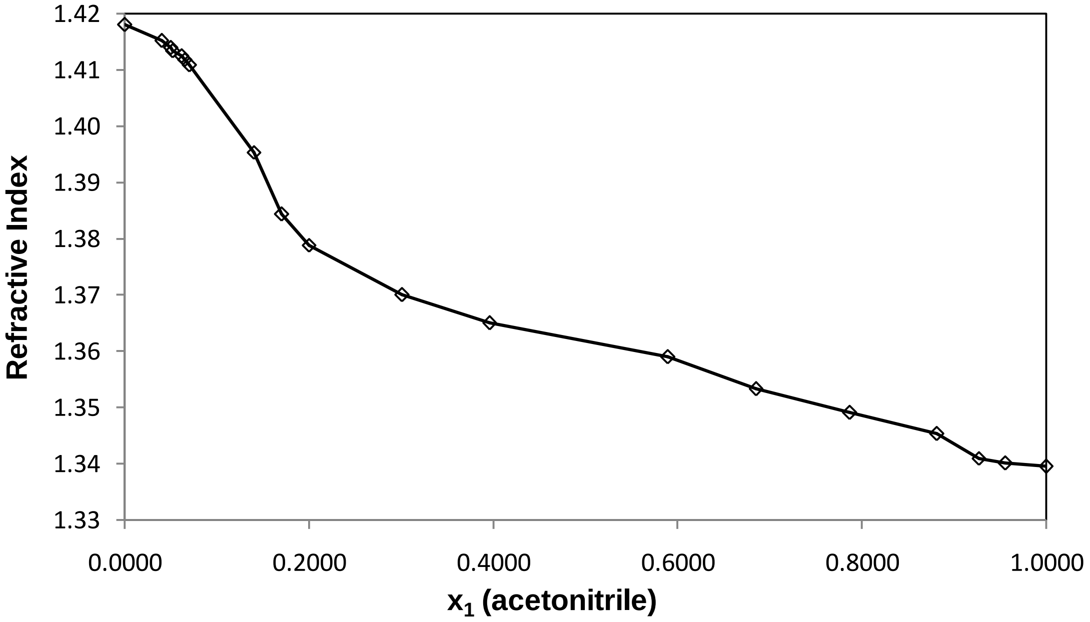

Figure 4.43 **Calibration curve for (acetonitrile + acetic acid + dodecane) system at 303.15 K.**

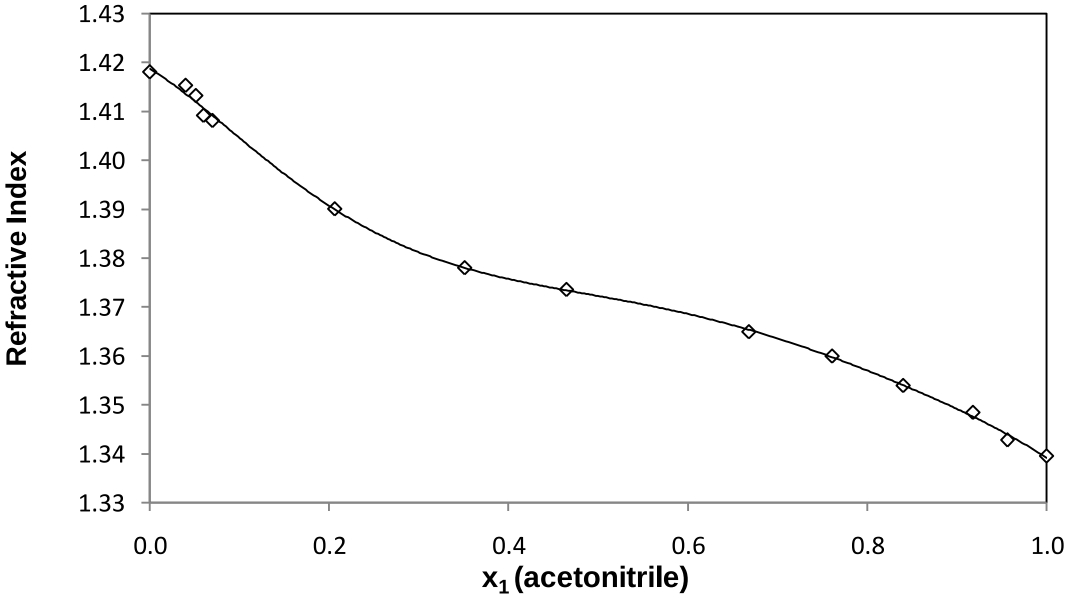

Figure 4.44 **Calibration curve for (acetonitrile + propanoic + dodecane) system at 303.15 K.**

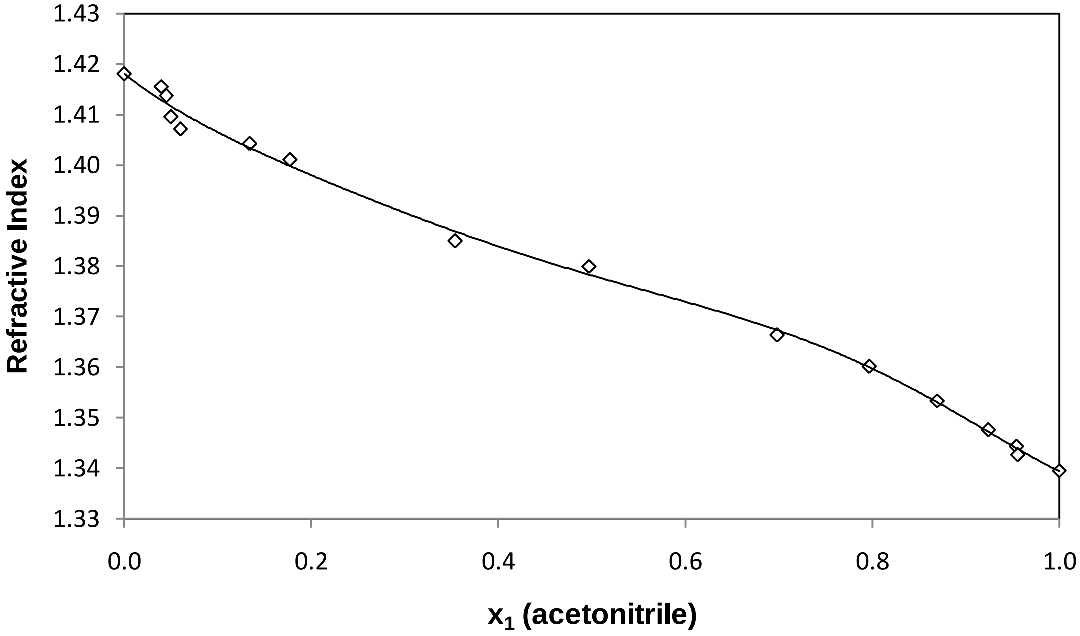

Figure 4.45 Calibration curve for (acetonitrile + butanoic + dodecane) system at 303.15 K.

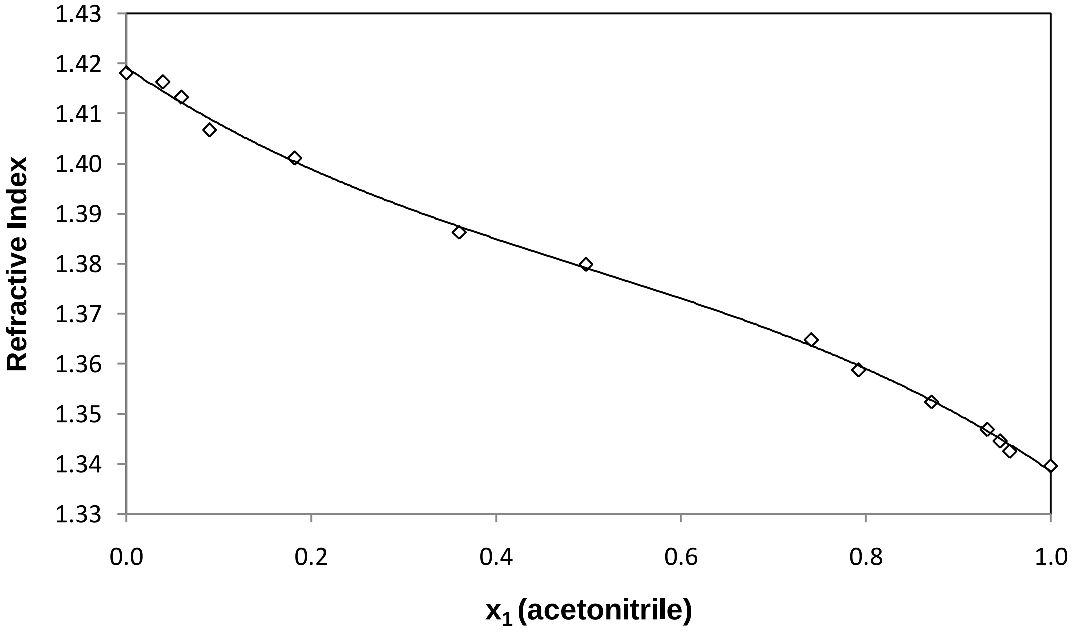

Figure 4.46 Calibration curve for (acetonitrile + 2-methylpropanoic + dodecane) system at 303.15 K.

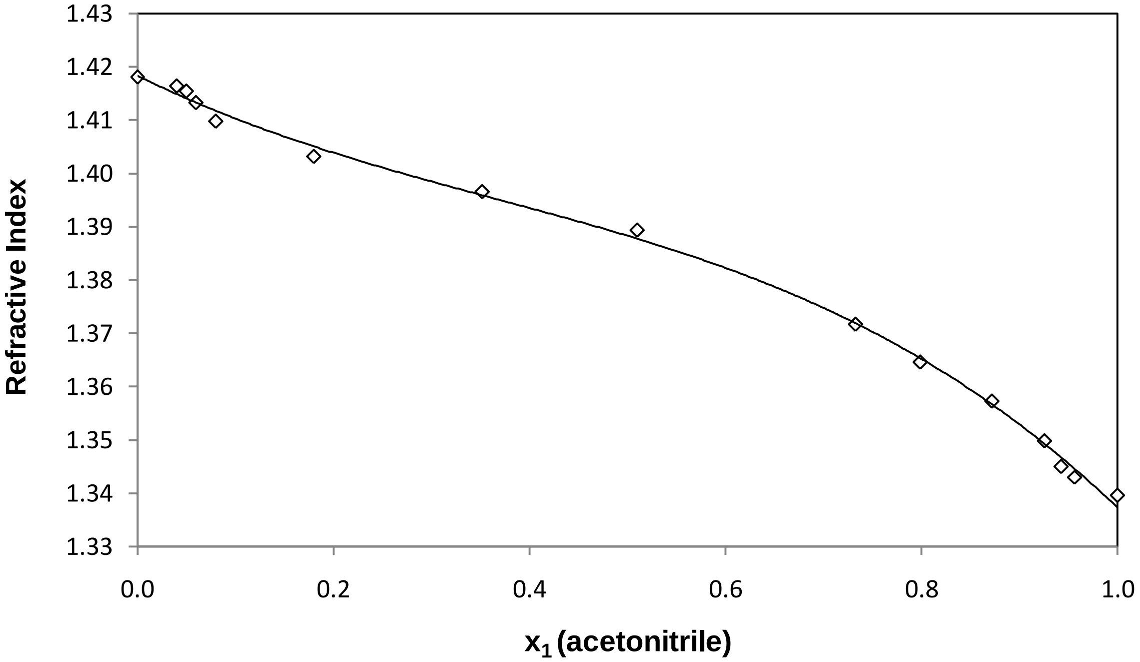

Figure 4.47 Calibration curve for (acetonitrile + pentanoic + dodecane) system at 303.15 K.

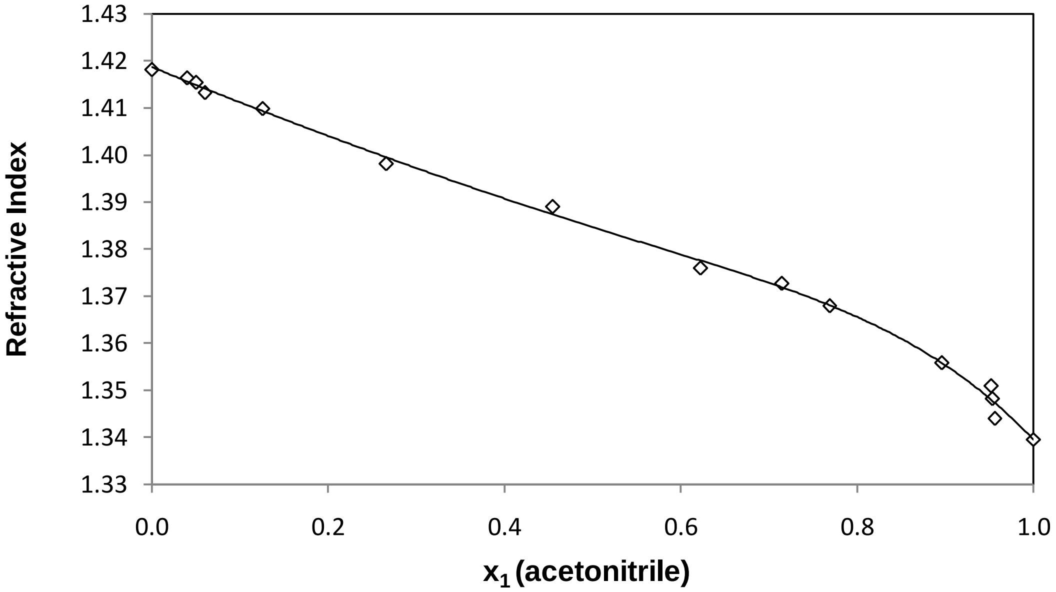

Figure 4.48 Calibration curve for (acetonitrile + 3-methylbutanoic + dodecane) system at 303.15 K.

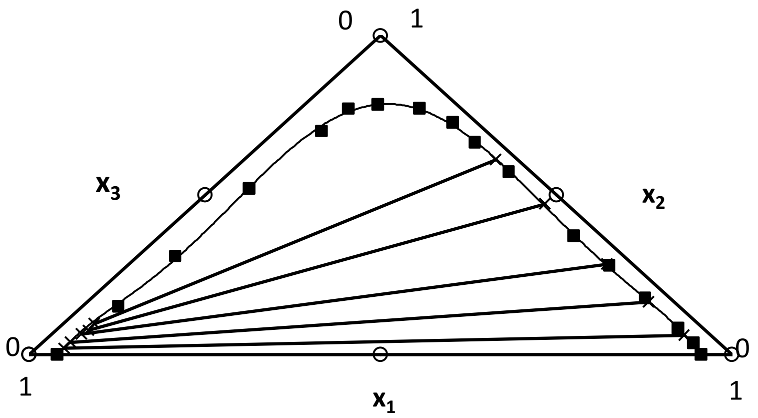

Figure 4.49 **Binodal curve for the liquid-liquid equilibrium data for the system: [Acetonitrile (1) + acetic acid (2) + dodecane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.**

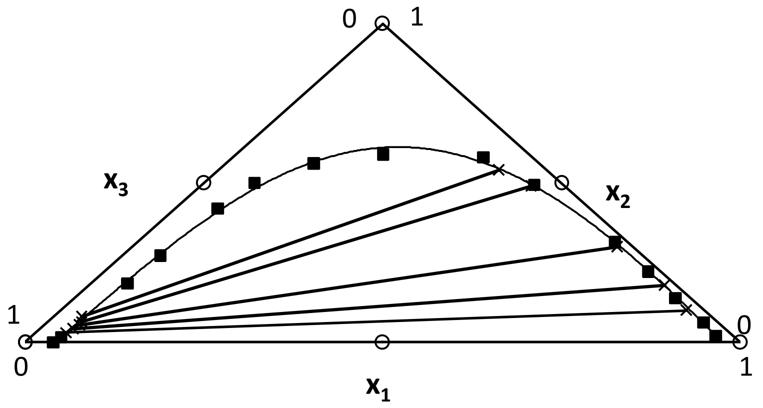

Figure 4.50 **Binodal curve for the liquid-liquid equilibrium data for the system: [Acetonitrile (1) + propanoic acid (2) + dodecane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.**

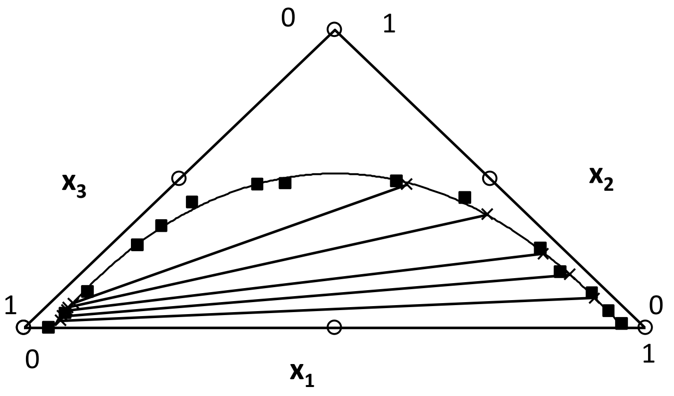

Figure 4.51 **Binodal curve for the liquid-liquid equilibrium data for the system: [Acetonitrile (1) + butanoic acid (2) + dodecane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.**

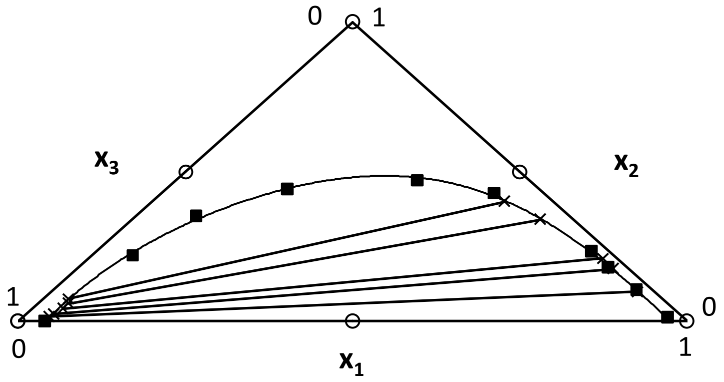

Figure 4.52 **Binodal curve for the liquid-liquid equilibrium data for the system: [Acetonitrile (1) + 2-methylpropanoic acid (2) + dodecane (3]) at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.**

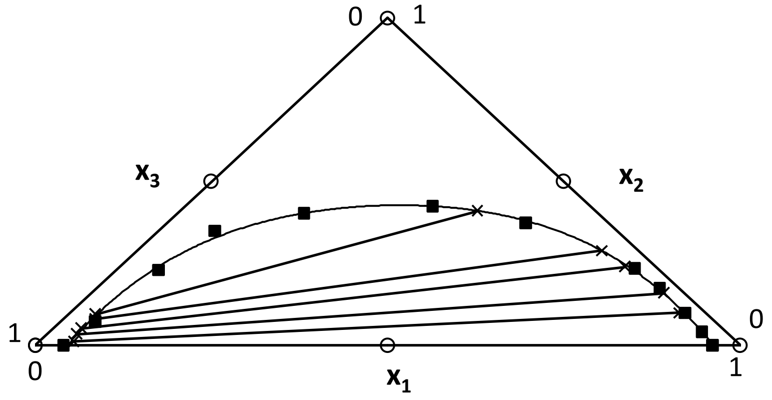

Figure 4.53 Binodal curve for the liquid-liquid equilibrium data for the system: [Acetonitrile (1) + pentanoic acid (2) + dodecane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

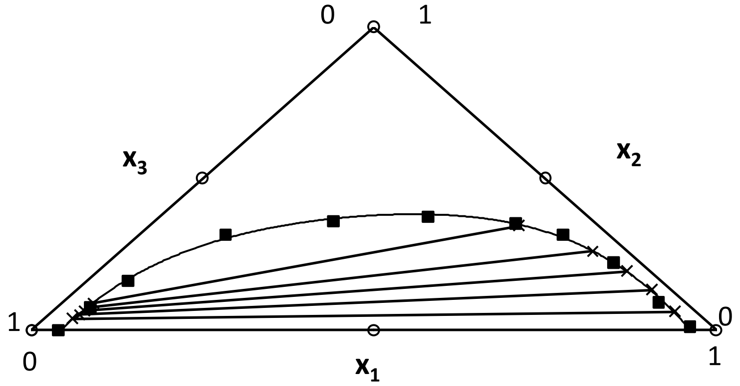

Figure 4.54 Binodal curve for the liquid-liquid equilibrium data for the system: [Acetonitrile (1) + 3-methylbutanoic acid (2) + dodecane (3)] at T = 303.15 K. Key: (x) experimental tie-lines and (■) experimental points.

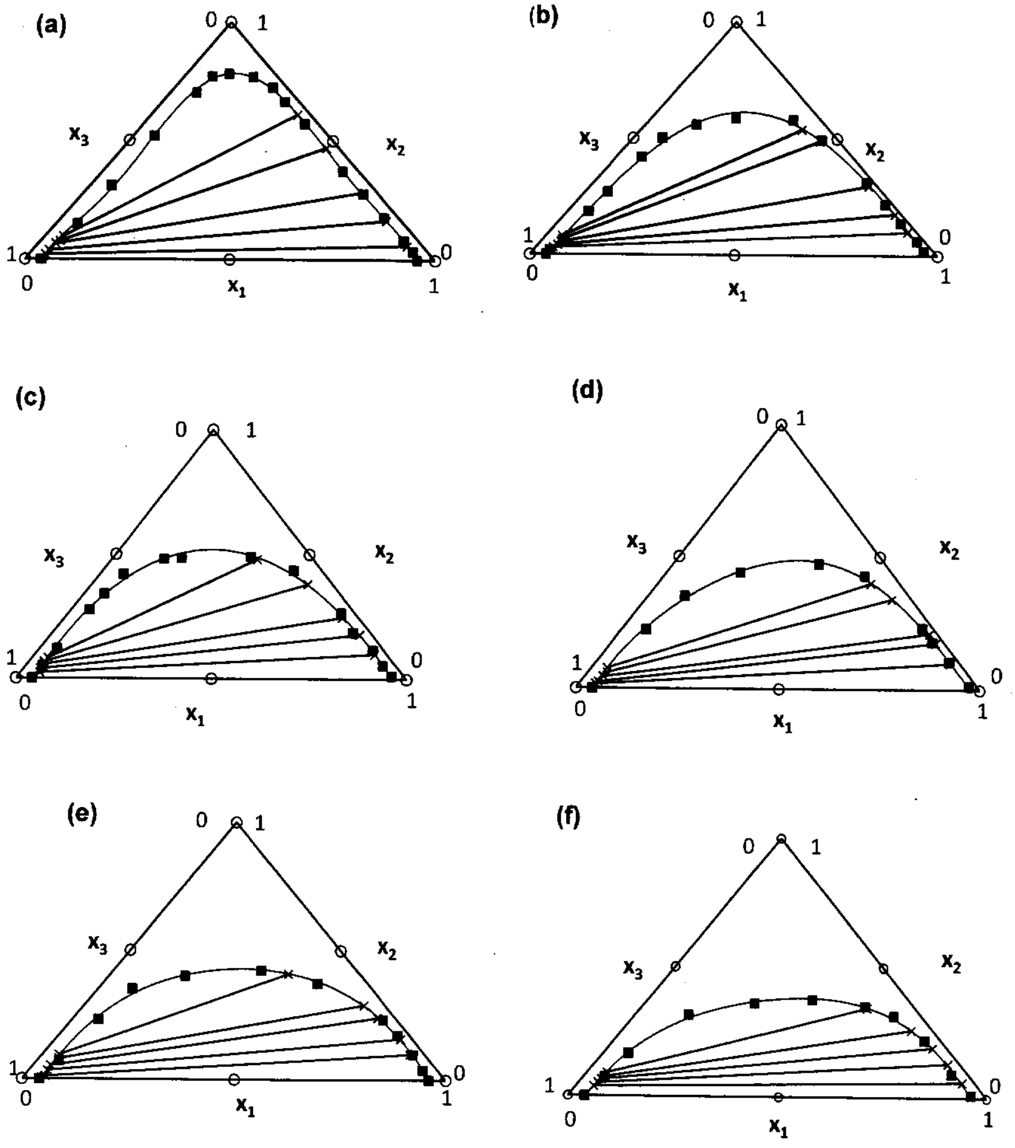

Figure 4.55 **Summary of liquid-liquid equilibrium data for the following systems at 303.15 K: (a) acetonitrile (1) + acetic acid (2) + dodecane (3); (b) acetonitrile (1) + propanoic acid (2) + dodecane (3); (c) acetonitrile (1) + butanoic acid (2) + dodecane (3); (d) acetonitrile (1) + 2-methylpropanoic acid (2) + dodecane (3); (e) acetonitrile (1) + pentanoic acid (2) + dodecane (3); (f) acetonitrile (1) + 3-methylbutanoic acid (2) + dodecane (3). Key: (×) experimental tie-lines; (■) experimental points.**

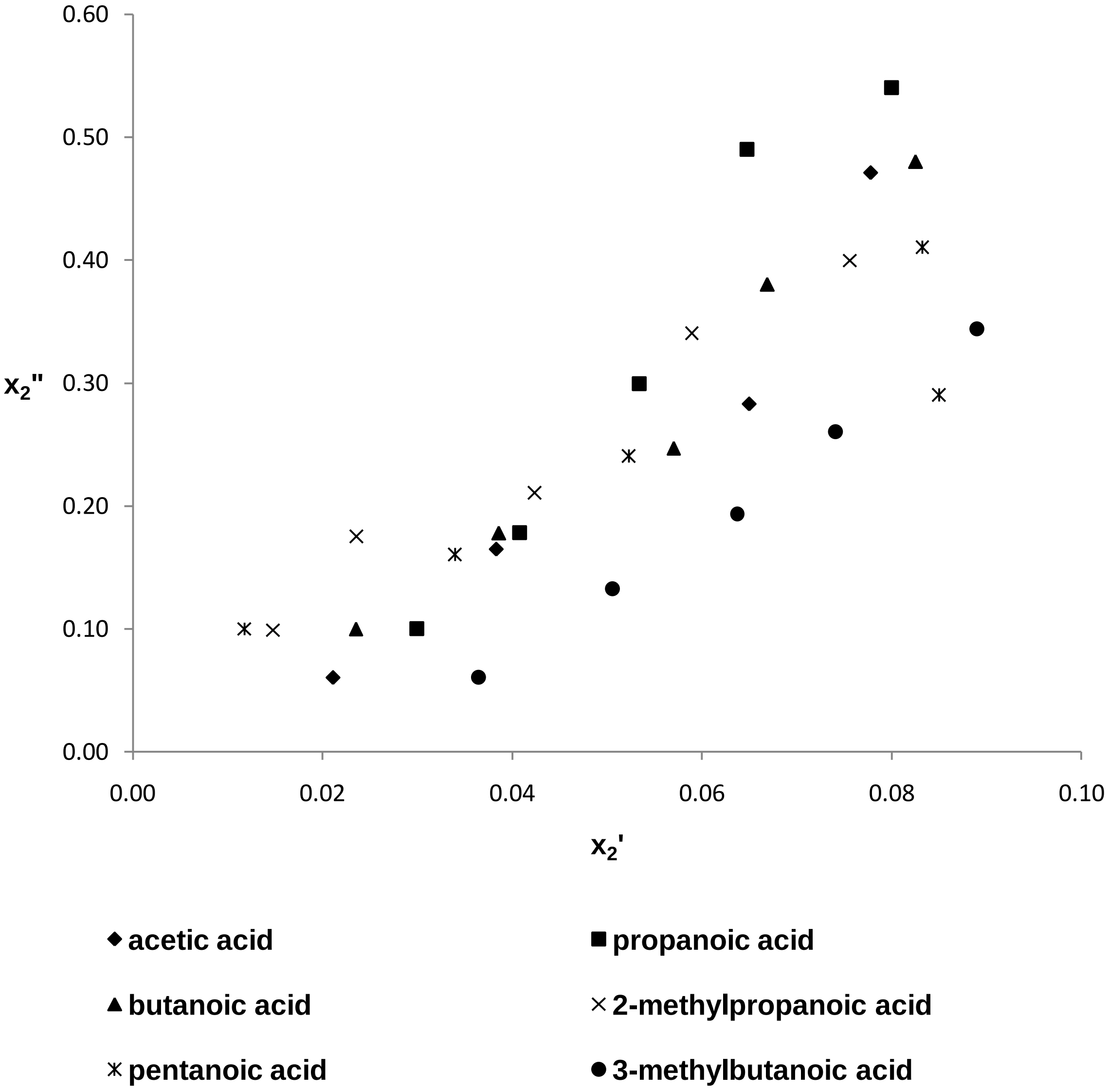

Figure 4.56 A plot of x_2'' against x_2' showing the relative solubilities of the carboxylic acids in the acetonitrile-rich and dodecane-rich layers at 303.15 K.

CHAPTER 5

DISCUSSION

5.1 Discussion of Ternary system involving [Sulfolane (1) + Carboxylic acid (2) + Pentane (3)] at 303.15 K.

Previous work:

Letcher and Redhi (2001) investigated the ternary systems of (acetonitrile + carboxylic acid + cyclohexane) at T = 298.15 K, and found that the mutual solubility of the components is increased as the carbon chain length of the acid is increased and that cyclohexane is most soluble in (acetonitrile + 3-methylbutanoic acid), or (acetonitrile + pentanoic acid) and least soluble in (acetonitrile + acetic acid).

LLE data on a number of ternary mixtures containing sulfolane have been reported in the literature. Kao and Lin (1999) reported the LLE of (sulfolane + 1.4 diisopropyl benzene + n-decane or n-dodecane or n-tetradecane) and their conclusion was that the addition of 1.4 diisopropyl benzene to sulfolane is found to increase the solubility of alkanes in the order of n-decane > n-dodecane > n-tetradecane. The relative mutual solubility of 1.4 diisopropyl benzene is higher in (n-decane + sulfolane) than in (n-dodecane + sulfolane) or (n-tertadecane + sulfolane) mixtures. The solubility effect was reflected in the size of the two phase region, increasingly slightly in the order of n-tetradecane > n-dodecane > n-decane at the same temperature.

Redhi (1996) studied the ternary mixtures of (sulfolane + benzene + 1-heptyne or p-xylene or heptane) at 303.15 K. His conclusion was that the two phase heterogeneous region decreases in the following order: 1-heptyne > p-xylene > benzene. Data presented in this study has not been reported before.

This work:

The measured compositions of equilibrium liquid phase of the ternary system [sulfolane (1) + carboxylic acid (2) + pentane (3)] at 303.15 K are reported in Tables 4.3 to 4.5 and illustrated in Figures 4.7 to 4.12. The feasibility of using sulfolane as a solvent to separate a mixture of carboxylic acids from a mixture of hydrocarbons was evaluated by tie-lines and evaluated by the distribution coefficient of carboxylic acids and hydrocarbons and, selectivity (ω) calculated from experimental data using the following equations.

$$\omega = \frac{\text{distribution coefficient of carboxylic acids}}{\text{distribution coefficient of pentane}}$$

$$\omega = (x_2 / x_3)_{\text{sulfolane-rich phase}} / (x_2 / x_3)_{\text{pentane-rich phase}} \qquad (5.1)$$

where x_2 refers to mole fraction of carboxylic acid and x_3 to mole fraction of pentane in the pentane-rich phase and the sulfolane- rich phase respectively.

The shape of the binodal curves show that the solubility of pentane in (sulfolane + a carboxylic acid) is very much dependent on the carbon number and the type of carboxylic acid. It is observed that the area of the two phase heterogeneous region for carboxylic mixtures is very large in the [sulfolane (1) + acetic acid (2) + pentane (3)] system compared to the area obtained for [propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid] as shown in Figures 4.13 (a) - (f). The area of the two phase heterogeneous region for the carboxylic mixtures decreases in the order of acetic acid > propanoic acid > 2-methylpropanoic acid ~ butanoic acid > pentanoic acid ~ 3-methylbutanoic acid.

According to Figure 4.7 to 4.12 it can be deduced that the single phase homogeneous region increases as the carbon chain length of the carboxylic acid increases but in the case of 3-methylbutanoic acid and 2-methylpropanoic acid, the single-phase heterogeneous phase becomes small compared to propanoic acid, butanoic acid and pentanoic acid. This could be attributed to the effect of the methyl groups on the terminal carbon of 3-

methylbutanoic and 2-methylpropanoic acids as opposed to their straight chain isomers.

The effectiveness of extraction of carboxylic acid (2) from pentane (3) by sulfolane is given by its selectivity (ω) which is a measure of the ability of sulfolane to separate carboxylic acids from hydrocarbons. The values of selectivity for the middle area of the measured tie-lines are 4.4, 2.5, 1.2, 33.9, 19.8, and 20.0 for acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid respectively, as presented in Table 4.6. Selectivity is an important factor in determining the ability of the extraction solvent. According to Table 4.6, selectivity in all cases is greater than one and this means extraction by sulfolane is possible.

The amount of hydrocarbon that is miscible in the (sulfolane + carboxylic acid) mixture is dependent on the carbon number and type of carboxylic acid. The larger the two-phase heterogeneous region, the smaller the amount of sulfolane that will be used in the separation of carboxylic acids from the pentane mixtures.

The relative solubility of carboxylic acids in sulfolane or pentane is evident from the tie-lines. The slopes of the tie-lines presented in Figures 4.1 to 4.6 shows that all the carboxylic acids are more soluble in pentane-rich than in sulfolane-rich mixture. The gradient of the tie-lines for 3-methylbutanoic is greater than for pentanoic acid. This could be attributed to the greater solubilising effect of the two methyl groups on the terminal carbon of 3-methylbutanoic acid as opposed to straight chain isomer. A similar effect is noted for 2-methylpropanoic acid as compared to butanoic acid. This effect was noted by (Letcher and Redhi 2001), when looking at the (acetonitrile + carboxylic acid + cyclohexane) systems at T = 298.15 K.

The minimum concentration of a carboxylic acid that is soluble in any concentration of (sulfolane + pentane) mixture for acetic acid is 0.7499 mole fraction, for propanoic acid it is 0.5523 mole fraction, for butanoic acid it is 0.5195 mole fraction, for 2-methylpropanoic acid is 0.6010 mole fraction, for pentanoic acid it is 0.4953 mole fraction and for 3-methylbutanoic acid it is 0.6122 mole fraction. The heterogeneous phase region is largest in the (sulfolane + acetic acid + pentane) system compared to the other systems, indicating that a small amount of sulfolane will be required to separate the carboxylic acids from pentane. The solubility effect is reflected in the size of the two-phase region, with acetic acid having a large area and pentane is least soluble in the (sulfolane - acetic acid) mixture.

The standard deviations, σ, Hlavatý, beta and logγ have been used in this work. The three equations have been fitted to the data following the work of Hlavatý, (1972). The modified Hlavatý, with an average standard deviation value of 0.012 gave the best overall fit compared to the β and logγ functions.

The NRTL and the UNIQUAC models were used to correlate ternary liquid-liquid equilibrium data for mixtures of (sulfolane + a carboxylic acid + pentane) at 303.15 K. All non-randomness factors (α_{ij}) in the NRTL model were fixed at 0.2 and not adjusted during the correlation. The root mean square deviation (rmsd) is a measure of agreement between the experimental data and the calculated values. The rmsd values are defined as follows (Rapel *et al.,* 2002):

$$\text{rmsd} = \left(\sum_i \sum_l \sum_m [x_{lm}^{exp} - x_{ilm}^{calc}]^2 / 6k\right)^{1/2} \qquad (3.10)$$

where x is the mole fraction, *k* is the number of tie-lines and the subscript *i, l* and *m* denotes the component, phase and tie-line respectively.

The NRTL equation fitted the experimental data far better than the UNIQUAC equation as can be observed in Table 4.8, where the average root mean square deviation phase composition error was 0.072 mole fraction for the NRTL as compared to 0.359 mole fraction for the UNIQUAC model.

5.3 Discussion of Ternary system involving [Sulfolane (1) + Carboxylic acid (2) + Hexane (1)] at 303.15 K.

The measured compositions of equilibrated liquid phases of the ternary system [sulfolane (1) + carboxylic acid (2) + hexane (3)] at 303.15 K are presented in Tables 4.11 to 4.13 and Figures 4.21 to 4.26. The amount of hexane that is miscible with a mixture of (sulfolane + carboxylic acid) is dependent on the number of carbons and the type of the acid. In Figures 4.21 to 4.26 it is observed that hexane is most soluble in the system containing [sulfolane (1) + propanoic acid (2) + hexane (3)].

The area of the two-phase heterogeneous region decreases in the order of: acetic acid > propanoic acid > butanoic acid > 2-methylpropanoic acid > pentanoic acid > 3-methylbutanoic acid. The single phase homogeneous region increases as the carbon chain length is increased. The (sulfolane + acetic acid + hexane) system has a large two phase heterogeneous region and a small single phase homogeneous region. The gradient of the tie-lines showed that all the acids are more soluble in the hexane-rich layer than in the sulfolane-rich layer.

Representative values of selectivity for the middle area of the measured tie-lines are 2.6, 3.5, 3.1, 9.2, 5.4 and 4.2 for acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid respectively. All the selectivity values obtained are greater than one meaning that extraction of carboxylic acid from hexane mixtures using sulfolane is possible.

The large two-phase heterogeneous region for the (sulfolane + acetic acid + hexane) system suggests that the entrainer sulfolane has high capacity or loading of solute per mole fraction of sulfolane, meaning small quantities of sulfolane would be needed for efficient separation of acetic acid from hexane.

The minimum concentration of a carboxylic acid that is soluble in the concentration of (sulfolane + hexane) mixtures is 0.7989 mole fraction for acetic acid, 0.6119 mole fraction for propanoic acid, 0.6019 mole fraction for butanoic acid, 0.6016 mole fraction for 2-methylpropanoic acid, 0.5357 mole fraction for pentanoic acid and 0.5910 mole fraction for 3-methylbutanoic acid.

The modified Hlavatý, β and logγ equations, were fitted to the binodal curve data points. Lower average standard deviations (σ) of 0.010 was obtained for the modified Hlavatý equations compared to β function and logγ function as listed in Table 4.15.

The NRTL and the UNIQUAC models were used to correlate ternary liquid-liquid equilibrium data. All non-randomness factors (α_{ij}) in the NRTL model were fixed at 0.2 and not adjusted during the correlation. The root mean square deviation (rmsd) is a measure of agreement between the experimental data and the calculated values.

The results for the correlation of the NRTL and UNIQUAC models for the tie-line data for mixtures of (sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + hexane) at T = 303.15 K, are given in Table 4.16. The average root mean square deviation phase composition error was 0.040 mole fraction for NRTL and 0.375 mole fraction for UNIQUAC. This shows that the NRTL model provides a much better fit to the experimental data compared to UNIQUAC model.

5.4 Discussion of Ternary system involving Sulfolane (1) + Carboxylic acid (2) + Hexadecane (1) at 303.15 K.

The measured compositions of the equilibrium liquid phase of sulfolane (1) + carboxylic acids (2) + hexadecane (3) are shown in Tables 4.19 to 4.21 and Figures 4.36 to 4.40. The feasibility of using sulfolane as a solvent to perform extraction of hydrocarbons from carboxylic acid mixtures was evaluated using parameters such as tie lines and selectivity.

The results show that the system (sulfolane + acetic acid + hexadecane) has a large two phase heterogeneous region compared to the other systems. It was observed that hexadecane is most soluble in the systems containing butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid. The slopes of the tie-lines presented in Figures 4.36 to 4.40 show that carboxylic acids are more soluble in hexadecane-rich mixture than in sulfolane-rich mixture. It is also observed that the relative mutual solubility of carboxylic acids is higher for (sulfolane + acetic acid) mixture than the other corresponding mixtures. This solubility effect is reflected in the size of the two-phase region, decreasing in the order acetic acid > propanoic acid > butanoic acid ~ 2-methylpropanoic acid > pentanoic acid ~ 2-methylbutanoic acid.

The partitioning of the carboxylic acid between hexadecane-rich and sulfolane-rich layers for systems is expressed in Figure 4.42, where the mole fraction of each carboxylic acid in the conjugate layers has been plotted. All the carboxylic acids are more soluble in the hexadecane-rich layer than in the sulfolane-rich layer. The relatively large two-phase heterogeneous region for the (sulfolane + acetic acid + hexadecane) system suggests that the entrainer sulfolane has a high capacity or loading of solute per mole fraction of solvent (sulfolane) meaning that smaller quantities of the solvent would be needed for efficient separation.

The minimum concentration of a carboxylic acid that is soluble in the concentration of (sulfolane + hexadecane) mixture is 0.7989 mole fraction for acetic acid, 0.7926 mole fraction for propanoic acid, 0.7364 mole fraction for butanoic acid, 0.7317 mole fraction for 2-methylpropanoic acid, 0.6997 mole fraction for pentanoic acid and 0.6972 mole fraction for 3-methylbutanoic acid.

Representative values of selectivity for the middle area of the measured tie lines are presented in Table 4.22, which are 2.4, 1.3, 2.9, 5.4, 6.7 and 7.9 for acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid respectively. All the selectivity values obtained are greater than one meaning that extraction of carboxylic acid from hexadecane mixtures using sulfolane is feasible.

The modified Hlavatý, β and logγ equations, were fitted to the binodal curve data points and again show that all are capable of fitting binodal curve data points. However, the modified Hlavatý gave a significantly better fit than the beta and logγ equations as presented in Table 4.23.

The NRTL and UNIQUAC equations have been fitted to the experimental tie-line data for the liquid mixtures of (sulfolane + a carboxylic acid + hexadecane) at 303.15 K. The nonrandomness parameter, α_{ij}, was set to the value of 0.2 for all the six ternary systems. The NRTL model fitted the experimental data better than the UNIQUAC model as shown in Table 4.24 with the average mean square deviation of 0.068 mole fraction as compared to 0.341 mole fraction for UNIQUAC.

5.5 Discussion of Ternary system involving [Acetonitrile (1) + Carboxylic acid (2) + Dodecane (3)] at 303.15 K.

Previous Work:

Liquid-liquid equilibria data of ternary systems have been reported in the literature (acetonitrile + a carboxylic acid + cyclohexane) by Letcher and Redhi, (2001). In their study of the LLE data of (acetonitrile + acetic acid, or propanoic acid, or butanoic acid, or 2-methylpropanoic acid, or pentanoic acid or 3-methylbutanoic acid + cyclohexane) at T = 298.15 K, the relative mutual solubility of each carboxylic acid was higher in the acetonitrile layer than in the hydrocarbon layer.

This Work:

The amount of hydrocarbon that is miscible with an (acetonitrile + carboxylic acid) mixture is dependent on the carbon number and type of the carboxylic acid. In the ternary systems, shown in Figure 4.55 (a) to (f), it can be observed that dodecane is most soluble in the systems containing butanoic acid, 2-methylbutanoic acid, pentanoic or 3-methylbutanoic acid because the single- phase region is larger than that for the acetic acid and to a lesser extent propanoic acid. Their two-phase heterogeneous regions are smaller compared to the two-phase heterogeneous regions of the acetic acid and propanoic acid.

The single phase homogenous region increases as the carbon chain length of the acid increased. It is found that dodecane is most soluble in the (3-methylbutanoic acid + acetonitrile), (pentanoic acid + acetonitrile) and (2-methylpropanoic acid +acetonitrile) and least soluble in the (acetic acid + acetonitrile) or (propanoic acid + acetonitrile) mixtures.

The relative solubility of a carboxylic acid in acetonitrile or dodecane is evident from the tie lines. The gradients of the tie lines obtained in this study show that all the acids are more soluble in the acetonitrile layer than in dodecane layer.

The relatively large two phase heterogeneous area for the (acetonitrile + acetic acid + dodecane) or (acetonitrile + propanoic acid + dodecane) systems indicates that the entrainer acetonitrile has high capacity or loading of solute per mole fraction of the solvent implying that small quantities of acetonitrile will be needed to separate the (acetic acid or propanoic acid + dodecane) mixtures. The minimum concentration of a carboxylic acid that is soluble in any concentration of (dodecane + acetonitrile) mixtures decreases from acetic acid (0.8400 mole fraction), propanoic acid (0.5900 mole fraction), butanoic acid (0.4911 mole fraction), 2-methylpropanoic acid (0.4701 mole fraction), pentanoic acid (0.4243 mole fraction), 3-methylbutanoic acid (0.3712 mole fraction).

The area of the two-phase heterogeneous region for the carboxylic acid mixtures decreases in the order: acetic acid > propanoic acid > butanoic acid > 2-methylbutanoic acid > pentanoic acid > 3-methylbutanoic acid. This implies that the mutual solubility of the components is decreased with an increased in the carbon chain length. Similar trends were observed in the ternary systems of [acetonitrile or butanitrile or benzonitrile + carboxylic acids + heptanes or water or cyclohexane] (Redhi, 2003). Their investigation showed that the mutual solubility is very much dependent on the length and structure of the carbon chain of the carboxylic acid. Acetic acid with two carbons is too short. The slopes of the tie lines for acetic acid system were steeper compared to other acids and this suggested that the separation of acetic acid from heptanes by extraction with acetonitrile can be achieved in fewer steps.

From the Table 4.30, selectivity values are represented for the middle area of the measured tie lines are 126, 166, 92, 5, 112 and 61 for acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic, pentanoic acid and 3-methylbutanoic acid respectively. If selectivity is greater than one then

extraction is feasible. It can therefore be concluded that the separation of all the carboxylic acids from dodecane by extraction is possible. It can also be concluded that acetonitrile is an especially good solvent for the separation of mixtures of (acetic acid and dodecane) or (propanoic acid and dodecane).
The modified Hlavatý, β and logγ equations, were fitted to the binodal curve data points. The modified Hlavatý gave the best fit of 0.010 for all the ternary systems as presented in Table 4.31.

The NRTL and UNIQUAC equations have been fitted to the experimental tie-line data for the liquid mixtures of (acetonitrile + a carboxylic acid + dodecane) at 303.15 K. The nonrandomness parameter, α_{ij}, was set to the value of 0.2 for each of the six ternary systems. The NRTL model fitted the experimental data better than the UNIQUAC model as shown in Table 4.33, with the average mean square deviation of 0.003 mole fraction as compared to 0.287 mole fraction for UNIQUAC.

CHAPTER 6

CONCLUSIONS

6.1 EXCESS MOLAR VOLUMES

In chapter 2, the excess molar volumes, V_m^E for the systems of [sulfolane (1) + a carboxylic acid (2)] at three different temperatures namely 298.15 K, 303.15 K and 308.15 K were determined; the carboxylic acids used being acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid.

The excess molar volumes for all the systems are negative over the entire mole fraction at the three temperatures, meaning that there is contraction in volume. At T = 298.15 K the magnitude of the area of the excess molar volumes increases in the following order: acetic acid < propanoic acid < butanoic acid < 2-methylpropanoic acid < pentanoic acid < 3-methylbutanoic acid.

At T = 303.15 K the magnitude of the area of the excess molar volumes increases in the following order: butanoic acid < acetic acid < propanoic acid < 2-methylpropanoic acid < 3-methylbutanoic acid < pentanoic acid.

At T = 308.15 K the magnitude of the area of the excess molar volumes increases in the following order: acetic acid < 2-methylpropanoic acid < propanoic acid < butanoic acid < pentanoic acid < 3-methylbutanoic acid.

The excess molar volumes are most negative in the case of 3-methylbutanoic acid at T = 298.15 K and 303.15 K compared to 308.35 K. It is observed that an increase in the carbon chain causes the excess molar volumes to be more negative leading to increased contraction in volume. Also an increase in temperature decreases the area under the excess molar volume curve.

It is observed that the position of the minima for excess molar volumes for (sulfolane + acetic acid) shifts progressively to the sulfolane-rich region of the mole fraction as the methylation increases. This is explained by the increased in steric hindrance caused by additional methyl groups which results in decrease in the association between sulfolane and carboxylic acids. The increasing size differences lead to change in dipole-dipole maxima interactions which increases towards the sulfolane-rich region as the methylation of acetic acid increases.

An increase in temperature decreases the magnitude and area of the excess molar volumes, and this is caused primarily by the kinetic energy of molecules increasing when temperature is increased, which leads to the contraction of volume (Wang *et al.*, 2004). The interactions of molecules decreases within a mixture at high temperatures.

6.2 LIQUID-LIQUID EQUILIBRIUM

New liquid-liquid equilibria data have been reported for the following systems:

(a) [Sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic + pentane] at 303.15 K.
(b) [Sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic + hexane] at 303.15 K.

(c) [Sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic + hexadecane] at 303.15 K.
(d) [Acetonitrile + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic + dodecane] at 303.15 K.

6.2.1 Liquid-liquid equilibria for the mixtures of [Sulfolane + a carboxylic acid + pentane or hexane or hexadecane] at 303.15 K

From the experimental results, the following conclusions can be made:

The shape of the binodal curves show that the solubility of hydrocarbons in (sulfolane + carboxylic acid) is very much dependent on the carbon number of the carboxylic acid. The area of the two-phase heterogeneous region is significantly larger in the (sulfolane + acetic acid + pentane or hexane or hexadecane) in all the ternary systems studied. The slope of the tie-lines indicates that the carboxylic acid is more soluble in hydrocarbon than in sulfolane.

The relative mutual solubility of carboxylic acid is higher in the system of (sulfolane + hexadecane) than in (sulfolane + pentane) or (sulfolane + hexane) mixtures at the same temperature. This effect is reflected in the size of the two-phase heterogeneous region, increasingly slightly in the order of pentane < hexane < hexadecane at the same temperature. The large two-phase heterogeneous region of the (sulfolane + acetic acid + pentane or hexane or hexadecane) mixtures indicates that a smaller amount of sulfolane will be used in the separation of carboxylic acids from the hydrocarbon mixtures.

From the selectivity data obtained (which is greater than one in all the three ternary systems), it is concluded that the separation of carboxylic acids from pentane, hexane and hexadecane is feasible with sulfolane as an extraction solvent.

The standard deviations, σ, of the three fitted equations to the binodal curves, namely the modified Hlavatý, β and $\log\gamma$, show that all are capable of fitting binodal curve point data points. However, the Hlavatý equation gave the best overall fit of 0.012 to the experimental binodal curve data for all the ternary systems whilst the β equation gave 0.021 and $\log\gamma$ equation gave 0.022.

The average root-mean square deviation phase composition error for the ternary systems involving sulfolane is 0.061 for the NRTL model, as compared to 0.358 for UNIQUAC model. The calculation based on the NRTL and UNIQUAC equations showed that the best results are given by the NRTL model.

The solvent, sulfolane has a higher capacity (large heterogeneous region) for (carboxylic acid + hexadecane) mixtures as opposed to (carboxylic acid + pentane) and (carboxylic acid + hexane) mixtures at the same temperature. Thus sulfolane is a better solvent for extracting carboxylic acids from hexadecane, than in pentane and hexane.

6.2.2 Liquid-liquid equilibria for the mixtures of [Acetonitrile + a carboxylic acid + dodecane] at 303.15 K

Liquid-liquid equilibrium data for the six ternary mixtures of (acetonitrile + acetic acid / propanoic acid / butanoic acid / 2-methylpropanoic acid / pentanoic acid / 3-methylbutanoic acid + dodecane) were determined at 303.15 K.

The area of two-phase heterogeneous region for the carboxylic mixtures increases in the order: 3-methylbutanoic acid < pentanoic acid < 2-methylpropanoic acid < butanoic acid < propanoic < acetic acid. The large two-phase heterogeneous area for the (acetonitrile + acetic acid + dodecane) and (acetonitrile + propanoic acid + dodecane) systems indicates that smaller quantities of acetonitrile will be needed to separate the (acetic acid or propanoic acid + dodecane) mixtures. The gradients of the tie-lines for acetic acid system were steeper compared to the other carboxylic acids and this indicates that the separation of acetic acids from dodecane by extraction with acetonitrile can be achieved in fewer steps.

The selectivity data showed that the separation of acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid from dodecane by extraction with acetonitrile is feasible.

The calculation based on Hlavatý, β and logγ showed that the best results are given by Hlavatý with the average standard deviation error of 0.011 compared to β with 0.027and logγ 0.018. The correlation obtained with the NRTL model was significantly better with the average root mean square deviation value of 0.003 than that obtained with the UNIQUAC model with the average root mean square of 0.287.

Sulfolane and acetonitrile solvents are both feasible for the separation of carboxylic acids from hydrocarbon mixtures at 303.15 K but selection of the best solvent depends on the economical considerations.

CHAPTER 7

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