DURBAN
UNIVERSITY of
TECHNOLOGY

PHASE EQUILIBRIUM STUDIES OF SULFOLANE MIXTURES CONTAINING CARBOXYLIC ACIDS

PHASE EQUILIBRIUM STUDIES OF SULFOLANE MIXTURES CONTAINING CARBOXYLIC ACIDS

NOMPUMELELO PRETTY SITHOLE

B.Tech: Chemistry (DUT)

Submitted in fulfilment of the academic requirements for the

Masters degree in Technology

in the Department of Chemistry, Durban University of Technology,

Durban, South Africa

2012

PREFACE

This work was done in the Department of Chemistry, Durban University of Technology, M L Sultan Campus in Durban, KwaZulu Natal Province, South Africa

DECLARATION

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

……………………………… ………………………………………..

N P Sithole Date

I hereby certify that the above statement is correct.

……………………………… ………………………………

Professor G G Redhi Date

DEDICATION

I would like to dedicate this thesis to my late big brother Mr Mzomuhle Moses Sithole

ACKNOWLEDGMENTS

I would like to record my appreciation to the following:

- God Almighty for guiding me through this journey to finish this project, it was not an easy one but His endless guidance saw me through it all.
- Prof G. G. Redhi from Durban University of Technology, Chemistry Department, my supervisor for his unlimited guidance, help, support and patience throughout the course of the project.
- My mother Mrs Zolani Sithole for her pep talk and motivation to pursue my dreams and never to give up even if it becomes tough.
- My husband Mr Thokozani Nyangayibizwa Cele for his unlimited support and motivation throughout the course of this project.
- My friends, Thabile, Cathrine, Thobeka, Nokukhanya and Myalo for their support and help.
- National Research Foundation and Durban University of Technology: Postgraduate Department for providing me with financial support and electronic notebook to finish this project.
- The Chemistry laboratory staff from Durban University of Technology for the help with instrumentation and motivation.

ABSTRACT

In this work, the thermodynamics of ternary liquid mixtures involving carboxylic acids with sulfolane, hydrocarbons including cycloalkane, and alcohols are presented. In South Africa, Sasol is one of the leading companies that produce synthesis gas from low grade coal. Carboxylic acids together with many other oxygenate and hydrocarbons are produced by Sasol using the Fischer-Tropsch process. Carboxylic acids class is one of the important classes of compounds with great number of industrial uses and applications. The efficient separation of carboxylic acids from hydrocarbons and alcohols from hydrocarbons is of economic importance in the chemical industry, and many solvents have been tried and tested to improve such recovery. This work focussed on the use of the polar solvent sulfolane in the effective separation by solvent extraction and not by more common energy intensive method of distillation.

The first part of the experimental work focussed on ternary liquid-liquid equilibria of mixtures of [sulfolane (1) + carboxylic acid (2) + heptane (3) or cyclohexane or dodecane] at T = 303.15 K, [sulfolane (1) + alcohol (2) + heptane (3)] at T = 303.15 K. Carboxylic acid refers to acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid. Alcohol refers to methanol, ethanol, 1- propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol and 2-methyl-2-propanol. Ternary liquid- liquid equilibrium data are essential for the design and selection of solvents used from liquid- liquid extraction process.

The separation of carboxylic acids from hydrocarbons and the alcohols from hydrocarbons is commercially lucrative consideration and is an important reason of this study. The separation of carboxylic acids or alcohols from hydrocarbons by extraction with sulfolane was found to be feasible as all selectivity values obtained are greater than 1.

The modified Hlavatý, beta (β) and log γ equations were fitted to the experimental binodal data measured in this work. Hlavatý gave the best overall fit as compared to beta (β) and log γ function.

The NRTL (Non-Random, Two Liquid) and UNIQUAC Universal Quasichemical) model were used to correlate the experimental tie-lines and calculate the phase compositions of the ternary systems. The correlation work served three purposes:

- to summarise experimental data
- to test theories of liquid mixtures
- prediction of related thermodynamics properties.

The final part of the study was devoted to the determination of the excess molar volumes of mixtures of [sulfolane (1) + alcohol (2)] at T = 298.15 K, T = 303.15 K and T = 309.15 K. Density was used to determine the excess molar volumes of the mixtures of [sulfolane (1) + alcohols (2)]. Alcohol refers to methanol, ethanol, 1- propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol.

The work was done to investigate the effect of temperature on excess molar volumes of binary mixtures of alcohols and sulfolane, as well as to get some idea of interactions involved between an alcohol and sulfolane. The excess molar volume data for each binary mixture was fitted in the Redlich–Kister equation to correlate the composition dependence of the excess property.

CONTENTS

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: LIQUID-LIQUID EXTRACTION

CHAPTER 4: EXPERIMENTAL TECHNIQUES

CHAPTER 5: RESULTS

5. LIQUID –LIQUID EQUILIBRIA

5.5 EXCESS MOLAR VOLUMES

CHAPTER 6: DISCUSSION

6.1 LIQUID–LIQUID EQUILIBRIA

6.2 EXCESS MOLAR VOLUMES

CHAPTER 7: CONCLUSIONS

7.1 TERNARY LIQUID-LIQUID EQUILIBRIA

7.2 EXCESS MOLAR VOLUMES

CHAPTER 8: REFERENCES

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

T = temperature

K = kelvin

$\boldsymbol{\beta}$ = beta coefficient for Hlavatý equation

$\boldsymbol{\gamma}$ = coefficient for Hlavatý equation

$\boldsymbol{\rho}$ = density

V_m = molar volume

V_{m}^{E} = excess molar volume

M_1 = molar mass of component 1

M_2 = molar mass of component 2

n_D = refractive index

z = lattice coordination number

α_{12} = parameter in NTRL equation

ω = selectivity

λ_i = activity coefficient of component i

ϕ = segment fraction

$\boldsymbol{\theta}_i$ = area fraction

$\boldsymbol{\theta}_{ij}$ = local area fraction of sites belonging to molecule i around sites belonging to molecule j

$\boldsymbol{\theta}$ = molecular configuration

δ = root mean square deviation between calculated and experimental property

ξ_{ij} = local volume fraction of molecule i in the immediate neighbourhood of molecule j

w_{12} = potential energy of interaction

W_{12} = molar potential energy of interaction

τ = normalized parameter for symmetric systems

x_1 = mole fraction of sulfolane

x_2 = mole fraction of carboxylic acid (or alcohol)

x_3 = mole fraction of heptane (or dodecane, or cyclohexane)

x_1' = mole fraction of sulfolane in heptane (dodecane, or cyclohexane) rich layer

x_2' = mole fraction of carboxylic acid in heptane (dodecane, or cyclohexane) rich layer

x_1'' = Mole fraction of sulfolane in sulfolane- rich layer

x_2'' = Mole fraction of carboxylic acid in sulfolane-rich layer

exp = experimental value

lit = literature value

R = Volume Parameter

Q = Surface Parameter

PUBLICATIONS

1. **Sithole, N.P.**, Redhi G.G., Liquid-liquid equilibria for mixtures of (sulfolane + a carboxylic acid + heptane) at 303.15 K: *Submitted*

2. **Sithole, N.P.**, Redhi G.G., Liquid-liquid equilibria for mixtures of (sulfolane + a carboxylic acid + cyclohexane) at 303.15 K: *In preparation*

3. **Sithole, N.P.**, Redhi G.G., Liquid-liquid equilibria for mixtures of (sulfolane + a carboxylic acid + dodecane) at 303.15 K: *In preparation*

4. **Sithole, N.P.**, Redhi G.G., Liquid-liquid equilibria for mixtures of (sulfolane + an alcohol + heptane) at 303.15 K: *In preparation*

CHAPTER 1

INTRODUCTION

1.1 TECHNIQUE OF SEPARATION

Separation is the process of obtaining a product in pure form by removal of the unwanted reactant/chemicals. Separation processes are essential in refineries, in material processing, pharmaceutical and chemical industries (Letcher, 2004). Separation processes are one of the major activities in the chemical and petrochemical industries. It is important to use the most cost effective separation technology to minimize waste, improve energy efficiency and increase the efficiency of raw material used. It is vital for separation technologies to have the potential to minimize waste and maximize productivity by separating valuable materials that can still be re-used or sold as by-products from waste streams. Common methods use to separate waste streams are distillation, crystallization, adsorption, membrane processes, absorption and stripping, and liquid-liquid extraction (Letcher, 2004).

In South Africa, Sasol is one of the companies that produce synthesis gas from low grade coal. The products include petrol, diesel, liquefied petroleum gas and other synthetic liquid fuels, as well as industrial pipeline gas and chemical feedstocks. Sasol synthetic fuels produce most of South Africa's chemical and polymer building blocks, including ethylene, propylene, ammonia, phenolics, alcohols and ketones (Redhi, 1996).

Carboxylic acids together with many other oxygenates and hydrocarbons are produced by Sasol using the Fischer-Tropsch process (Letcher and Reddy, 2004). Carboxylic acids are an important class of compounds with a great number of industrial uses and applications.

The separation of carboxylic acid from mixtures of organic compound found in Fischer-Tropsch synthesis mixtures and crude oil mixtures is an important objective for physical chemists and for chemical engineers (Letcher and Whitehead, 1996). In chemical industries, liquid-liquid extraction or solvent extraction plays an important role in the separation process.

1.2 FISCHER TROPSCH CONVERSION

1.2.1 Introduction

Fischer Tropsch (FT) is a catalyzed chemical reaction in which carbon monoxide and hydrogen are converted into liquid hydrocarbons of various forms. Typical catalysts used are based on iron and cobalt. The purpose of this process is to produce a synthetic petroleum substitute for use as synthetic lubrication oil or synthetic fuel (Broughton *et al*, 1968). Sasol is one of the petroleum industries using this kind of synthesis, to produce a synthetic petroleum substitute, typically from coal, natural gas or biomass, for use as synthetic lubrication oil or as synthetic fuel for motor vehicles and some air craft engines.

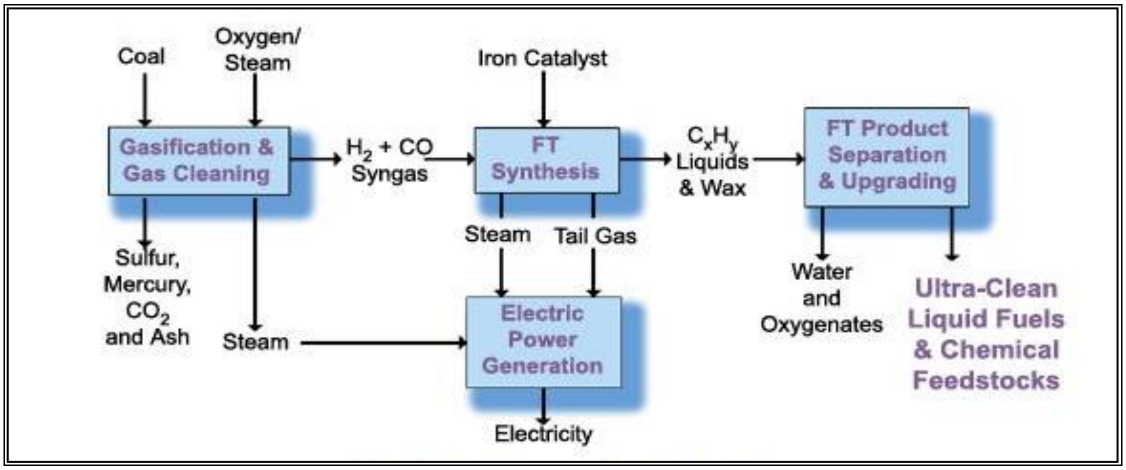


Figure 1.1: Production of liquid fuels from coal by Fischer Tropsch process

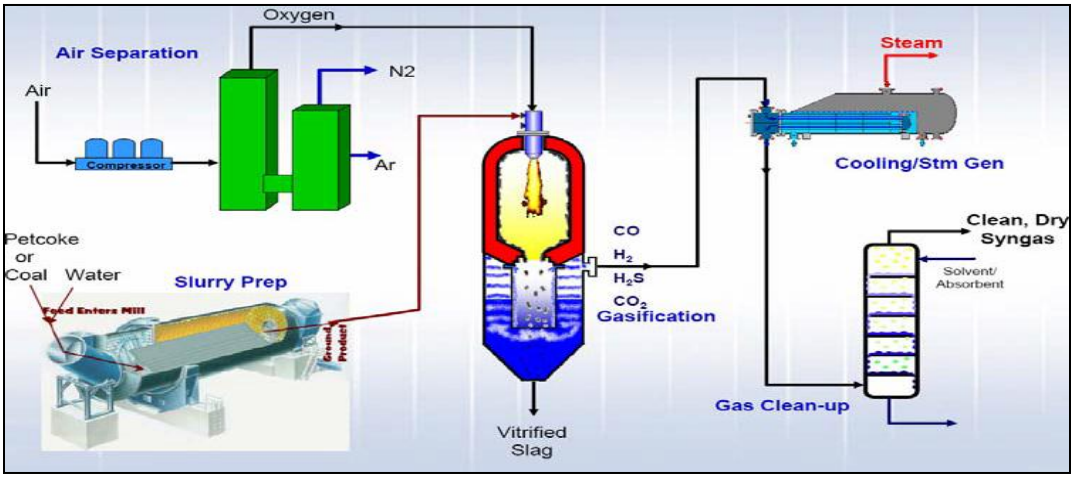


Figure 1.2: Gasification of coal (Bowen and Irwin, 2006)

1.2.2 Original Process

The original Fischer-Tropsch process is described by the following chemical equation

$$\boxed{(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O} \qquad (1.1)$$

where ‘n’ is a whole number

The initial reactants in the above reaction that is carbon monoxide and hydrogen can be produced by other reactions, such as the partial combustion of hydrocarbon:

$$\boxed{C_nH_{(2n+2)} + \tfrac{1}{2} nO_2 \rightarrow (n+1) H_2 + nCO} \qquad (1.2)$$

For example (when n = 1), methane in the case of gas to liquids applications:

$$\boxed{CH_4 + \tfrac{1}{2} O_2 \rightarrow 2H_2 + CO} \qquad (1.3)$$

Or by the gasification of coal or biomass

$$\boxed{C + H_2O \rightarrow H_2 + CO} \qquad (1.4)$$

The energy needed for this endothermic reaction of coal or biomass and steam is usually provided by exothermic combustion with air or oxygen. This lead to the following reaction:

$$\boxed{C + \tfrac{1}{2} O_2 \rightarrow CO} \qquad (1.5)$$

The mixture of carbon monoxide and hydrogen is called synthesis gas or syngas. The resulting hydrocarbon products are refined to produce the desired synthetic fuel. Carbon dioxide and carbon monoxide are generated by partial oxidation of coal and wood-based fuels.

The utility of the process is primarily to produce fluid hydrocarbons from solid feedstock, such as coal or solid carbon-containing wastes of various types. Non-oxidative pyrolysis of solid material produces syngas which can be used directly as fuel without being taken through Fischer-Tropsch transformations. If liquid petroleum-like fuel, lubricant, or wax is required, the Fischer-Tropsch process can be applied (Khodakov *et a*l, 2007).

1.3 TYPICAL SEPARATION PROCESSES

1.3.1 Introduction

The design and evaluation of industrial units for separation processes require reliable phase equilibrium data of the different mixtures involved in a given process (Rappel and Mattedi, 2002, Mohsen-Nia *et al,* 2005). One way to effectively separate a mixture of two compounds is to add a third compound usually a polar compound such as sulfolane to the mixture. The resultant selectivity or relative volatility of the species in the mixture can be use to design separation procedures via liquid- liquid extraction or extractive distillation.

1.3.2 Distillation

Large scale industrial distillation applications include both batch and continuous fractional, vacuum, azeotropic, extractive, and steam distillation (Letcher, 2004) The most widely used industrial applications of continuous, steady-state fractional distillation are in petroleum refineries, petrochemical and chemical plants and natural gas processing plants.

In this separation process, the high boiling entrainers (highly selective solvent) are introduced not far from the top of the extractive distillation column and they alter the volatilities of the compound to be separated. The presence of entrainers in the column during the separation process causes the aliphatic compounds to become more volatile. The products with the lowest boiling point exit from the top of the columns, and the rest of the products with the highest boiling point or both the aromatic hydrocarbons and the entrainer remain at the bottom of the column and exit from the bottom of the column, thereby making it easier for the aliphatic hydrocarbons to be separated.

In the second distillation column, a high boiling entrainer can easily be separated from the aromatic hydrocarbon and be recycled to the first column. Better purity of the product, is influenced by the number of theoretical stages realized, and the selectivity of the entrainer used (Letcher, 2004).

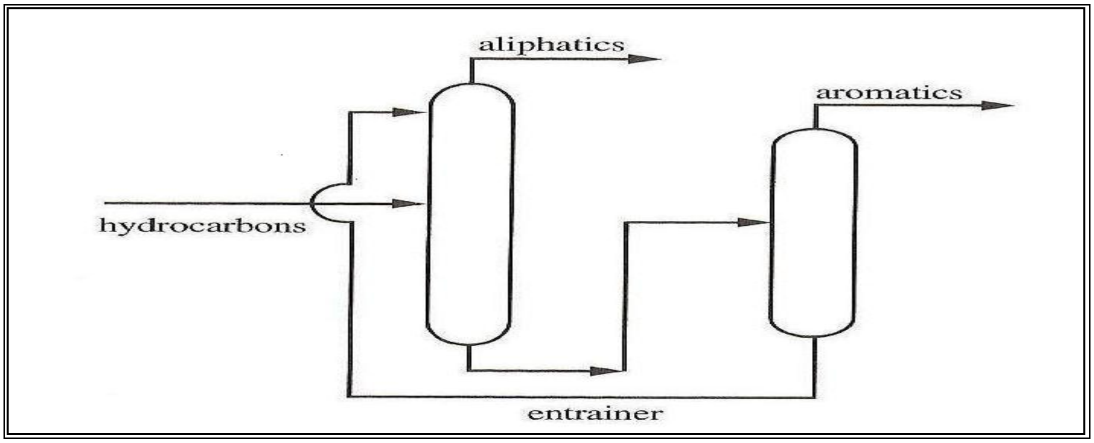


Figure 1.3 Schematic diagram of extractive distillation process (Letcher, 2004)

1.3.3 Liquid-liquid extraction

In liquid-liquid extraction, selective solvents are also required, which are partially miscible with the liquid mixture to be separated. In this process, selective solvent (extractant) is used to separate the aliphatic compounds from the aromatic compounds in the feed stream. Distillation is used for the removal of the selective solvent from the extract and raffinate mixture. This separation process is used in industry for the following separation processes for separation of systems with similar boiling points, separation of azeotropic mixtures, separation of temperature sensitive compounds; separation of mixtures with high boiling points and extraction of organic compounds from salt solutions (Letcher, 2004).

The selectivity, which strongly influences the number of separation stages, together with the capacity of the solvent, strongly influences the investment cost of a separation process. The entrainers with high selectivity and capacity are mostly required, but unfortunately, in most cases, high selectivity values are linked to low capacity values. The low capacity of water for example, is the reason that in spite of its high selectivity, it is not used for the separation of aliphatic and aromatic compounds (Letcher, 2004).

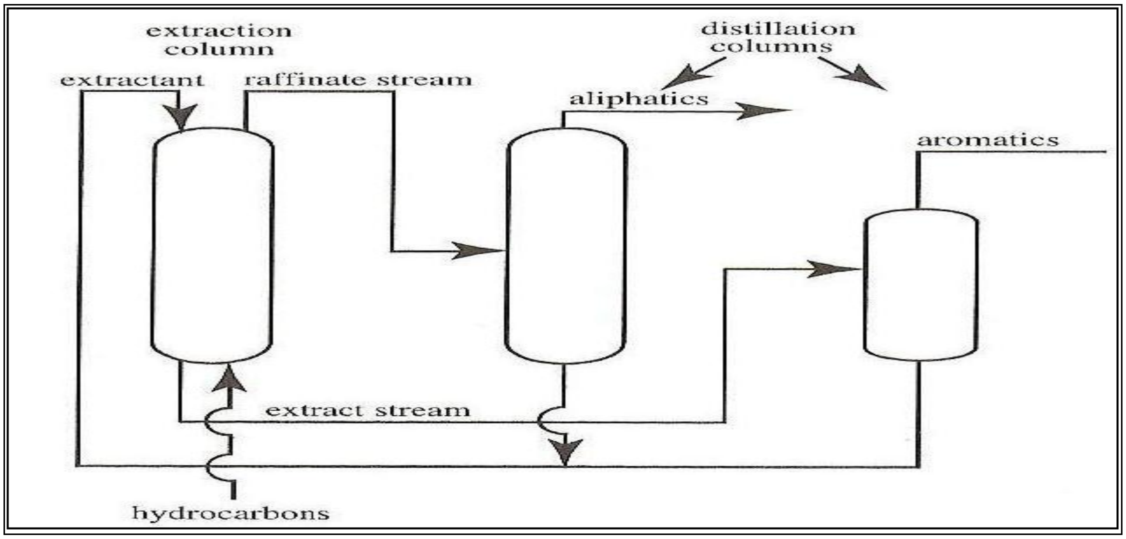


Figure 1.4 Schematic diagram of a typical liquid-liquid extraction process

1.3.3 Absorption

Absorption is the removal of one or more components from a gas stream using selective solvents. A selective solvent (absorbent) removes the undesired compounds from the raw gas in a multistage countercurrent process, while the purified gas leaves the absorber which is saturated with selective solvent. The absorbent is regenerated in a second column (desorber) and is recycled to the absorber. In the case of physical absorption, the absorber is operated at high pressures and low temperature, while the desorber is operated on the opposite conditions (Letcher, 2004).

1.4 CHOICE OF SOLVENT USED IN THIS WORK FOR SOLVENT EXTRACTION

1.4.1 Introduction

Solvent extraction depends on the physical and chemical properties of a solvent when used for separation of complex liquid mixtures such as the recovery of valuable products and removal of contaminants in effluent streams. The separation potential and feasibility of solvents for commercial applicability are dependent on the physical properties such as boiling point, thermal stability, and viscosity, ease of recovery, toxicity and corrosive nature of the solvent. Selectivity of the solvent is the important component in characterizing a solvent (Letcher and Reddy, 2004).

A solvent used for solvent extraction plays a vital role in the separation process, and the quality of the solvent used for extraction is important for the efficiency of the desired separation process (Rappel and Mattedi, 2002). Sulfolane is one of the most widely used in the chemical industry, as a solvent in the extraction of hydrocarbons and aromatic hydrocarbons from naphtha feed (Mohsen-Nia and Paikar, 2007). It has been widely used in the extraction and extractive distillation process to recover high–purity aromatic hydrocarbons from refinery process streams and pressurized washing processes to remove hydrogen sulphide and carbon dioxide from synthesis gas or natural gas.

Sulfolane is a popular solvent for extraction due its good physical and chemical properties (Senol, 2005). The quality of the solvent used in the generation and prediction of the liquid-liquid equilibrium data for systems of interest is essential for proper understanding of the solvent extraction process (Senol, 2005). Sulfolane is also an industrially valuable solvent having good thermal and hydrolytic stability, high density and high boiling point (Maciuca *et al*, 2008).

1.4.2 Description of sulfolane

Sulfolane is also known as tetramethylene sulfone or 2, 3, 4, 5-tetrahydrothiophene-1, 1-dioxide. It is a clear, colourless and commonly used in the chemical industry as an extractive distillation solvent or reaction solvent. It is a polar and aprotic organosulphur compound that is readily soluble in water.

Sulfolane was originally developed by the Shell Oil Company in the 1960`s as a solvent to purify butadiene (Shaohui, 2006)

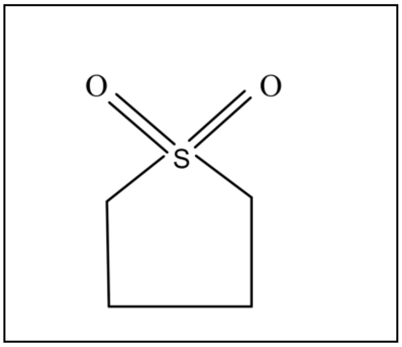


Figure 1.5 Structure of sulfolane

1.4.3 Chemical properties of sulfolane

Sulfolane is classified as a sulfone, a group of organosulphur compounds containing a sulfonyl functional group. The sulfonyl group is a sulphur atom doubly bonded to two oxygen atoms. 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 hydrocarbon mixtures (Shaohui, 2006).

Sulfolane is a specialty solvent which shows the following interesting properties:

- Versatility, it can be used in wide range of synthesis
- High polarity and miscible with a water
- Chemically and thermally stable, it has a high boiling point
- Aprotic, it has a no acidic hydrogen atom
- Recyclable, it is easy to recycle
- It is easy to handle due to its low hazard characteristic

It is these properties that allow sulfolane to be miscible in both water and hydrocarbons, resulting in its widespread use as a solvent for purifying hydrocarbon mixtures (Shaohui, 2006), and is the choosen solvent for this investigation.

1.4.4 Synthesis of sulfolene

Sulfolane can be prepared in the laboratory by the following reactions

1.4.4.1 Hydrogenation of 3-sulfolene

Industrially, sulfolane is synthesized by hydrogenation of 3-sulfolene, which is prepared through the reaction of butadiene and sulphur dioxide (Shaohui, 2006).

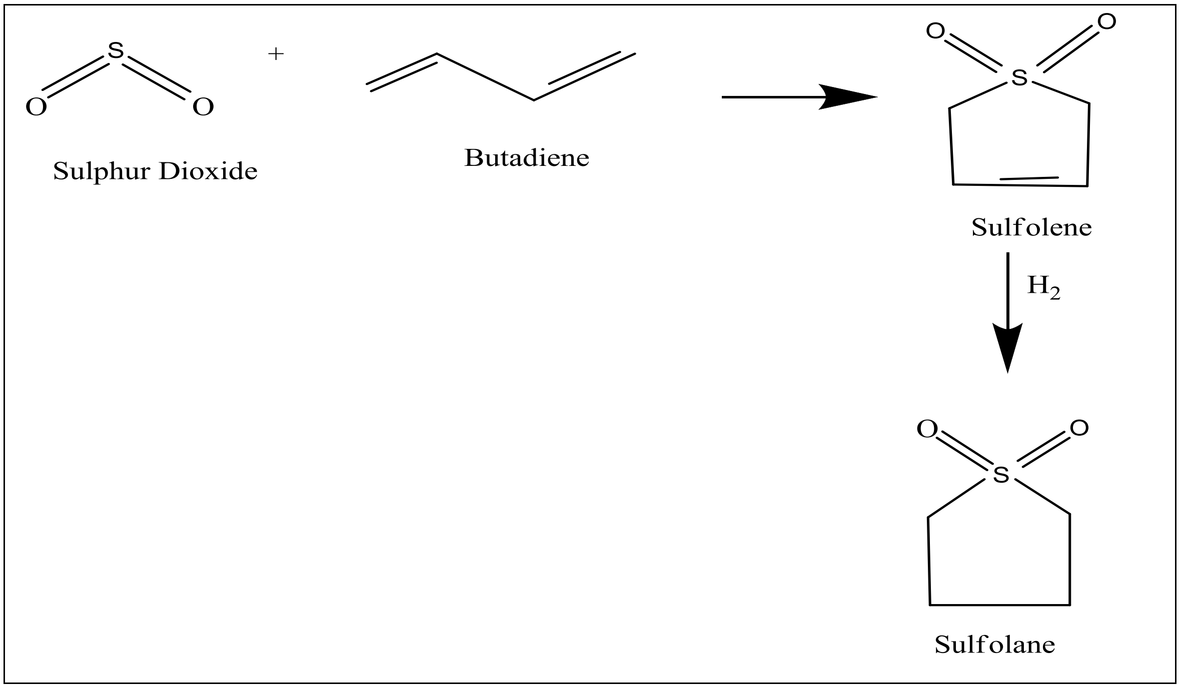


Figure 1.6 Preparation of sulfolane from sulphur dioxide

Sulfolane manufacturing using butadiene and sulphur dioxide was patented by Shell in 1944 (Goodehbour *et al* 1962). Developments have continued over the years, including in the catalyst used. Recently, it was found that Ni-B/MgO showed superior catalytic activity to that of Raney Nickel and other common catalysts that have been used in hydrogenation of sulfolene (Shaohui, 2006).

1.4.4.2 Oxidation of tetrahydrothiophene

Other synthetic routes have also been developed, such as oxidizing tetrahydrothiophene with hydrogen peroxide. This first produces tetramethylene sulfoxide, which can then be further oxidised to tetramethylene sulfone (sulfolane).

The first oxidation takes place at low temperature and the second at relatively higher temperature, the reaction can be controlled at each stage. This gives a greater freedom for manipulation of the reaction, which can potentially lead to higher yields and purity (Lal *et al,* 2003).

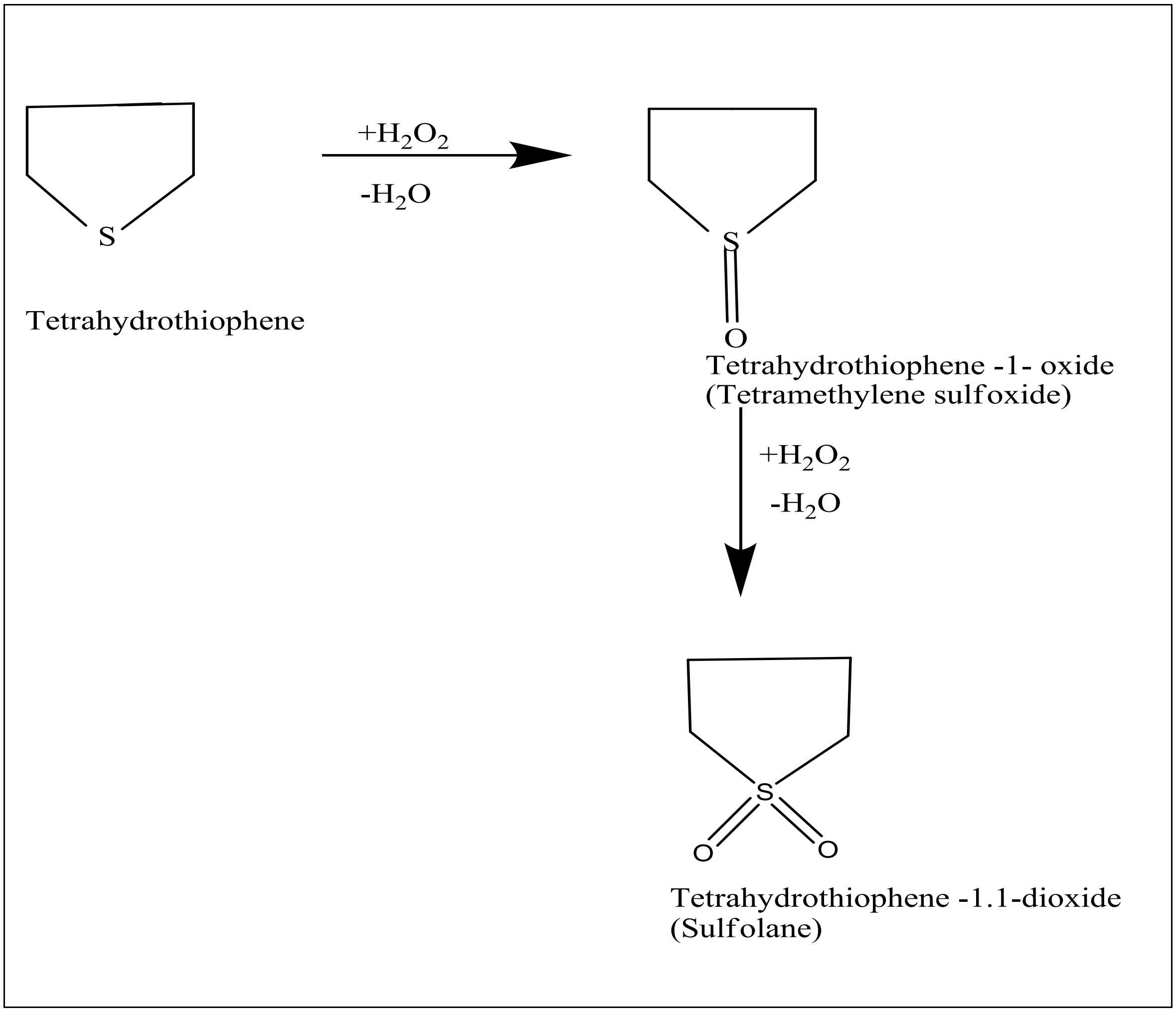


Figure 1.7 Preparation of sulfolane from tetrahydrothiophene

1.4.5 Uses of sulfolane

- Sulfolane is predominantly used as an extracting solvent of aromatic hydrocarbons like benzene, toluene and xylenes from aliphatic hydrocarbon mixtures and n-propyl alcohol and sec-butyl alcohol. It was found to be highly effective in separating the high purity hydrocarbon mixtures using liquid-liquid extraction. This process is still widely used today in refineries and in the petrochemical industry (Shaohui, 2006)
- It is used to purify natural gas streams and fractionation of fatty acids into saturated and unsaturated components
- It can be used in plasticize nylon, cellulose and cellulose esters to improve flexibility and increase elongation of polymers. It can be used alone on in combination with a co-solvent as a polymerization solvent for polyureas, polysulfones, polysiloxanes and polyether polyols (Goodenbour *et al*, 1962).
- Sulfolane has been tested as a solvent in lithium batteries due to its high dielectric constant, low volatility, solubilising characteristics and aprotonic nature.
- It is used in textile industry for preparation of dyes, fabric treating prior to dyeing and fibre treating.
- Sulfolane is also an industrial solvent for purifying aromatics, it operates at a low solvent-to-feed ratio making sulfolane units highly cost effective
- Sulfolane is highly stable and can therefore be re-used many times; it does eventually break down into acidic by-products. Some measures has been developed to remove the by-products thereby allowing sulfolane to be re-used and increasing the lifetime of a given supply. The methods include vacuum and steam distillation, back extraction, adsorption and also anion-cation exchange resin columns.

1.5 ORGANIC ACIDS

1.5.1 Introduction

Organic acids are compounds having the functional group –COOH and they behave like acids hence they are known as organic acids. The functional group –COOH is called the carboxyl group, and thus the organic acids are also known as carboxylic acids.

The bonds in a carboxyl group are such that the carbon has a double bond with the oxygen and a single bond with the hydroxyl group (OH) (Morrison and Boyd, 1992).

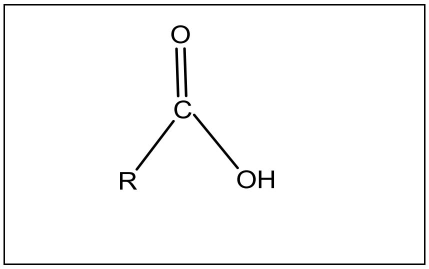


Figure 1.8 Structure of carboxylic acid

1.5.2 Synthesis of organic acids in laboratory

1.5.2.1 Oxidation of alcohol

Organic acids can be produced by oxidation of primary alcohols and aldehydes with strong oxidants such as the Jones reagent, potassium permanganate, or sodium chlorite.

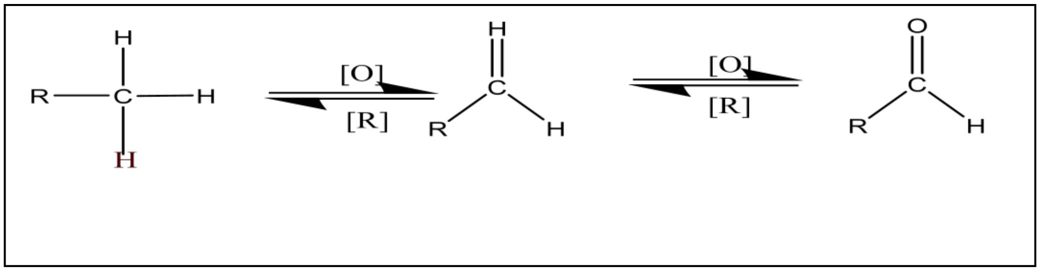


Figure 1.9 Synthesis of carboxylic acid from primary alcohol.

Jones reagent is a solution of chromium trioxide in diluted sulphuric acid that can be used for oxidation of secondary alcohols to ketones and of primary alcohols to carboxylic acids and in a few cases to aldehydes (Harding, 1975).

1.5.2.2 Hydrolysis of nitriles

Primary alkyl halide can be under goes a substitution reaction by reacting with sodium cyanide. The cynide ion will replace the halogen to form a nitrile and then can be hydrolysed by aqueous acid to form a carboxylic acid.

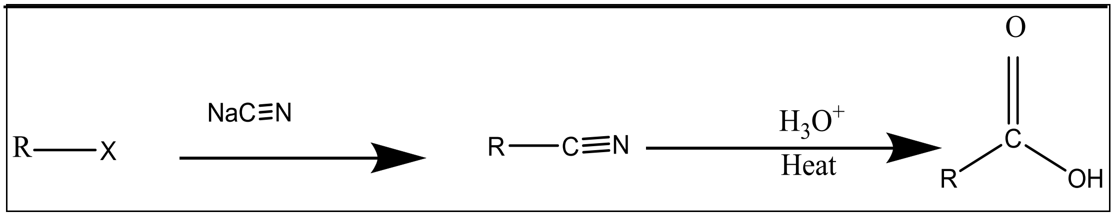


Figure 1.10 Synthesis of carboxylic acid from primary alkylhalide

1.5.2.3 Hydrolysis of esters

Carboxylic acid esters hydrolyse to parent carboxylic acid and alcohol, the process is called saponification. Reagents used are aqueous acid or aqueous sodium hydroxide together with heat.

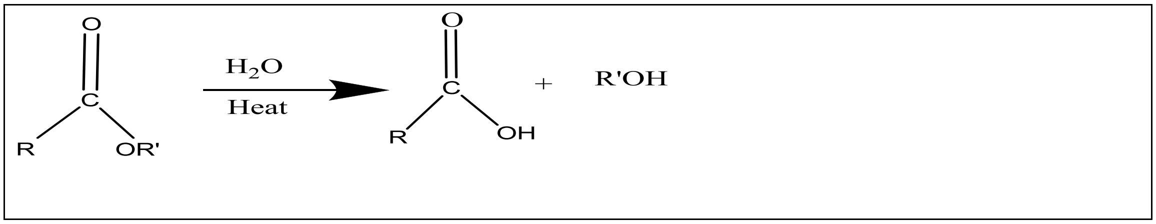


Figure 1.11 Synthesis of carboxylic acid from carboxylic acid esters

1.5.3 Properties of organic acids

1.5.3.1 Physical properties

The first three organic acids in the homologous series that is methanoic acid, ethanoic acid and propanoic acid are all colourless liquids at ordinary room temperature. Organic acids having a greater number of carbons are colourless oily liquids at ordinary room temperature. Organic acids with even higher number of carbon atoms are colourless wax like substances at ordinary room temperature. The first three organic acids have a pungent smell, the organic acids with four to nine carbon atoms smell like goat’s butter, and higher molecular weight organic acids are odourless (Morrison and Boyd, 1992).

The first homologous organic acids are soluble in water, but as the molecular weight increase the solubility in water decreases. Solubility is affected by the ratio of the size of hydrophilic to hydrophobic of the compound as hydrocarbons are non polar and hydrophobic whilst the hydrogen bonding is polar and hydrophilic (Yuen, 2003).

An acid is considered to be any chemical compound that when dissolved in water gives the solution a hydrogen ion activity greater than in pure water that is the pH less than 7.0. At equilibrium, the reaction of weak acid (HA) and water (H_2O) which act as a base given by

$$\boxed{HA\,(aq) + H_2O \rightarrow H_3O^+(aq) + A^-(aq)} \qquad (1.6)$$

The acidity constant (K_a) is the equilibrium constant for the reaction of HA with water

$$\boxed{K_a = \frac{[H_3O^+][A^-]}{[HA]}} \qquad (1.7)$$

The organic acids are weak acids in a sense that its ionization is incomplete. Strong acids have large Ka values, and the acidic nature of organic acids decreases as the number of carbon increases in the homologues series (Yuen, 2003).

1.5.3.2 Chemical Properties

Formic acid and acetic acid turns blue litmus paper red quite easily; and this indicates the acidic nature of the compounds. The higher members however of the organic acid do not show this test readily.

Organic acids react with sodium bicarbonate to release water and carbon dioxide. If acetic acid reacts with sodium bicarbonate, sodium ethanoate, an ester is also formed along with water and carbon dioxide.

The reaction show below:

$$\boxed{\mathbf{CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + H_2O + CO_2}} \qquad (1.8)$$

The sodium bicarbonate test is a test for the presence of the carboxyl group (-COOH) in a compound. A positive test for carboxylic acid causes effervescence resulting from the released of carbon dioxide.

Esters are formed when alcohols are made to react with organic acids in the presence of concentrated sulphuric acid. The reaction below shows the reaction of acetic acid with ethanol.

$$\boxed{\mathbf{CH_3COOH + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + H_2O}} \qquad (1.9)$$

Ethanol and acetic acid is mixed and warmed, a few drops of concentrated sulphuric acid is added and a sweet smell will emanate from the reaction. The sweet smell is the smell of the ester, ethyl ethanoate.

1.5.4 Applications of organic acids

- Simple organic acids like methanoic and ethanoic acids are used for oil and gas cell stimulation treatments
- Acetic acid is also used in some food items for example vinegar and it is used by medical industries for synthesis of asprin.

- Acetic acid is used for coagulation of latex; it is needed when rubber is made from latex in the rubber industry.
- Acetic acid is used for making cellulose acetate, which is an important starting material for making artificial fibres.
- Propanoic acid inhibits the growth of the mold and some bacteria, and as a result it is used as a preservative for both animal feed and food for human consumption (Bertleff *et al,* 2003).
- Propanoic acid is useful as an intermediate in the production of other chemicals, especially polymers, for example cellulose-acetate propionate is a useful thermoplastic used to make pesticides and pharmaceuticals.
- Esters of propanoic acid have fruit-like odours and are sometimes used as a solvents or artificial flavourings (Bertleff *et al,* 2003).
- Propanoic acid and its calcium, sodium and potassium salts are widely used throughout the food industry as preservatives (Ahmad and Othman, 2010)
- Propanoic acid as a preservative extends the shelf life of food products by inhibiting the growth of moulds and some bacteria (Ahmad and Othman, 2010)
- Butanoic acid is used in the preparation of various butanoate esters, low molecular weight esters of butanoic acid such as methyl butanaote, have mostly pleasant aromas or taste, and they are used as food and perfume additives.
- Pentanoic acid is primarily used to synthesis esters; volatile esters of pentanoic acid tend to have pleasant odours and are used in perfumes and cosmetics. Ethyl valerate and pentyl valerate are used as food additives because of their flavours.
- 2-Methylbutanoic acid is used for synthetic lubricants and is also used as a chemical intermediate for plasticizers, pharmaceuticals, metallic salts and vinyl stabilizers.

1.6 ALCOHOLS

1.6.1 Introduction

Alcohol is any organic compound in which a hydroxyl group is bound to a carbon atom of the alkyl or substituted alkyl group. An important group of alcohols is formed by the simple acyclic alcohols, the general formula for which is C_nH_{2n+1}

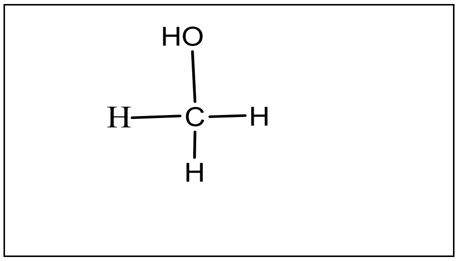


Figure 1.12 Structure of an Alcohol

1.6.2 Properties of alcohols

There are three major subsets of alcohols, which are primary, secondary and tertiary alcohols, which are based upon the number of carbon, and how the C-OH group is bonded**.** Alcohols are polar, and they can form hydrogen bonds to one another and other compounds.

Alcohols can be used as protonic solvents, two opposing solubility trends in alcohols are the tendency of the polar OH to promote solubility in water and the carbon chain resist it. Thus methanol, ethanol and propanol are miscible in water because they have a shorter carbon chain.

Butanol is moderately soluble in water, and alcohols that have five and more carbon are effectively insoluble in water. All simple alcohols are miscible in organic solvents. Alcohols have an odour that is often described as biting and as hanging in the nasal passages.

1.6.3 Applications of alcohol

- Ethanol is the only alcohol than can be used as an alcoholic beverage and has been consumed by humans since pre-historic times
- Methanol and ethanol can also be used as the alcohol fuel, the fuel performance can be increased in force induction internal combustion by injecting alcohol into the air intake, after the turbocharger or supercharger has pressurized the air.
- Alcohols can also be used in chemical industries as reagents or solvents because they of its low toxicity and ability to dissolve non polar substances.
- Ethanol can be used as a solvent in medical drugs. It canalso be used as an antiseptic to disinfect the skin before injections are given along with iodine.
- Alcohol gels has been common as hand sanitizers
- Ethanol is used as the preservative for specimens
- Ethanol-based soaps are becoming common in restaurants and are convenient because they require less drying due to the volatility of the compound.
- In organic synthesis alcohols serves as versatile intermediates.

1.7 AREA OF RESEARCH COVERED IN THIS WORK

This project involves an investigation into the feasibility of separation of carboxylic acids from hydrocarbons including a cyloalkane, using sulfolane as a solvent for extraction. Solvents for extraction should have a high selectivity for one of the components, high capacity, capacity to form two phases at reasonable temperatures, capability of rapid phase separation, be non-corrosive, non-reactive and show good thermal stability.

In the first part of this work, the effectiveness of solvent extraction by sulfolane was investigated for ternary systems at T = 303.15 K. The ternary systems consist of (sulfolane + carboxylic acid + hydrocarbon), (sulfolane + carboxylic acid + cycloalkane) and (sulfolane + alcohol + hydrocarbon).

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

- Sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + heptane
- Sulfolane + acetic acid or propanoic acid or butanoic acid 2-methylpropanoic acid or or pentanoic acid or 3-methylbutanoic acid + cyclohexane.
- Sulfolane + acetic acid or propanoic acid or butanoic acid 2-methylpropanoic acid or or pentanoic acid or 3-methylbutanoic acid + dodecane.
- Sulfolane + methanol or ethanol or 1- propanol or 2-propanol or 1-butanol or 2-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol + heptane.

The purpose of this project is develop a economically viable separation of carboxylic acids or alcohols from hydrocarbons using sulfolane serves two purposes, polluted aqueous streams can be cleaned up and high valued chemicals can be produced relatively cheaply. This in turn will save South Africa valuable foreign exchange as many of these compounds are imported.

The liquid-liquid equilibria work in this project was aimed at finding the following effect of the ternary mixtures [sulfolane (1) + a carboxylic acid (2) or alcohol (2) + hydrocarbon (3)] on the phase equilibria

- Increasing the carbon chain length of carboxylic acid
- Increasing the carbon chain length of the hydrocarbon

The second part of this work is the fitting of the binodal models to the experimental binodal data determined. The modified Hlavatý, beta (β) and log γ equations will be fitted to the experimental binodal data. The NRTL (Non-Random, Two Liquid) and UNIQUAC Universal Quasichemical) model would be used to correlate the experimental tie-lines and calculate the phase compositions of the ternary systems.

The structures for the six carboxylic acids, eight alcohols and hydrocarbons used in this work are shown in figure 1.13.

CH_3COOH	acetic acid
CH_3CH_2COOH	propanoic acid
$CH_3CH_2CH_2COOH$	butanoic acid
$(CH_3)CHCOOH$	2-methylpropanoic acid
$CH_3CH_2CH_2CH_2COOH$	pentanoic acid
$(CH_3)_2CHCH_2COOH$	3-methylbutanoic acid
CH_3OH	methanol
CH_3CH_2OH	ethanol
$CH_3CH_2CH_2OH$	1-propanol
$CH_3CH(OH)CH_3$	2-propanol
$CH_3CH_2CH_2CH_2OH$	1-butanol
$CH_3CH(CH_3)CH_2(OH)$	2-methyl-1-propanol
$CH_3CH(OH)(CH_3)CH_3$	2-methyl-2-propanol
$CH_3(CH_2)_5CH_3$	heptane
C_7H_{14}	cyclohexane
$C_{12}H_{26}$	dodecane

Figure 1.13 Structures of carboxylic acids, alcohols and hydrocarbons used in the study

The third part of this work involves investigating of the excess molar volumes of the binary mixtures (sulfolane + an alcohol) T = 298.15 K, T = 303.15 K and T = 308.15 K. The sulfolane mixtures were [sulfolane (1) + methanol or ethanol or 1-propanol or 2- propanol or 1-butanol or 2-butanol or 2-methyl-1-propanol or 2-methyl-2-propano (2)]. Excess molar volume data is a useful parameter in the design of the technological separation processes for the components, and can be used to predict vapour liquid equilibria using appropriate equation of state models. Redlich–Kister equation was used to correlate the excess molar volume data obtained.

CHAPTER 2

LITERATURE REVIEW

2.1 LIQUID-LIQUID EQUILIBRIUM FOR TERNARY MIXTURES

Solvent extraction is a major technique and its operation is based entirely on limited liquid miscibility and the distribution of solutes between two liquid phases. The separation of two components in solution is achieved by the addition of the third component, that is the third liquid which is added to the solution mixture to bring about the extraction. This solvent takes up part of the components of the original solution and forms an immiscible layer composed of the remainder of the original solution plus some of the solvent (Redhi, 2003). Sulfolane is popular solvent for extraction due its physical and chemical properties.

Lee and Kim (1995) presented liquid-liquid equilibrium data for the systems (sulfolane + octane + benzene), (sulfolane + octane + toluene) and (sulfolane + octane + p-xylene) at T = 298.15 K, T = 308.15 K and T = 318.15 K. It was reported that the size of the two phase region decrease with an increase in the temperature. The tie line data were satisfactory correlated by the Othmer and Tobias method, and the experimental data were compared to the values calculated by the UNIQUAC and NRTL models. It was concluded that although good quantitative agreement was obtained with both these models, the NRTL model values were found to be substantially better than UNIQUAC model values.

Chen-Feng and Wen-Churng (1999) presented the liquid-liquid equilibria of alkane C10/C12/C14) + octylbenzene + sulfolane) at T = 323.15 K, T = 348.15 K and T = 373.15 K. The addition of octylbenzene to sulfolane was found to increase the solubility of alkanes in the order of n-decane > n-dodecane > n-tetradecane. It was concluded that the higher the temperature, the larger the distribution coefficient value. An increase in solvent capacity (distribution coefficient) of sulfolane leads to a decrease in its selectivity, therefore in-order to choose the optimum values of the selectivity and solvent capacity, a compromise between the two parameters must be achieved by adjusting the temperature or adding a second component like water to the solvent.

Chen-Feng and Wen-Churng (1999) studied the ternary liquid-liquid equilibria of alkane ((C10/C11/C12/C14) + 1.4 disopropylbenzene + sulfolane) at T = 322.15 K, T = 348.15 K and T = 373.15 K. The addition of 1.4, diisopropylbenzene to sulfolane was found to increase the solubility of alkanes 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 the (n-dodecane + sulfolane) or (n-tetradecane + sulfolane) mixtures. The size of the two phase region was found to decrease with an increase in temperature, and from the selectivity data, it can be concluded that the separation of 1.4-diisopropylbenzene from n-decane, n-dodecane or n-tetradecane is feasible with sulfolane as a solvent.

Chen *et al.*, (2000) studied the liquid-liquid equilibrium data of six ternary systems: (n-hexane + benzene + sulfolane), (n-hexane + toluene + sulfolane, n-hexane + xylene + sulfolane), (n-octane + benzene + sulfolane, n-octane + toluene + xylene + sulfolane), three quaternary systems: (n-hexane + n-octane + benzene + sulfolane), (n-hexane + benzene + toluene + sulfolane, n-octane + toluene + xylene + sulfolane), one quinary system: (n-hexane + n-octane + benzene + toluene + sulfolane).

Chen *et al.*, found that NRTL and UNIQUAC parameters between n-hexane and n-octane, benzene and toluene, benzene and xylene, toluene and xylene are suggested to be zero. The results from the quarternary and quinary systems showed RMDS are < 0.01. The maximum deviation is 0.018 for the mole fraction of sulfolane in the system (n-hexane + n-octane + benzene + sulfolane).

Letcher and Redhi (2001) presented the liquid-liquid equilibrium data for (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 of the carboxylic acids was higher in the acetonitrile than in the hydrocarbon layer. The influence of 3-methylbutanoic acid, pentanoic acid, 2-methylpropanoic acid and butanoic acid on the solubility of the hydrocarbon in acetonitrile was greater than that of acetic acid and propanoic acid. The separation of carboxylic acid from the cyclohexane by extraction with acetonitrile was feasible.

Wen-Churng and Nein-Hsin (2002) presented equilibrium tie line data at T = 323.15 K, T = 348.15 K and T = 373.15 K for the ternary liquid- liquid equilibria of octane + (benzene or toluene or m-xylene + sulfolane) systems. The mutual solubility of benzene was higher than that of toluene or m-xylene in (octane + sulfolane) mix. Correlation of tie line data showed that calculated values based on the NRTL were found to be better than those based on UNIQUAC equation.

Rappell *et al*., (2002) studied the ternary systems of (sulfolane + *p*-xylene + cyclohexane), (sulfolane + *p*-xylene + *n*-hexane) and (sulfolane + toluene + n-hexane) at T = 308.15 K and T = 323.15 K. The systems were compared at different temperatures and the results showed that the two-phase region was enlarged as the temperature was increased, indicating that at higher temperature, sulfolane is more selective solvent for aromatic compounds. The experimental data was better fitted with the NRTL than the UNIQUAC model.

Ahmad *et al*., (2004) presented interaction parameters for multi-component aromatic extraction with sulfolane. Activity coefficient models were used to predict the behaviour of ternary data of systems at different temperatures. The parameter estimation procedure was modified to estimate the parameters simultaneously for different systems involving common pairs that were used for parameter estimation. It was reported that the results of separate estimation showed that the binary interaction parameters for the same pairs are different for different systems. The objective function was modified to estimate the binary interaction parameters using three systems with common pairs simultaneously.

Mohsen-Nia *et al*., (2005) studied the ternary mixtures of (solvent + aromatic hydrocarbon + alkane) at different temperatures from T = 298.15 K to T = 313.15 K. The aromatic hydrocarbon was toluene or m-xylene and the alkane was n-heptane or n-octane or cyclohexane and the solvent was sulfolane or dimethyl sulfoxide or ethylene carbonate. It was reported that the size of the two phase region decreased with increase in temperature.

The selectivity and distribution coefficient of the used solvents were compared in this study. It was also reported that in extraction of aromatics from non aromatics, the solvent with higher selectivity and distribution coefficient, was preferred, and based on calculated selectivity and distribution coefficient indicated the superiority of ethylene carbonate and dimethyl sulfoxide. It was concluded based on the very strong and bad odour, as well as recovery difficulties of dimethyl sulfoxide, ethylene carbonate was considered a better solvent than dimethyl sulfoxide.

Im *et al*., (2006) studied the liquid- liquid equilibrium of the binary of sulfolane and branched cycloalkanes (methylcyclopentane, methylcyclohexane, and ethylcyclohexane) over the temperature range around T = 300 K to T = 460 K.

The compositions of both branched cycloalkane-rich and sulfolane-rich phases were analyzed by on-line gas chromatography. The quantitative description of liquid-liquid equilibria of industrial interest containing sulfolane and branched cycloalkanes was gathered to accurately simulate and optimize the extractive distillation units, where these systems were involved.

Mohsen-Nia and Paikar (2007) presented the liquid-liquid equilibrium data for ternary and quaternary systems containing (*n*-hexane, toluene, *m*-xylene, propanol, sulfolane and water) were at T = 303.15 K. The efficiency of extraction of toluene or *m*-xylene from *n*-hexane by using sulfolane as the pure-solvent and (sulfolane + propanol) or (sulfolane + water) as the mixed-solvents is evaluated by comparison of the selectivity factors and distribution coefficients. It was concluded that the extraction of toluene an *m*-xylene from *n*-hexane the mixed-solvent (sulfolane + propanol) has lower selectivity factor and higher distribution coefficient than the pure solvent sulfolane at T = 303.15 K.

Santiago and Aznar (2007) studied the liquid- liquid data for three quaternary systems containing (sulfolane, nonane + undecane + benzene + sulfolane), (nonane + undecane + toluene + sulfolane), and (nonane + undecane + *m*-xylene + sulfolane) at T = 298.15 K and T = 313.15 K and ambient pressure. The size of the two-phase region was reported to decrease with an increase in temperature. The effect was mostly observed in the systems containing the m-xylene. It was observed that toluene, benzene and m-xylene were more soluble in the hydrocarbon than in the sulfolane. The slope of the tie lines showed that toluene, benzene and *m*-xylene are soluble in hydrocarbon-rich mixture than in sulfolane-rich mixture. The solubility effect was reported to be reflected in the size of the two-phase region, which increased slightly in order benzene > toluene > *m*-xylene at the same temperature. It was concluded that the effect of temperature was very small on the liquid –liquid equilibrium data.

Santiago and Aznar (2007) the presented the liquid- liquid data three quinary mixtures (nonane + undecane + benzene + toluene + sulfolane), (nonane + undecane + benzene +*m*-xylene + sulfolane) and (nonane + undecane + toluene + *m*-xylene + sulfolane) at T = 298.15 K and T= 313.15 K and ambient pressure. Liquid–liquid equilibrium data of the three quinary systems, (nonane + undecane + benzene or toluene or *m*-xylene) was investigated. It was reported that the size of the two-phase region decreased with an increase in temperature. This effect was observed to be stronger in the systems containing *m*-xylene. The data also showed that toluene, benzene and *m*-xylene were more soluble in the aliphatic-rich phase than in sulfolane-rich phase. This solubility effect was reflected in the size of the two-phase region, which increased slightly in the order benzene > toluene > *m*-xylene, at the same temperature.

Awwad *et al*., (2008) presented the liquid-liquid equilibria for pseudo-ternary systems for [sulfolane + 2-ethyoxyethanol (1) + octane (2) + toluene (3)] at T = 293.15 K. It was reported the solvent (sulfolane + 0.75% ethoxyethanol) showed higher capacity for toluene compared to pure sulfolane and for that reason it could be used for higher recovery of aromatics at lower solvent to feed ratios and temperatures. It was concluded from the selectivity values that the separation of toluene from octane by extraction with (sulfolane + mass % 2-ethyoxyethanol) was feasible. The comparison between experimental selectivity data of (sulfolane + mass % 2-ethyoxyethanol) with that of (sulfolane + 2-methoxyethanol) for the extraction of toluene from (toluene + octane) mixture at T = 293.15 K was more efficient using (sulfolane + mass % 2-methoxyethanol).

Mohmoudi *et al*., (2010) studied the liquid-liquid equilibrium properties for the binary systems containing (n-formoylmorpholine + benzene + n-hexane), (sulfolane + benzene + n-hexane) and quaternary mixed solvent system (sulfolane + N-formolymorphiline + benzene + n-hexane) measured at temperature ranging from T = 298.15 K to T = 318.15 K and at atmospheric pressure. The experimental distribution coefficients and selectivity factors were presented to evaluate the efficiency of the solvents for extraction of benzene from n-hexane. The liquid-liquid equilibria results reported indicated that increasing temperature decreased the selectivity for all solvents. It was concluded from the result that sulfolane has highest selectivity and n-formoylmorpholine has the highest distribution coefficient whilst the mixed solvent (sulfolane + n-formoylmorpholine has higher selectivity factor than n-formoylmorpholine and higher distribution coefficient than sulfolane. It was concluded that all solvents are feasible for separation, but selection of the best solvent depends on the most economically viable.

2.2 EXCESS MOLAR VOLUMES MIXTURES

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). The volume change on mixing of binary liquid mixtures,V_m^E, at constant pressure and temperature is of interest to chemists and chemical engineers, and is an indicator of the non-idealities present in real mixtures. It is important to thermochemists because it serves as a sensitive indicator for the applicability of liquid mixtures (Redhi, 2003).

Benoit and Charbonneau (1969) presented molar excess free energies for the systems of (sulfolane + benzene) and (sulfolane + dichloromethane) were calculated from static vapour pressure measurement at T = 303.15 K.

Refractive indexes, excess partial molar volumes of mixing and enthalpies of mixing at infinite dilution of benzene and dichloromethane were also determined. The excess Gibbs free energy was observed to be negative and the heat of solution at infinite dilution of dichloromethane was exothermic. It was concluded that the complex-forming interactions between the solvent and molecules and such complexes are known to exist in other binary systems of dichloromethane with a proton acceptor.

Yang-Xin and Yi-Gui (1998) presented the excess molar volume data on mixing for binary mixtures of sulfolane with toluene, o-xylene, m-xylene, p-xylene, ethylbenzene and 1,2,4-trimethylbenzene at T = 298.15 K. It was found that all mixtures exhibited negative excess volumes over the entire mole fraction range for all binary systems. It was reported that the negative excess molar volumes were due to the expansion in volume due to mutual loss of dipolar association and the difference in size of and shape of the component molecules and that contraction in volume comes from the dipole-induced and dipole-dipole interactions and donor acceptor interactions between unlike molecules. The molar volumes for equimolar mixtures were found to vary in the order of toluene > p-xylene > m-xylene > ethylbenzene > o-xylene > 1,2,4-trimethylbenzene.

Letcher *et al*., (2000) studied the excess molar volumes and excess molar enthalpies were measured as a function of mole fraction at T= 303.15 K and atmospheric pressure for each of the mixtures (1-heptyne, or 1-octyne + sulfolane). The excess molar volumes were also measured for mixtures of (1-hexyne + sulfolane).

The 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 (1-alkyne + sulfolane) measured were very large, negative and slightly asymmetrical in form. The increase in the molar excess volume was in the sequence 1-hexyne >1-heptyne > 1-octyne

Yang-Xin e*t al*., (2000) presented data on two binary mixtures of (water + sulfolane) and (water + tetraethylene glycol). The excess molar volumes for both binary mixtures were negative and it was shifted towards the water-rich region for the (water + sulfolane) and (water + tetra-ethylene glycol) systems. Excess molar volumes for aqueous tetraethylene glycol solutions are smaller than those for the other systems of sulfolane and water. This effect was explained as follows: the increase in the order of the system is due to the formation of hydrogen bonds between water and tetra-ethylene glycol molecules.

Yang *et al*., (2004) presented densities and viscosities of the binary systems of (sulfolane + ethylbenzene, sulfolane + p-xylene) at T = 303.1 K to T = 353.15 K and at atmospheric pressure. It was reported that the excess molar volume of the two mixtures exhibited negative excess molar volumes on the entire composition range for the two systems. It was also found that excess molar volumes and viscosity deviation showed a systematic change with increasing temperature.

Wang *et al*., (2004) presented the excess molar volumes of (cyclohexanone + benzene, or toluene, or ethylbenzene, or styrene), obtained from the densities over the composition range at temperature T = (293.15 K, 303.15 K, 313.15 K, 323.15 K, 333.15 K, 343.15 K and 353.15 K) and atmospheric pressure.

It was reported that the excess molar volumes had shifted in a regular way with the increasing temperature from T = 293.15 K to 313.15 K.

In each system, a slight decrease in the excess molar volumes over the whole mole fraction range was noticeable with increasing temperature. It was concluded that by comparison of the minimum values of excess molar volumes for three mixtures containing an aromatic hydrocarbon at the same temperature, styrene was the most favourable one to form close packing with cylohexanone.

Chen *et al*., (2005) presented viscosities and densities for binary mixtures of n-methylpiperazine with methanol, ethanol, n-propanol, isopropanol, n-butanol and isobutanol at T = 293.15 K, T = 298.15 K and T = 303.15 K and atmospheric pressure. It was reported that all the investigated systems exhibited very large positive values of viscosity deviation, and excess Gibbs energy and excess molar volumes were negative over the entire composition range. The deviations were attributed to the strong cross association between the alkonol and n-methylpiperazine molecules through the hydrogen bond of O-H-N. It was also reported the temperature had a significant effect on viscosity deviation, and relatively slight effect on the excess molar volumes and excess Gibbs energy.

Šerbanović *et al*., (2006) presented the four binary mixtures of (methanol + benzene), (ethanol + benzene), (methanol + chlorobenzene) and (ethanol + chlorobenzene) at six different temperatures, T= (288.15 K, 293.15 K, 303.15 K, 308.15 K and 313.15 K). It was reported that the results were analysed in terms of specific molecular interactions present in the mixtures taking into considerations the effect of temperature on them. Šerbanović *et al* also found that excess molar volumes increased with an increase in temperature and concluded that excess molar volumes increased with an increase in temperature.

Ho *et al*., (2007) presented heat capacities of aqueous solutions of sulfolane with 2-amino-2-methyl-1-propanol over the range from T = 303.15 K to T = 353.15 K using the differential calorimeter. The liquid heat capacities of sulfolane alone and binary mixtures were also studied.

It was reported that the heat capacities of sulfolane and (sulfolane + water) were found to be agreement with those values reported on literature. It was concluded that the heat capacities of aqueous mixtures of sulfolane and amino-2-methyl-1-propanol, in general, are of sufficient accuracy for most engineering-design calculations.

Kinart *et al*., (2007) presented densities and relative permittivities of the binary mixtures of sulfolane with ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol, measured as function of composition at T = 303.15 K. It was reported that the excess molar volumes were negative over the entire mole fraction composition range for all the systems, and the magnitude of molar excess volume became more negative as the number of oxyethylene groups in the glycols increased. It was concluded that the globular molecules of sulfolane had no significant intermolecular hydrogen bonding capability in pure liquid and the molecules of glycols are self-associated liquids though inter- and intramolecular hydrogen bonding. The formation of intramolecular hydrogen bonds in the liquid ethylene gylocols was more favourable when the molecules of these solvents are in the gauche formations.

Aguila-Hernandez *et al*., (2008) presented kinematic viscosities for the binary systems composed of N-methylpyrrolidone + monoethanolamine and N-methylpyrrolidone + diethanolamine throughout the concentration range at eight different in a range of temperature from T = 303.15 K to T = 373.15 K. The experimental results of both pure and binary systems showed a decrease in viscosities with the increase in temperature.

In binary systems, the change of viscosity with concentration for two sets of mixtures of N-methylpyrrolidone was very large in the range T = 303.15 K to T = 353.15 K, whereas it was small in the range T = 363.15 K to T = 373.15 K. The observed behavior in the change of viscosity with concentration of sulfolane with monoethanolamine was reported to be have deviated from that shown by (sulfolane with diethanolamine) at T = 303.15 K to T = 373.15 K.

The system of (N-methylpyrrolidone + monoethanolane) was reported to have a minima viscosity point in the sulfolane-rich region whilst the (N-methylpyrrolide + diethanolamine) system showed large variations of viscosity at low sulfolane concentration at T = 303.15 K and T = 323.15 K, whereas at T = 353.15 K the viscosity values were changed smoothly between those for the two pure components.

Chen *et al*., (2010) presented four binary mixtures of (benzene + nonane), (toluene + *o*-xylene), (*m*-xylene + sulfolane) and (*o*-xylene + sulfolane) at T = 333.15 K and T = 353.15 K. The excess molar volumes of (benzene + nonane), (*m*-xylene + sulfolane) and (*o*-xylene + sulfolane) at T = 333.15 K and T = 353.15 K were positive. It was concluded that the toluene + o-xylene mixture was close to the ideal solution whereas three systems of (benzene +nonane), (m-xylene + sulfolane) and (*o*-xylene + sulfolane) mixtures showed an apparent deviation from the ideal solution. The associated binary interaction parameters between each component for four mixtures were correlated with the Wilson, NRTL and UNIQUAC models.

CHAPTER 3

LIQUID-LIQUID EXTRACTION

3.1 LIQUID-LIQUID EXTRACTION AS A TECHNIQUE

3.1.1 Introduction

An important step within the processes in the petrochemical industry is the recovery of high–purity hydrocarbons from naphtha. Aromatic compounds are separated from the aliphatic hydrocarbons present in naphtha through solvent extraction since distillation is not suitable (Santiago and Aznar, 2007). Solvent extraction is one of the most important methods to produce high-purity aromatic extracts from catalytic reformates (Yang-Xin *et al*, 2001).

As an effective method, extraction and extractive distillation, with the separating agent especially a polar solvent have been used to separate the slightly polar compound from the non-polar compound (Im *et al*, 2006). The separation is based entirely on limited liquid miscibility and the distribution of solutes between two liquid phases. The separation of two components in solution is achieved by addition of the third component. The liquid third component which is added to the solution to bring about the extract is known as the solvent or entrainer. This solvent takes up part of the components of the original solution and forms an immiscible layer composed of the remainder of the original solution plus some of the solvent, termed as the raffinate (Redhi, 2003).

Phase equilibrium involves the transfer of substance from one phase to another. When two phases are bought into contact they exchange their constituents until the composition of each phase attains a constant value and equilibrium has been attained. The equilibrium composition of the two phases can be very different from one another and it is this difference which enables mixtures to be separated by distillation, extraction and other phase contacting operations (Redhi, 2003).

3.1.2 Principle of liquid-liquid extraction

In the design of such processes, it is necessary to know the data that can be used to calculate the composition of the two phases in equilibrium. It is essential that liquid mixture and the solvent are at least partially if not completely immiscible, and in essence, three stages are involved:

(i) Bringing the mixture and the solvent into intimate contact
(ii) Separation of the resulting two phases,
(iii) Removal and recovery of the solvent from each phase

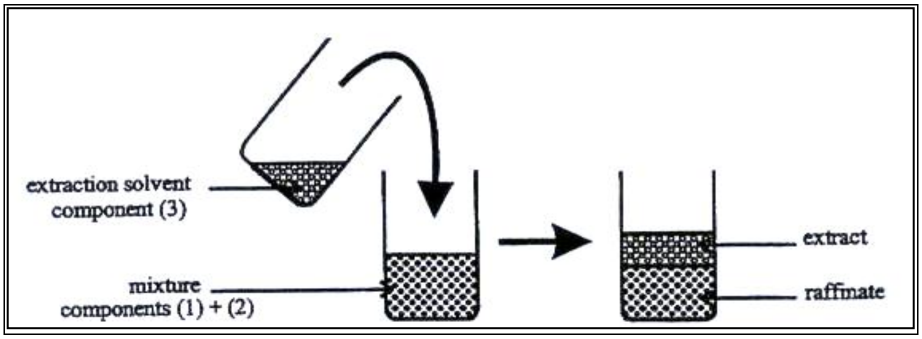


Figure 3.1 Principle of liquid-liquid extraction

The equilibrium phase depends on variables such as temperature, pressure, chemical nature and concentration of the various substances involved. Phase equilibrium thermodynamics seeks to establish the relationship between the various properties when the system is at equilibrium. Phase equilibrium is related quantitatively to the intensive properties that is temperature and pressure which describe the equilibrium state of two or more homogenous phases (Naicker, 2000).

3.2 CRITERIA USED TO SELECT POTENTIAL SOLVENT FOR SOLVENT EXTRACTION

The choice of solvents for solvent extraction processes involves a systematic approach, which is influenced by the following considerations of solvent properties (Reddy, 2003).

3.2.1 Selectivity

The selectivity, ω, is the ratio of the mole fractions of two components that are to be separated in the one phase to the ratio of the same two components in the other phase.

$$\boxed{\textbf{Selectivity } (\omega) = \frac{(x_2/x_3)\ \text{phase}_1}{(x_2/x_3)\ \text{phase}_2}} \qquad (3.1)$$

Where x_2 and x_3 are the mole fractions of the components to be separated. For an efficient separation the value of selectivity, ω, must not be 1, as this means that the overall composition of the two phases in equilibrium with each other is the same (Reddy, 2003).

3.2.2 The distribution coefficient

The capacity is described by distribution coefficient, K, which is the ratio of the concentration of component to be separated in the solvent rich (extract) phase to the ratio of the same component in the solvent depleted (raffinate) phase. K should be large for a chosen solvent.

$$\boxed{K = \frac{(x_2)\ \text{phase}_1}{(x_2)\ \text{phase}_2}} \qquad (3.2)$$

3.2.3 Ease of Recovery

Ideally a solvent which is easily separated from the mixture and then purified so that it can be recycled and be re-used is desirable. For effective separation, there should be a large difference in volatilities of the components in relation to the solvent. There should be a high boiling point difference between the solvent and the extracted components to ensure that the solvent can easily be recovered by distillation.

3.2.4 Solvent Solubility

The solvent should have low solubility in one of the components, and separation in the two phases region should be large. The latter presents a larger composition range in which the solvent can be used.

A ternary phase diagram with the large two phase region implies a relatively high mutual insolubility of the components in the ternary mixture. This is an advantage as the useful composition range over which the extraction solvent entrainer can be utilized is large as shown in figure 3.2 (Redhi, 2003).

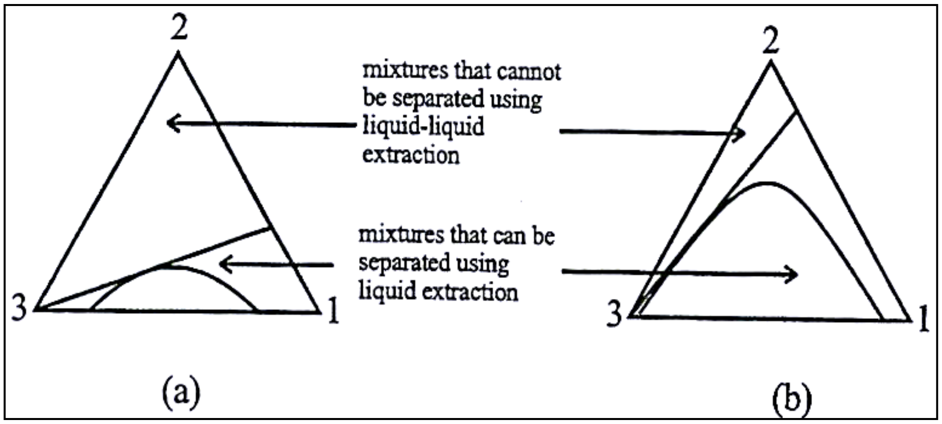


Figure 3.2 (a) Ternary liquid-liquid phase diagram with a small two phase region. (b) Ternary liquid-liquid phase diagram with a large two-phase region

3.2.5 Density and viscosity

A large density difference between the equilibrium conjugate phases in the mixture is ideal to favour phase separation, as this facilitates rapid phase separation. The density difference between the two phases should be large and the interfacial tension of the solvent must be large. Both properties ensure rapid separation of the two phases. A low viscosity solvent is preferred from a theoretical and practical point of view. The density difference between the two phases should be large and the interfacial tension of the solvent must be large. Large differences in these properties ensure rapid separation of the two phases.

3.2.6 Toxicity and availability

The solvent should have low toxicity from vapour inhalation or skin contact. When extraction is used as a pre-treatment for waste water before being finally discharged to a stream, low toxicity to aquatic life is vital. Another important factor which determines the economic viability of solvent extraction potential of prospective solvent, is its ease if availability and unit cost.

3.3 THEORY AND REPRESENTATION OF TERNARY LIQUID-LIQUID EQUILIBRIA

3.3.1 Introduction

The condition of phase equilibrium inherently involves the transfer of the solute particles from one phase to another phase in a dynamic fashion. It is achieved when the composition of the phase in contact with one another becomes constant, that is, there is no net transfer of solute particles between the phases

3.3.2 Phase rule

In one of the most elegant calculations in the field of chemical thermodynamics J.W. Gibbs deduced the phase rule. According to the Phase Rule (Barrow, 1996):

$$\boxed{F = C - P + 2} \qquad (3.3)$$

Where F is the variance of the system, which the number of intensive variables that can changed, without changing the number of phases in equilibrium. C refers to the number of the components in the system and P is the number of phases (Atkins, 2002). For a three component system (this work):

$$\boxed{F = 5 - P} \qquad (3.4)$$

Holding the temperature and pressure constant leaves two degrees freedom, that is, the mole fractions of two of the components.

3.4 TRIANGULAR PHASE DIAGRAMS

Phase diagrams show the region of thermodynamic stability and in particular are appropriate visual aids in observing the miscibility of the components in ternary liquid systems.

In this work, representation of ternary liquid-liquid equilibria data are as shown in Figure 3.3

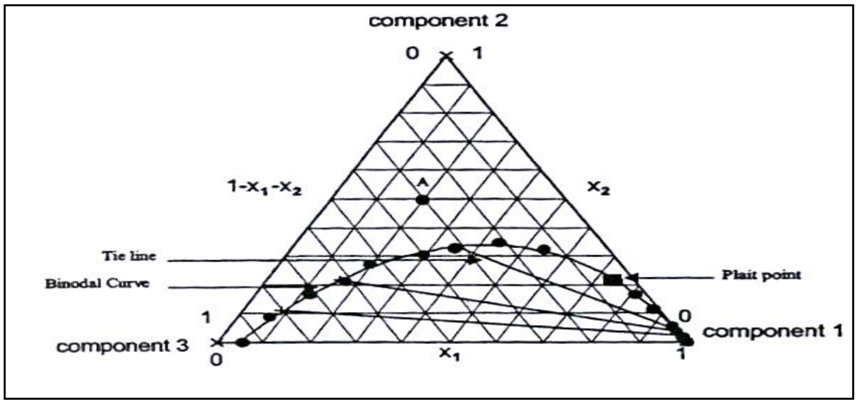


Figure 3.3 Representation of Ternary liquid- liquid equilibria using a triangular phase diagram

In Figure 3.3 the curve separating the two-phase region (below the curve) from the single-phase (above the curve) is called a binodal curve. The two-phase region is formed as a result of the system not in being able to maintain homogeneity across the composition range and shows immiscibility by separating into two phases in equilibrium with each other at a particular composition range. The tie line is the line that intersects the binodal curve at two points and it serves to give the compositions of the two liquid phases (conjugate) in equilibrium at the experimental temperature of the system. The plait point or critical point is approached as tie lines become shorter and shorter, until the plait point is reached where only one phase exists. It is the point where the composition of the two phases in equilibrium is identical (Naicker, 1997)

3.5 FITTING MATHEMATICAL EQUATIONS TO THE BINODAL CURVE DATA

For ternary liquid mixture with only one pair of immiscible liquids, the equation of Hlavatý (1972) has until fairly recently been the only successful method in fitting and equation to the binodal curve. Three equations have been fitted to the ternary data for each system following the work of Hlavatý (1972)

The coefficient A_i relate to modified Hlavatý equation

$$\boxed{x_2 = A_1 x_A \ln x_A + A_2 x_B \ln x_B + A_3 x_A \ln x_B} \qquad (3.5)$$

The coefficient B_i relate to a β-function equation

$$\boxed{x_2 = B_1(1 - x_A)^{B2}\, x_A^{B3}} \qquad (3.6)$$

The coefficient C_i relate to the log γ equation

$$\boxed{x_2 = C_1\,(-\ln x_A)^{C2}\, x_A^{C3}} \qquad (3.7)$$

where

$$\boxed{x_A = (\, x_1 + 0.5\, x_2 \; - x_2 - x_1{}^{0}) \,/\, (x_{11}^{0} - x_1^{0})} \qquad (3.8)$$

$$\boxed{x_B = \; (x_{11}^{0} \; - \; x_1 - 0.5x_2) \,/\, (x_{11}^{0} - x_1^{0})} \qquad (3.9)$$

x_1 refers to mole fraction composition 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 binodal curve which cuts the $x_2 = 0$ axis and have been used to summarize the binodal curve data.The standard deviation (σ) is given by equation (3.7) – (3.9)

$$\boxed{\sigma \quad = \sum[x_2\ (\text{calc}) - x_2\ (\text{exp})]^2 \ / \ (n - 3\ )^{1/2}} \tag{3.10}$$

Where n is the number of data points and 3 is the number of estimated coefficients (Sen and Srivastava, 1990).

3.6 CORRELATION OF TERNARY LIQUID-LIQUID EQUILIBRIA

3.6.1 Introduction

A significant fraction of chemical process design is concerned with separation of fluid mixtures by diffusional operations. All design methods for such separations require quantitative estimates of fluid-phase equilibria, and liquid phase activity coefficients must be known.

Two models will be discussed, namely Non-Random, Two Liquid (NRTL) equation, and Universal Quasi-Chemical (UNIQUAC) equation.

In the NTRL equation, the consideration is given to the prediction of ternary vapour and ternary liquid-liquid equilibria based on the binary data and UNIQUAC is applicable to multicomponent mixtures of non-polar and polar liquids and encountered in typical chemical and petrochemicals systems (Redhi, 2003).

3.6.2 The NRTL (Non Random, two liquid) equation

To take into account non- randomness mixing, it is assumed that the relation between the local fraction x_{21} and x_{11} is given by a modification of the equation

$$\boxed{\frac{x_{21}}{x_{11}} = \frac{x_2\exp(-g_{21}/RT)}{x_1\exp(-g_{11}/RT)}} \qquad (3.11)$$

to the following equation

$$\boxed{\frac{x_{21}}{x_{11}} = \frac{x_2\exp(\alpha_{12}-g_{21}/RT)}{x_1\exp(\alpha_{12}-g_{11}/RT)}} \qquad (3.12)$$

where α_{12} is constant characteristic of the non-randomness of the mixture.

Interchanging subscripts 1 and 2, yield

$$\boxed{\frac{x_{21}}{x_{11}} = \frac{x_2\exp(\alpha_{12}-g_{12}/RT)}{x_1\exp(\alpha_{12}-g_{22}/RT)}} \qquad (3.13)$$

The local mole fractions are related by:

$$\boxed{x_{21} + x_{11} = 1} \qquad (3.14)$$

$$\boxed{x_{12} + x_{22} = 1} \qquad (3.15)$$

From equation (3.11) and (3.14) we obtain for local mole fractions

$$\boxed{x_{21} = \frac{x_2 \exp[-\alpha_{12}(g_{21} - g_{11})/RT]}{x_1 + x_2 \exp[-\alpha_{12} (g_{21} - g_{11})]}} \quad (3.16)$$

and similarly from equation (3.14) and (3.17)

$$\boxed{x_{12} = \frac{x_1 \exp[-x_{12}(g_{12} - g_{22})/RT]}{x_2 + x_1 \exp[-g_{12} (g_{21} - g_{22})/RT]}} \quad (3.17)$$

The residual energy for a cell containing molecule at its centre is $g^{(1)}$ is given by

$$\boxed{g^{(1)} = x_{11}g_{11} + x_{21}g_{21}} \quad (3.18)$$

If we consider pure liquid, l, $x_{11} = 1$ and $x_{21} = 0$

In this case residual Gibbs energy for a cell containing a molecule 1 at its centre

$$\boxed{g^{(1)}_{pure}\text{, is } g^{(1)}_{pure} = g_{11}} \quad (3.19)$$

and

$$\boxed{g^{(2)}_{pure} = g_{22}} \quad (3.20)$$

The molar Gibbs energy for binary solution is the sum of the two changes in residual energy, therefore,

$$\boxed{g^E = (x_1(g^{(1)} - g^{(1)}_{pure}) + (x_2(g^{(2)} - g^{(2)}_{pure})} \qquad (3.21)$$

Substituting equations (3.14), (3.15), (3.16), (3.17), (3.18), (3.19) and (3.20) into (3.21)

$$\boxed{G^E = x_1x_{22}(g_{21} - g_{11}) + x_2x_{12}(g_{12} - g_{22})} \qquad (3.22)$$

Where x_1 and $x_{12}$are given by equations (3.17) and (3.18)

We call equation (3.22) coupled with equation (3.17) and (3.18) the NRTL (non-random, two liquid) equation.

With the local composition equations, prediction of the properties of multicomponent systems is possible without additional ternary or higher order parameters. For the NTRL equation, the excess Gibbs energy is derived from the liquid theory by taking into account only two-body interactions, and there is no need to introduce higher order interactions in the treatment of multicomponent systems when they were neglected for binary mixtures. The NTRL equation is a good and general equation for the prediction of ternary vapour-liquid as well ternary liquid-liquid equilibria using only data for binary mixtures, but no ternary constant, if the optimum value of x_{12} for each binary is chosen.

3.6.3. The UNIQUAC equation

Abrams *et al,* (1995), derived an equation which in a sense extends the quasi-chemical theory of Guggenheim for non random mixtures to solutions containing molecules of different size. This extension was therefore called the universal quasi-chemical theory.

Lattice partition is given by

$$\boxed{Z_{lattice} = \sum_{all\ \Theta} w(\Theta)\exp[-U_o(\Theta)/kT]} \qquad (3.23)$$

Where the w = the combinatorial factor (number of ways that the molecule can be arranged in space)

U_o = potential energy of the lattice, it is closely related to the energy of isothermal vaporization from liquid to ideal gas state.

Both w and U_o depend on the molecular configuration of the mixture, designated by variable Θ

Φ is the average segment fraction:

$$\boxed{\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}} \qquad (3.24)$$

$$\boxed{\Phi_2 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}} \qquad (3.25)$$

The activity coefficient for component 1 is given by the following equation

$$\boxed{\ell n\gamma i = \ell n \frac{\phi_i}{x_i} + \frac{(z)}{(2)} q_i \ \ell n \frac{\Theta_i}{\phi_i} q_i \ \ell_i - \frac{\phi_i}{x_i} \sum_j x_j \ell_j} \tag{3.26}$$

$$\boxed{-q_i \ \ell n \sum_j \Theta_j \tau_{ji} + q_i - q_i \sum_j \frac{\Theta_j \tau_{ij}}{\sum_k \Theta_k \tau_{kj}}} \tag{3.27}$$

where $\ell_j = (z/2)\ (r_j - q_j) - (r_j - 1)$ and the average area function Θ and average segment fraction ϕ are defined by Θ is

$$\boxed{\Theta_i = \frac{q_i N_i}{\sum_i q_i N_j} = \frac{q_i x_i}{\sum j q_i x_j}} \tag{3.28}$$

and

$$\boxed{\phi_i = \frac{r_i N_i}{\sum_i r_i N_j} = \frac{r_i x_i}{\sum j r_i x_j}} \tag{3.29}$$

Since the derived equation is based on the generalization or extension of Guggenheim's quasi-chemical model, the equation is referred to as the UNIQUAC. The UNIQUAC model results in two contributions, the combinatorial term which is evaluated using group contributions to compute size parameters and the residual term which is has two adjustable parameters for each binary system that is to be fitted to experimental data.

CHAPTER 4

EXPERIMENTAL TECHNIQUES

4.1 Introduction

In principle the measurement of phase equilibria involves simply the measurements of pressure, temperature, phase compositions and phase amounts. In practise, however, it is not a simple matter to obtain experimental data of sufficient accuracy, care must be taken to assure that equilibrium really exists, that the temperature and pressure measured at the position where equilibrium really exists, and that taking of samples for analysis does not disturb the equilibrium appreciably (Redhi, 2003).

4.1.1 Phase diagram of mixtures

Phase diagram of a substance is a map that shows the conditions of temperature and pressure at which its vapour or liquid phases are thermodynamically most stable. Phase boundaries are the boundaries between the regions and they show the values of temperature and pressure at which the two neighbouring phases are equilibrium. Vapour pressure is a pressure of the vapour in equilibrium with its condensed.

Phase diagram, of pure substances mixture show which phase is most stable for a given condition. Composition is now a variable in addition to the pressure and temperature (Barrow, 1998).

4.2 DETERMINATION OF THE BINODAL CURVES IN A TERNARY SYSTEM

4.2.1 Titration Method

Although the binodal curve does not yield complete information on phase equilibria since it defines only the heterogeneous region, it can be used to determine the composition of the conjugate phases when the properties of the system studied are known (Redhi, 2003).

The titration method involves the addition of the third component to homogenous binary mixtures of the components 1 and 2 until the appearance of the turbidity or the attainment of the cloud-point (Reddy, 2003). The mixtures are well agitated and kept at constant temperature. The determination of the tie line compositions is to develop a standard curve that relates the composition of points, through the concentration of one of the components of the binodal curve, to an easily determined physical or chemical property such as density or refractive index (Reddy, 2003, Naicker, 1997)

Two–phase mixtures across the entire mole fraction range were prepared and allowed to reach equilibrium at constant temperature by allowing the mixtures to mix and then separate completely from one another. The composition of the conjugate phases were the analysed for the same physical property upon which the standard curve was established. This measurement of physical property is then correlated by means of the standard curve to obtain the compositions of the conjugate phases and hence to establish the tie line.

This work the titration method, adapted from that Briggs and Comings (1943) and modified by Letcher et al, (1989) was used. The binodal curve was first determined by an analysis using refractive index, in order to determine the tie line.

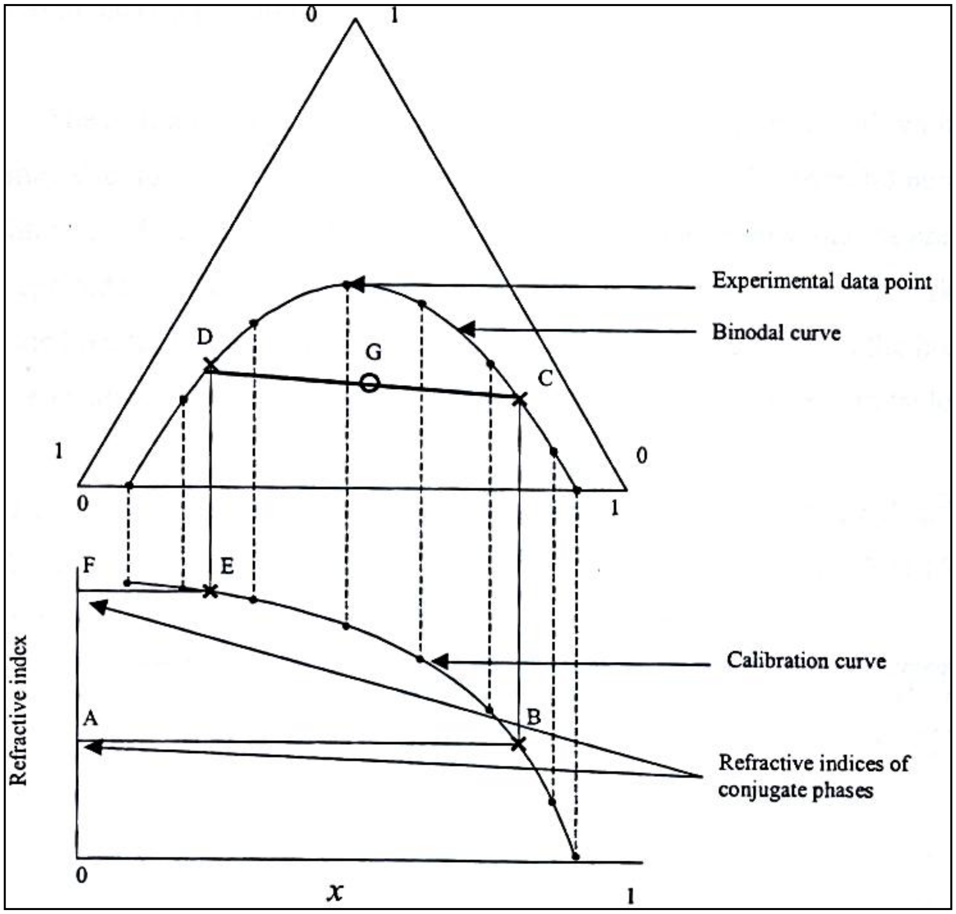


Figure 4.1 Binodal curve, calibration curve and tie line.

The dashed lines represent the perpendicular lines that determine the calibration curve. A mixture, G, with overall composition in the two phase region splits into two phases with the compositions represented by points C and D. The refractive indices of the phases are F and A respectively. These refractive indices are extended to points E and B on the calibration curve and this allows the determination of points C and D on the binodal curve (Naicker, 2000).

4.3 DETERMINATION OF TIE-LINES IN A TERNARY SYSTEMS USING THE BINODAL CURVE

4.3.1 Introduction

Measurement of refractive index or density of the mixture at equilibrium permits the determination of corresponding position on the binodal curve, and thus tie-line can be found.

4.3.2 Karl Fischer titration

As an alternative to refractive index method, tie lines could also be determined using the Karl Fischer Method provides one of the components is water. In this method the Karl Fischer reagent is used to titrate against the water in each phase present. In this way the aqueous content of each can be determined, and these compositions are located on the binodal curve and the tie lined are drawn.

4.4 DETERMINATION OF THE CRITICAL POINT (PLAIT POINT) IN THREE COMPONENT SYSTEMS

The plait point or critical point is approached as tie lines become shorter and shorter, until the plait point is reached where only one phase exists. It is the point where the composition of the two phases in equilibrium is identical (Naicker, 1997)

The plait point is determined by means of the Treybal method. The method of Treybal involves producing plots of

$$\left(\frac{x''_1}{x''_2}\right) \quad \text{vs} \quad \left(\frac{x'_1}{x'_2}\right) \tag{4.1}$$

where x'_2, x'_3, x''_1, x''_2 are the mole fraction compositions of the conjugate mixtures and

$$\left(\frac{x_2}{x_1}\right) \quad \text{vs} \quad \left(\frac{x_2}{x_1}\right) \tag{4.2}$$

where x_1, x_2 and x_3 are the mole fraction compositions of components 1, 2 and 3, respectively, of the mixture on the binodal curve. The plait point is that point of intersection of the curves of (4.1) and (4.2).

4.5 REFRACTOMETRY

4.5.1 Introduction

The speed of light in a vacuum is always the same, but when light moves through any other medium it travels more slowly since it is constantly being absorbed and re-emitted by the atoms in the material.

The ratio of the speed of light in a vacuum to the speed of light in another substance is defined as the **index of refraction** (**refractive index** or **n**) for the substance,

$$\text{Refractive Index of substance} = \frac{(\text{Speed of light in a vacuum})}{(\text{Speed of light in a substance})}$$

Figure 4.2 Bellingham and Stanely RFM 340 Refractometer

4.5.2 Principle of operation refractometry

Whenever light changes speed as it crosses a boundary from one medium into another its direction of travel also change, that is, refraction.

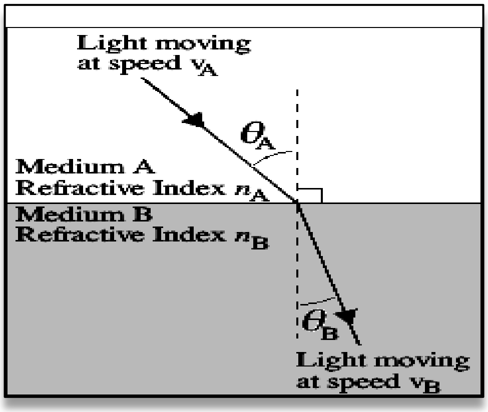


Figure 4.3 Refraction of light when passing from medium A to medium B

The relationship between speed of light in two mediums (A and B), the angles of incidence (θ_A) and refraction (θ_B) and the refractive indeces of the two mediums (n_A and n_B) is shown below:

$$\boxed{\frac{A}{B} = \frac{\sin \theta_A}{\sin \theta_B} = \frac{n_B}{n_A}} \qquad (4.3)$$

Thus, it is not necessary to measure the speed of light in a sample in order to determine its index of refraction. Instead, by measuring the angle of refraction, and knowing the index of refraction of the layer that is in contact with the sample, it is possible to determine the refractive index of the sample quite accurately (Webb *et al*, 2004).

4.5.3 Operation of a refractometer

In the refractometer the liquid sample is sandwiched into a thin layer between an illuminating prism and a refracting prism

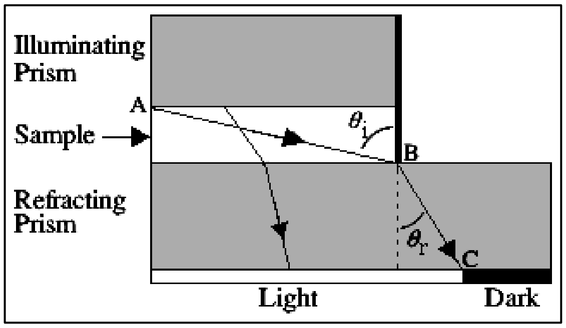


Figure 4.4 Cross section of Refractometer

The refracting prism is made of a glass with a high refractive index and the refractometer is designed to be used with samples having a refractive index smaller than that of the refracting prism. A light source is projected through the illuminating prism, the bottom surface of which is ground, so each point on this surface can be thought of as generating light rays travelling in all directions (Webb and Jones, 2004)

Inspection of Figure 4.4 shows that light travelling from point A to point B will have the largest angle of incidence (θ_i) and hence the largest possible angle of refraction (θ_r) for that sample. All other rays of light entering the refracting prism will have smaller θ_r and hence lie to the left of point C. Thus, a detector placed on the back side of the refracting prism would show a light region to the left and a dark region to the right. In an actual refractometer there is no a detector on the back of the refracting prism, but includes additional optics.

In most liquids and solids the speed of light, and hence the index of refraction, varies significantly with wavelength. This variation is referred to as **dispersion,** and it is what causes white light moving through a prism to be refracted into a rainbow of colours. Shorter wavelengths are normally refracted more than longer ones. Thus, for the most accurate measurements it is necessary to use monochromatic light. The most widely used wavelength of light for refractometry is the sodium D line at 589 nm.

4.6 EXCESS MOLAR VOLUMES

Excess molar data, like many data are more informative and easier to handle when expressed relative to some of ideal behavior. The excess molar volume, V_m^E, is defined as:

$$\boxed{V_m^E = V_{mixture} - \sum x_1 V_1{}^o} \tag{4.4}$$

where x_1 is the mole fraction of component 1, $V_{mixture}$ is the molar volume of mixture and $V_i{}^o$ a molar of the component i. For binary mixture,

$$\boxed{V_m^E = V_{mixture} - (x_1 V_1^o + x_2 V_2{}^o)} \tag{4.5}$$

The change in the volume on mixing two liquids, especially two liquids, 1 and 2 can be attributed to a number of processes.

(a) the breakdown of 2-1 and 2-2 intermolecular interactions which have positive effect on the volume,

(b) the formation of 1-2 intermolecular interactions which results in a dimunition of the volume of the mixture,

(c) packing effects caused by difference in the size shape of the component species and which may have positive or negative effect on the particular species involved, and,

(d) formation of new chemical species

Volume changes on mixing of binary liquid mixtures, V_m^E, at constant pressure and temperature is of interest to chemists and chemical engineers, and is an indicator of the non idealities present in real mixtures. There are great difficulties in treating excess volumes and one major problem is the packing effect. However, this has not deterred some theoreticians and a number of theories abound.

4.6.1 Measurement of excess molar volumes

The excess molar volume, V_m^E, is a helpful parameter in the design of the technological processes of the reaction (Letcher and Reddy, 2002). The volume changes of binary mixtures can be determined experimentally in one of two ways, namely,

(i) indirectly from density measurements or

(ii) from the more direct dilatomeric method, that is by determining the resultant volume change upon mixing of two components (Redhi, 2003).

Indirect determination

Density (p) is defined as:

$$\boxed{\rho = \frac{M}{V}} \qquad (4.6)$$

where **M** is the mass of the substance, and **V** is the volume.

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

$$\boxed{= \frac{(x_1 m_1 + x_2 m_2)}{\rho_{mixture}} - \frac{(x_1 m_1)}{\rho_1} + \frac{(x_2 m_2)}{\rho_2}} \qquad (4.7)$$

where x_1 and x_2 are the mole fractions of components 1 and 2 respectively, m_1 and m_2 molar masses of components 1 and 2 respectively and ρ_1, ρ_2, $\rho_{mixture}$ are the densities of component 1, component 2 and mixture respectively.

4.6.2 The Anton Paar Densimeter

The densities of the mixture as well as the corresponding pure compounds were measured using a vibrating tube densitometer, Anton Paar DMA 38, with a precision of (±1 x 10^{-5}g/ cm^3), achieved by determining the period of oscillation of the liquid in a U-tube.

Figure 4.5 Anton Paar DMA 38 densimeter

The natural vibration period of the tube, which depends on the density of the liquid, is measured with a high-resolution digital frequency meter (Grguric *et al*, 2002).

$$\boxed{\Delta\rho = \rho - \rho_0 = (A\tau^2 - \tau_0^2)} \tag{4.8}$$

Equation 4.8 is used to relate the density (ρ) and the period (τ) for the investigated liquids ρ_0 and τ_0, corresponding to the reference fluid. The value of the constant A is determined by calibration using fluids of known densities. Air and de-ionised water (Millipore quality) were used as reference fluids to determine the constant of the densimeter.

The densimeter was calibrated each time measurements were done according the procedure prescribed by the manufacturer. All measurements were in static mode. The sample was introduced in a U-shaped sample tube, and the time taken to equilibrate was typically between 5 to 7 minutes, after which the period of oscillation was read from the numerical dial.

Between two successive measurements, the sample tube was cleaned with acetone and dried for 5 minutes using the built in pump. This was the time necessary for the period of empty sample tube to return to its previous value. The density determination was based upon measurement of oscillations of vibrating U-shape sample tube. The U-shaped tube was filled with liquid sample mixture and the relationship between the between the period $\boldsymbol{\tau}$ and the density of the mixture $\boldsymbol{\rho}$ is given by:

$$\boxed{\rho = A + B\tau^2} \tag{4.9}$$

The constant **A** and **B** are instrument constants for each individual oscillator and they can be determined by two calibration measurements with samples of known density that is air and deionised water (Grguric, 2002).

For each binary mixture, the Redlich-Kister equation was fitted to the experimental excess molar volume data to correlate the composition dependence of the excess property.

$$\boxed{V^E = x(1 - x) \sum_{i=0}^{j} A_i (1 - 2x)^i} \qquad (4.10)$$

where x denotes the mole fraction of component, A_i is the polynomial coefficients, and j is the polynomial degree, respectively.

The coefficient Ai was obtained by fitting equation 4.10 to the experimental results using a least-squares regression method with all points weighted equally. In each case, the optimum number of coefficients was ascertained from examination of the variation in the standard deviation (σ).

The standard deviation (σ) is calculated using

$$\boxed{\sigma = [\sum^{n} (V_m^E (\text{calc}, i) - V_m^E (\text{exp}, i) / (n-j)]^{1/2}} \qquad (4.11)$$

where n is the number of experimental data and j is the number of fitting coefficients (Wang et al, 2004).

4.7 EXPERIMENTAL SECTION

4.7.1 Materials used

The solvents were kept in the dry box before use. Molecular sieves (4 nm) were used to extract trace amount of moisture and the liquid were degassed in an ultrasonic bath for one hour before use. The carboxylic acids and hydrocarbon compounds were analysed by Karl-Fischer and showed that the water content was less than 0.01 mass%. A summary of the materials used in this work, their suppliers and purities is given in the table below.

Table 4.1 Materials used, their suppliers and mass % purities.

COMPOUND	SUPPLIER	% PURITY
Acetic acid	Riedel-de Haën	99.8
Propanoic Acid	Riedel-de Haën	99.8
Butanoic Acid	Riedel-de Haën	99.8
2- Methylpropanoic acid	Riedel-de Haën	99.8
Pentanoic acid	Riedel-de Haën	99.8
3-Methylbutanoic acid	Riedel-de Haën	99.8
Methanol	Sigma -Aldrich	99.9
Ethanol	Sigma -Aldrich	99.9
1-Propanol	Sigma -Aldrich	99.9
2-Propanol	Sigma -Aldrich	99.9
1-Butanol	Sigma -Aldrich	99.9
2-Butanol	Sigma -Aldrich	99.9
2-Methyl-1-propanol	Sigma -Aldrich	99.9
2-Methyl-2-propanol	Sigma -Aldrich	99.9
Sulfolane	Fluka	99.5
Heptane	Sigma -Aldrich	99.5
Dodecane	Fluka	99.5
Cyclohexane	Fluka	99.5

Table 4.2 Densities and refractive indices of pure components at T = 303.15 K, Refractive indices n_D, Density ρ.

Component	n_D exp	ρ exp
Acetic acid	1.3716	1.0437
Propanoic Acid	1.3829	0.9881
Butanoic Acid	1.3947	0.9535
2- Methylpropanoic acid	1.3913	0.9431
Pentanoic acid	1.4047	0.9346
3-Methylbutanoic acid	1.3977	0.9216
Methanol	1.3291	0.7984
Ethanol	1.3601	0.7813
1-Propanol	1.3835	0.7962
2-Propanol	1.3762	0.7771
1-Butanol	1.3981	0.8026
2-Butanol	1.3952	0.7987
2-Methyl-1-propanol	1.3945	0.7952
2-Methyl-2-propanol	1.3853	0.7778
Sulfolane	1.4815	1.2614
Heptane	1.3844	0.6787
Dodecane	1.4187	0.7449
Cyclohexane	1.4222	0.7730

4.7.2 Samples used for ternary system

4.7.2.1 System I

Carboxylic acids, that is, acetic acid (C_2), propanoic acid (C_3), butanoic acid (C_4), 2-methylpropanoic acid (C_4), pentanoic acid (C_5) and 3-methylbutanoic acid (C5) as well as heptane and sulfolane were stored under 4nm molecular sieves before use. Analysis of moisture content by Karl Fischer technique showed that in all cases the water content was less than 0.01 mass %. Sulfolane was supplied by Fluka and used without further purification. A summary of the materials, their suppliers and purities, used in this work is given in table 4.1. Mixtures of sulfolane and carboxylic acids were prepared in conical flasks.

4.7.2.2 System II

Carboxylic acids, that is, acetic acid (C_2), propanoic acid (C_3), butanoic acid (C_4), 2-methylpropanoic acid (C_4) pentanoic acid (C_5) and 3-methylbutanoic acid (C5) as well as cyclohexane and sulfolane were stored under 4nm molecular sieves before use. Analysis of moisture content by Karl Fischer technique showed that in all cases the water content was less than 0.01 mass %. Sulfolane was supplied by Fluka and used without further purification. A summary of the materials, their suppliers and purities, used in this work is given in table 4.1. Mixtures of sulfolane and carboxylic acids were prepared in conical flasks

4.7.2.3 System III

Carboxylic acids, that is, acetic acid (C_2), propanoic acid (C_3), butanoic acid (C_4), 2-methyl propanoic acid (C_4) pentanoic acid (C_5) and 3-methyl butanoic acid (C5) as well as dodecane and sulfolane were stored under 4nm molecular sieves before use. Analysis of moisture content by Karl Fischer technique showed that in all cases the water content was less than 0.01 mass %. Sulfolane was supplied by Fluka and used without further purification. A summary of the materials, their suppliers and purities, used in this work is given in table 4.1. Mixtures of sulfolane and carboxylic acids were prepared in conical flasks.

4.7.2.4 System IV

Alcohols, that is, methanol (C_1), ethanol (C_2), 1-propanol (C_3), 2-propanol (C3), 1-butanol (C_4), 2-butanol (C_4), 2-methyl-1-propanol (C_4), 2-methyl-2-propanol (C_4), as well as heptane and sulfolane were stored under 4nm molecular sieves before use. Analysis of moisture content by Karl Fischer technique showed that in all cases the water content was less than 0.01 mass %. Sulfolane was supplied by Fluka and used without further purification. A summary of the materials, their suppliers and purities, used in this work is given in table 4.1. Mixtures of sulfolane and alcohols were prepared in conical flasks.

4.7.3 Procedure

In this study, the “method of titration”, that is a method adapted from Briggs and Comings (1943) as described by Letcher and Siswana (1992) was used to determine the ternary liquid-liquid equilibrium data. Here the binodal curve was first obtained and tie-lines were then determined.

The points on the curve were obtained in the following way, a mixture of two of the miscible components, that is the carboxylic acid and sulfolane, were prepared accurately by weighing. The mixtures were then left to equilibrate in a water bath maintained at 30 ±0.1 ^{0} C for at least 1 hour. The third component, the hydrocarbon (heptane or cyclohexane or dodecane) was then added dropwise from a weighed gas tight syringe until the mixture turned cloudy. The syringe was weighed to determine the mass of hydrocarbon added.

To ensure the maintenance of one phase a measured drop of the carboxylic acid was added in each case. At the hydrocarbon-rich end of the binodal curve the binary mixture was made up of sulfolane and carboxylic acid (or alcohol), and the third component added was the hydrocarbon. The mixtures of two of the miscible components, the sulfolane and carboxylic acid (or alcohol), were accurately prepared by weighing. The mixtures were then left to equilibrate in a water bath at 30 ±0.1^{0}C for at least one hour.

The refractive index of the clear mixture was measured using a Bellingham & Stanely RFM 340 Refractometer set at 30 ± 0.1^{0}C. A 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 mole fraction axis. The tie lines were determined from carefully made up solutions in the miscible regions of the phase diagram.

The samples were then well shaken and left in a controlled water bath at 30 ± 0.1^{0}C for at least 24 hours to facilitate phase separation to ensure equilibrium. Samples of the separate phases were then withdrawn using a warmed, gas tight syringe and analysed immediately using the refractive index method. The refractive indices of the different phases were then related to the compositions of the binodal curve by the linear interpolation of the refractive indices against the sulfolane axis using Figure 4.1.

Each tie-line was checked to ensure that the line joining the two points representing the compositions of the solution pairs at equilibrium, passed through the composition of the overall mixture.

4.8 EXCESS MOLAR VOLUMES

4.8.1. Materials used

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

Table 4.3 Materials used, their suppliers and mass % purities

COMPOUND	SUPPLIER	% PURITY
Methanol	Sigma -Aldrich	99.9
Ethanol	Sigma -Aldrich	99.9
1-Propanol	Sigma -Aldrich	99.9
2-Propanol	Sigma -Aldrich	99.9
1-Butanol	Sigma -Aldrich	99.9
2-Butanol	Sigma -Aldrich	99.9
2-Methyl-1-propanol	Sigma -Aldrich	99.9
2-Methyl-2-propanol	Sigma -Aldrich	99.9
Sulfolane	Fluka	99.5
Heptane	Sigma -Aldrich	99.5

Table 4.4 Densities of pure components at various temperatures, Density (ρ).

Component	Experimental Density (ρ)		
	298.15 K	303.15 K	308.15 K
Methanol	0.7876	0.7826	0.7789
Ethanol	0.7859	0.7813	0.7775
1-Propanol	0.8006	0.7962	0.7931
2- Propanol	0.7816	0.7771	0.7730
1-Butanol	0.8066	0.8026	0.7995
2-Butanol	0.8033	0.7987	0.7952
2-Methyl-1-propanol	0.7826	0.7776	0.7731
2-methyl-2-propano l	0.8028	0.8001	0.7965
Sulfolane	1.2656	1.2614	1.2572

4.8.2 Validation of experimental technique

The validity of the technique was established by measuring the excess molar volumes of the mixtures (sulfolane + toluene) at T = 298.15 K and comparing the results obtained to the literature data for these mixtures (Yang-Xin and Yi-Gui, 1998). A comparison between this work and the literature data is shown on Table 4.5 and graphically represented on figure 4.8

Table 4.5 Comparison of the V_m^E results obtained in this work with the literature results (Yang-Xin and Yi-Gui, 1998) for the mixtures of [sulfolane (1) + toluene (2)] at T = 298.15 K

x_1	V_m^E (exp) cm^3mol^{-1}	V_m^E (lit) cm^3mol^{-1}	x_1	V_m^E (exp) cm^3mol^{-1}	V_m^E (lit) cm^3mol^{-1}
0.0000	0.000	0.000	0.5796	-1.017	-1.019
0.0634	-0.310	-0.320	0.6159	-0.980	-0.981
0.1104	-0.512	-0.510	0.6553	-0.930	-0.932
0.1638	-0.682	-0.681	0.6903	-0.872	-0.874
0.2250	-0.838	-0.839	0.7371	-0.781	-0.780
0.2814	-0.938	-0.939	0.7854	-0.673	-0.675
0.3081	-0.980	-0.980	0.8931	-0.531	-0.533
0.3406	-1.090	-1.010	0.9187	-0.275	-0.277
0.398	-1.051	-1.052	0.9626	-0.128	0.129
0.4507	-1.078	-1.079	1.0000	0.000	0.000
0.5042	-1.070	-1.072			

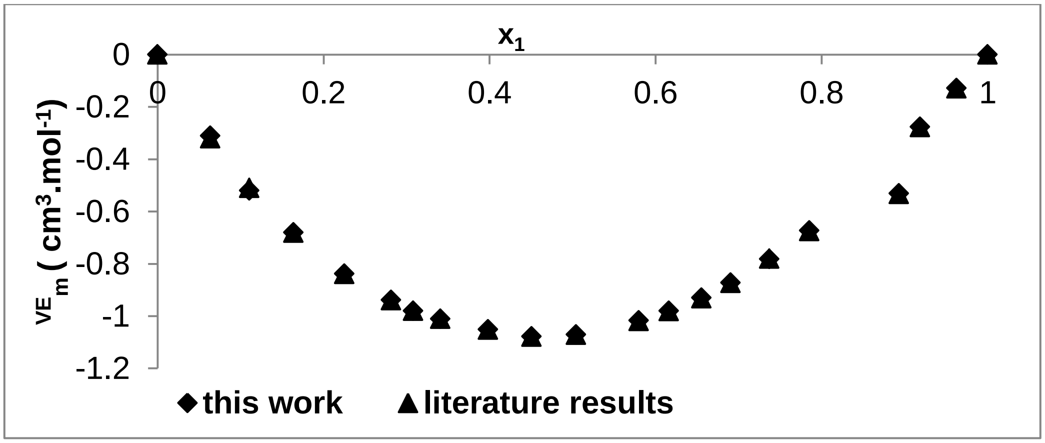


Figure 4.6 **Comparison of V_m^E results from this work with literature results (Yang-Xin and Yi-Gui, 1998) for the mixture [sulfolane (1) + toluene (2)].**

4.8.3 Preparation of samples mixtures

The pure solvents were initially degassed in an ultrasonic bath for at least 1 hour, as aerated solvents tend to give errors in density measurements as well as tend to lead to non- reproducible readings. Moisture was removed by drying pure solvent with molecular sieves (0.4nm). The mixtures were made up in glass vial of 12 mL fitted with a lid. Mixtures with compositions spanning the entire mole-fraction scale were made up gravimetrically. Care was taken to first add the least volatile component into the vial and the complete mixture should have left a small space, just large enough to aid the mixing in the vial. The mixtures were made up just before use, and were shaken vigorously before injection.

4.8.4 Operation procedure for the instrument

Prior to each experimental run, the cell was first flushed with absolute ethanol (>99.5%) and then acetone. After flushing, compressed air was blown through the cell. The value of the constant periodic value, $\boldsymbol{\tau}$**,** for the sample tube filled with air was then noted.

Double de-ionised Milli-Q water was then introduced into the cell by means of a glass syringe with a Leur tip ensuring a snug and leak proof fit at the sample cell syringe junction. The injection process was carried out slowly but steadily enabling the liquid mixture to properly wet the walls of the cell, and also to alleviate the risk of trapping air bubbles in the U-tube. The U-tube was first flushed with 2 mL of the sample and the syringe then filled again with the sample and introduced into the injection port.

Each measuring cycle was allowed to continue until a constant period value was obtained. Period values for water, pure solvents and air were determined between each solution injection, not only for density calculations, but as it also permitted a continuous check on both sample purity and densitometer operation.

The density meter U tube cell was flushed with 10 % ethanol water solution after each measurement to avoid the formation of air bubbles in the U tube. The instrument was cleaned regularly with two vials of cleaning solution for the Anton Paar Densimeter that was supplied by Swiss Lab, Instrument Supplier.

The densities of the mixture as well as the pure liquids were then determined from the periodic values measured, and subsequent application of equation

$$\boxed{V_m^E = V_{mixture} - \sum x_1 V_1{}^o} \qquad (4.12)$$

Using the density and compositions of these mixtures V_m^E was determined according to equation

$$\boxed{V_m^E = V_{mixture} - (x_1 V_1{}^o + x_2 V_2{}^o)} \qquad (4.13)$$

The temperature of the Anton Paar DMA 38 Densimeter was maintained at 303.15 + 0.002 K which was controlled by the internal solid-state thermostat.

CHAPTER 5

RESULTS

5. LIQUID–LIQUID EQUILIBRIA

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

- Sulfolane (1) + Carboxylic Acid (2) + Heptane (3) at T = 303.15 K
- Sulfolane (1) + Carboxylic Acid (2) + Cyclohexane (3) at T = 303.15 K
- Sulfolane (1) + Carboxylic Acid (2) + Dodecane (3) at T = 303.15 K
- Sulfolane (1) + Alcohol (2) + Heptane (3) at T = 303.15 K

For each section, tables of results for binodal curve data, calibration curve data, tie-line data and coefficients of fitted equation, values of the parameters for NTRL and UNIQUAC equations and selectivity data are tabulated. Ternary phase diagrams, where UNIQUAC and NTRL thermodynamic models are used to correlate the experimental data have been produced. Calibration curves as well as distribution curves have also been included. The interaction parameters for each model were determined with the aid of an LLE programme.

5.1 LIQUID–LIQUID EQUILIBRIA FOR MIXTURES OF SULFOLANE + CARBOXYLIC ACID + HEPTANE AT T = 303.15 K

Table 5.1 Physical Properties of the Pure Components at T = 303.15 K, Molar Volumes, V_{mi}, Refractives Index, n_D, Volume and Surface Parameters, R and Q.

Component	$V_{mi}/cm^3.mol^{-1}$	n_D	R	Q
Acetic Acid	57.73	1.3716	2.202[a]	2.072[a]
Propanoic Acid	75.34	1.3829	2.877[a]	2.612[a]
Butanoic Acid	92.93	1.3947	3.551[a]	3.152[a]
2-Methylpropanoic Acid	93.46	1.3913	3.550[a]	3.148[a]
Pentanoic Acid	109.78	1.4047	4.226[a]	3.692[a]
3-Methylbutanoic Acid	111.34	1.3997	4.225[a]	3.688[a]
Heptane	147.40	1.3844	5.174[b]	4.396[b]
Sulfolane	95.30	1.4815	4.036[b]	3.200[b]

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

[b] Mohsen- Nia *et al*.(2005)

Table 5.2 Composition of points on the binodal curve at T = 303.15 K for the systems: [Sulfolane (1) + Carboxylic Acid (2) + Heptane (3)], equilibrium Mole fraction, x_1, x_2

x_1	x_2	x_1	x_2
	Acetic Acid		
0.0060	0.0000	0.1941	0.7664
0.0085	0.1050	0.2713	0.6986
0.0110	0.1950	0.4730	0.5046
0.0120	0.2834	0.5647	0.4220
0.0130	0.3859	0.6782	0.3079
0.0150	0.4964	0.8326	0.1554
0.0180	0.5863	0.9060	0.0803
0.0215	0.7320	0.9360	0.0471
0.0262	0.7825	0.9850	0.0000
0.0525	0.8202		
0.1164	0.8170		
	Propanoic Acid		
0.0060	0.0000	0.2135	0.6293
0.0079	0.0090	0.3112	0.6033
0.0109	0.1090	0.5110	0.4351
0.0123	0.1890	0.6186	0.3442
0.0169	0.2862	0.7280	0.2421
0.0179	0.3821	0.8519	0.1234
0.0217	0.4309	0.9143	0.0687
0.0410	0.4946	0.9528	0.0278
0.1260	0.6123	0.9850	0.0000
	Butanoic Acid		
0.0060	0.0000	0.3259	0.5237
0.0065	0.0235	0.5577	0.3827
0.0074	0.0635	0.6372	0.3094
0.0085	0.1072	0.7428	0.2051
0.0254	0.2110	0.8668	0.1031
0.0388	0.3179	0.9296	0.0541
0.0450	0.4644	0.9743	0.0249
0.1287	0.5617	0.9850	0.0000
0.2139	0.5652		

Table 5.2 Continued

x_1	x_2	x_1	x_2
2-Methylpropanoic Acid			
0.0060	0.0000	0.3399	0.5462
0.0085	0.1991	0.5517	0.3943
0.0094	0.2959	0.6559	0.3097
0.0256	0.3744	0.7588	0.2054
0.0300	0.4065	0.8541	0.1048
0.0585	0.5060	0.9143	0.0531
0.1392	0.5727	0.9497	0.0253
0.2029	0.5836	0.9850	0.0000
Pentanoic Acid			
0.0060	0.0000	0.3582	0.4983
0.0089	0.2340	0.5736	0.3619
0.0250	0.2961	0.6726	0.2716
0.0345	0.3366	0.7901	0.1810
0.0432	0.3467	0.8806	0.0919
0.0572	0.4850	0.9315	0.0405
0.1529	0.5659	0.9521	0.0258
0.2494	0.5394	0.9850	0.0000
3-Methylbutanoic Acid			
0.0060	0.0000	0.3600	0.5018
0.0069	0.1323	0.5783	0.3522
0.0090	0.1961	0.6910	0.2687
0.0319	0.2681	0.7938	0.1808
0.0522	0.3917	0.8971	0.0849
0.0690	0.5190	0.9326	0.0497
0.1526	0.5752	0.9559	0.0243
0.2643	0.5451	0.9850	0.0000

Table 5.3 Mole Fraction and Refractive Indices: [Sulfolane (1) + Carboxylic Acid (2) + Heptane (3)] at T = 303.15 K.

x_1	n_D	x_1	n_D
	Acetic Acid		
0.0000	1.3844	0.2713	1.4391
0.0150	1.3892	0.4730	1.4416
0.0180	1.3893	0.5647	1.4610
0.0215	1.3894	0.6782	1.4703
0.0262	1.3896	0.8326	1.4726
0.0525	1.3897	0.9060	1.4765
0.1164	1.4061	0.9360	1.4780
0.1941	1.4175	1.0000	1.4815
	Propanoic Acid		
0.0000	1.3844	0.5110	1.4301
0.0179	1.3857	0.6186	1.4482
0.0217	1.3858	0.7280	1.4559
0.0410	1.3859	0.8519	1.4641
0.1260	1.3864	0.9143	1.4728
0.2135	1.3865	0.9528	1.4787
0.3112	1.4234	1.0000	1.4815
	Butanoic Acid		
0.0000	1.3844	0.6372	1.4458
0.0254	1.3904	0.7428	1.4610
0.0388	1.3915	0.8668	1.4677
0.0450	1.3924	0.9296	1.4742
0.1287	1.3936	0.9743	1.4806
0.2139	1.4349	1.0000	1.4815
0.3259	1.4416		

Table 5.3 Continued

x_1	n_D	x_1	n_D
2-Methylpropanoic Acid			
0.0000	1.3844	0.5517	1.4597
0.0256	1.3952	0.6559	1.4638
0.0300	1.3960	0.7588	1.4691
0.0585	1.3984	0.8541	1.4746
0.1392	1.3986	0.9143	1.4796
0.2029	1.4273	0.9497	1.4803
0.3399	1.4485	1.0000	1.4815
Pentanoic Acid			
0.0000	1.3844	0.5736	1.4552
0.0345	1.3944	0.6726	1.4619
0.0432	1.3945	0.7901	1.4654
0.0572	1.3948	0.8806	1.4705
0.1529	1.3961	0.9315	1.4758
0.2494	1.3962	0.9521	1.4789
0.3582	1.4481	1.0000	1.4815
3-Methylbutanoic Acid			
0.0000	1.3844	0.5783	1.4539
0.0319	1.3935	0.6910	1.4542
0.0522	1.3949	0.7938	1.4555
0.0690	1.3951	0.8971	1.4620
0.1526	1.3953	0.9326	1.4661
0.2643	1.3956	0.9559	1.4708
0.3600	1.3965	1.0000	1.4815

Table 5.4 Composition of the conjugate solutions, x_1', x_2' and x_1'', x_2'' at T = 303.15 K for the systems: [Sulfolane (1) + Carboxylic Acid (2) + Heptane (3)], Refractive Index, n_D

Heptane Rich			Sulfolane Rich		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) + Acetic Acid (2) + Heptane (3)					
0.0045	0.1050	1.3897	0.9678	0.0201	1.4061
0.0082	0.2711	1.3896	0.9671	0.0252	1.4175
0.0114	0.3829	1.3894	0.9495	0.0414	1.4416
0.0137	0.5507	1.3893	0.9230	0.0620	1.4610
0.0321	0.7542	1.3892	0.8794	0.1086	1.4726
Sulfolane (1) + Propanoic Acid (2) + Heptane (3)					
0.0107	0.1002	1.3864	0.9782	0.0095	1.4610
0.0117	0.2450	1.3861	0.9724	0.0212	1.4559
0.0127	0.2839	1.3859	0.9569	0.0311	1.4482
0.0154	0.3429	1.3858	0.9244	0.0612	1.4301
0.0252	0.4547	1.3857	0.8922	0.0853	1.4234
Sulfolane (1) + Butanoic Acid (2) + Heptane (3)					
0.0075	0.0909	1.3936	0.9879	0.0071	1.4742
0.0165	0.1635	1.3924	0.9801	0.0168	1.4677
0.0283	0.2909	1.3915	0.9490	0.0327	1.4610
0.0505	0.4410	1.3905	0.9171	0.0560	1.4458
0.0620	0.4851	1.3904	0.8861	0.0904	1.4416
Sulfolane (1) + 2-Methylpropanoic Acid (2) + Heptane (3)					
0.0129	0.0950	1.3986	0.9578	0.0186	1.4746
0.0127	0.1600	1.3984	0.9388	0.0248	1.4691
0.0108	0.2250	1.3960	0.9165	0.0435	1.4638
0.0104	0.3057	1.3956	0.8955	0.0654	1.4597
0.0099	0.3843	1.3892	0.8651	0.0942	1.4485

Table 5.4 Continued

Heptane Rich			Sulfolane Rich		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) + Pentanoic Acid (2) + Heptane (3)					
0.0052	0.0750	1.3962	0.9631	0.0123	1.4758
0.0081	0.1763	1.3961	0.9579	0.0260	1.4705
0.0145	0.2992	1.3948	0.9476	0.0328	1.4654
0.0324	0.3592	1.3945	0.9257	0.0438	1.4619
0.0421	0.4229	1.3944	0.9149	0.0654	1.4551
Sulfolane (1) + 3-Methylbutanoic Acid (2) + Heptane (3)					
0.9592	0.0109	1.4708	0.0107	0.0811	1.3956
0.9579	0.0219	1.4661	0.0197	0.1835	1.3953
0.9560	0.0288	1.4620	0.0253	0.2959	1.3951
0.9519	0.0378	1.4555	0.0509	0.3957	1.3949
0.9456	0.0453	1.4542	0.0658	0.4841	1.3935

Table 5.5 Coefficients A_i, B_i, and C_i in equation (3.5) – (3.7) respectively, for the systems: [Sulfolane (1) + Carboxylic Acid (2) + Heptane (3)] at T = 303.15 K, standard deviation, σ, in equation (3.10)

Hlavatý	**Beta**	**Log γ**
Sulfolane (1) + Acetic Acid (2) + Heptane (3)		
$A_1 = 1.432$	$B_1 = 4.32$	$C_1 = 3.815$
$A_2 = 1.294$	$B_2 = 1.246$	$C_2 = 1.202$
$A_3 = 6.884$	$B_3 = 1.293$	$C_3 = 1.729$
$\sigma = 0.027$	$\sigma = 0.031$	$\sigma = 0.032$
Sulfolane (1) + Propanoic Acid (2) + Heptane (3)		
$A_1 = 0.582$	$B_1 = 3.083$	$C_1 = 2.494$
$A_2 = 0.0659$	$B_2 = 1.173$	$C_2 = 1.103$
$A_3 = 4.223$	$B_3 = 1.161$	$C_3 = 1.493$
$\sigma = 0.008$	$\sigma = 0.010$	$\sigma = 0.017$
Sulfolane (1) + Butanoic Acid (2) + Heptane (3)		
$A_1 = 0.356$	$B_1 = 2.906$	$C_1 = 2.651$
$A_2 = 0.216$	$B_2 = 1.206$	$C_2 = 1.001$
$A_3 = 1.089$	$B_3 = 1.195$	$C_3 = 1.134$
$\sigma = 0.007$	$\sigma = 0.012$	$\Sigma = 0.013$
Sulfolane (1) + 2- Methylpropanoic Acid (2) + Heptane (3)		
$A_1 = 0.406$	$B_1 = 3.468$	$C_1 = 3.188$
$A_2 = 0.626$	$B_2 = 1.311$	$C_2 = 1.285$
$A_3 = 0.3782$	$B_3 = 1.205$	$C_3 = 1.707$
$\sigma = 0.005$	$\sigma = 0.011$	$\sigma = 0.014$

Table 5.5 Continued

Hlavatý	Beta	Log γ
Sulfolane (1) + Pentanoic Acid (2) + Heptane (3)		
A_1 = 0.244	B_1 = 2.848	C_1 = 2.659
A_2 = 0.426	B_2 = 1.207	C_2 = 1.187
A_3 = 3.119	B_3 = 1.144	C_3 = 1.615
σ = 0.012	σ = 0.011	σ = 0.012
Sulfolane (1) + 3-Methylpropanoic Acid (2) + Heptane (3)		
A_1 = 0.247	B_1 = 2.508	C_1 = 2.299
A_2 = 0.39	B_2 = 1.112	C_2 = 1.087
A_3 = 3.102	B_3 = 1.077	C_3 = 1.485
σ = 0.012	σ = 0.013	σ = 0.012

Table 5.6 Values of the Parameters for NRTL and UNIQUAC Equations, determined from Ternary Liquid- Liquid Equilibria for the systems Sulfolane (1) + Carboxylic Acid (2) + Heptane (3) as well as the calculated Root Mean Square Deviation, rmsd.

	Parameters ($J.mol^{-1}$)			
	NRTL[a]		**UNIQUAC**	
Component ***i-j***	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ji}
Sulfolane (1) + Acetic Acid (2) + Heptane (3)				
	(0.086)		(0.334)	
1-2-2-1	2192.74	-4883.75	2.24	1.65
1-3-3-1	23023.16	21443.94	2.21	-0.57
2-3-3-2	2185.69	20626.01	-15.64	14.40
Sulfolane (1) + Propanoic Acid (2) + Heptane (3)				
	(0.026)		(0.403)	
1-2-2-1	-38976.14	98662.81	1.91	0.001
1-3-3-1	117442.20	84995.29	0.01	0.002
2-3-3-2	-13056.11	-27129.40	3.323	-203.58
Sulfolane (1) + Butanoic Acid (2) + Heptane (3)				
	(0.003)		(0.343)	
1-2-2-1	-19881.81	51555.27	0.99	-0.173
1-3-3-1	67523.92	219516.65	0.61	0.055
2-3-3-2	-1661.34	82458.19	-2.82	-0.55

Table 5.6 continued

	Parameters (J.mol^{-1})			
	NRTL[a]		UNIQUAC	
Component				
i-j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ji}
	Sulfolane (1) + 2-Methylpropanoic Acid (2) + Heptane (3)			
	(0.001)		(0.326)	
1-2-2-1	2206.58	70093.45	5.88	2.88
1-3-3-1	62002.38	79540.18	-4.74	0.67
2-3-3-2	17204.11	73345.67	0.30	-11.11
	Sulfolane (1) + Pentanoic Acid (2) + Heptane (3)			
	(0.001)		(0.371)	
1-2-2-1	97856.43	-49982.31	-0.08	-0.61
1-3-3-1	69797.57	96355.36	0.12	0.89
2-3-3-2	25897.94	38562.27	0.55	-0.98
	Sulfolane (1) + 3-Methylbutanoic Acid (2) + Heptane (3)			
	(0.001)		(0.337)	
1-2-2-1	18437.48	-10048.74	3.33	20.80
1-3-3-1	82469.77	78134.01	-0.43	0.08
2-3-3-2	-2681.33	68032.48	-2.10	-9.67

[a] Calculated with α_{ij} =0.2

Table 5.7 Representative selectivity values of sulfolane for the separation of carboxylic acids from heptane using equation (3.1)

Carboxylic Acid	**Selectivity (ω)**
Acetic Acid	7
Propanoic Acid	7
Butanoic Acid	10
2-Methylpropanoic Acid	3
Pentanoic Acid	5
3-Methylbutanoic Acid	5

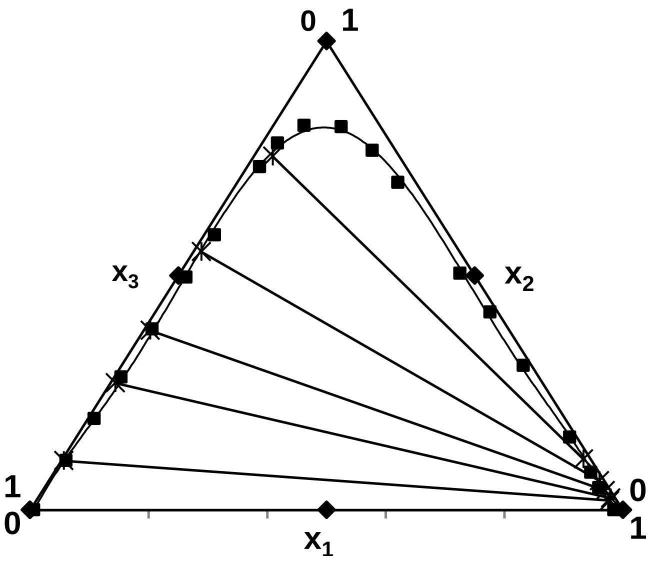


Figure 5.1 Liquid-liquid equilibrium data for the system [sulfolane (1) + acetic acid (2) + heptane (3)] at T = 303.15 K

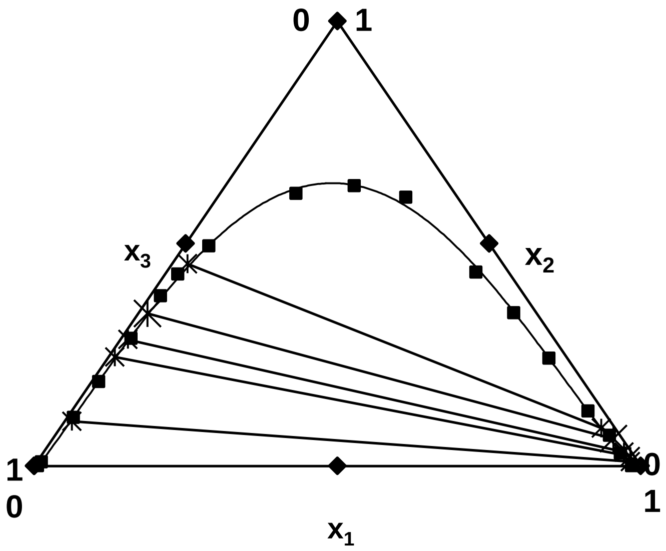


Figure 5.2 Liquid-liquid equilibrium data for the system [sulfolane (1) + propanoic acid (2) + heptane (3)] at T = 303.15 K.

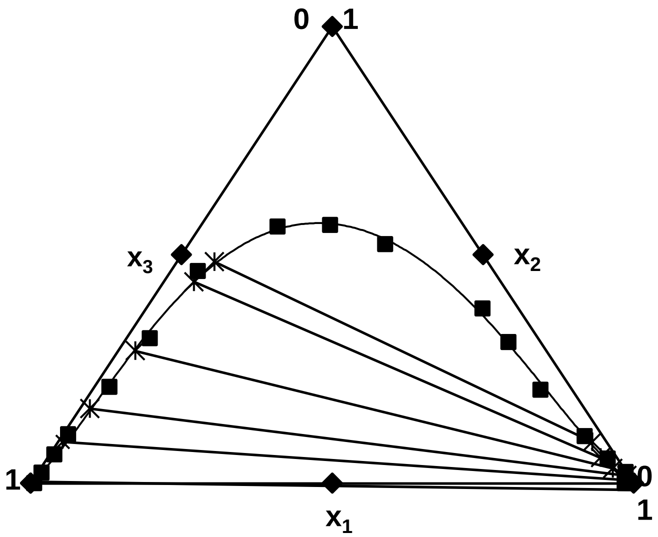


Figure 5.3 Liquid-liquid equilibrium data for the system [sulfolane (1) + butanoic acid (2) + heptane (3)] at T = 303.15 K

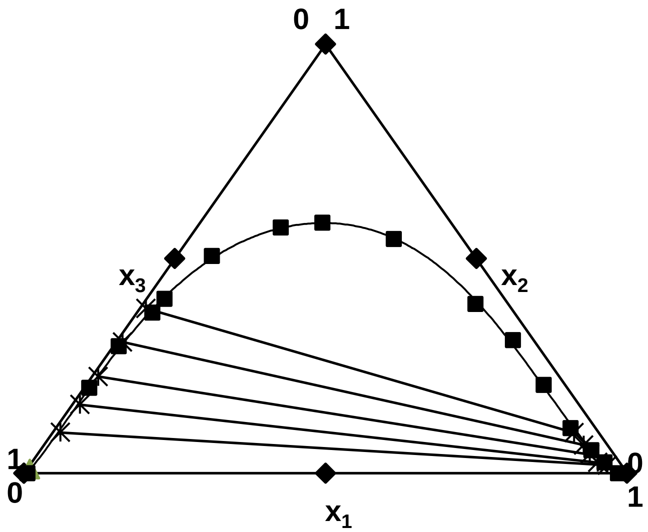


Figure 5.4 Liquid-liquid equilibrium data for the system [sulfolane (1) +2-methylpropanoic acid (2) + heptane (3)] at T = 303.15 K

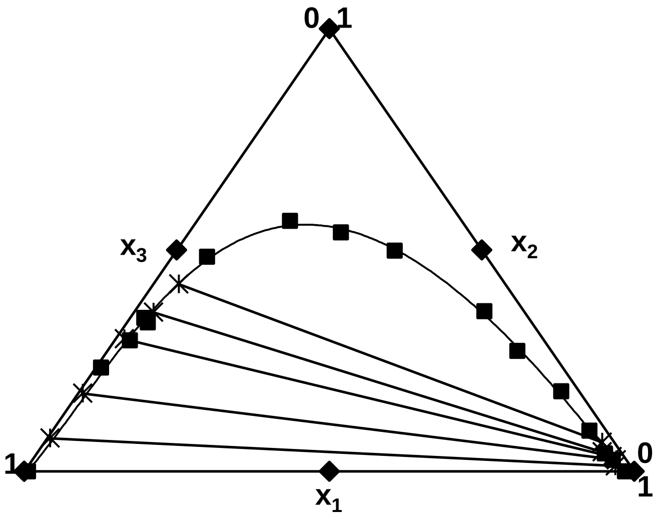


Figure 5.5 Liquid-liquid equilibrium data for the system [sulfolane (1) + pentanoic acid (2) + heptane (3)] at T = 303.15 K

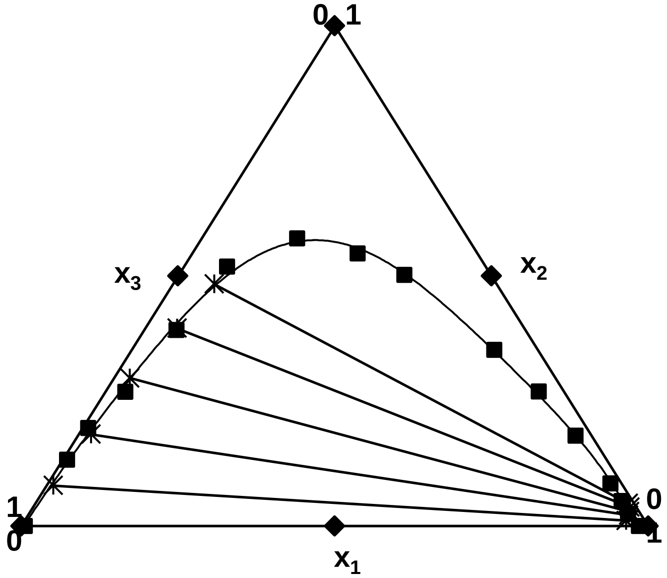
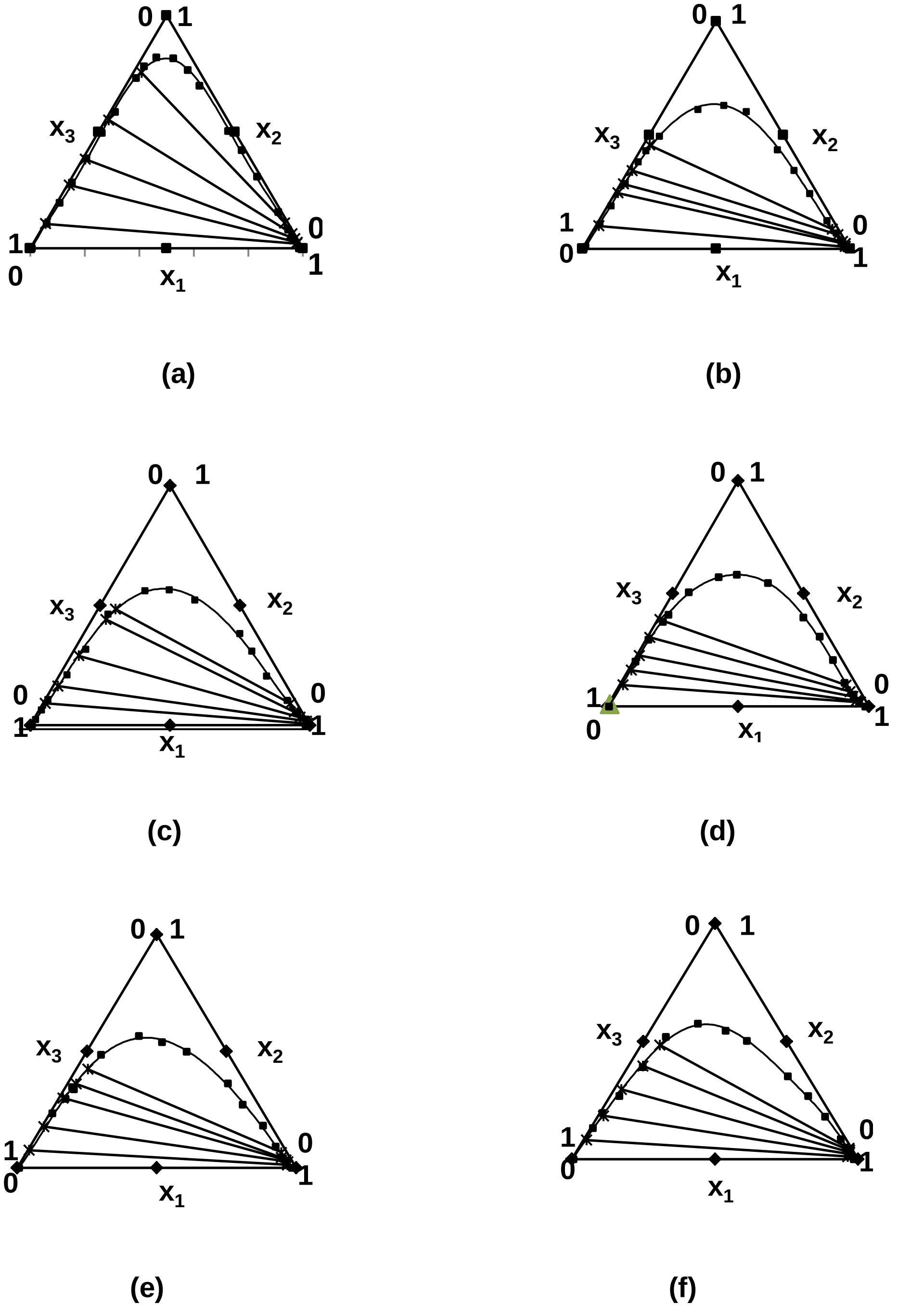


Figure 5.6 Liquid-liquid equilibrium data for the system [sulfolane (1) + 3-methylbutanoic acid (2) + heptane (3)] at T = 303.15 K



(a) (b)

(c) (d)

(e) (f)

Figure 5.7 Summary of Liquid-liquid equilibrium data for the following systems at T = 303.15 K: [(a) sulfolane(1) + acetic acid (2) + heptane (3), (b) sulfolane (1) + propanoic acid (2) + heptane (3), (c) sulfolane(1) + butanoic acid (2) + heptane (3), (d) sulfolane (1) + 2-methylpropanoic acid (2) + heptane (3), (e) sulfolane (1) + pentanoic acid (2) + heptane(3), (f) sulfolane (1) + 3-methylbutanoic acid (2) + heptane (3)]. [Key: experimental points (▪), experimental tie lines(x)]

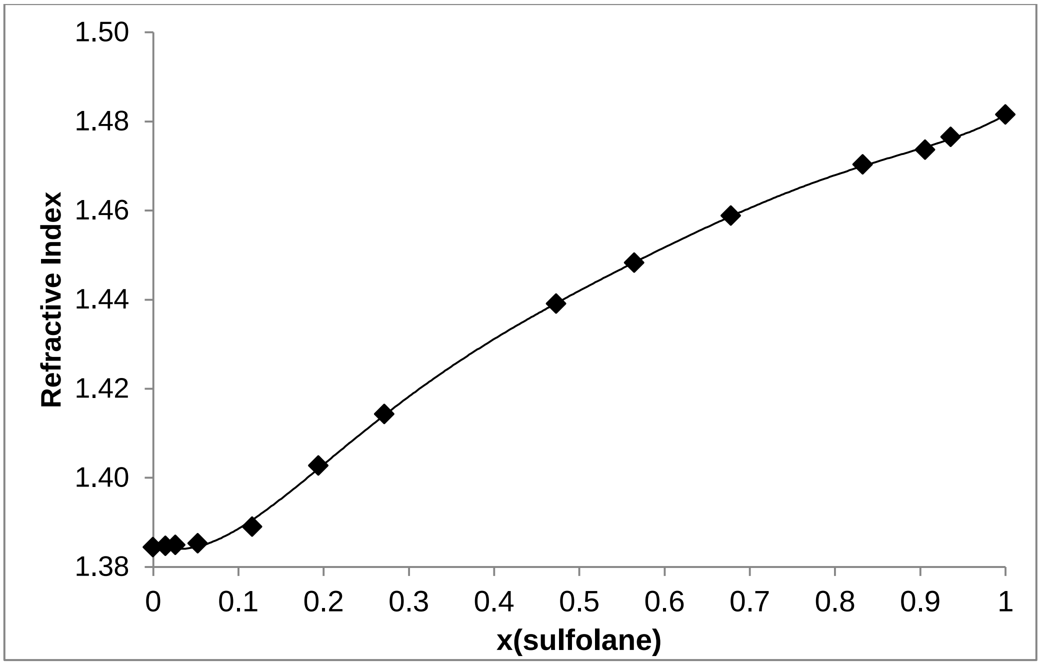


Figure 5.8 Calibration curve for the system: [sulfolane (1) + acetic acid (2) + heptane (3)] at T = 303.15 K

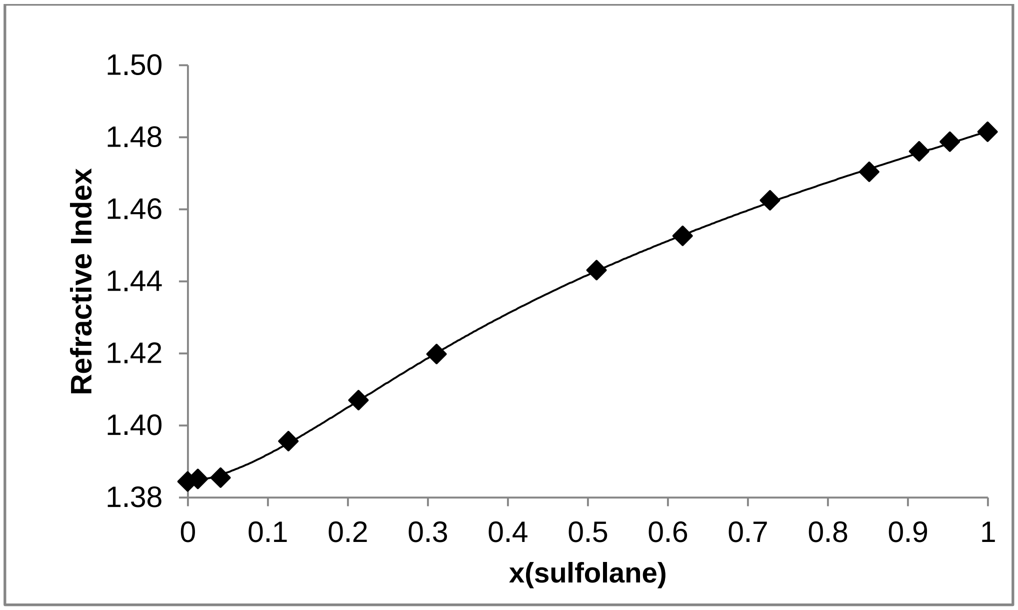


Figure 5.9 Calibration curve for the system: [sulfolane (1) + propanoic acid (2) + heptane (3)] at T= 303.15 K

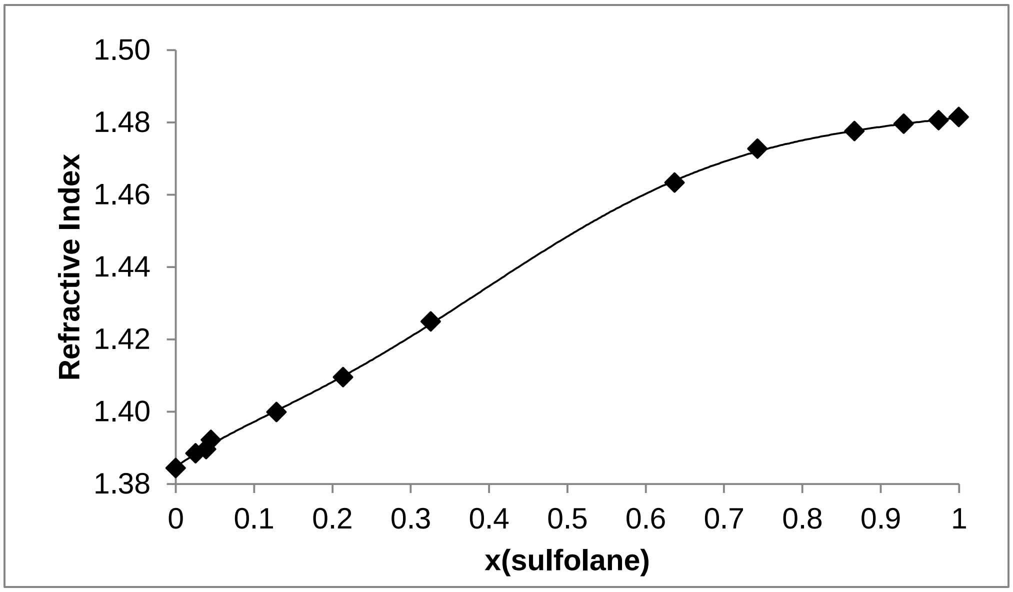


Figure 5.10 Calibration curve for the system: [sulfolane (1) + butanoic acid (2) + heptane (3)] at T = 303.15 K

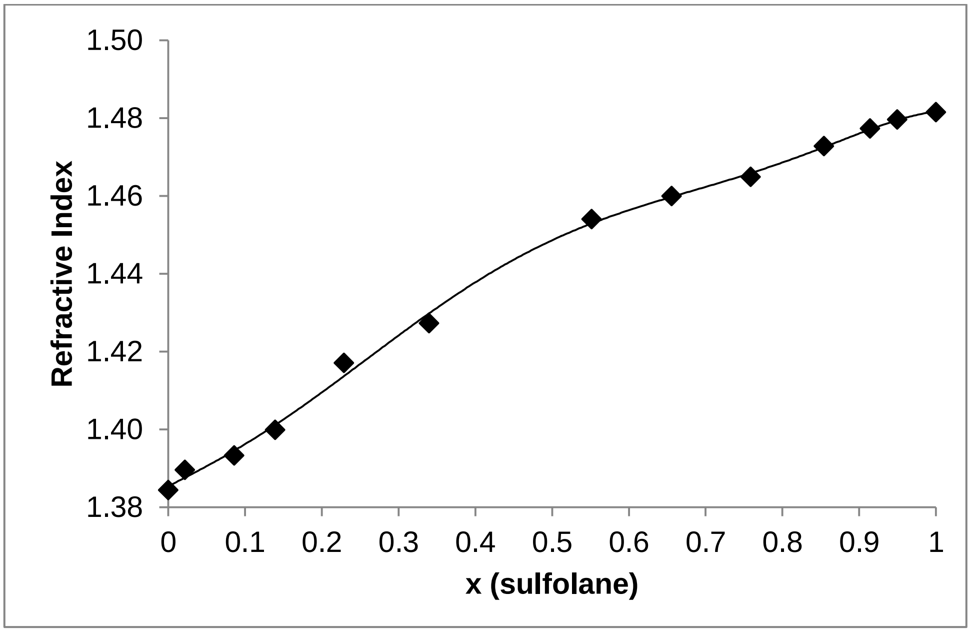


Figure 5.11 Calibration curve for the system:
[sulfolane (1) + 2-methypropanoic acid (2) + heptane (3)] at T = 303.15 K

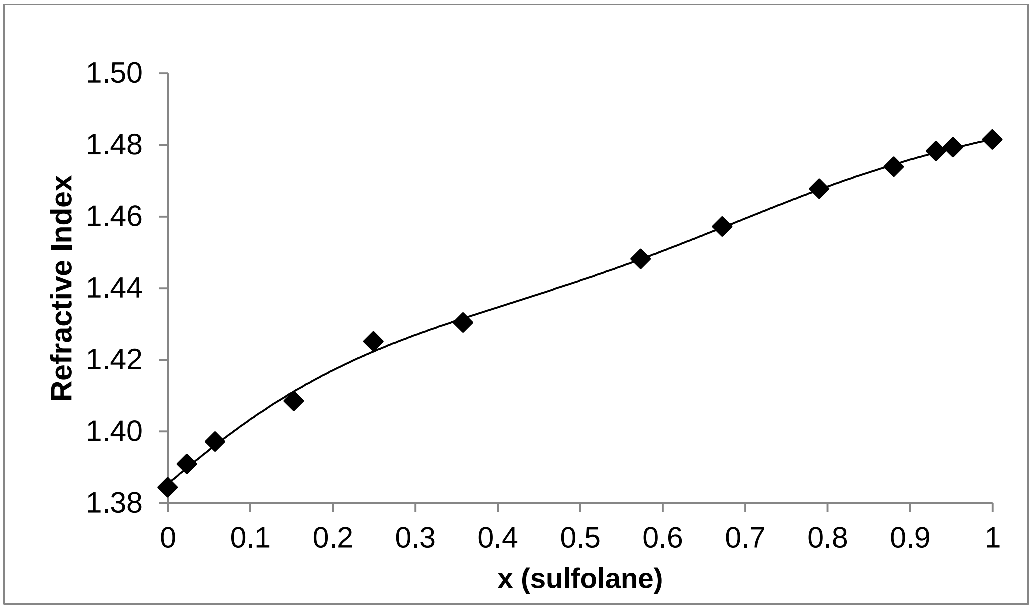


Figure 5.12 Calibration curve for the system: [sulfolane (1) + pentanoic acid (2) + heptane (3)] at T = 303.15 K

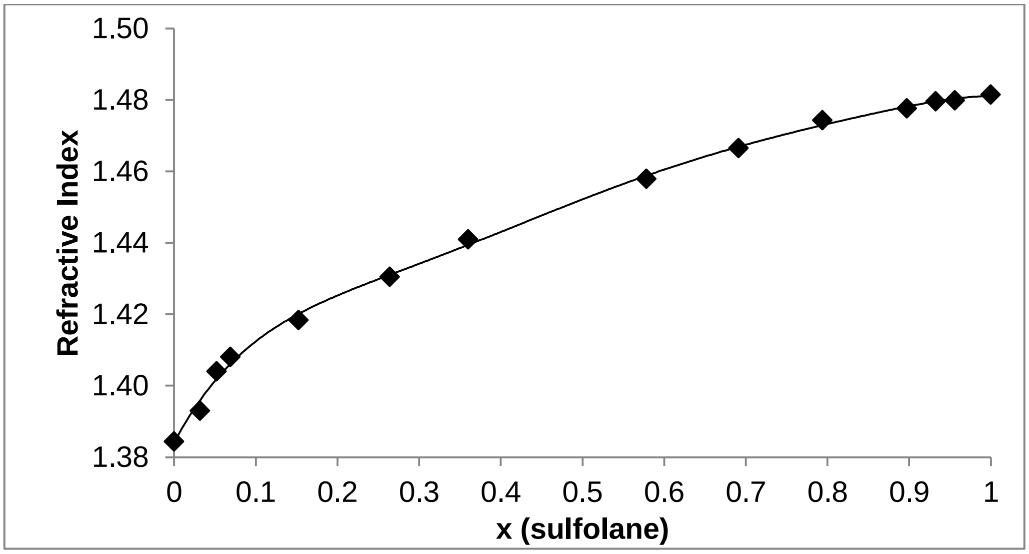


Figure 5.13 Calibration curve for the system: [sulfolane (1) + 3-methylbutanoic acid (2) + heptane (3)] at T = 303.15 K

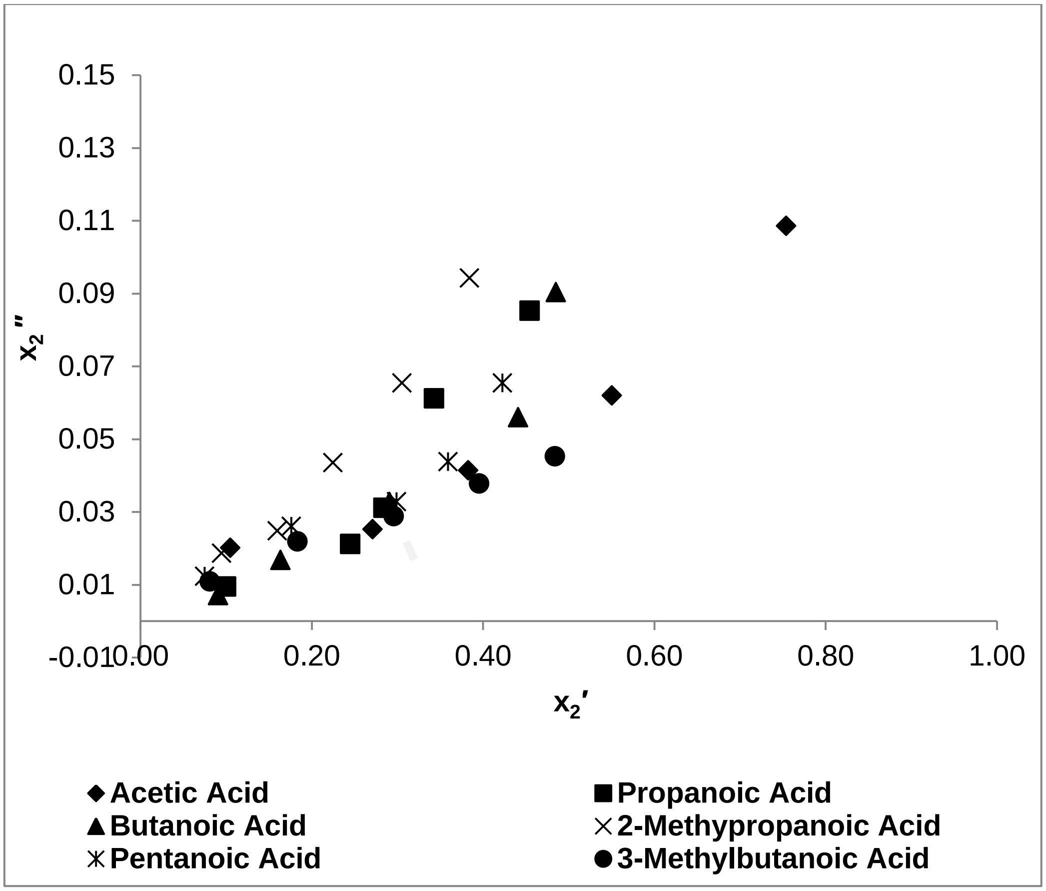


Figure 5.14 A plot of x_2'' against x_2' showing the relative solubilities of the carboxylic acid in the sulfolane-rich and heptane- rich layers

5.2 LIQUID–LIQUID EQUILIBRIA FOR MIXTURES OF SULFOLANE + CARBOXYLIC ACID + CYCLOHEXANE AT T = 303.15 K

Table 5.8 Physical Properties of the Pure Components at T = 303.15 K, Molar Volumes, $V_{mi,}$ Refractives Index, n_D, Volume and Surface Parameters, R and Q.

Component	$V_{mi}/cm^3.mol^{-1}$	n_D	R	Q
Acetic Acid	57.73	1.3716	2.022[a]	2.072[a]
Propanoic Acid	75.34	1.3829	2.877[a]	2.612[a]
Butanoic Acid	92.93	1.3947	3.551[a]	3.152[a]
2-Methylpropanoic Acid	93.46	1.3913	3.550[a]	3.148[a]
Pentanoic Acid	109.78	1.4047	4.226[a]	3.692[a]
3-Methylbutanoic Acid	111.34	1.3997	4.225[a]	3.688[a]
Cyclohexane	108.75	1.4222	4.046[b]	3.240[b]
Sulfolane	95.30	1.4815	4.036[b]	3.200[b]

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

[b] Mohsen- Nia *et al* (2005)

Table 5.9 Composition of points on the binodal curve at T = 303.15 K for the systems: [Sulfolane (1) + Carboxylic Acid (2) + Cyclohexane (3)], equilibrium Mole Fraction, x_1, x_2

x_1	x_2	x_1	x_2
Acetic Acid			
0.0056	0.0000	0.2881	0.5686
0.0079	0.0532	0.4623	0.4577
0.0081	0.0831	0.5679	0.3624
0.0101	0.1500	0.6995	0.2313
0.0128	0.2608	0.8340	0.1103
0.0322	0.3686	0.8876	0.0770
0.0671	0.4700	0.9263	0.0439
0.1314	0.5961	0.9943	0.0000
0.2099	0.6096		
Propanoic Acid			
0.0056	0.0000	0.4426	0.4219
0.0458	0.1645	0.5304	0.3622
0.0951	0.2784	0.6369	0.2793
0.1257	0.3789	0.7463	0.1980
0.1380	0.4801	0.8440	0.1093
0.2002	0.5062	0.8890	0.0685
0.2494	0.5130	0.9864	0.0120
0.2886	0.4984	0.9943	0.0000
0.3484	0.4754		
Butanoic Acid			
0.0056	0.0000	0.4030	0.4767
0.0157	0.0485	0.4957	0.4018
0.0234	0.0827	0.6112	0.3292
0.0430	0.1268	0.7264	0.2394
0.0634	0.2189	0.8449	0.1324
0.0867	0.2971	0.9022	0.0840
0.1087	0.3905	0.9538	0.0373
0.1722	0.4791	0.9678	0.0318
0.2573	0.5170	0.9943	0.0000

Table 5.9 Continued

x_1	x_2	x_1	x_2
2-Methylpropanoic Acid			
0.0056	0.0000	0.5906	0.3540
0.0211	0.1012	0.7203	0.2405
0.0523	0.2511	0.8433	0.1291
0.1021	0.3456	0.8939	0.0982
0.1177	0.4266	0.9219	0.0759
0.2069	0.5242	0.9867	0.0108
0.2952	0.5199	0.9943	0.0000
0.4953	0.4190		
Pentanoic Acid			
0.0056	0.0000	0.6106	0.3497
0.0110	0.1002	0.7459	0.2210
0.0211	0.2612	0.8376	0.1166
0.0412	0.4402	0.9258	0.0584
0.0713	0.6314	0.9561	0.0267
0.1290	0.6703	0.9717	0.0128
0.3100	0.6136	0.9851	0.0012
0.4902	0.4602	0.9943	0.0000
0.5662	0.3853		
3-Methylbutanoic Acid			
0.0056	0.0000	0.2889	0.5497
0.0171	0.1067	0.5092	0.3971
0.0345	0.1730	0.6280	0.2831
0.0248	0.2732	0.7060	0.2180
0.0435	0.3296	0.8466	0.1191
0.0625	0.4139	0.9107	0.0654
0.1176	0.4990	0.9580	0.0295
0.1948	0.5793	0.9943	0.0000

Table 5.10 Mole fraction and Refractive Indices: [Sulfolane (1) + Carboxylic Acid (2) + Cyclohexane (3)] at T = 303.15 K.

x_1	n_D	x_1	n_D
Acetic Acid			
0.0000	1.4222	0.4623	1.4270
0.0128	1.4224	0.5679	1.4398
0.0322	1.4247	0.6995	1.4495
0.0671	1.4249	0.8340	1.4606
0.1314	1.4259	0.8876	1.4714
0.2099	1.4262	0.9263	1.4796
0.2881	1.4269	1.0000	1.4815
Propanoic Acid			
0.0000	1.4222	0.6369	1.4743
0.2002	1.4228	0.7463	1.4590
0.2494	1.4229	0.8440	1.4664
0.2886	1.4232	0.8890	1.4736
0.3484	1.4237	0.9864	1.4782
0.4426	1.4239	1.0000	1.4815
0.5304	1.4512		
Butanoic Acid			
0.0000	1.4222	0.7264	1.4641
0.1087	1.4228	0.8449	1.4692
0.1722	1.4229	0.9022	1.4758
0.2573	1.4232	0.9538	1.4789
0.4030	1.4237	0.9678	1.4808
0.4957	1.4239	1.0000	1.4815
0.6112	1.4597		

Table 5.10 Continued

x_1	n_D	x_1	n_D
2-Methylpropanoic Acid			
0.0000	1.4222	0.7203	1.4654
0.1021	1.4237	0.8433	1.4742
0.1177	1.4246	0.8939	1.4762
0.2069	1.4255	0.9219	1.4799
0.2952	1.4266	0.9867	1.4805
0.4953	1.4372	1.0000	1.4815
0.5906	1.4489		
Pentanoic Acid			
0.0000	1.4222	0.6106	1.4582
0.0412	1.4226	0.7459	1.4628
0.0713	1.4235	0.8376	1.4646
0.1290	1.4237	0.9561	1.4764
0.3100	1.4238	0.9717	1.4799
0.4902	1.4240	0.9851	1.4800
0.5662	1.4389	1.0000	1.4815
3-Methylbutanoic Acid			
0.0000	1.4222	0.5092	1.4583
0.0248	1.4224	0.6280	1.4650
0.0435	1.4227	0.7060	1.4768
0.0625	1.4233	0.8466	1.4792
0.1176	1.4239	0.9107	1.4799
0.1948	1.4244	0.9580	1.4805
0.2889	1.4477	1.0000	1.4815

Table 5.11 Compositions of the conjugate solutions, x_1', x_2' and x_1'', x_2'' at T = 303.15 K for the systems: [Sulfolane (1) + Carboxylic Acid (2) + Cyclohexane (3)], Refractive Index, n_D

Cyclohexane Rich			**Sulfolane Rich**		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) + Acetic Acid (2) + Cyclohexane (3)					
0.0095	0.0544	1.4269	0.9567	0.0203	1.4796
0.0171	0.1569	1.4249	0.9345	0.0457	1.4714
0.0182	0.2349	1.4259	0.9071	0.0658	1.4606
0.0240	0.3411	1.4249	0.8851	0.0759	1.4495
0.0375	0.4365	1.4247	0.8615	0.0930	1.4398
Sulfolane (1) + Propanoic Acid (2) + Cyclohexane (3)					
0.0211	0.0709	1.4242	0.9638	0.0208	1.4782
0.0490	0.1499	1.4234	0.9432	0.0380	1.4736
0.0862	0.2852	1.4232	0.9263	0.0492	1.4664
0.1033	0.3535	1.4229	0.9054	0.0655	1.4590
0.1210	0.4071	1.4228	0.8867	0.0766	1.4512
Sulfolane (1) + Butanoic Acid (2) + Cyclohexane (3)					
0.0213	0.0812	1.4239	0.9780	0.0129	1.4789
0.0414	0.1540	1.4237	0.9744	0.0234	1.4758
0.0656	0.2303	1.4232	0.9540	0.0347	1.4692
0.0880	0.3284	1.4229	0.9431	0.0458	1.4641
0.1086	0.3842	1.4228	0.9321	0.0567	1.4597
Sulfolane (1) + 2-Methylpropanoic Acid (2) + Cyclohexane (3)					
0.0231	0.1084	1.4236	0.9808	0.0135	1.4784
0.0412	0.2121	1.4233	0.9710	0.0218	1.4758
0.0713	0.3130	1.4229	0.9597	0.0328	1.4709
0.0910	0.3751	1.4227	0.9456	0.0437	1.4619
0.1243	0.4300	1.4226	0.9391	0.0550	1.4542

Table 5.11 Continued

Cyclohexane Rich			Sulfolane Rich		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) + Pentanoic Acid (2) + Cyclohexane (3)					
0.0102	0.1191	1.4240	0.9685	0.0108	1.4800
0.0202	0.2195	1.4238	0.9574	0.0219	1.4764
0.0211	0.3330	1.4237	0.9363	0.0425	1.4724
0.0431	0.4397	1.4235	0.9135	0.0585	1.4646
0.0757	0.5266	1.4226	0.9022	0.0690	1.4582
Sulfolane (1) + 3-Methylbutanoic Acid (2) + Cyclohexane (3)					
0.0115	0.0890	1.4244	0.9709	0.0142	1.4804
0.0211	0.1740	1.4239	0.9577	0.0242	1.4792
0.0311	0.2199	1.4233	0.9457	0.0366	1.4768
0.0507	0.3216	1.4227	0.9306	0.0476	1.4650
0.0811	0.4690	1.4224	0.9124	0.0596	1.4583

Table 5.12 Coefficients A_i, B_i, and C_i in equation (3.5) – (3.7) respectively, for the systems: [Sulfolane (1) + Carboxylic Acid (2) + Cyclohexane (3)] at T = 303.15 K, standard deviation, σ, equation (3.10)

Hlavatý	**Beta**	**Log γ**
Sulfolane (1) + Acetic Acid (2) + Cycohexane (3)		
$A_1 = 0.589$	$B_1 = 3.483$	$C_1 = 2.896$
$A_2 = 1.098$	$B_2 = 1.415$	$C_2 = 1.345$
$A_3 = 4.694$	$B_3 = 1.187$	$C_3 = 1.641$
$\sigma = 0.013$	$\sigma = 0.017$	$\sigma = 0.022$
Sulfolane (1) + Propanoic Acid (2) + Cyclohexane (3)		
$A_1 = 0.960$	$B_1 = 1.147$	$C_1 = 1.117$
$A_2 = 0.950$	$B_2 = 0.786$	$C_2 = 0.781$
$A_3 = 4.638$	$B_3 = 0.735$	$C_3 = 1.057$
$\sigma = 0.012$	$\sigma = 0.053$	$\sigma = 0.052$
Sulfolane (1) + Butanoic Acid (2) + Cyclohexane (3)		
$A_1 = 0.534$	$B_1 = 0.727$	$C_1 = 0.704$
$A_2 = 0.16$	$B_2 = 0.592$	$C_2 = 0.587$
$A_3 = 2.945$	$B_3 = 0.696$	$C_3 = 0.916$
$\sigma = 0.012$	$\sigma = 0.080$	$\sigma = 0.079$
Sulfolane (1) + 2- Methylpropanoic Acid (2) + Cyclohexane (3)		
$A_1 = 0.528$	$B_1 = 6.157$	$C_1 = 1.428$
$A_2 = 0.298$	$B_2 = 1.623$	$C_2 = 0.834$
$A_3 = 3.183$	$B_3 = 1.466$	$C_3 = 1.249$
$\sigma = 0.012$	$\sigma = 0.027$	$\sigma = 0.030$

Table 5.12 Continued

Hlavatý	**Beta**	**Log γ**
Sulfolane (1) + Pentanoic Acid (2) + Cyclohexane (3)		
A_1 = 0.942	B_1 = 6 157	C_1 = 5.474
A_2 = 1.193	B_2 = 1.623	C_2 = 1.592
A_3 = 5.565	B_3 = 1.466	C_3 = 2.06
σ = 0.015	σ = 0.027	σ = 0.034
Sulfolane (1) + 3-Methylpropanoic Acid (2) + Cyclohexane (3)		
A_1 = 0.594	B_1 = 2.537	C_1 = 2.307
A_2 = 0.94	B_2 = 1.197	C_2 = 1.168
A_3 = 4.307	B_3 = 1.125	C_3 = 1.563
σ = 0.018	σ = 0.024	σ = 0.023

Table 5.13 Values of the Parameters for NRTL and UNIQUAC Equations, determined from Ternary Liquid- Liquid Equilibria for the systems Sulfolane (1) + Carboxylic Acid (2) + Cyclohexane (3) as well as the calculated Root Mean Square Deviation, rmsd.

	Parameters ($J.mol^{-1}$)			
	NRTL[a]		**UNIQUAC**	
Component *i-j*	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ji}
	Sulfolane (1) + Acetic Acid (2) + Cyclohexane (3)			
	(0.004)		(0.305)	
1-2-2-1	17790.28	60070.40	2.00	-0.99
1-3-3-1	51337.05	84965.4	2.00	0.01
2-3-3-2	2645.78	22879.88	-42.78	42.77
	Sulfolane (1) + Propanoic Acid (2) + Cyclohexane (3)			
	(0.003)		(0.292)	
1-2-2-1	29566.30	31043.22	2.50	1.37
1-3-3-1	67599.67	64960.79	-0.07	-0.03
2-3-3-2	-45268.52	10293.17	-83.62	-2.41
	Sulfolane (1) + Butanoic Acid (2) + Cyclohexane (3)			
	(0.002)		(0.297)	
1-2-2-1	69959.93	-4571.14	-2051.41	1.28
1-3-3-1	86201.21	59326.61	-0.080	0.03
2-3-3-2	33871.93	-11397.20	-182.567	-159.46

Table 5.13 Continued

	Parameters (J.mol^{-1})			
	NRTL[a]		UNIQUAC	
Component				
i-j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ji}
Sulfolane (1) + 2-Methylpropanoic Acid (2) + Cyclohexane (3)				
	(0.001)		(0.315)	
1-2-2-1	63057.67	-1610.79	-0.50	0.01
1-3-3-1	87529.42	69230.10	1.28	3.40
2-3-3-2	-29279.78	39842.58	-4.66	4.66
Sulfolane (1) + Pentanoic Acid (2) + Cylohexane (3)				
	(0.097)		(0.328)	
1-2-2-1	10915.02	23221.47	2.00	2.00
1-3-3-1	22664.71	22692.32	-1.14	-0.02
2-3-3-2	16443.94	-15111.51	-21.58	21.58
Sulfolane (1) + 3-Methylbutanoic Acid (2) + Cyclohexane (3)				
	(0.003)		(0.321)	
1-2-2-1	49906.45	19057.41	2.00	-0.13
1-3-3-1	61416.69	78482.73	-0.03	-0.04
2-3-3-2	-2747.85	23411.62	-15.03	14.99

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

Table 5.14 **Representative selectivity values of sulfolane for the separation of carboxylic acids from cyclohexane using equation (3.1)**

Carboxylic Acid	**Selectivity (ω)**
Acetic Acid	8
Propanoic Acid	8
Butanoic Acid	19
2-Methylpropanoic Acid	11
Pentanoic Acid	3
3-Methylbutanoic Acid	6

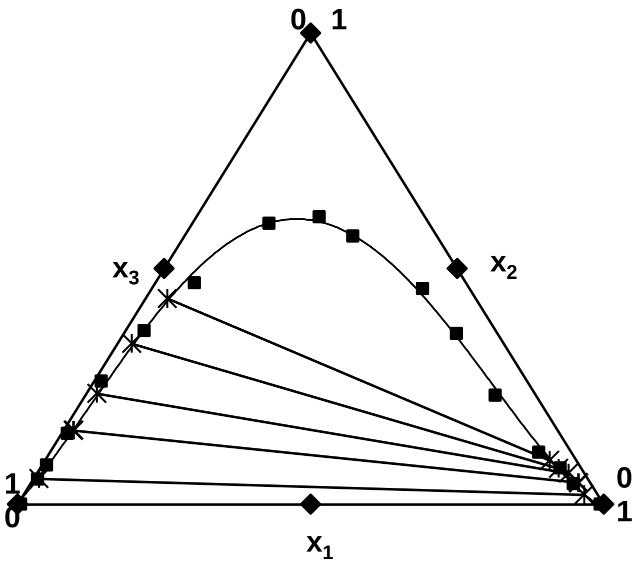


Figure 5.15: Liquid-liquid equilibrium data for the system [sulfolane (1) + acetic acid (2) + cyclohexane (3)] at T = 303.15 K

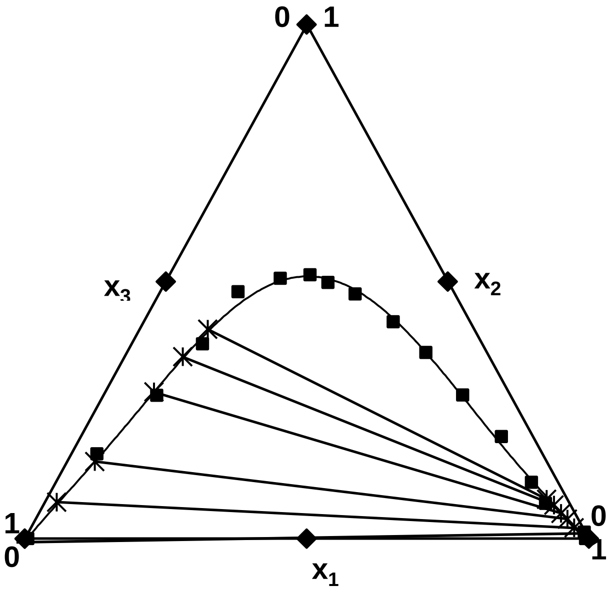


Figure 5.16 Liquid-liquid equilibrium data for the system [sulfolane (1) + propanoic acid (2) + cyclohexane (3)] at T = 303.15 K

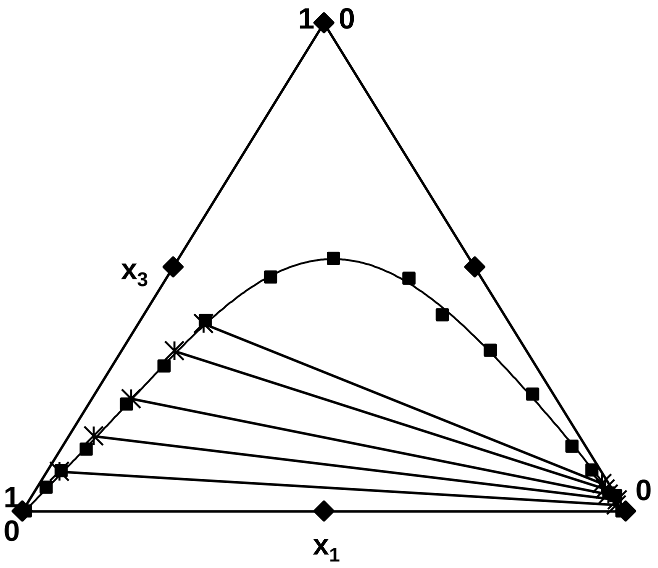


Figure 5.17 Liquid-liquid equilibrium data for the system [sulfolane (1) + butanoic acid (2) + cyclohexane (3)] at T= 303.15 K

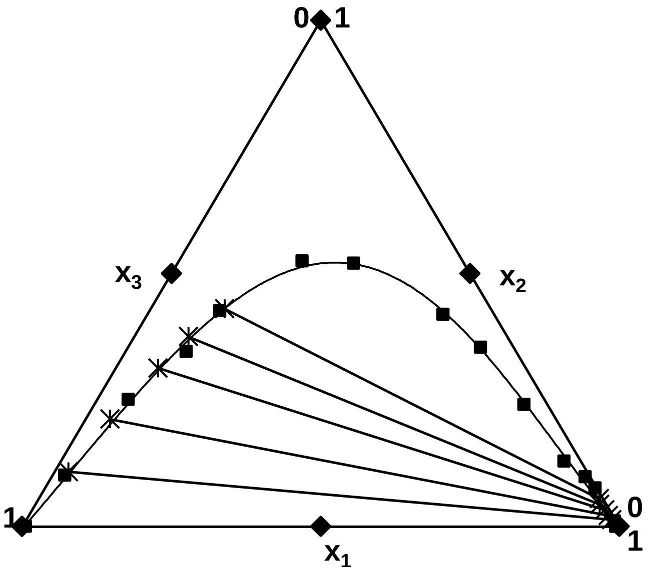


Figure 5.18 Liquid-liquid equilibrium data for the system [sulfolane (1) + 2-methylpropanoic acid (2) + cyclohexane (3)] at T= 303.15 K

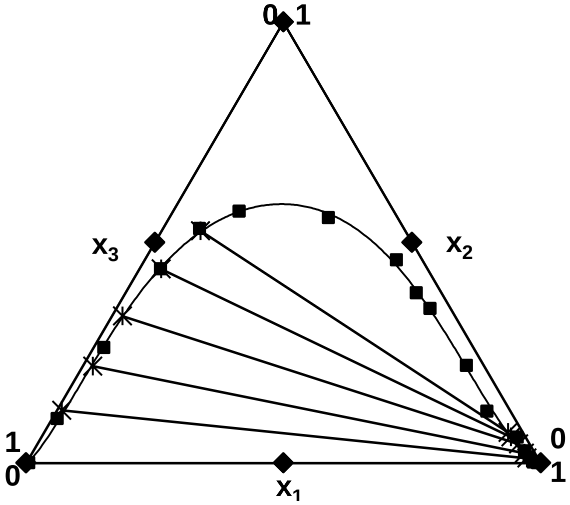


Figure 5.19 Liquid-liquid equilibrium data for the system [sulfolane (1) + pentanoic acid (2) + cyclohexane (3)] at T = 303.15 K

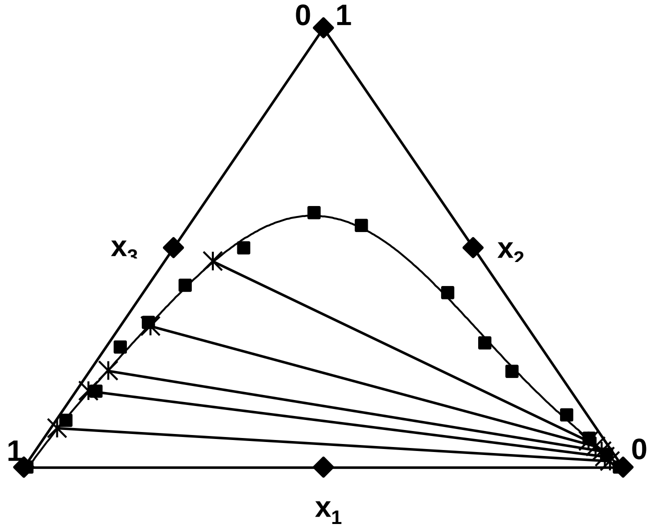


Figure 5.20 Liquid-liquid equilibrium data for the system [sulfolane (1) + 3-methylbutanoic acid (2) + cyclohexane (3)] at T= 303.15 K

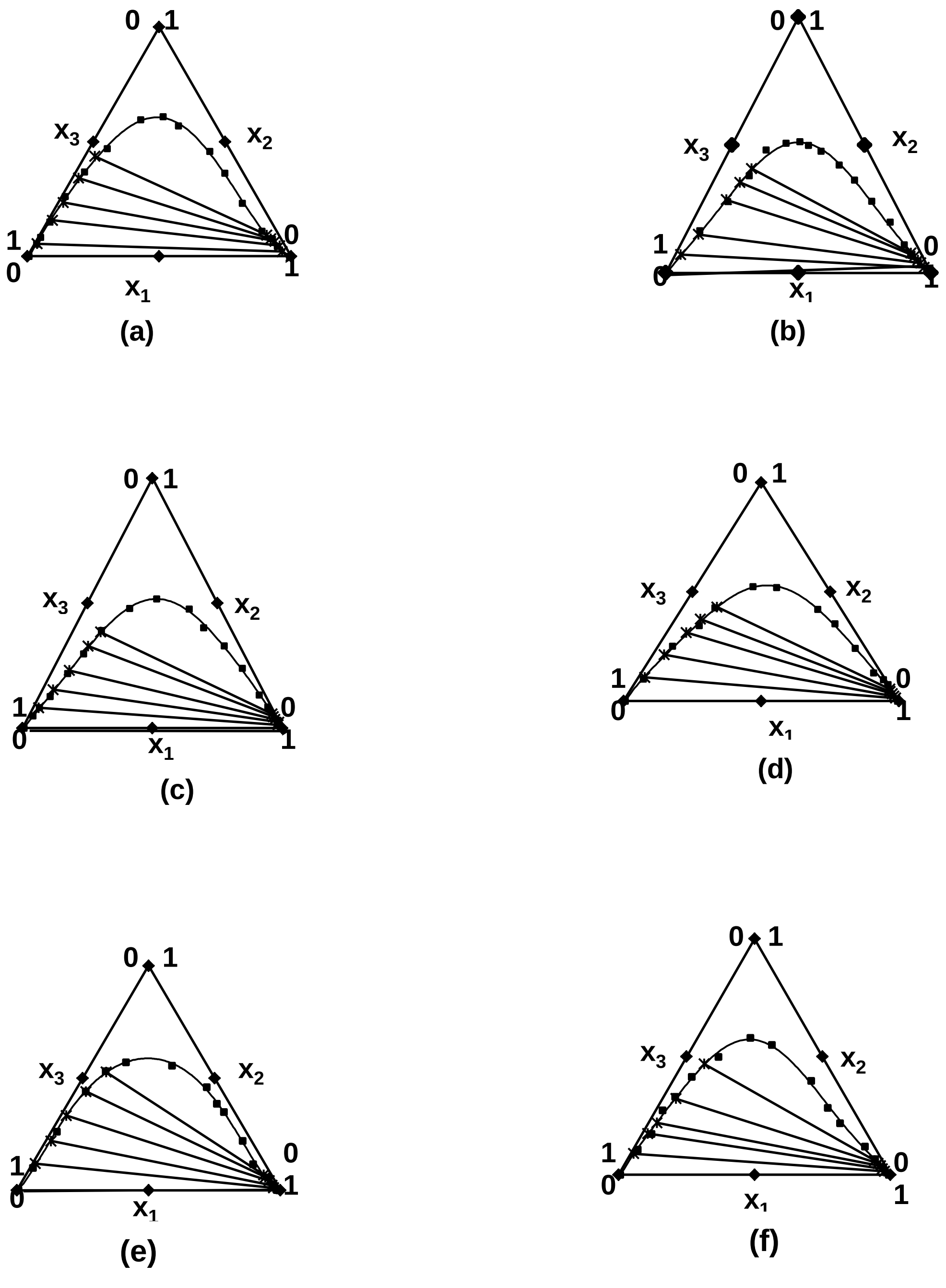


Figure 5.21 Summary of Liquid-liquid equilibrium data for the following systems at T = 303.15 K: [(a) sulfolane(1) + acetic acid (2) + cyclohexane (3), (b) sulfolane (1) + propanoic acid (2) + cyclohexane (3), (c) sulfolane(1) + butanoic acid (2) + cyclohexane (3), (d) sulfolane (1) + 2-methylpropanoic acid (2) + cyclohexane (3), (e) sulfolane (1) + pentanoic acid (2) + cyclohexane(3), (f) sulfolane (1) +3-methylbutanoic acid (2) + cyclohexane (3)]. [Key: experimental points (▪), experimental tie lines(x)]

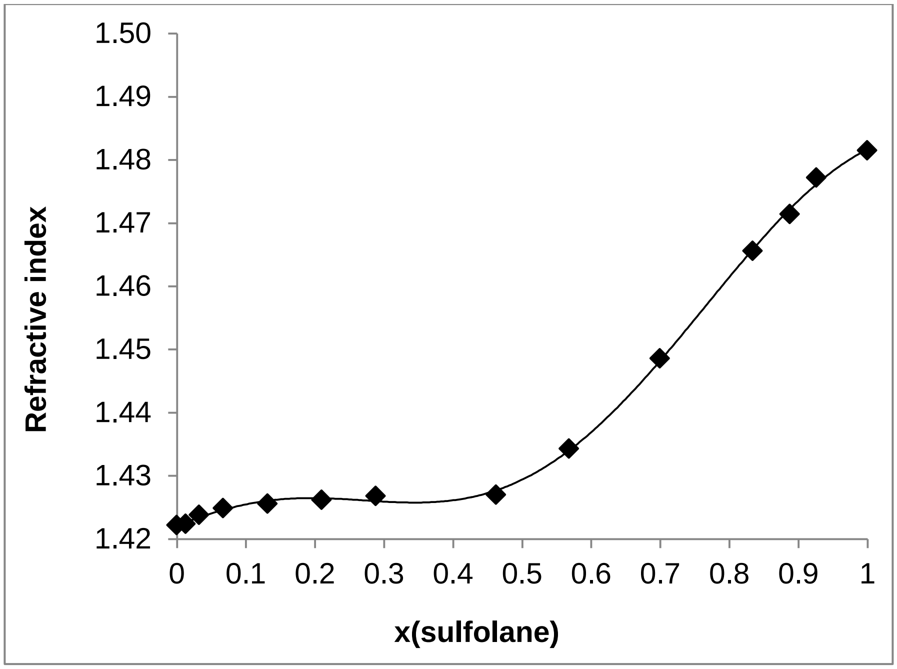


Figure 5.22 Calibration curve for the system: [sulfolane (1) + acetic acid (2) + cyclohexane (3)] at T = 303.15 K

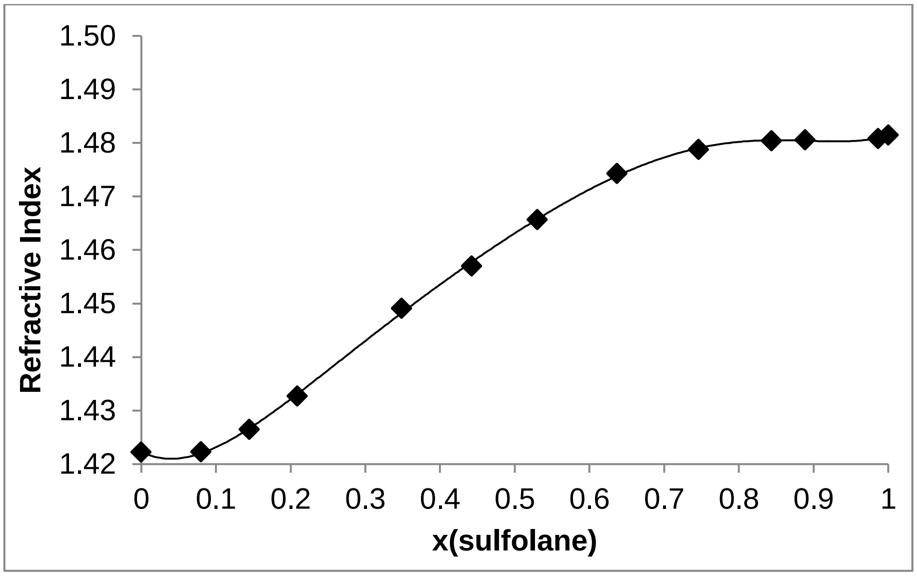


Figure 5.23 Calibration curve for the system: [sulfolane (1) + propanoic acid (2) + cyclohexane (3)] at T = 303.15 K

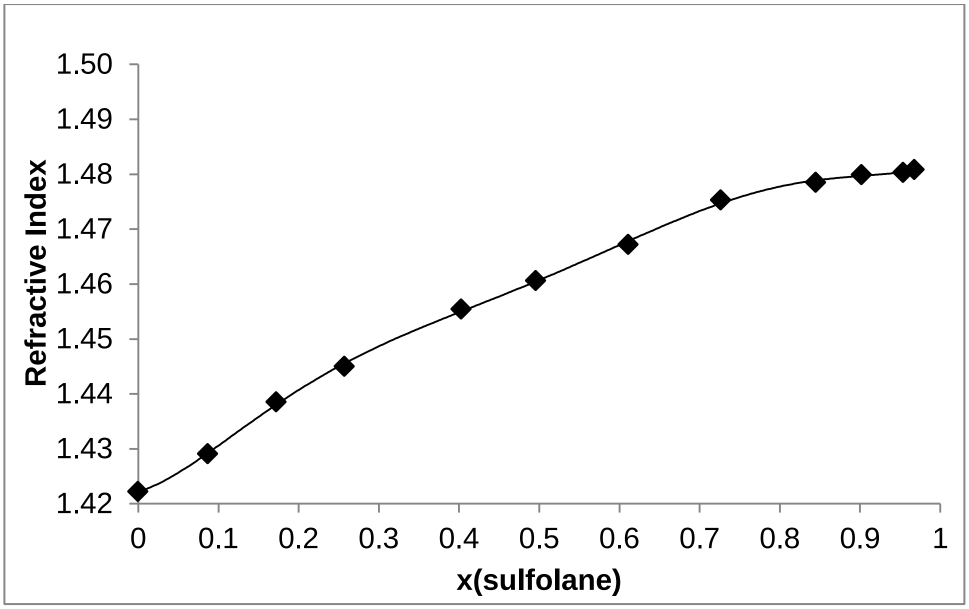


Figure 5.24 Calibration curve for the system: [sulfolane (1) + butanoic acid (2) + cyclohexane (3)] at T = 303.15 K

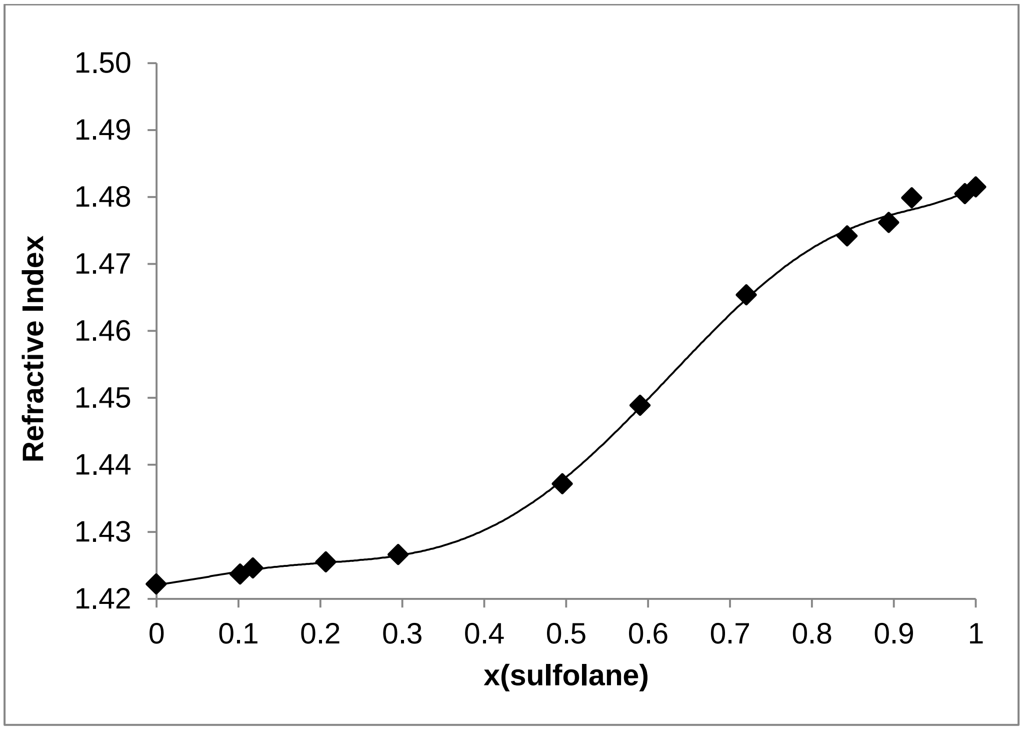


Figure 5.25 Calibration curve for the system: [sulfolane (1) + 2-methylpropanoic acid (2) + cyclohexane (3)] at T = 303.15 K

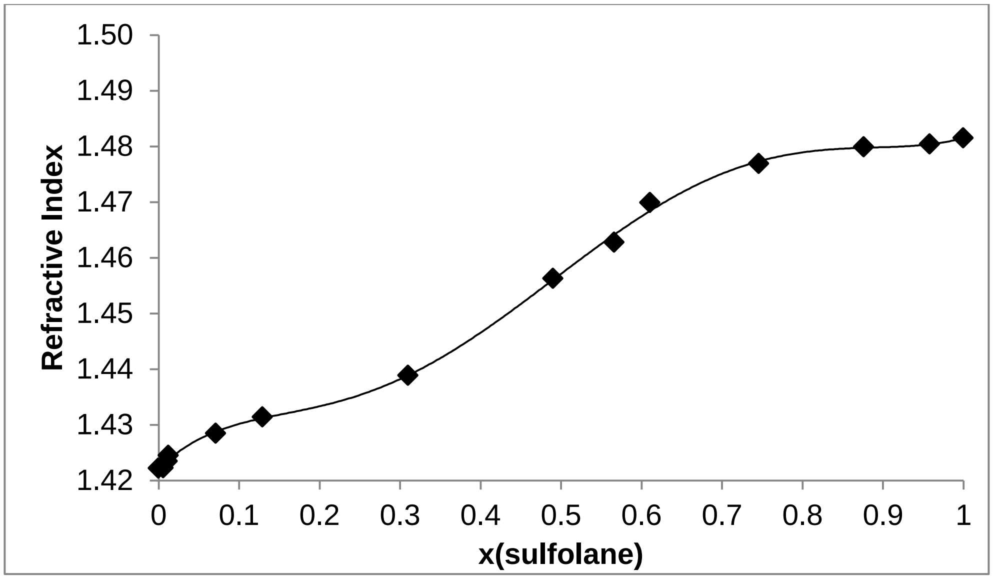


Figure 5.26 Calibration curve for the system: [sulfolane (1) + pentanoic acid (2) + cyclohexane (3)] at T = 303.15 K

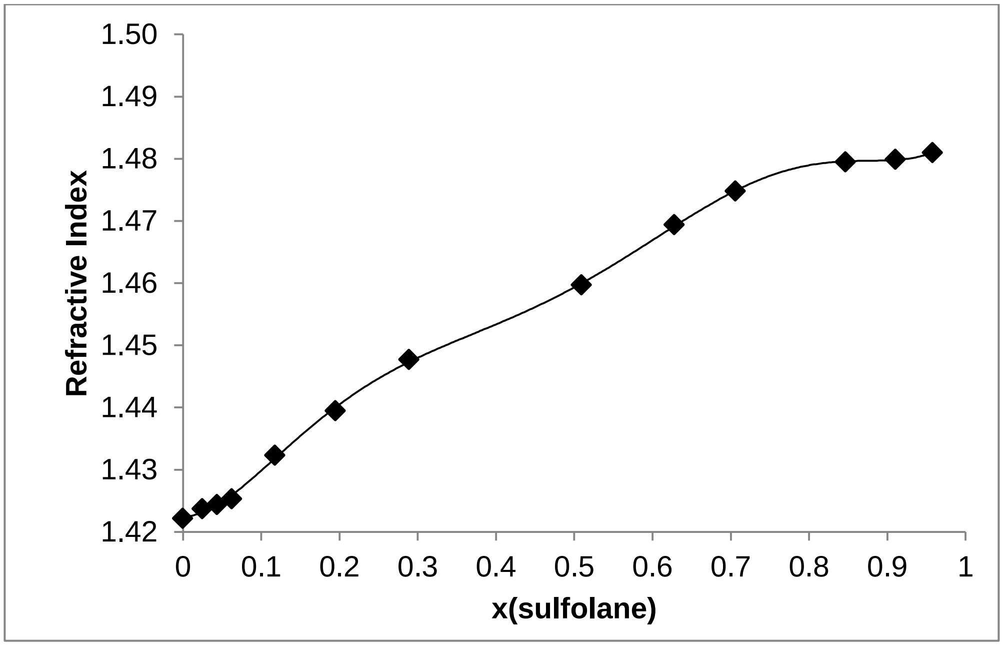


Figure 5.27 Calibration curve for the system: [sulfolane (1) + 3-methylbutanoic acid (2) + cyclohexane (3)] at T = 303.15 K

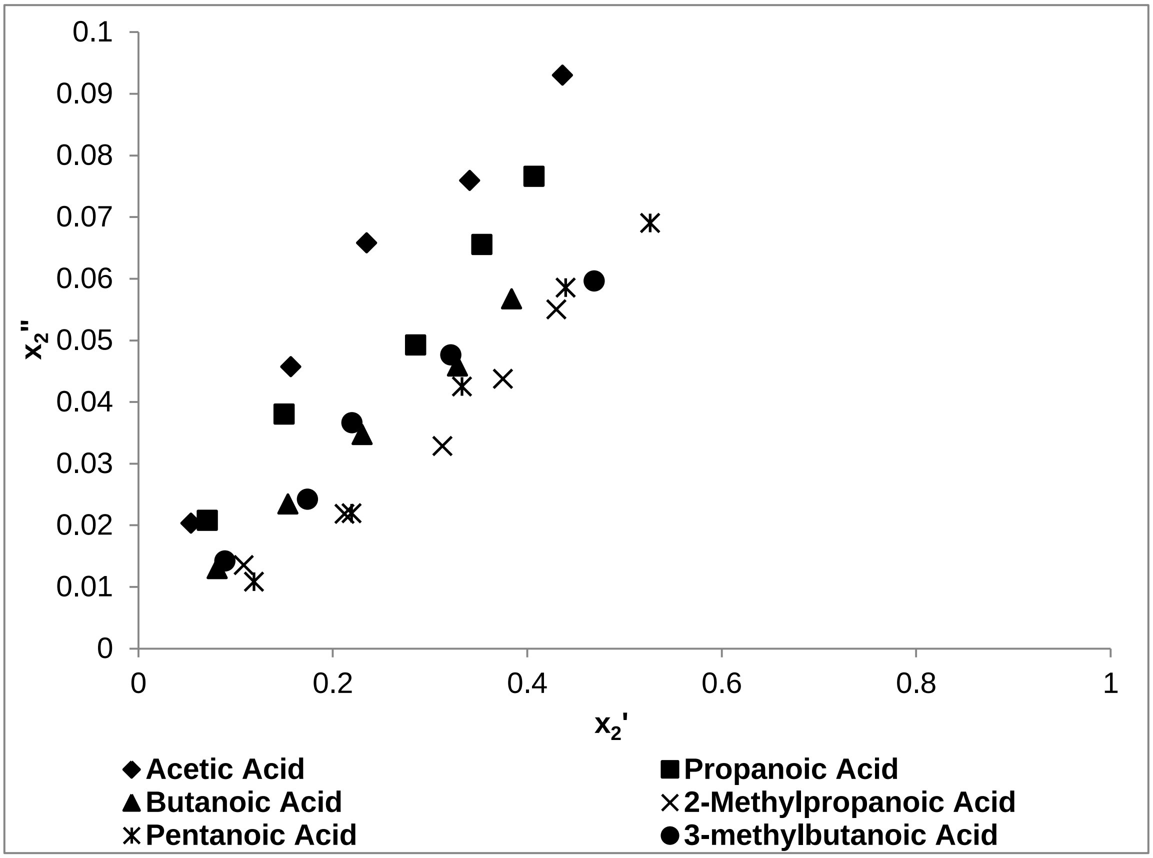


Figure 5.28 A plot of x_2'' against x_2' showing the relative solubilities of the carboxylic acid in the sulfolane-rich and cyclohexane-rich layers

5.3 LIQUID–LIQUID EQUILIBRIA FOR MIXTURES OF SULFOLANE + CARBOXYLIC ACID + DODECANE AT T = 303.15 K

Table 5.15 Physical Properties of the Pure Components at T = 303.15 K, Molar Volumes, V_{mi}, Refractives Index, n_D, Volume and Surface Parameters, R and Q.

Component	V_{mi}/cm^3.mol^{-1}	n_D	R	Q
Acetic Acid	57.73	1.3716	2.022[a]	2.072[a]
Propanoic Acid	75.34	1.3829	2.877[a]	2.612[a]
Butanoic Acid	92.93	1.3947	3.551[a]	3.152[a]
2-Methylpropanoic Acid	93.46	1.3913	3.550[a]	3.148[a]
Pentanoic Acid	109.78	1.4047	4.226[a]	3.692[a]
3-Methylbutanoic Acid	111.34	1.3997	4.225[a]	3.688[a]
Dodecane	228.60	1.4187	7.096[c]	8.546[c]
Sulfolane	95.30	1.4815	4.036[b]	3.200[b]

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

[b] Mohsen- Nia *et al.*(2005)

[c] Mohsen- Nia *et al.*(2006)

Table 5.16 Composition of points on the binodal curve at T = 303.15 K for the systems: [Sulfolane (1) + Carboxylic Acid (2) + Dodecane (3)], equilibrium Mole Fraction, x_1, x_2

x_1	x_2	x_1	x_2
	Acetic Acid		
0.0027	0.0000	0.1157	0.7818
0.0215	0.1050	0.1803	0.7583
0.0272	0.2382	0.2851	0.6828
0.0327	0.3143	0.4591	0.5119
0.0397	0.4750	0.5680	0.3932
0.0436	0.5635	0.6594	0.3016
0.0498	0.6717	0.7722	0.1925
0.0546	0.7406	0.8651	0.1081
0.0634	0.7689	0.9301	0.0510
0.0863	0.7806	0.9950	0.0000
	Propanoic Acid		
0.0027	0.0000	0.2566	0.6248
0.0110	0.1591	0.3271	0.5624
0.0183	0.2450	0.4972	0.4160
0.0290	0.3650	0.5995	0.3267
0.0308	0.4401	0.6981	0.2267
0.0319	0.5052	0.8059	0.1325
0.0434	0.5662	0.8949	0.0660
0.0486	0.6244	0.9294	0.0384
0.1209	0.6470	0.9950	0.0000
	Butanoic Acid		
0.0027	0.0000	0.2347	0.6299
0.0199	0.1010	0.3231	0.5829
0.0351	0.2750	0.4980	0.4186
0.0419	0.3901	0.5733	0.3513
0.0451	0.4500	0.6960	0.2394
0.0532	0.5178	0.8051	0.1492
0.0595	0.5496	0.8692	0.0897
0.0646	0.5993	0.9315	0.0536
0.1550	0.6598	0.9950	0.0000

Table 5.16 Continued

x_1	x_2	x_1	x_2
	2-Methylpropanoic Acid		
0.0027	0.0000	0.1894	0.6267
0.0222	0.1450	0.2673	0.5796
0.0249	0.2850	0.3578	0.6182
0.0263	0.3403	0.5476	0.4212
0.0298	0.3955	0.7035	0.2639
0.0360	0.4700	0.7511	0.2176
0.0390	0.5149	0.8590	0.1104
0.0404	0.5963	0.9437	0.0560
0.0497	0.6358	0.9698	0.0300
0.0943	0.6706	0.9950	0.0000
	Pentanoic Acid		
0.0027	0.0000	0.3895	0.5146
0.0150	0.1267	0.4526	0.4618
0.0186	0.2345	0.6378	0.3026
0.0200	0.3060	0.7228	0.2199
0.0324	0.3968	0.8295	0.1186
0.0387	0.4751	0.8928	0.0684
0.0643	0.5791	0.9372	0.0326
0.1710	0.6431	0.9950	0.0000
0.2686	0.6180		
	3-Methylbutanoic Acid		
0.0027	0.0000	0.2724	0.6036
0.0098	0.0500	0.3879	0.5341
0.0135	0.0721	0.5927	0.3649
0.0216	0.1345	0.6900	0.2714
0.0341	0.2476	0.7812	0.1801
0.0381	0.3796	0.8845	0.0909
0.0538	0.4845	0.9281	0.0464
0.0634	0.5623	0.9578	0.0262
0.1566	0.6434	0.9950	0.0000

Table 5.17 Mole Fraction and Refractive Indices: [Sulfolane (1) + Carboxylic Acid (2) + Dodecane (3)] at T = 303.15 K

x_1	n_D	x_1	n_D
	Acetic Acid		
0.0000	1.4187	0.4591	1.4308
0.0546	1.4188	0.5680	1.4350
0.0634	1.4190	0.6594	1.4407
0.0863	1.4195	0.7722	1.4515
0.1157	1.4199	0.8615	1.4610
0.1803	1.4238	0.9301	1.4726
0.2851	1.4287	1.0000	1.4815
	Propanoic Acid		
0.0000	1.4187	0.4972	1.4654
0.0319	1.4193	0.5995	1.4736
0.0434	1.4198	0.6981	1.4784
0.0486	1.4201	0.8059	1.4801
0.1209	1.4302	0.8949	1.4805
0.2566	1.4309	0.9294	1.4810
0.3271	1.4565	1.0000	1.4815
	Butanoic Acid		
0.0000	1.4187	0.4980	1.4645
0.0532	1.4190	0.5733	1.4701
0.0595	1.4192	0.6960	1.4789
0.0646	1.4194	0.8051	1.4799
0.1550	1.4204	0.8692	1.4801
0.2347	1.4451	0.9315	1.4810
0.3231	1.4590	1.0000	1.4815

Table 5.17 Continued

x_1	n_D	x_1	n_D
	2-Methylpropanoic Acid		
0.0000	1.4187	0.5476	1.4530
0.0404	1.4193	0.7035	1.4619
0.0497	1.4194	0.7511	1.4709
0.0943	1.4195	0.8590	1.4759
0.1894	1.4198	0.9437	1.4808
0.2673	1.4218	1.0000	1.4815
0.3578	1.4483		
	Pentanoic Acid		
0.0000	1.4187	0.6378	1.4685
0.0387	1.4194	0.7228	1.4727
0.0643	1.4199	0.8295	1.4773
0.1710	1.4201	0.8928	1.4778
0.3686	1.4202	0.9372	1.4799
0.3895	1.4547	1.0000	1.4815
0.5264	1.4638		
	3-Methylbutanoic Acid		
0.0000	1.4187	0.6900	1.4496
0.0538	1.4189	0.7812	1.4635
0.0634	1.4194	0.8845	1.4689
0.1566	1.4195	0.9281	1.4735
0.2724	1.4197	0.9578	1.4784
0.3879	1.4199	0.9735	14804
0.5927	1.4202	1.0000	1.4815

Table 5.18 Compositions of the conjugate solutions, x_1', x_2' and x_1'', x_2'' at T = 303.15 K for the systems: [Sulfolane (1) + Carboxylic Acid (2) + Dodecane (3)], Refractive Index, n_D

Dodecane Rich			Sulfolane Rich		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) + Acetic Acid (2) + Dodecane (3)					
0.0206	0.1550	1.4308	0.9708	0.0182	1.4726
0.0361	0.3005	1.4302	0.9659	0.0294	1.4610
0.0403	0.3950	1.4287	0.9436	0.0383	1.4515
0.0441	0.5150	1.4238	0.9185	0.0565	1.4407
0.0480	0.6630	1.4190	0.9093	0.0688	1.4305
Sulfolane (1) + Propanoic Acid (2) + Dodecane (3)					
0.0107	0.2075	1.4309	0.9504	0.0285	1.4784
0.0170	0.3163	1.4302	0.9161	0.0407	1.4610
0.0211	0.4075	1.4201	0.9043	0.0522	1.4381
0.0370	0.5316	1.4198	0.8933	0.0609	1.4361
0.0685	0.6362	1.4193	0.8723	0.0799	1.4309
Sulfolane (1) + Butanoic Acid (2) + Dodecane (3)					
0.0211	0.0917	1.4204	0.9758	0.0147	1.4801
0.0326	0.1730	1.4198	0.9577	0.0237	1.4701
0.0417	0.3110	1.4194	0.9281	0.0452	1.4645
0.0493	0.4598	1.4192	0.9195	0.0566	1.4590
0.0577	0.5621	1.4190	0.8926	0.0769	1.4451
Sulfolane (1) + 2-Methylpropanoic Acid (2) + Dodecane (3)					
0.0110	0.0927	1.4808	0.9689	0.0251	1.4218
0.0212	0.1877	1.4709	0.9568	0.0348	1.4198
0.0291	0.2902	1.4619	0.9368	0.0548	1.4195
0.0305	0.5101	1.4530	0.9107	0.0769	1.4194
0.0318	0.6655	1.4483	0.8901	0.0920	1.4193

Table 5.18 Continued

Dodecane Rich			Sulfolane Rich		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) + Pentanoic Acid (2) + Dodecane (3)					
0.0079	0.0705	1.4202	0.9693	0.0159	1.4778
0.0159	0.1865	1.4201	0.9543	0.0290	1.4727
0.0192	0.2421	1.4199	0.9369	0.0402	1.4685
0.0211	0.3285	1.4197	0.9070	0.0569	1.4638
0.0291	0.4350	1.4194	0.8904	0.0681	1.4547
Sulfolane (1) + 3-Methylbutanoic Acid (2) + Dodecane (3)					
0.0108	0.0750	1.4199	0.9790	0.0120	1.4784
0.0270	0.1769	1.4197	0.9578	0.0212	1.4735
0.0341	0.2995	1.4195	0.9466	0.0340	1.4689
0.0403	0.3995	1.4194	0.9255	0.0550	1.4635
0.0514	0.4964	1.4189	0.9044	0.0752	1.4196

Table 5.19 Coefficients A_i, B_i, and C_i in equation (3.5) - (3.6) respectively, for the systems: [Sulfolane (1) + Carboxylic Acid (2) + Dodecane (3)] at T = 303.15 K, standard deviation, σ, in equation 3, in equation (3.10).

Hlavatý	**Beta**	**Log γ**
Sulfolane (1) + Acetic Acid (2) + Dodecane (3)		
A_1 = 1.948	B_1 = 5.691	C_1 = 4.976
A_2 = 1.891	B_2 = 1.479	C_2 = 1.432
A_3 = 8.300	B_3 = 1.498	C_3 = 2.029
σ = 0.028	σ = 0.029	σ = 0.03
Sulfolane (1) + Propanoic Acid (2) + Dodecane (3)		
A_1 = 0.977	B_1 = 4.597	C_1 = 4.035
A_2 =1.970	B_2 = 1.560	C_2 = 1.513
A_3 = 6.090	B_3 = 1.344	C_3 = 1.917
σ = 0.019	σ = 0.017	σ = 0.017
Sulfolane (1) + Butanoic Acid (2) + Dodecane (3)		
A_1 =1.13	B_1 = 3.647	C_1 = 3.224
A_2 = 1.448	B_2 = 1.353	C_2 = 1.310
A_3 = 6.073	B_3 = 1.277	C_3 = 1.917
σ = 0.020	σ = 0.027	σ = 0.017

Table 5.19 Continued

Hlavatý	Beta	Log γ
Sulfolane (1) + 2- Methylpropanoic Acid (2) + Dodecane (3)		
A_1 = 1.924	B_1 = 4.022	C_1 = 3.695
A_2 = 1.865	B_2 = 1.240	C_2 = 1.214
A_3 = 8.296	B_3 = 1.301	C_3 = 1.772
σ = 0.025	σ = 0.047	σ = 0.045
Sulfolane (1) + Pentanoic Acid (2) + Dodecane (3)		
A_1 = 0.94	B_1 = 4.73	C_1 = 4.144
A_2 = 1.367	B_2 = 1.553	C_2 = 1.506
A_3 = 5.684	B_3 = 1.376	C_3 = 1.941
σ = 0.012	σ = 0.01	σ = 0.013
Sulfolane (1) + 3-Methylpropanoic Acid (2) + Dodecane (3)		
A_1 = 0.891	B_1 = 3.673	C_1 = 3.137
A_2 = 0.994	B_2 = 1.340	C_2 = 1.288
A_3 = 5.094	B_3 = 1.269	C_3 = 1.713
σ = 0.011	σ = 0.014	σ = 0.018

Table 5.20 Values of the Parameters for NRTL and UNIQUAC Equations, determined from Ternary Liquid- Liquid Equilibria for the systems Sulfolane (1) + Carboxylic Acid (2) + Dodecane (3) as well as the calculated Root Mean Square Deviation, rmsd.

	Parameters (J.mol^{-1})			
	NRTL[a]		UNIQUAC	
Component				
i-j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ji}
	Sulfolane (1) + Acetic Acid (2) + Dodecane (3)			
	(0.108)		(0.270)	
1-2-2-1	21284.30	24756.72	11220.35	7714.50
1-3-3-1	18024.65	18131.41	-14275.25	-1282.34
2-3-3-2	-3469.16	1616.26	-3861.83	-6058.20
	Sulfolane (1) + Propanoic Acid (2) + Dodecane (3)			
	(0.093)		(0.213)	
1-2-2-1	19835.49	2999.97	-0.08	-0.61
1-3-3-1	19506.03	2060.13	0.12	0.89
2-3-3-2	2097.98	2980.79	0.55	-0.98
	Sulfolane (1) + Butanoic Acid (2) + Heptane (3)			
	(0.428)		(0.112)	
1-2-2-1	20343.56	30017.38	0.72	0.34
1-3-3-1	17778.78	18306.30	-0.91	0.04
2-3-3-2	-22283.03	1131.83	-0.45	0.60

Table 5.20 Continued

	Parameters (J.mol^{-1})			
	NRTL[a]		**UNIQUAC**	
Component				
i-j	$g_{ij}-g_{jj}$	$g_{ji}-g_{ii}$	Δu_i	Δu_{ji}
Sulfolane (1) + 2-Methylpropanoic Acid (2) + Dodecane (3)				
	(0.003)		(0.425)	
1-2-2-1	21226.56	73433.39	5.88	2.88
1-3-3-1	78429.22	64070.80	-4.74	0.67
2-3-3-2	20961.82	6165.73	0.031	-11.11
Sulfolane (1) + Pentanoic Acid (2) + Dodecane (3)				
	(0.005)		(0.422)	
1-2-2-1	11557.05	80172.07	10.40	-6.40
1-3-3-1	54352.89	81259.05	-0.18	0.38
2-3-3-2	-21030.83	30670.34	1.08	-0.31
Sulfolane (1) + 3-Methylbutanoic Acid (2) + Heptane (3)				
	(0.003)		(0.425)	
1-2-2-1	26951.40	35997.76	0.005	0.001
1-3-3-1	6043.793	7326.281	-0.001	-0.001
2-3-3-2	3332.301	-3376.383	-18.85	18.85

[a] Calculated with α_{ij} =0.2

5.21 Representative selectivity values of sulfolane for the separation of carboxylic acids from dodecane using equation (3.1)

Carboxylic Acid	**Selectivity (ω)**
Acetic Acid	6
Propanoic Acid	2
Butanoic Acid	6
2-Methylpropanoic Acid	16
Pentanoic Acid	6
3-Methylbutanoic Acid	6

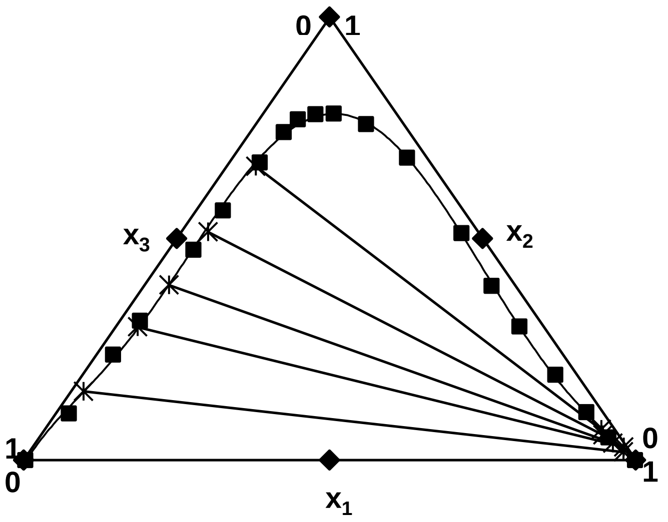


Figure 5.29 Liquid-liquid equilibrium data for the system [sulfolane (1) + acetic acid (2) + dodecane (3)] at T= 303.15 K

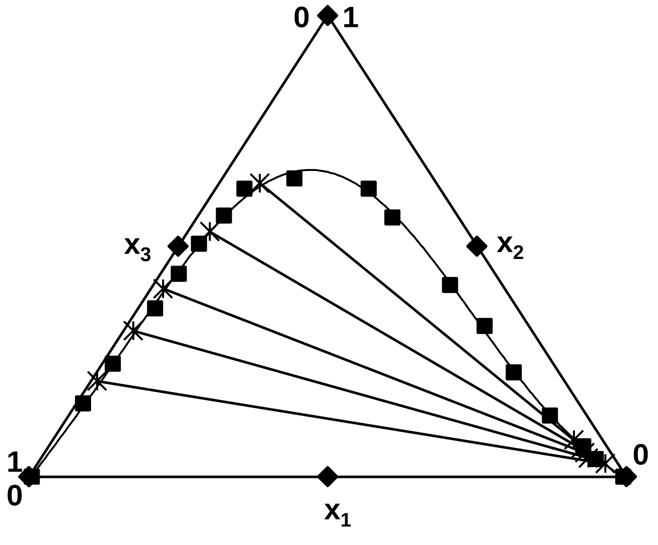


Figure 5.30 Liquid-liquid equilibrium data for the system [sulfolane (1) + propanoic acid (2) + dodecane (3)] at T = 303.15 K

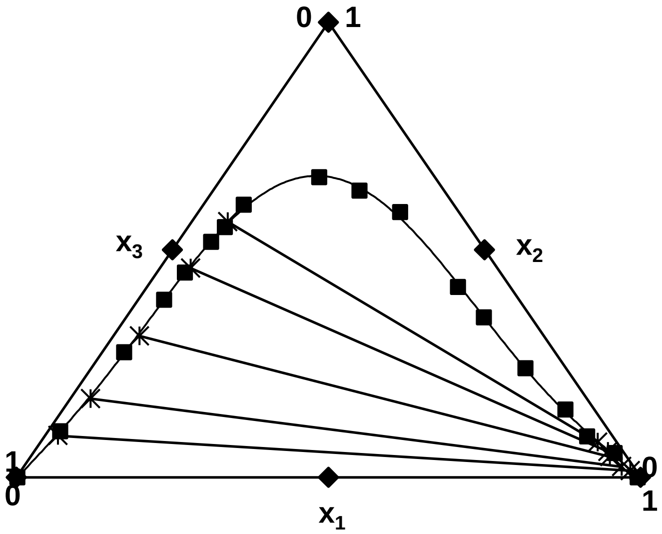


Figure 5.31 Liquid-liquid equilibrium data for the system [sulfolane (1) + butanoic acid (2) + dodecane (3)] at T= 303.15 K

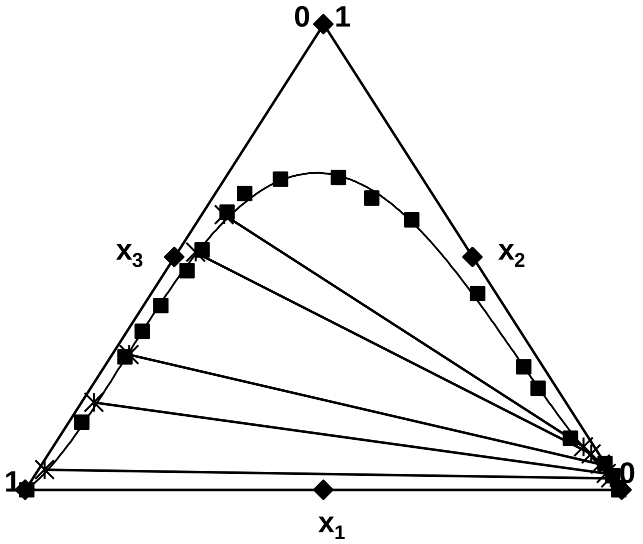


Figure 5.32 Liquid-liquid equilibrium data for the system [sulfolane (1) + 2-methylpropanoic acid (2) + dodecane (3)] at T= 303.15 K

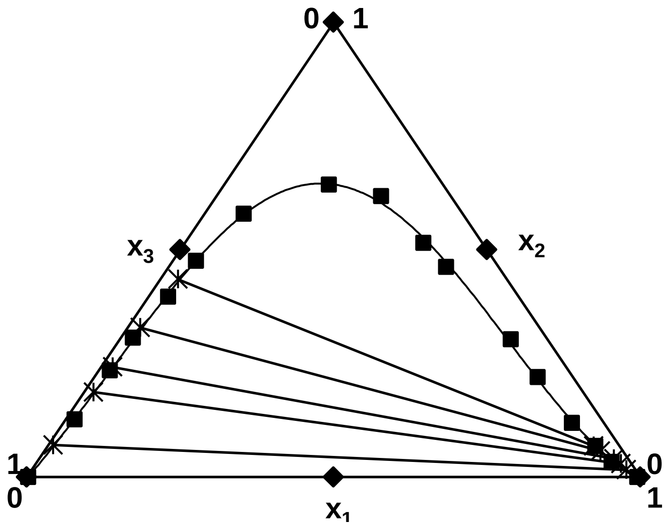


Figure 5.33 Liquid-liquid equilibrium data for the system [sulfolane (1) + pentanoic acid (2) + dodecane (3)] at T= 303.15 K

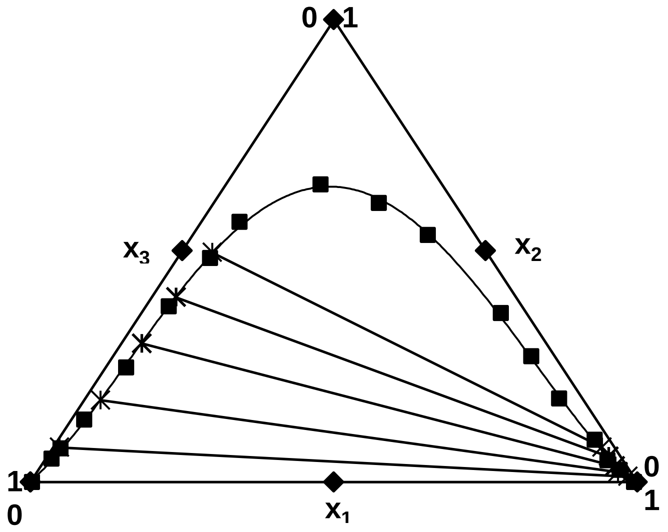
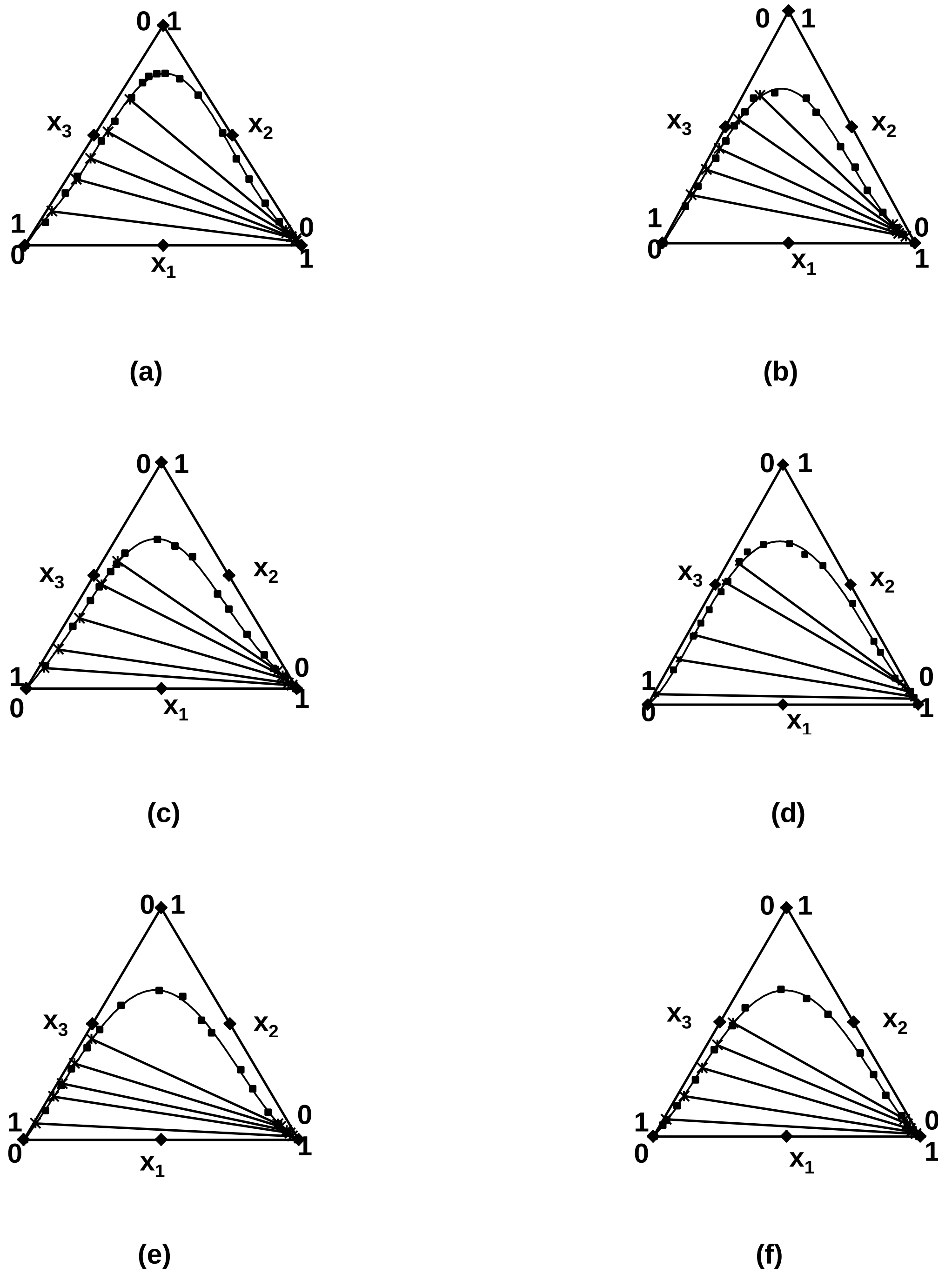


Figure 5.34 Liquid-liquid equilibrium data for the system [sulfolane (1) + 3-methylbutanoic acid (2) + dodecane (3)] at T= 303.15 K



(a)

(b)

(c)

(d)

(e)

(f)

Figure 5.35 Summary of Liquid-liquid equilibrium for data for the following systems at T = 303.15 K: [(a) sulfolane(1) + acetic acid (2) + dodecane (3), (b) sulfolane (1) + propanoic acid (2) + dodecane (3), (c) sulfolane(1) + butanoic acid (2) + dodecane (3), (d) sulfolane (1) + 2-methylpropanoic acid (2) + dodecane (3), (e) sulfolane (1) + pentanoic acid (2) + dodecane (3), (f) sulfolane (1) +3-methylbutanoic acid (2) + dodecane (3)] at T = 303.15 K [Key: experimental points (▪), experimental tie lines(x)]

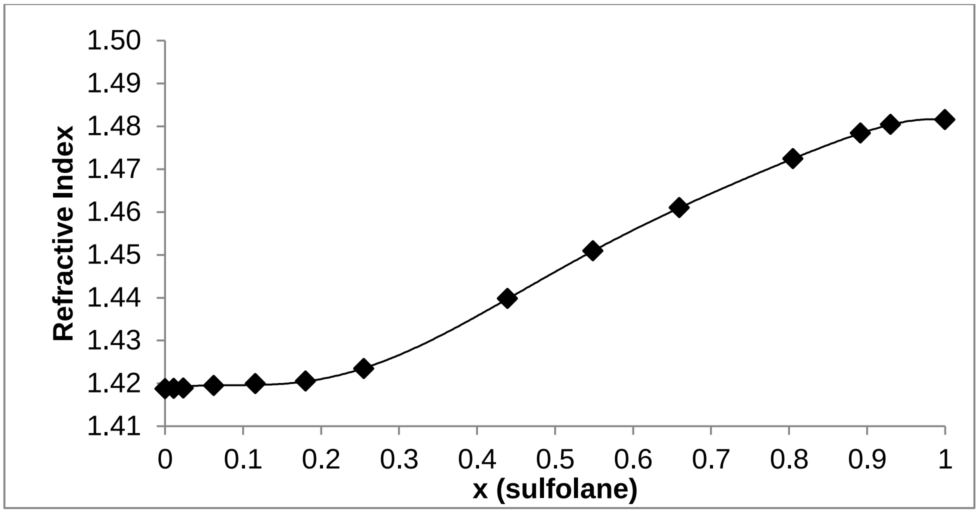


Figure 5.36 Calibration curve for the system: [sulfolane (1) + acetic acid (2) + dodecane (3)] at T = 303.15 K

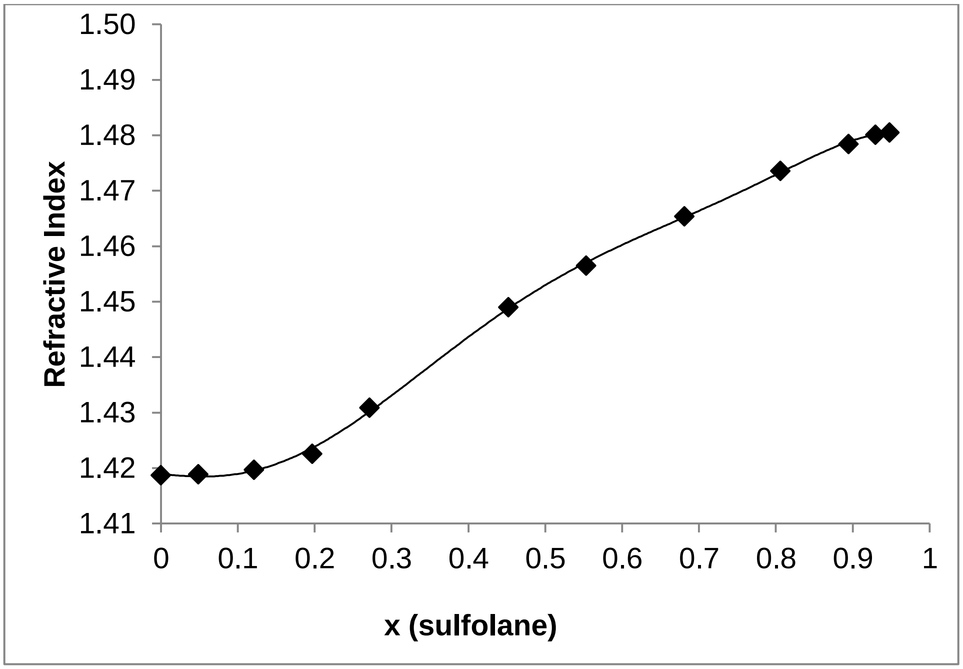


Figure 5.37 Calibration curve for the system: [sulfolane (1) + propanoic acid (2) + dodecane (3)] at T = 303.15 K

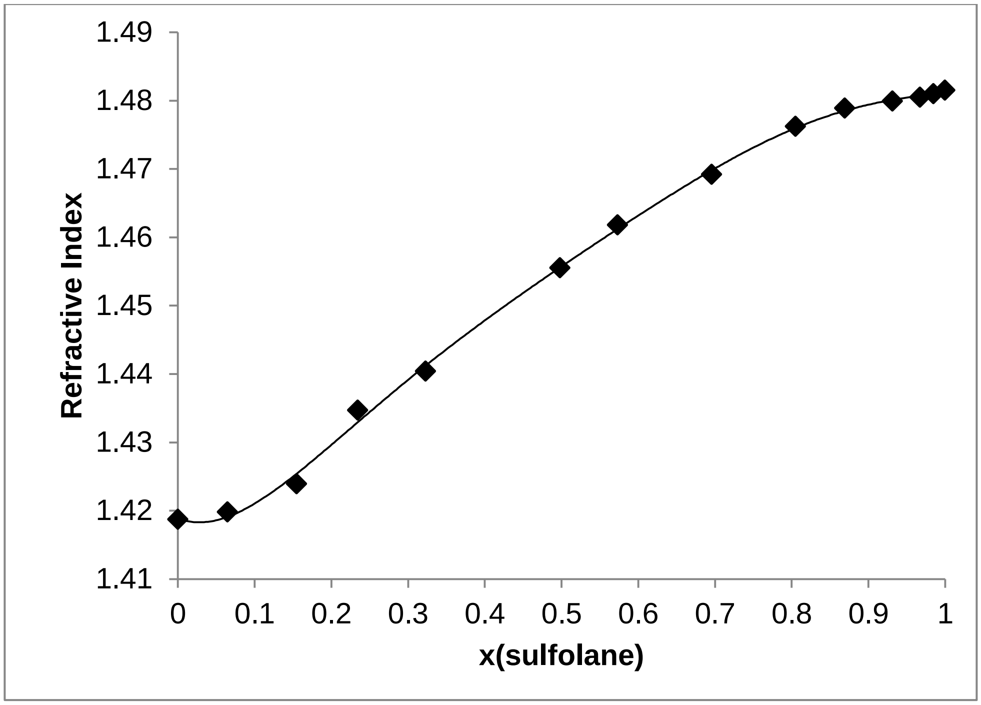


Figure 5.38 Calibration curve for the system: [sulfolane (1) + butanoic acid (2) + dodecane (3)] at T = 303.15 K

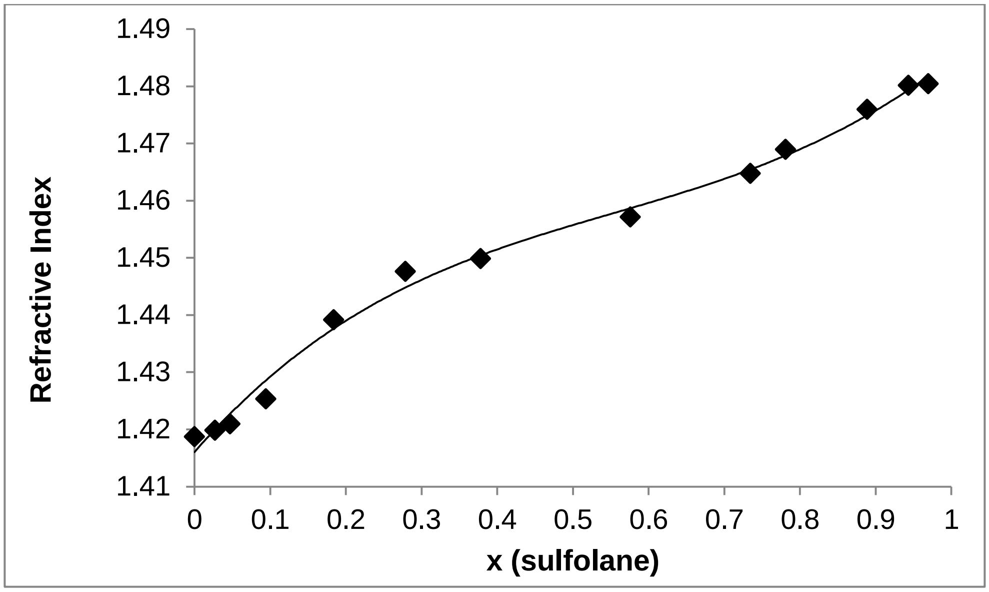


Figure 5.38 Calibration curve for the system:
[sulfolane (1) + 2-methylpropanoic acid (2) + dodecane (3)] at T = 303.15 K

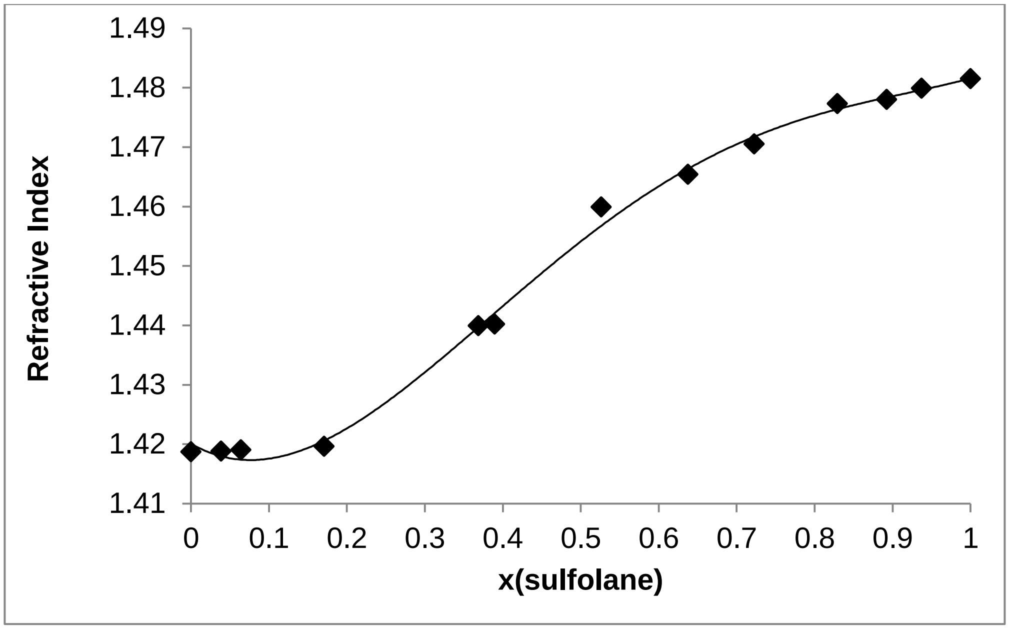


Figure 5.40 Calibration curve for the system: [sulfolane (1) + pentanoic acid (2) + dodecane (3)] at T = 303.15 K

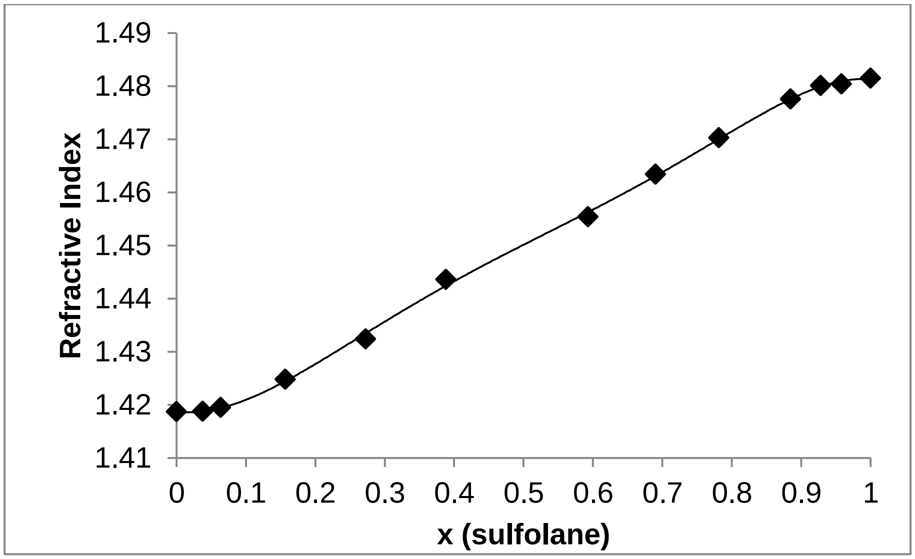


Figure 5.41 Calibration curve for system: [sulfolane (1) + 3-methylbutanoic acid (2) + dodecane (3)] at T = 303. 15 K

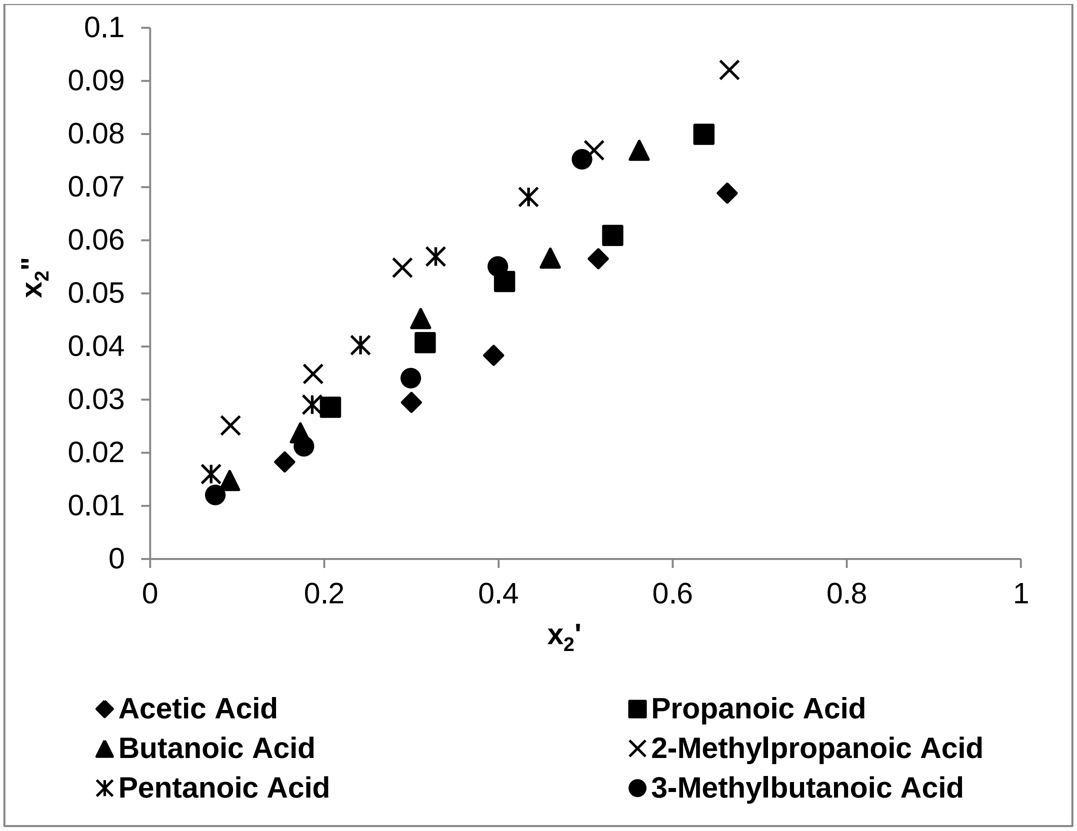


Figure 5.42 A plot of x_2'' against x_2' showing the relative solubilities of the carboxylic acid in the sulfolane-rich and dodecane-rich layers

5.4 LIQUID–LIQUID EQUILIBRIA FOR MIXTURES OF SULFOLANE + ALCOHOL + HEPTANE AT T = 303.15 K

Table 5.22 Physical Properties of the Pure Components at 303.15 K, Molar Volumes, V_{mi}, Refractives Indeces, n_D, Volume and Surface Parameters, R and Q.

Component	V_{mi}/cm^3.mol^{-1}	n_D	R	Q
Methanol	40.13	1.3261	1.863[a]	1.953[a]
Ethanol	58.96	1.3587	2.495[a]	2.661[a]
1-Propanol	75.49	1.3822	3.128[a]	3.369[a]
2-Propanol	77.34	1.3744	2.961[a]	3.343[a]
1-Butanol	92.35	1.3966	3.760[a]	4.077[a]
2-Butanol	92.80	1.3936	3.593[a]	4.051[a]
2-Methyl-1-propanol	93.21	1.3929	3.760[a]	4.092[a]
2-Methyl-2-propanol	95.29	1.3835	3.220[a]	4.017[a]
Heptane	147.40	1.3844	5.174[b]	4.396[b]
Sulfolane	95.30	1.4815	4.036[b]	3.200[b]

[a] Redhi (1996)

[b] Mohsen- Nia *et al*. (2005)

Table 5.23 Composition of points on the binodal curve at T = 303.15 K for the systems: [Sulfolane (1) + Alcohol (2) + Heptane (3)], equilibrium Mole Fraction, x_1, x_2

x_1	x_2	x_1	x_2
	Methanol		
0.0060	0.0000	0.0789	0.7276
0.0080	0.0690	0.1159	0.7536
0.0098	0.1577	0.2274	0.7258
0.0105	0.2432	0.3189	0.6474
0.0110	0.3597	0.4499	0.5149
0.0115	0.4745	0.6569	0.3093
0.0117	0.5684	0.7437	0.2237
0.0238	0.6484	0.8553	0.1348
0.0472	0.6964	0.9850	0.0000
	Ethanol		
0.0060	0.0000	0.3205	0.4991
0.0296	0.0975	0.4970	0.3681
0.0470	0.165	0.5598	0.3188
0.0764	0.2872	0.6512	0.2470
0.0821	0.3941	0.8244	0.1086
0.1501	0.5142	0.9101	0.0532
0.2508	0.5301	0.9850	0.0000
	1-Propanol		
0.0060	0.0000	0.2726	0.5340
0.0150	0.0630	0.4318	0.4238
0.0180	0.1939	0.5070	0.3651
0.0210	0.3105	0.6187	0.2591
0.0283	0.4198	0.7237	0.1865
0.0379	0.4621	0.8263	0.1099
0.0455	0.5058	08377	0.0456
0.1266	0.6133	0.9850	0.0000
0.1938	0.5964		

Table 5.23 Continued

x_1	x_2	x_1	x_2
2-Propanol			
0.0060	0.0000	0.3002	0.4909
0.0085	0.0945	0.4861	0.4528
0.0114	0.2146	0.5837	0.3644
0.0129	0.3220	0.6825	0.2749
0.0146	0.4296	0.8050	0.1472
0.0290	0.5399	0.8768	0.0965
0.1256	0.6705	0.9065	0.0644
0.2145	0.6687	0.9850	0.0000
1-Butanol			
0.0060	0.0000	0.6596	0.2767
0.0408	0.0922	0.7256	0.1830
0.0586	0.1630	0.8449	0.1091
0.0671	0.2922	0.8964	0.0764
0.0791	0.3699	0.9465	0.0432
0.1463	0.4285	0.9513	0.0322
0.2449	0.5298	0.9623	0.0219
0.3212	0.5142	0.9841	0.0130
0.5001	0.4262	0.9850	0.0000
2-Butanol			
0.0060	0.0000	0.2589	0.6970
0.0190	0.0450	0.3013	0.6584
0.0218	0.1512	0.3976	0.5658
0.0242	0.2158	0.5578	0.3983
0.0262	0.3199	0.6709	0.2794
0.0388	0.4392	0.8577	0.1136
0.0458	0.5832	0.9378	0.0432
0.0646	0.6881	0.9850	0.0000
0.1099	0.7447		

Table 5.23 Continued

x_1	x_2	x_1	x_2
2-Methyl-1-propanol			
0.0060	0.0000	0.2925	0.5350
0.0199	0.1034	0.4672	0.4281
0.0291	0.2121	0.5615	0.3533
0.0316	0.2932	0.6777	0.2642
0.0427	0.3297	0.7917	0.1649
0.0615	0.3954	0.8518	0.0852
0.0844	0.4965	0.8849	0.0323
0.1310	0.5595	0.9745	0.0176
0.2070	0.5574	0.9850	0.0000
2-Methyl-2-propanol			
0.0060	0.0000	0.3155	0.6703
0.0094	0.1727	0.4222	0.5405
0.0162	0.2799	0.5469	0.4192
0.0316	0.4822	0.6509	0.3205
0.0388	0.5691	0.7520	0.2240
0.0584	0.6790	0.8980	0.0842
0.0968	0.7186	0.9850	0.0000
0.1985	0.7128		

Table 5.24 Mole fraction and Refractive Indices: [Sulfolane (1) + Alcohol (2) + Heptane] at T = 303.15 K

x_1	n_D	x_1	n_D
	Methanol		
0.0000	1.3844	0.2274	1.4204
0.0110	1.3853	0.3129	1.4378
0.0117	1.3854	0.4499	1.4517
0.0238	1.3855	0.6569	1.4677
0.0472	1.3862	0.7437	1.4728
0.0789	1.3877	0.8553	1.4776
0.1159	1.3886	1.0000	1.4815
	Ethanol		
0.0000	1.3844	0.3205	1.4613
0.0296	1.3854	0.4970	1.4700
0.0470	1.3866	0.5598	1.4754
0.0764	1.3868	0.6512	1.4770
0.0821	1.3869	0.8244	1.4787
0.1501	1.4468	0.9101	1.4799
0.2508	1.4576	1.0000	1.4815
	1-Propanol		
0.0000	1.3844	0.5070	1.4449
0.0455	1.3854	0.6187	1.4518
0.1266	1.3860	0.7237	1.4567
0.1938	1.3895	0.8263	1.4631
0.2726	1.4039	0.8377	1.4718
0.4318	1.4349	1.0000	1.4815
	2-Propanol		
0.0000	1.3844	0.5837	1.4539
0.0290	1.3856	0.6825	1.4630
0.1256	1.3860	0.8050	1.4711
0.2145	1.3866	0.8768	1.4758
0.3002	1.3869	0.9065	1.4776
0.4861	1.4463	1.0000	1.4815

Table 5.24 Continued

x_1	n_D	x_1	n_D
	1-Butanol		
0.0000	1.3844	0.7256	1.4634
0.1463	1.3972	0.8449	1.4689
0.2449	1.3983	0.8964	1.4747
0.3212	1.3992	0.9513	1.4800
0.5001	1.3999	0.9623	1.4806
0.6096	1.4548	0.9841	1.4809
0.6596	1.4590	1.0000	1.4815
	2-Butanol		
0.0000	1.3844	0.3976	1.4522
0.0458	1.3947	05578	1.4603
0.0646	1.3967	0.6709	1.4637
0.1099	1.3970	0.8577	1.4685
0.2589	1.4318	0.9678	1.4732
0.3013	1.4461	1.0000	1.4815
	2-Methyl-1-propanol		
0.0000	1.3844	0.6777	1.4664
0.0844	1.3930	0.7917	1.4754
0.1310	1.3943	0.879	1.4785
0.2070	1.3952	0.8849	1.4799
0.2925	13962	0.9451	1.4805
0.4672	1.4590	0.9745	1.4810
0.5615	1.4638	1.0000	1.4815
	2-Methyl-2-propanol		
0.0000	1.3844	0.3155	1.4395
0.0162	1.3853	0.4222	1.4407
0.0316	1.3855	0.5469	1.4426
0.0388	1.3858	0.6509	1.4586
0.0584	1.3863	0.7520	1.4658
0.0968	1.4259	0.8980	1.4731
0.1985	1.4332	1.0000	1.4815

Table 5.25 Compositions of the conjugate solutions, x_1', x_2' and x_1'', x_2'' at T = 303.15 K for the systems: [Sulfolane (1) + Alcohol (2) + Heptane (3)], Refractive Index, n_D

Heptane Rich			**Sulfolane Rich**		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) + Methanol (2) + Heptane (3)					
0.0203	0.0950	1.3886	0.9644	0.0209	1.4776
0.0497	0.3082	1.3877	0.9470	0.0322	1.4728
0.0525	0.4255	1.3855	0.9354	0.0436	1.4517
0.0594	0.5468	1.3854	0.9231	0.0549	1.4378
0.0650	0.6322	1.3853	0.8829	0.0894	1.4204
Sulfolane (1) + Ethanol (2) + Heptane (3)					
0.0313	0.1024	1.3869	0.9637	0.0192	1.4770
0.0515	0.1929	1.3868	0.9472	0.0280	1.4754
0.0716	0.3147	1.3866	0.9325	0.0364	1.4700
0.0924	0.4048	1.3859	0.9104	0.0505	1.4576
0.1260	0.4852	1.3854	0.8903	0.0654	1.4468
Sulfolane (1) + 1-Propanol (2) + Heptane (3)					
0.0149	0.1283	1.4039	0.9467	0.0229	1.4718
0.0170	0.2410	1.3895	0.9368	0.0354	1.4631
0.0218	0.3524	1.3892	0.9156	0.0456	1.4567
0.0304	0.4392	1.3860	0.8959	0.0568	1.4518
0.0523	0.5150	1.3855	0.8836	0.0737	1.4449
Sulfolane (1) + 2-Propanol (2) + Heptane (3)					
0.0128	0.0967	1.3869	0.9578	0.0240	1.4758
0.0313	0.1974	1.3866	0.9476	0.0344	1.4711
0.0415	0.2758	1.3860	0.9268	0.0460	1.4630
0.0581	0.3994	1.3858	0.9185	0.0549	1.4539
0.0710	0.4905	1.3856	0.9045	0.0654	1.4463

Table 5.25 Continued

Heptane Rich			Sulfolane Rich		
x_1'	x_2'	n_D	x_1''	x_2''	n_D
Sulfolane (1) + 1-Butanol (2) + Heptane (3)					
0.0158	0.0672	1.3999	0.9457	0.0335	1.4806
0.0121	0.1521	1.3992	0.9380	0.0433	1.4747
0.0117	0.2081	1.3989	0.9273	0.0531	1.4689
0.0103	0.3086	1.3983	0.9162	0.0628	1.4634
0.0095	0.3707	1.3972	0.8905	0.0794	1.4590
Sulfolane (1) + 2-Butanol (2) + Heptane (3)					
0.0043	0.1001	1.3970	0.9708	0.0140	1.4732
0.0064	0.1903	1.3967	0.9655	0.0209	1.4685
0.0079	0.2764	1.3959	0.9420	0.0342	1.4637
0.0090	0.3525	1.3947	0.9289	0.0476	1.4603
0.0117	0.4363	1.3843	0.9067	0.0691	1.4522
Sulfolane (1) + 2- Methyl-1-propanol (2) + Heptane (3)					
0.0072	0.0816	1.3962	0.9658	0.0215	1.4785
0.0079	0.1650	1.3952	0.9480	0.0345	1.4757
0.0089	0.2702	1.3949	0.9267	0.0459	1.4664
0.0091	0.3460	1.3943	0.9195	0.0565	1.4638
0.0107	0.4299	1.3930	0.9088	0.0688	1.4590
Sulfolane (1) + 2- Methyl-2-propanol (2) + Heptane (3)					
0.0114	0.0626	1.3863	0.9725	0.0126	1.4731
0.0212	0.1582	1.3858	0.9648	0.0235	1.4658
0.0283	0.2508	1.3855	0.9544	0.0341	1.4586
0.0315	0.3880	1.3853	0.9431	0.0453	1.4510
0.0592	0.4530	1.3851	0.9241	0.0657	1.4426

Table 5.26 Coefficients A_i, B_i, and C_i in equation (3.5) – (3.6) respectively, for the systems: Sulfolane (1) + Alcohol (2) + Heptane (3) at 303.15 K, standard deviation, σ, in equation (3.10)

Hlavatý	Beta	Log γ
Sulfolane (1) + Methanol (2) + Heptane (3)		
$A_1 = 1.842$	$B_1 = 5.516$	$C_1 = 4.641$
$A_2 = 1.459$	$B_2 = 1.455$	$C_2 = 1.381$
$A_3 = 7.425$	$B_3 = 1.529$	$C_3 = 2.017$
$\sigma = 0.024$	$\sigma = 0.023$	$\sigma = 0.027$
Sulfolane (1) + Ethanol (2) + Heptane (3)		
$A_1 = 0.847$	$B_1 = 3.057$	$C_1 = 2.711$
$A_2 = 1.162$	$B_2 = 1.371$	$C_2 = 1.327$
$A_3 = 4.814$	$B_3 = 1.290$	$C_3 = 1783$
$\sigma = 0.008$	$\sigma = 0.020$	$\sigma = 0.019$
Sulfolane (1) + 1-Propanol (2) + Heptane (3)		
$A_1 = 0.614$	$B_1 = 3.644$	$C_1 = 3.096$
$A_2 = 1.188$	$B_2 = 1.409$	$C_2 = 1.348$
$A_3 = 4.844$	$B_3 = 1.249$	$C_3 = 1.723$
$\sigma = 0.013$	$\sigma = 0.012$	$\sigma = 0.011$
Sulfolane (1) + 2- Propanol (2) + Heptane (3)		
$A_1 = 1.217$	$B_1 = 3.789$	$C_1 = 3.333$
$A_2 = 1.120$	$B_2 = 1.320$	$C_2 = 1.274$
$A_3 = 5.782$	$B_3 = 1.314$	$C_3 = 1.778$
$\sigma = 0.021$	$\sigma = 0.024$	$\sigma = 0.026$

Table 5.26 Continued

Hlavatý	Beta	Log γ
Sulfolane (1) +1-Butanol (2) + Heptane (3)		
A_1 = 1.314	B_1 = 3.895	C_1 = 3.425
A_2 = 1.005	B_2 = 1.284	C_2 = 1.320
A_3 = 5.810	B_3 = 1.330	C_3 = 1.782
σ = 0.023	σ = 0.025	σ = 0.021
Sulfolane (1) +2-Butanol (2) + Heptane (3)		
A_1 = 1.426	B_1 = 4.131	C_1 = 3.608
A_2 = 1.376	B_2 = 1.284	C_2 = 1.239
A_3 = 6.705	B_3 = 1.344	C_3 = 1.783
σ = 0.025	σ = 0.030	σ = 0.031
Sulfolane (1) + 2-Methyl-1-propanol (2) +Heptane (3)		
A_1 = 0.558	B_1 = 1.866	C_1 = 1.751
A_2 = 0.761	B_2 = 0.956	C_2 = 0.939
A_3 = 4.03	B_3 = 0.981	C_3 = 1.341
σ = 0.011	σ = 0.033	σ = 0.030
Sulfolane (1) + 2-Methyl-2-propanol (2) + Heptane (3)		
A_1 = 1.498	B_1 = 4.364	C_1 = 3.971
A_2 = 1.311	B_2 = 1.295	C_2 = 1.262
A_3 = 6.744	B_3 = 1.373	C_3 = 1.860
σ = 0.019	σ = 0.023	σ = 0.022

Table 5.27 Values of the Parameters for NRTL and UNIQUAC Equations, determined from Ternary Liquid- Liquid Equilibria for the systems Sulfolane (1) + Carboxylic Acid (2) + Dodecane (3) as well as the calculated Root Mean Square Deviation, rmsd.

	Parameters (J.mol^{-1})			
	NRTL^{a}		**UNIQUAC**	
Component *i-j*	g_{ij} -g_{jj}	g_{ji} -g_{ii}	Δu_{ij}	Δu_{ji}
	Sulfolane (1) + Methanol (2) + Heptane (3)			
	(0.090)		(0.342)	
1-2-2-1	20652.14	27319.74	0.04	4.37
1-3-3-1	19702.23	19774.49	2.38	2.03
2-3-3-2	-2431.28	-2551.34	-0.12	0.12
	Sulfolane (1) + Ethanol (2) + Heptane (3)			
	(0.006)		(0.329)	
1-2-2-1	51749.73	25085.29	-0.02	-1.03
1-3-3-1	55939.26	55430.92	2.97	-1.53
2-3-3-2	68370.72	-26291.18	-1.56	0.84
	Sulfolane (1) + 1-Propanol (2) + Heptane (3)			
	(0.005)		(0.312)	
1-2-2-1	26192.30	53455.03	-0.03	0.45
1-3-3-1	41979.01	92327.44	0.05	-0.05
2-3-3-2	-27249.59	44696.65	-0.30	0.12

Table 5.27 Continued

	Parameters (J.mol^{-1})			
	NRTL[a]		**UNIQUAC**	
Component **i-j**	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ji}
	Sulfolane (1) + 2-Propanol (2) + Heptane (3)			
	(0.103)		(0.319)	
1-2-2-1	11914.00	25083.08	0.65	0.77
1-3-3-1	18737.89	22867.93	0.006	-0.02
2-3-3-2	4937.57	-18661.94	-0.29	0.09
	Sulfolane (1) + 1-Butanol (2) + Heptane (3)			
	(0.004)		(0.213)	
1-2-2-1	16147.69	126181.15	-0.17	-0.50
1-3-3-1	56327.12	78031.74	0.64	0.96
2-3-3-2	37089.90	6351.67	0.11	0.64
	Sulfolane (1) + 2-Butanol (2) + Heptane (3)			
	(0.004)		(0.337)	
1-2-2-1	16593.96	35691.37	0.41	-0.31
1-3-3-1	62280.03	217070.41	0.43	0.55
2-3-3-2	42946.12	-50825.51	0.34	0.86

Table 5.27 Continued

	Parameters (J.mol^{-1})			
	NRTL[a]		UNIQUAC	
Component *i-j*	$g_{ij}-g_{jj}$	$g_{ji}-g_{ii}$	Δu_{ij}	Δu_{ji}
	Sulfolane (1) + 2-Methyl-1-propanol (2) + Heptane (3)			
	(0.003)		(0.336)	
1-2-2-1	33957.98	39328.79	0.53	-0.17
1-3-3-1	57924.81	16408.25	-0.01	-0.07
2-3-3-2	2846.29	21180.06	0.21	0.23
	Sulfolane (1) + 2-Methyl-2-propanol (2) + Heptane (3)			
	(0.002)		(0.353)	
1-2-2-1	43371.93	24834.39	0.38	0.68
1-3-3-1	71078.28	81110.37	0.61	-0.66
2-3-3-2	-5704.28	20830.61	-0.83	0.92

[a] Calculated with α_{ij} =0.2

Table 5.28 Representative selectivity values of sulfolane for the separation of alcohol from heptane using equation (3.1)

Alcohol	**Selectivity (ω)**
Methanol	5
Ethanol	8
1-Propanol	3
2-Propanol	6
1-Butanol	11
2-Butanol	5
2-Methyl-1-propanol	8
2-Methyl-2-propanol	9

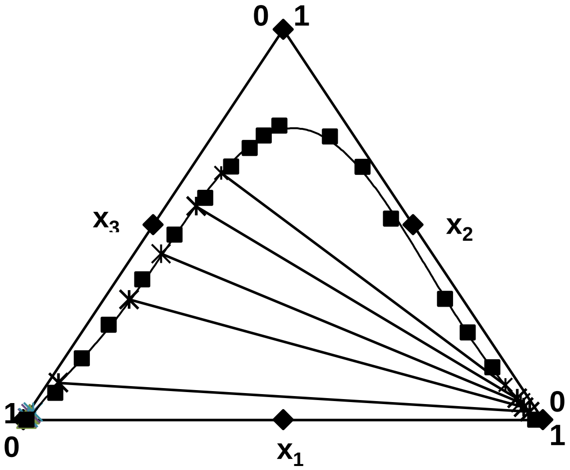


Figure 5.43 Liquid-liquid equilibrium data for the system [sulfolane (1) + methanol (2) + heptane (3)] at T = 303.15 K

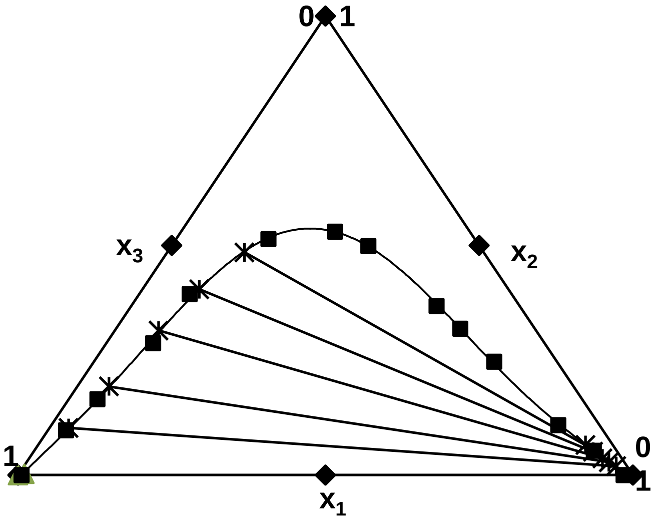


Figure 5.43 Liquid-liquid equilibrium data for the system [sulfolane (1) + ethanol (2) + heptane (3)] at T = 303.15 K

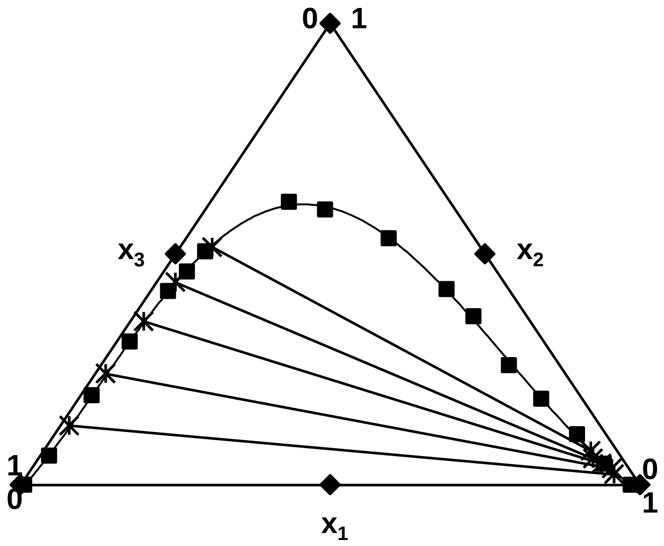


Figure 5.45 Liquid-liquid equilibrium data for the system [sulfolane (1) + 1-propanol (2) + heptane (3)] at T= 303.15 K

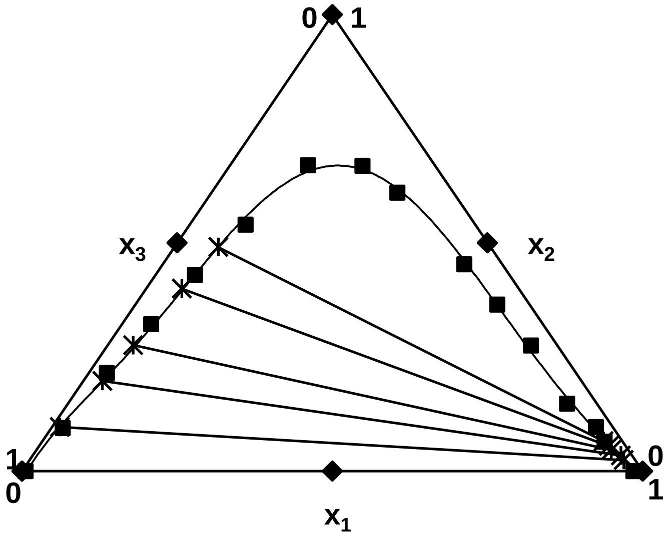


Figure 5.46 Liquid-liquid equilibrium data for the system [sulfolane (1) + 2-propanol (2) + heptane (3)] at T= 303.15 K

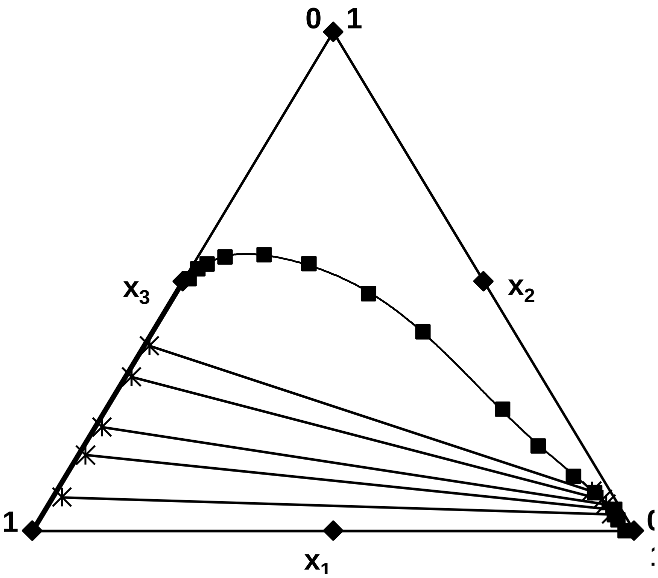


Figure 5.47 Liquid-liquid equilibrium data for the system [sulfolane (1) + 1-butanol (2) + heptane (3)] at T= 303.15 K

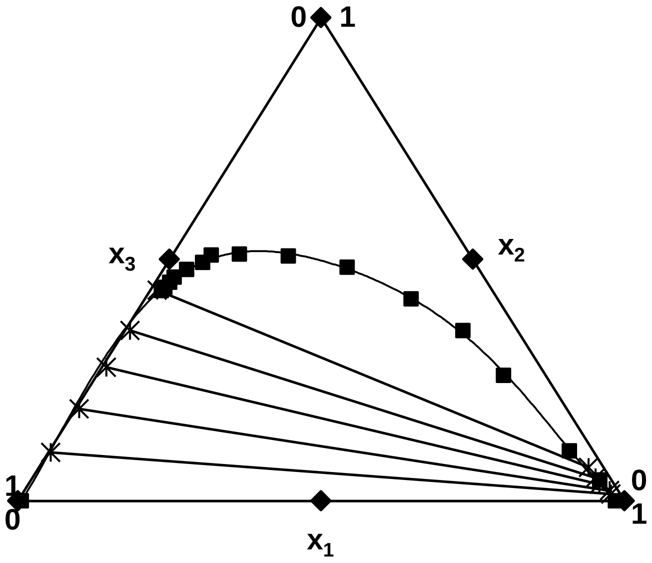


Figure 5.48 Liquid-liquid equilibrium data for the system [sulfolane (1) + 2-butanol (2) + heptane (3)] at T = 303.15 K

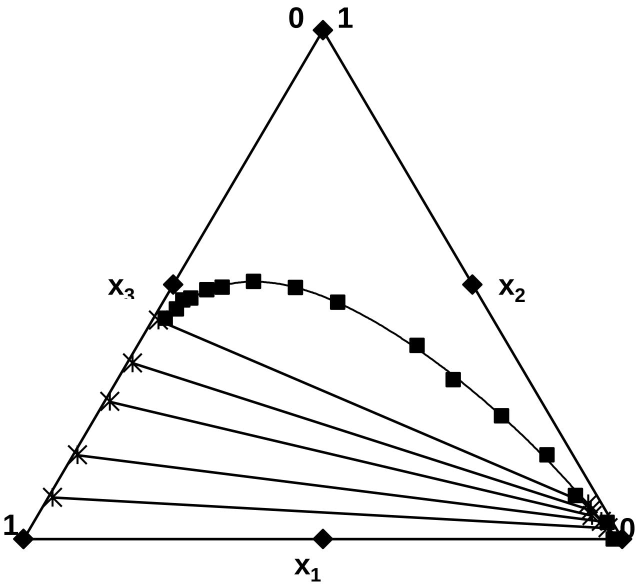


Figure 5.49 Liquid-liquid equilibrium data for the system [sulfolane (1) + 2-methyl-1-propanol (2) + heptane (3)] at T= 303.15 K

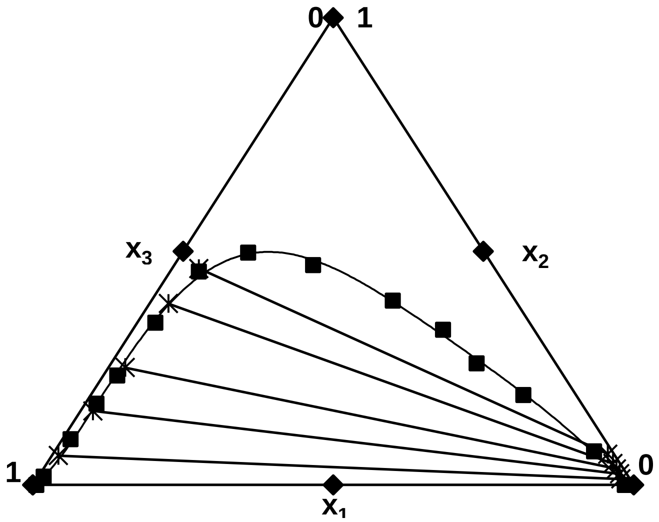
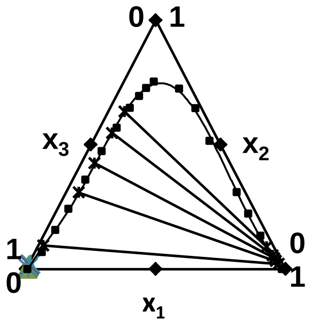
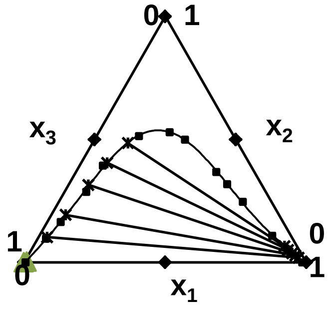


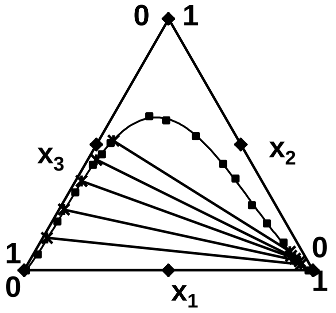
Figure 5.50 Liquid-liquid equilibrium data for the system [sulfolane (1) + 2-methyl-2-propanol (2) + heptane (3)] at T= 303.15 K


0
1
x_3
x_2
1
0
0
1
x_1

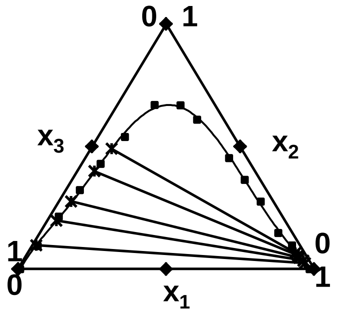
(a)


0
1
x_3
x_2
1
0
0
1
x_1

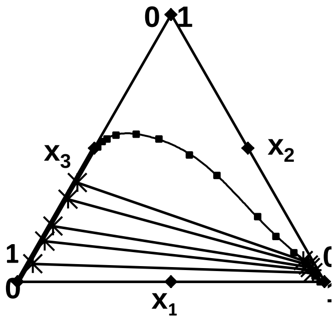
(b)


0
1
x_3
x_2
1
0
0
1
x_1

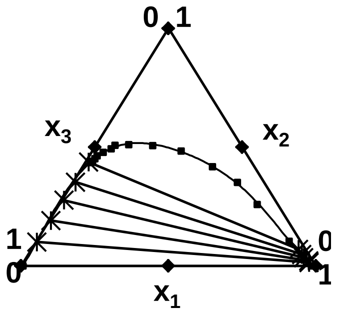
(c)


0
1
x_3
x_2
1
0
0
1
x_1

(d)


0
1
x_3
x_2
1
0
x_1

(e)


0
1
x_3
x_2
1
0
0
1
x_1

(f)

(g) (h)

Figure 5.51 Summary of Liquid-liquid equilibrium data for the following systems at 303.15 K: (a) sulfolane(1) + methanol (2) + heptane (3), (b) sulfolane + ethanol (2) + heptane (3), (c) sulfolane(1) + 1-propanol (2) + heptane (3), (d) sulfolane (1) + 2-propanol (2) + heptane (3), (e) sulfolane (1) + 1-butanol (2) + heptane (3), (f) sulfolane (1) + 2-butanol (2) + heptane (3), (g) sulfolane (1) + 2-methyl-1-propanol (2) + heptane (3) and (h) sulfolane (1) +2-methyl-2-propanol (2) + heptane (3) at T = 303.15 K. [Key: experimental points (▪), experimental tie lines (x)]

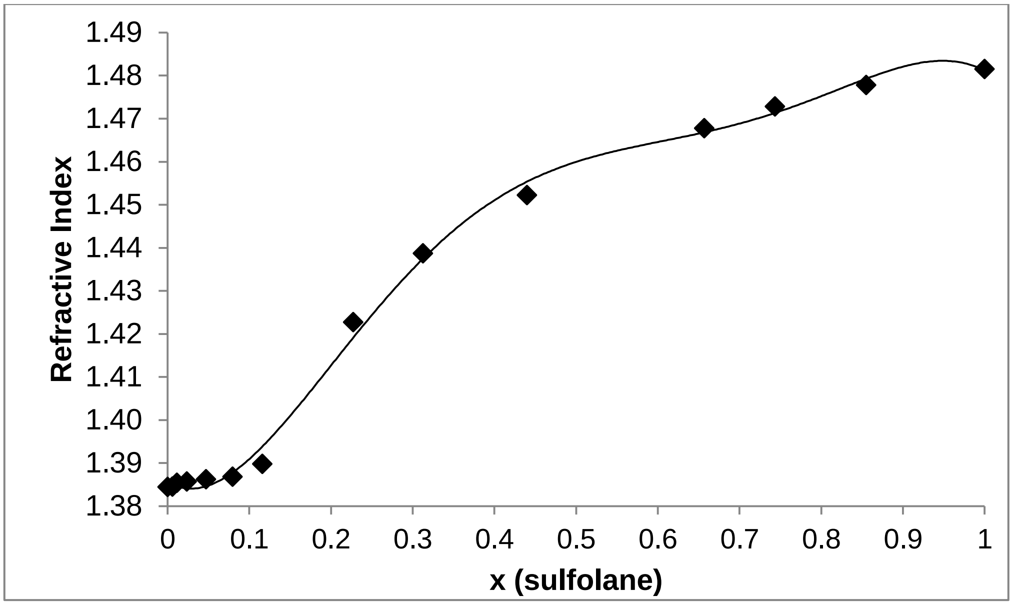


Figure 5.52 Calibration curve for system: [sulfolane (1) + methanol (2) + heptane (3)] at T= 303.15 K

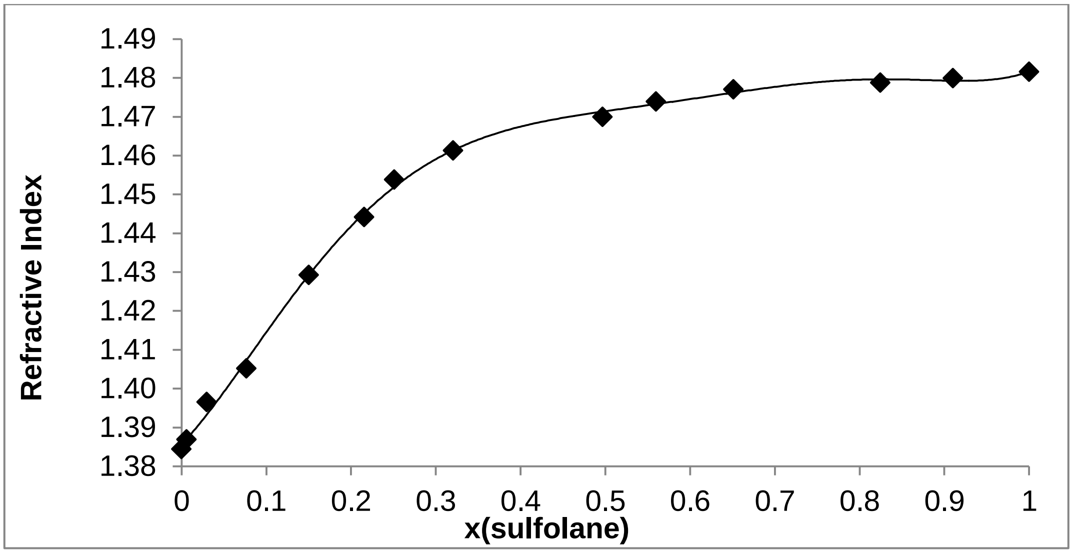


Figure 5.53 Calibration curve for system: [sulfolane (1) + ethanol (2) + heptane (3)] at T= 303.15 K

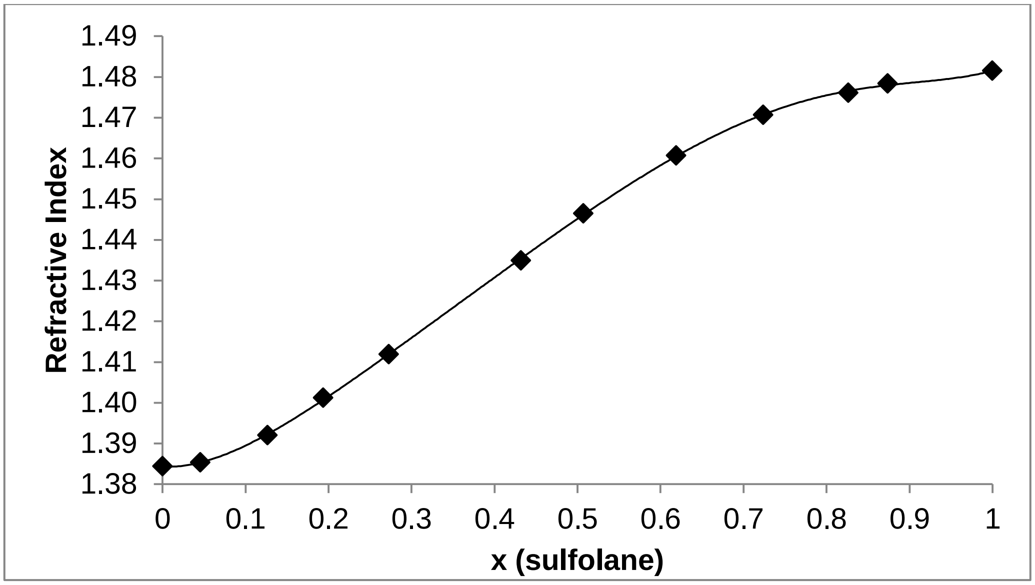


Figure 5.54 Calibration curve for system: [sulfolane (1) + 1-propanol (2) + heptane (3)] at T= 303.15 K

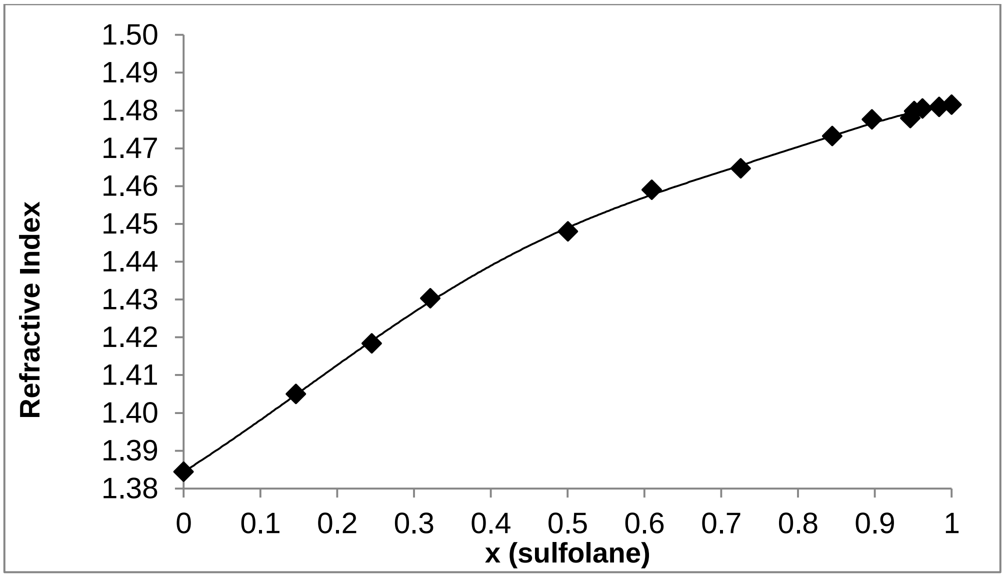


Figure 5.55 Calibration curve for system: [sulfolane (1) + 2-propanol (2) + heptane (3)] at T= 303.15 K

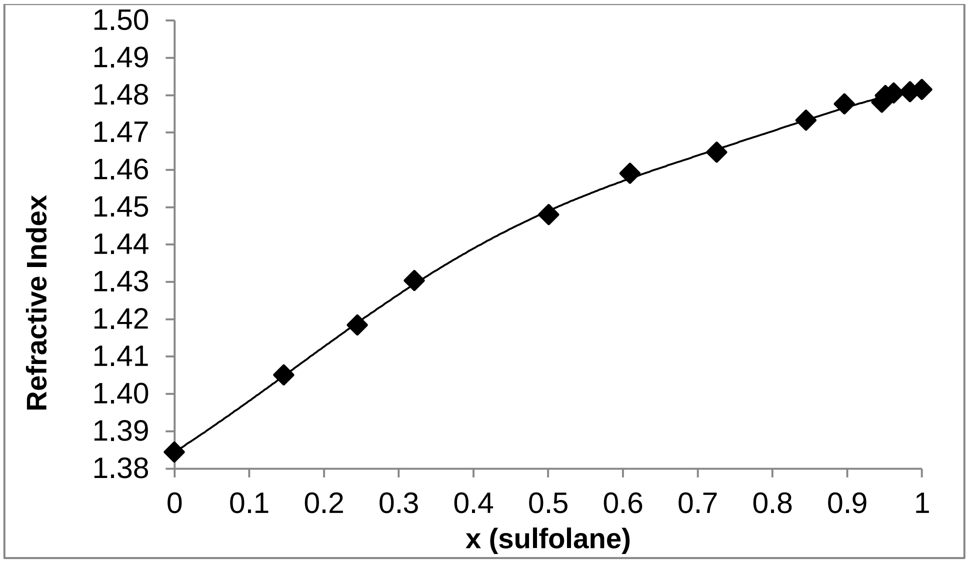


Figure 5.56 Calibration curve for system: [sulfolane (1) + 1- Butanol (2) + heptane (3)] at T= 303.15 K

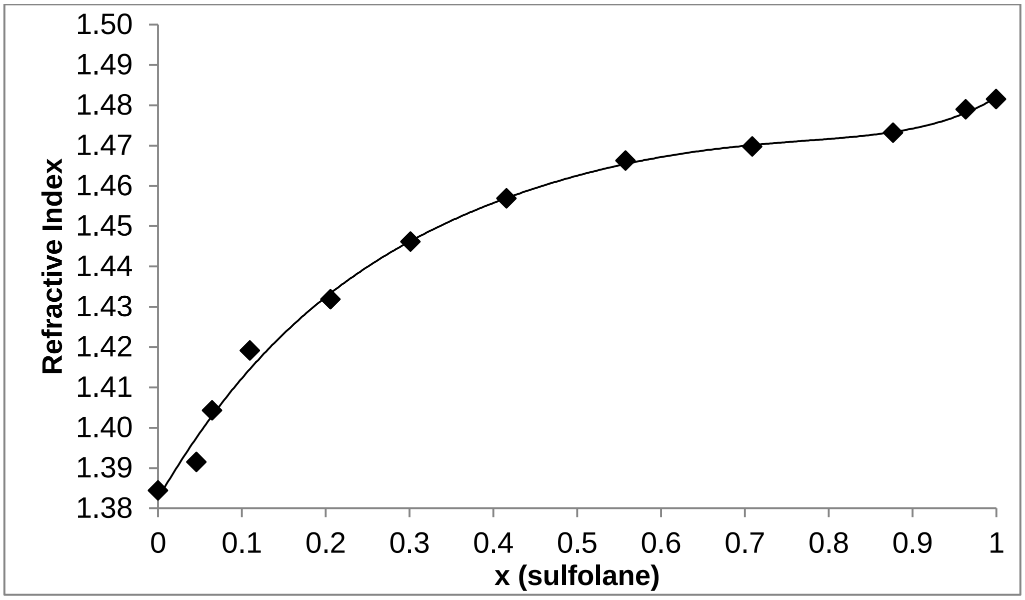


Figure 5.57 Calibration curve for system: [sulfolane (1) + 2- Butanol (2) + heptane (3)] at T= 303.15 K

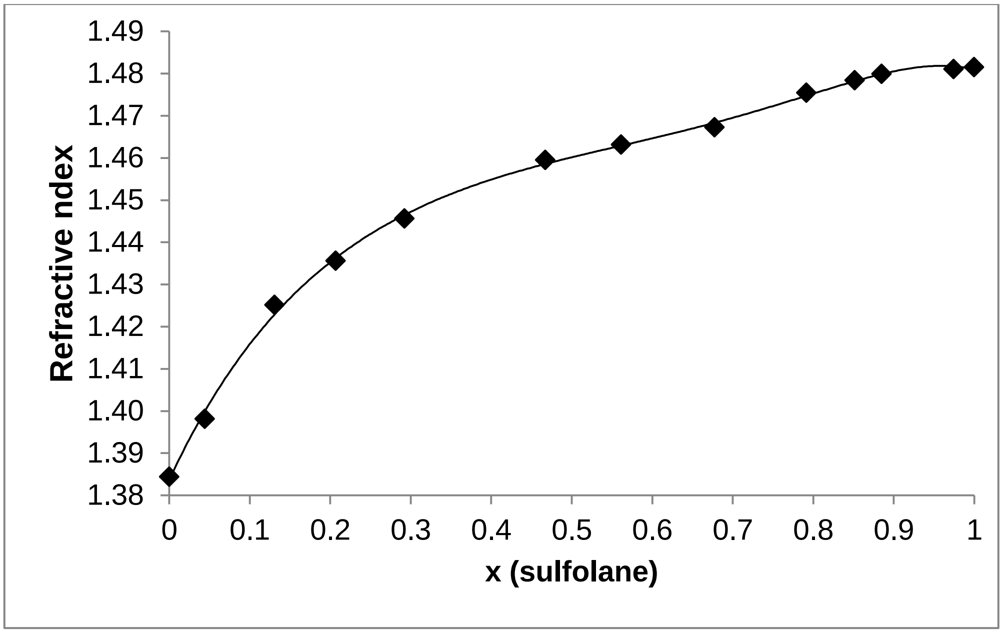


Figure 5.58 Calibration curve for system: [sulfolane (1) + 2-methyl-1-propanol (2) + heptane (3)] at T= 303.15 K

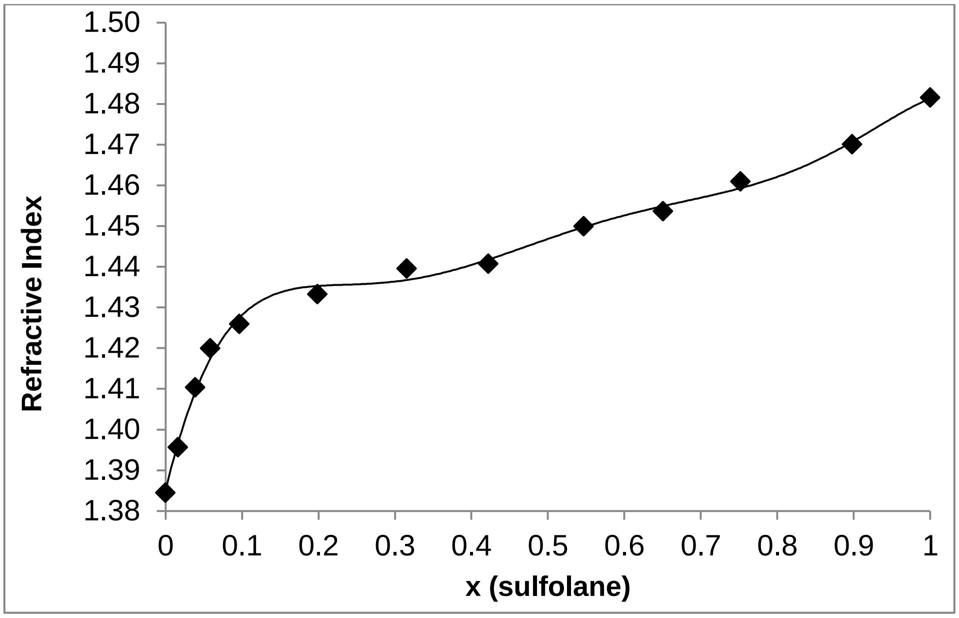


Figure 5.59 Calibration curve for system: [sulfolane (1) + 2-methyl-2-propanol (2) + heptane (3)] at T = 303.15 K

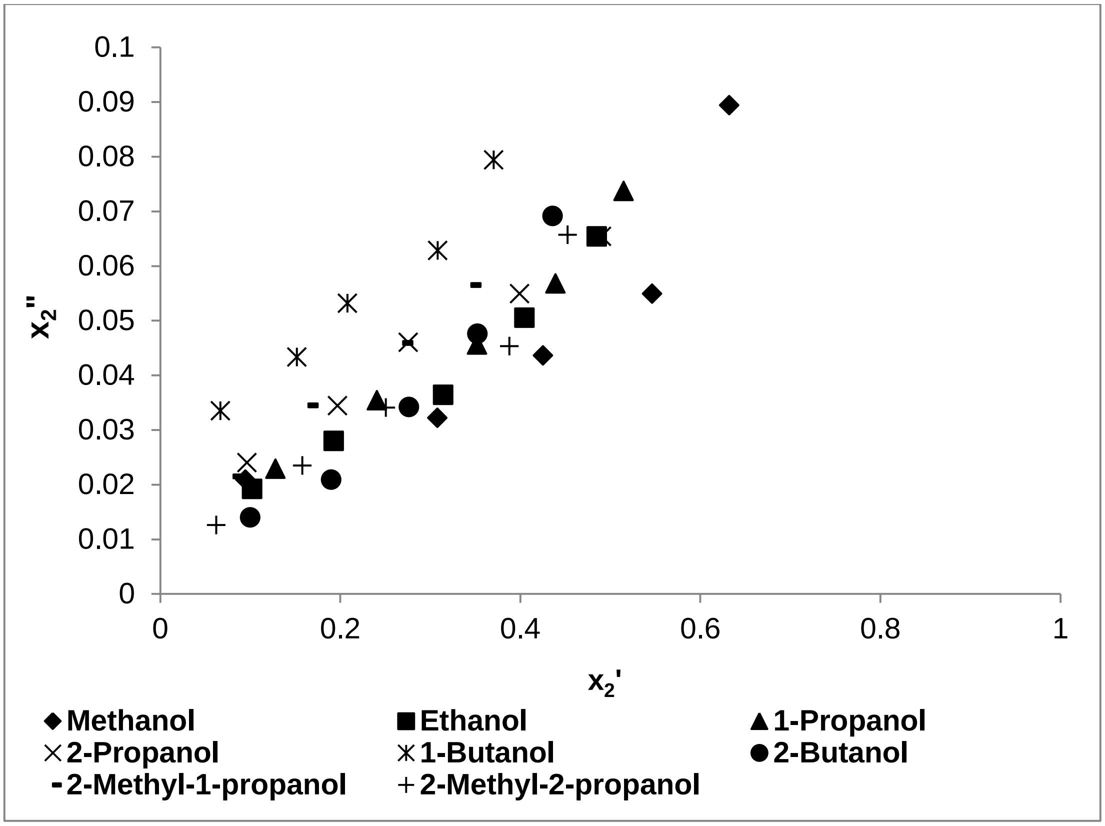


Figure 5.60 A plot of x_2'' against x_2' showing the relative solubilities of the alcohols in the sulfolane-rich and heptane-rich layers

5.5 EXCESS MOLAR VOLUMES

5.5.1 BINARY MIXTURES OF SULFOLANE (1) + ALCOHOL (2) AT T = 298.15 K.

Table 5.29 Densities of pure components at T = 298.15 K, Density ρ.

Compound	**Density / g.cm^{-3}**
Methanol	0.8033
Ethanol	0.7859
1-Propanol	0.8002
2-Propanol	0.7816
1-Butanol	0.8063
2-Butanol	0.8033
2-Methyl-1-Propanol	0.7994
2-Methyl-2-Propanol	0.7827
Sulfolane	1.2640[a]

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

Table 5.30 Densities, ρ, and excess molar volumes, V_{m}^{E} , for the systems: [Sulfolane (1) + Alcohol (2)] at T = 298.15 K.

x_1	V_{m}^{E} ($cm^3.mol^{-1}$)	$\delta V_{\mathrm{m}}^{E}$ ($cm^3.mol^{-1}$)	x_1	V_{m}^{E} ($cm^3.mol^{-1}$)	$\delta V_{\mathrm{m}}^{E}$ (cm^3mol^{-1})
Sulfolane (1) + Methanol (2)					
0.0000	0.0000	0.0000	0.4944	-1.1004	0.0050
0.0222	-0.0655	-0.0180	0.5437	-1.1121	0.0070
0.0595	-0.1680	-0.0120	0.5920	-1.1099	0.0180
0.0970	-0.2864	0.0140	0.6547	-1.0100	-0.0300
0.1396	-0.3796	-0.0010	0.6948	-0.9000	0.0210
0.1743	-0.4793	-0.0070	07636	-0.7964	-0.0300
0.2091	-0.5714	0.0130	0.7900	-0.6911	0.0250
0.2570	-0.6940	0.0036	0.8510	-0.4566	-0.0090
0.2806	-0.7955	0.0040	0.8956	-0.2797	0.0030
0.3265	-0.8667	-0.3100	1.0000	0.0000	0.0000
0.4030	-0.9984	-0.0170			
Sulfolane (1) + Ethanol (2)					
0.0000	0.0000	0.0000	0.4388	-2.0198	-0.0200
0.0130	-0.0671	-0.0024	0.5025	-2.1357	-0.0890
0.0525	-0.1047	0.0810	0.5519	-2.1340	-0.0540
0.0958	-0.4281	-0.0660	0.6598	-2.1403	0.0210
0.1254	-0.5471	-0.0520	0.7269	-1.8357	0.0470
0.1361	-0.6199	-0.0750	0.7936	-1.4917	0.1110
0.2035	-0.8617	0.0200	0.8668	-0.9611	0.0300
0.2450	-0.9973	0.1070	0.9190	-0.6450	-0.0680
0.2879	-1.2885	0.0440	0.9533	-0.4208	-0.0620
0.3213	-1.4952	0.0100	1.0000	0.0000	0.0000
0.3923	-1.8199	0.0120			
Sulfolane (1) +1-Propanol (2)					
0.0000	0.0000	0.0000	0.5469	-1.4133	0.0050
0.0139	-0.0266	0.0200	0.6460	-1.3131	0.0290
0.0496	-0.1089	0.2800	0.6911	-1.2011	0.0070
0.1088	-0.2859	0.0290	0.7069	-1.1988	-0.0220
0.1297	-0.3932	-0.0240	0.7572	-1.0276	-0.0570
0.1460	-0.4395	-0.0100	0.8280	-0.7455	0.0050
0.1681	-0.5452	-0.0350	0.8608	-0.5206	-0.0100
0.2015	-0.7496	-0.0240	0.8866	-0.4328	0.0380
0.3273	-1.1857	-0.0020	0.9360	-0.2385	0.0310
0.3926	-1.2951	0.0070	1.0000	0.0000	0.0000
0.4485	-1.3844	0.0350			

Table 5.30 Continued

x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^3.mol^{-1})	x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^{3}mol^{-1})
			Sulfolane (1) + 2-Propanol (2)		
0.0000	0.0000	0.0000	0.5147	-2.0399	-0.0500
0.0535	-0.1908	0.0200	0.5747	-2.0418	-0.4700
0.0832	-0.3214	0.0160	0.6100	-2.0552	-0.5500
0.1252	-0.5421	-0.0160	0.6283	-1.9995	0.0200
0.1833	-0.8364	-0.0320	0.7240	-1.7419	0.1920
0.2333	-1.0385	0.0120	0.7529	-1.5889	-0.0880
0.2586	-1.1617	0.0120	0.8029	-1.2384	-0.0280
0.2759	-1.2741	-0.0170	0.8787	-0.6907	0.0220
0.3564	-1.5891	0.0270	0.9190	-0.4227	0.0240
0.3824	-1.6865	0.0310	1.0000	0.0000	0.0000
0.4652	-1.9828	0.0020			
			Sulfolane (1) + 1-Butanol (2)		
0.0000	0.0000	0.0000	0.5890	-1.1425	-0.0170
0.0258	-0.0868	0.0320	0.6590	-1.1218	-0.0220
0.1021	-0.2966	-0.0060	0.6859	-1.0592	0.1070
0.1257	-0.3620	0.0025	0.7124	-0.9880	-0.0500
0.1642	-0.5444	0.0080	0.7641	-0.8479	-0.0590
0.2494	-0.7379	-0.0510	0.8118	-0.6878	-0.0510
0.3141	-0.9589	-0.0280	0.8357	-0.5924	0.0260
0.3428	-1.0196	-0.0050	0.8790	-0.4313	0.0760
0.3965	-1.1283	0.0340	0.9277	-0.2141	0.00023
0.4558	-1.1800	0.0180	1.0000	0.0000	0.0000
0.5133	-1.1673	0.0020			
			Sulfolane (1) + 2-Butanol (2)		
0.0000	0.0000	0.0000	0.5502	-1.2181	0.0120
0.0489	-0.0944	0.0090	0.5942	-1.1921	0.0160
0.1106	-0.3207	0.0340	0.6618	-1.1299	0.0080
0.1640	-0.5124	0.0160	0.6852	-1.1022	-0.0150
0.1965	-0.6707	0.0010	0.7243	-1.0178	-0.0140
0.2502	-0.8283	-0.0460	0.8053	-0.7655	-0.0530
0.3153	-0.9905	-0.3200	0.8543	-0.5437	0.0220
0.3459	-1.0541	-0.0250	0.8979	-0.3278	-0.0130
0.4025	-1.1521	0.0210	0.9384	-0.2103	0.0770
0.4524	-1.1925	0.0390	1.0000	0.0000	0.0000
0.5052	-1.2092	0.0140			

Table 5.30 Continued

x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^3.mol^{-1})	x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^{3}mol^{-1})
Sulfolane (1) + 2- Methyl-1-propanol (2)					
0.0000	0.0000	0.0000	0.6161	-1.1200	-0.0072
0.0599	-0.1290	0.0510	0.6571	-1.0928	-0.0043
0.0716	-0.1921	0.0020	0.7167	-1.0050	-0.029
0.1949	-0.2731	0.0120	0.7324	-0.9062	-0.0300
0.2394	-0.5705	-0.1400	0.7935	-0.7655	-0.0210
0.2830	-0.8171	-0.0500	0.8533	-0.4919	0.0530
0.3487	-0.9951	-0.1400	0.8933	-0.3262	0.0140
0.3986	-1.0024	0.0130	0.9289	-0.1204	-0.0320
0.4444	-1.1021	0.0110	0.9533	-0.0281	0.0300
0.4965	-1.1621	0.0230	1.0000	0.0000	0.0000
0.5513	-1.1937	0.0200			
Sulfolane (1) + 2-Methyl-2-propanol (2)					
0.0000	0.0000	0.0000	0.4563	-1.2325	-0.0340
0.0136	-0.0290	-0.0970	0.5217	-1.2451	0.0650
0.0591	-0.1485	-0.0700	0.6263	-1.2367	0.0070
0.0835	-0.2248	0.1060	0.7114	-1.1168	-0.0270
0.1054	-0.3484	0.0070	0.7523	-0.9833	0.0460
0.1285	-0.4234	0.0230	0.7815	-0.8765	-0.0040
0.1540	-0.5306	0.0230	0.8470	-0.5433	0.0250
0.1935	-0.6412	-0.0050	0.9289	-0.2156	-0.0670
0.2191	-0.7948	-0.1100	0.9533	-0.1481	0.0060
0.2836	-1.0099	-0.0340	1.0000	0.0000	0.0000
0.3441	-1.1297	-0.0380			

Table 5.31 Coefficients, A_r and standard deviations from equation for the excess molar volumes of systems [Sulfolane (1) + Alcohol (2)] at T = 298.15 K.

Alcohol	A_0	A_1	A_2	A_3	σ
			T = 298.15 K		
Methanol	-4.509	0.584	3.117	-2.909	0.020
Ethanol	-8.573	3.003	6.024	-3.740	0.064
1-Propanol	-2.477	0.959	0.531	-0.132	0.028
2-Propanol	-8.092	2.654	4.120	-2.418	0.059
1-Butanol	-4.645	1.343	2.936	-0.720	0.045
2-Butanol	-2.791	3.309	0.894	-2.816	0.032
2-Methyl-1-propanol	-5.302	-2.449	5.392	4.058	0.050
2-Methyl-2-propanol	-4.175	3.056	3.420	-3.805	0.029

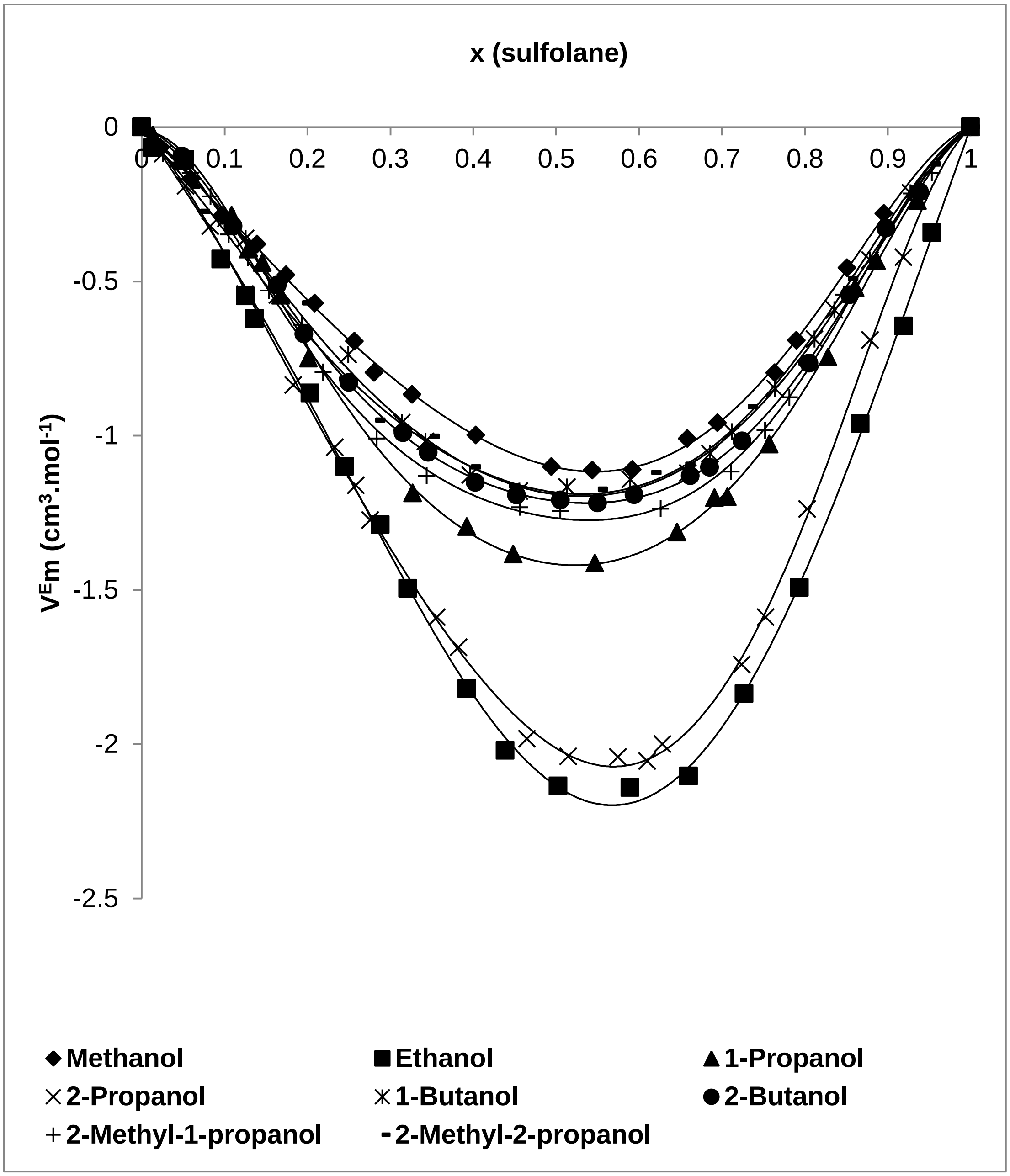


Figure 5.61 Plot of excess molar volume, V_{m}^{E}, for binary mixtures of [sulfolane(1) + methanol (2)], [sulfolane (1) + ethanol (2)], [sulfolane (1) + 1-propanol (2)], [sulfolane (1) + 2-propanol (2)], [sulfolane (1) + 1-butanol (2)], [sulfolane (1) + 2-butanol (2)], [sulfolane (1) + 2-methyl-1-propanol (2)], [sulfolane (1) +2-methyl-2-propanol (2)] at T = 298.15 K, as a function of mole fraction of x (sulfolane)

5.5.2 BINARY MIXTURES OF SULFOLANE (1) + ALCOHOL (2) AT T = 303.15 K.

Table 5.32 Densities of pure components at T = 303.15 K, Density ρ.

Compound	**Density / g.cm^{-3}**
Methanol	0.7984
Ethanol	0.7813
1-Propanol	0.7962
2-Propanol	0.7771
1-Butanol	0.7987
2-Butanol	0.7987
2-Methyl-1-propanol	0.7952
2-Methyl-2-propanol	0.7778
Sulfolane	1.2609

Table 5.33 Densities, ρ, and excess molar volumes, V_{m}^{E}, for the systems: [Sulfolane (1) + Alcohol (2)] at T = 303.15 K.

x_1	V_{m}^{E} ($cm^3.mol^{-1}$)	$\delta V_{\mathrm{m}}^{E}$ ($cm^3.mol^{-1}$)	x_1	V_{m}^{E} ($cm^3.mol^{-1}$)	$\delta V_{\mathrm{m}}^{E}$ (cm^3mol^{-1})
Sulfolane (1) + Methanol (2)					
0.0000	0.0000	0.0000	0.3436	-0.8291	0.0210
0.0222	-0.0924	0.0290	0.3569	-0.8992	0.0280
0.0456	-0.1274	-0.0420	0.3892	-0.9598	-0.0440
0.0700	-0.2134	-0.0110	0.4128	-1.0030	-0.0320
0.1496	-0.2844	-0.0160	0.5483	-1.1165	-0.0340
0.1824	-0.3515	-0.0090	0.6256	-0.9993	0.0290
0.2052	-0.4697	0.0260	0.6700	-0.8497	0.0250
0.2317	-0.5147	0.0160	0.8103	-0.4374	0.0240
0.2544	-0.5772	0.0060	0.8560	-0.2552	-0.0420
0.2765	-0.6582	0.0130	1.0000	0.0000	0.0000
0.3130	-0.7690	-0.0090			
Sulfolane (1) + Ethanol (2)					
0.0000	0.0000	0.0000	0.4388	-2.0890	-0.0460
0.0302	-0.2364	-0.0060	0.5025	-2.1658	-0.0017
0.0523	-0.4730	-0.0810	0.5519	-2.0920	0.0040
0.0958	-0.6789	0.0120	0.5982	-1.8982	0.0220
0.1254	-0.9510	-0.0700	0.6823	-1.6481	-0.0120
0.1361	-1.0511	0.0450	0.7363	-1.3219	0.0480
0.2035	-1.3104	0.0190	0.8267	-0.8646	-0.0140
0.2450	-1.4539	0.0790	0.8841	-0.5195	-0.0060
0.2879	-1.6024	0.0350	0.9171	-0.2876	-0.0027
0.3213	-1.8213	-0.0160	1.0000	0.0000	0.0000
0.3923	-2.0249	-0.0530			
Sulfolane (1) + 1-Propanol (2)					
0.0000	0.0000	0.0000	0.4690	-1.4204	-0.0111
0.0439	-0.2553	-0.0850	0.5716	-1.3204	0.0360
0.0855	-0.3737	-0.0330	0.6109	-1.2865	0.0071
0.1629	-0.6338	0.0260	0.6554	-1.1991	-0.0040
0.1970	-0.7694	0.0240	0.7266	-0.9870	0.0010
0.2096	-0.8249	0.0160	0.7822	-0.7498	0.0440
0.2962	-1.0847	0.0430	0.8108	-0.6983	-0.0120
0.3290	-1.2034	0.0110	0.8660	-0.4784	-0.0070
0.4140	-1.4143	-0.0460	0.9360	-0.2504	0.0430
0.4379	-1.4195	-0.0270	1.0000	0.0000	0.0000
0.4485	-1.4290	-0.0290			

Table 5.33 Continued

x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^3.mol^{-1})	x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^{3}mol^{-1})
Sulfolane (1) + 2-Propanol (2)					
0.0000	0.0000	0.0000	0.5147	-1.9799	-0.0030
0.0535	-0.2588	0.0051	0.5747	-2.0420	-0.0140
0.0832	-0.4431	0.0140	0.6100	-2.0556	-0.0200
0.1252	-0.5501	-0.0270	0.6276	-2.0520	0.0180
0.1833	-0.6984	0.0270	0.6971	-1.8552	0.0090
0.2333	-0.8769	0.0350	0.7529	-1.5979	0.0050
0.2586	-0.9871	0.0240	0.8029	-1.2830	0.0070
0.2932	-1.2010	-0.0470	0.8787	-0.7582	-0.0260
0.3564	-1.4310	-0.0080	0.9190	-0.4228	0.0130
0.4038	-1.6413	-0.0220	1.0000	0.0000	0.0000
0.4652	-1.8065	0.0360			
Sulfolane (1) + 1-Butanol (2)					
0.0000	0.0000	0.0000	0.5896	-1.1875	0.0050
0.0582	-0.0953	0.0310	0.5904	-1.1800	0.0120
0.1021	-0.1907	0.0470	0.6736	-1.1037	-0.0520
0.1571	-0.4596	-0.0680	0.7124	-0.9321	0.0150
0.1942	-0.4961	0.0060	0.7641	-0.7832	-0.0070
0.2494	-0.6794	-0.0100	0.8118	-0.6428	-0.0470
0.3141	-0.8549	0.0040	0.8357	-0.4266	0.0750
0.3428	-0.9510	-0.0150	0.8790	-0.3446	-0.0120
0.3965	-1.0285	0.0330	0.9277	-0.1621	0.0007
0.4558	-1.1630	-0.0007	1.0000	0.0000	0.0000
0.5713	-1.1978	0.0090			
Sulfolane (1) + 2-Butanol (2)					
0.0000	0.0000	0.0000	0.5502	-1.2651	-0.0220
0.0489	-0.1090	-0.0510	0.5942	-1.1989	0.0080
0.1106	-0.2762	-0.0560	0.6618	-1.0987	-0.0080
0.1640	-0.3932	0.0100	0.6852	-0.9965	0.0340
0.1959	-0.4699	0.0490	0.7243	-0.8653	0.0280
0.2502	-0.6568	0.0550	0.8053	-0.6439	-0.0160
0.3153	-0.8998	0.0110	0.8318	-0.5432	0.0170
0.3459	-1.0121	-0.0260	0.8786	-0.3219	-0.0110
0.4025	-1.1621	-0.0340	0.9384	-0.1410	-0.0370
0.4524	-1.2169	-0.0020	1.0000	0.0000	0.0000
0.5052	-1.2846	-0.0140			

Table 5.33 Continued

x_1	V_m^E ($cm^3.mol^{-1}$)	δV_m^E ($cm^3.mol^{-1}$)	x_1	V_m^E ($cm^3.mol^{-1}$)	δV_m^E (cm^3mol^{-1})
			Sulfolane (1) + 2 Methyl-1-propanol (2)		
0.0000	0.0000	0.0000	0.5133	-1.3982	-0.0290
0.0577	-0.0864	-0.0240	0.6161	-1.2251	-0.0010
0.0991	-0.1825	-0.0047	0.6709	-1.1033	0.0100
0.1572	-0.3410	-0.0060	0.7167	-0.9799	0.0060
0.2049	-0.4694	0.0340	0.7324	-0.8892	0.0460
0.2541	-0.6547	0.0290	0.7935	-0.7104	0.0060
0.2830	-0.7782	0.0090	0.8334	-0.5675	-0.0070
0.3487	-0.8867	0.0420	0.8918	-0.3510	-0.0190
0.3856	-1.0957	-0.0020	0.9309	-0.2183	-0.0270
0.4444	-1.2056	-0.0350	1.0000	0.0000	0.0000
0.4965	-1.2106	-0.0170			
		Sulfolane (1) + 2 Methyl-2-propanol (2)			
0.0000	0.0000	0.0000	0.5633	-1.2409	-0.0960
0.0598	-0.0913	-0.0150	0.5922	-1.0100	-0.0350
0.1113	-0.2131	0.0020	0.6826	-0.8664	-0.0120
0.1635	-0.4243	-0.0270	0.7114	-0.6910	0.0640
0.2117	-0.5425	0.0370	0.7523	-0.5206	0.0840
0.2285	-0.6811	-0.0380	0.7815	-0.4926	0.0020
0.2854	-0.8478	-0.0010	0.8347	-0.2856	0.0140
0.3535	-0.9697	0.0760	0.8921	-0.1744	-0.0530
0.4069	-1.2402	0.0180	0.9281	-0.0871	-0.0045
0.4586	-1.2303	-0.0250	1.0000	0.0000	0.0000
0.5840	-1.2085	0.0040			

Table 5.34 Coefficients, A_r and standard deviations from equation for the excess molar volumes of systems [Sulfolane (1) + Alcohol (2)] at T = 303.15 K.

Alcohol	**A_0**	**A_1**	**A_2**	**A_3**	**σ**
	T = 303.15 K				
Methanol	-4.569	0.276	2.826	-4.445	0.028
Ethanol	-8.406	-0.963	3.206	-1.681	0.042
1-propanol	-5.645	-0.387	2.38	-0.052	0.035
2-Propanol	-7.770	5.002	3.391	-6.321	0.024
1-Butanol	-4.821	1.249	3.306	-1.699	0.035
2-Butanol	-4.544	-0.816	4.103	0.910	0.033
2-Methyl-1-propanol	-5.122	1.173	4.011	-0.292	0.028
2-Methyl-2-propanol	-4.840	-0.605	5.110	0.090	0.047

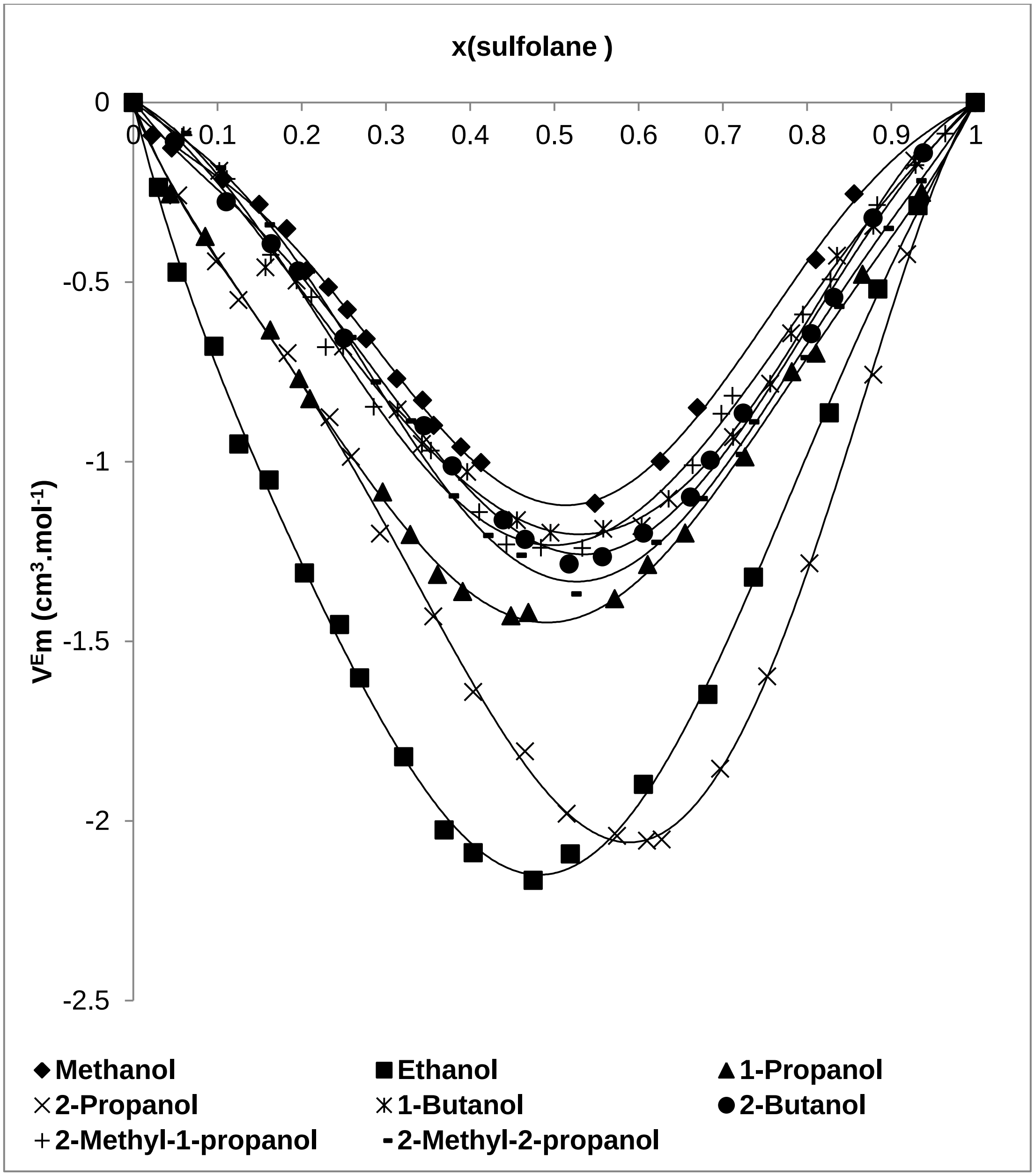


Figure 5.62 Plot of excess molar volume, V_{m}^{E}, for binary mixtures of [sulfolane(1) + methanol (2)], [sulfolane (1) + ethanol (2], [sulfolane (1) + (1-propanol (2)], [sulfolane (1) +2-propanol (2)], [sulfolane (1) +1-butanol (2)], [sulfolane (1) + 2-butanol (2)], [sulfolane (1) +2-methyl-1-propanol (2)], [sulfolane (1) +2-methyl-2-propanol (2)] at T= 303.15 K, as a function of mole fraction x (sulfolane)

5.5.3 BINARY MIXTURES OF SULFOLANE (1) + ALCOHOL (2) AT T = 308.15 K.

Table 5.35 Densities of pure components at T = 308.15 K, Density ρ.

Compound	**Density/g.cm^{-3}**
Methanol	0.7941
Ethanol	0.7775
1-Propanol	0.7929
2-Propanol	0.7730
1-Butanol	0.7952
2-Butanol	0.7952
2-Methyl-1-propanol	0.7921
2-Methyl-2-propanol	0.7728
Sulfolane	1.2570

Table 5.36 Densities, ρ, and excess molar volumes, V_{m}^{E}, for the systems: [Sulfolane (1) + Alcohol (2)] at T = 308.15 K.

x_1	V_{m}^{E} ($cm^3.mol^{-1}$)	$\delta V_{\mathrm{m}}^{E}$ ($cm^3.mol^{-1}$)	x_1	V_{m}^{E} ($cm^3.mol^{-1}$)	$\delta V_{\mathrm{m}}^{E}$ (cm^3mol^{-1})
Sulfolane (1) + Methanol (2)					
0.0000	0.0000	0.0000	0.3436	-1.1155	0.0050
0.0222	-0.0341	0.0190	0.3687	-1.1524	0.0170
0.0456	-0.1079	0.0120	0.3920	-1.1724	0.0340
0.0703	-0.2196	-0.0200	0.4283	-1.1934	0.0510
0.0962	-0.2693	0.0220	0.5483	-1.2046	0.0100
0.1243	-0.3486	0.0470	0.6256	-1.0994	-0.0240
0.2125	-0.6919	0.0380	0.6700	-0.9857	-0.0250
0.2170	-0.7654	-0.0200	0.8103	-0.5350	-0.0310
0.2381	-0.8762	-0.0560	0.8560	-0.2990	0.0510
0.2650	-0.9687	-0.0590	1.0000	0.0000	0.0000
0.2962	-1.0339	-0.0310			
Sulfolane (1) + Ethanol (2)					
0.0000	0.0000	0.0000	0.4388	-2.3983	-0.0590
0.0302	-0.2467	-0.0220	0.5025	-2.3727	-0.0690
0.0523	-0.4757	-0.0790	0.5519	-2.2249	-0.0140
0.0958	-0.8218	-0.0810	0.5982	-2.1086	-0.0290
0.1254	-0.9823	-0.0100	0.6823	-1.6904	0.0650
0.1361	-1.0683	-0.0140	0.7363	-1.4232	0.0650
0.1820	-1.3215	0.0660	0.8167	-1.0660	0.0810
0.2150	-1.5435	0.0600	0.8841	-0.7530	-0.0420
0.2879	-1.9182	0.0740	0.9471	-0.4393	-0.1020
0.3213	-2.1030	0.0200	1.0000	0.0000	0.0000
0.3923	-2.3277	0.0280			
Sulfolane (1) +1-Propanol (2)					
0.0000	0.0000	0.0000	0.4990	-1.4793	-0.109
0.0386	-0.0571	-0.0320	0.5362	-1.4530	0.023
0.0552	-0.1257	-0.0690	0.6409	-1.2178	0.057
0.0991	-0.2545	-0.0910	0.6855	-1.0967	0.037
0.1370	-0.3545	-0.0100	0.7427	-0.8565	0.064
0.1691	-0.4827	-0.0450	0.7822	-0.7396	-0.016
0.2136	-0.6404	0.0660	0.8108	-0.6192	0.0007
0.2579	-0.8373	0.0860	0.8660	-0.4590	-0.046
0.3354	-1.1094	0.0940	0.9360	-0.2080	-0.033
0.3942	-1.3290	0.0200	1.0000	0.0000	0.0000
0.4145	-1.3591	-0.0180			

Table 5.36 Continued

x_1	V_m^E ($cm^3.mol^{-1}$)	δV_m^E ($cm^3.mol^{-1}$)	x_1	V_m^E ($cm^3.mol^{-1}$)	δV_m^E (cm^3mol^{-1})
Sulfolane (1) + 2-Propanol (2)					
0.0000	0.0000	0.0000	0.5147	-1.7376	0.0550
0.0535	-0.1273	0.0400	0.5747	-1.9947	0.0160
0.0832	-0.2039	0.0380	0.6100	-2.0081	0.0430
0.1252	-0.3543	-0.0090	0.6828	-2.0292	0.0040
0.1833	-0.5190	-0.0160	0.6457	-2.0591	-0.1190
0.2333	-0.6579	0.0100	0.7529	-1.5976	-0.0009
0.2586	-0.7818	-0.0190	0.8029	-1.1082	0.0230
0.2759	-0.8593	-0.0290	0.8787	-0.7937	-0.0180
0.3564	-1.1996	-0.0130	0.9190	-0.3486	0.0730
0.3824	-1.4027	-0.0210	1.0000	0.0000	0.0000
0.4652	-1.6577	0.0200			
Sulfolane (1) + 1-Butanol (2)					
0.0000	0.0000	0.0000	0.5609	-1.2347	0.0240
0.0822	-0.2754	0.0300	0.5960	-1.2104	-0.0020
0.1321	-0.5170	-0.0200	0.6380	-1.1093	-0.0090
0.1871	-0.6924	0.0060	0.6731	-1.1093	-0.0070
0.2194	-0.8208	-0.0070	0.7067	-0.9904	-0.0170
0.2494	-0.9230	0.0360	0.7453	-0.7653	-0.0230
0.3141	-1.1243	-0.0310	0.7780	-0.6590	-0.0002
0.3464	-1.1920	-0.0290	0.8248	-0.4638	0.0320
0.4040	-1.2713	-0.0220	0.8977	-0.2862	0.0140
0.5158	-1.2973	0.0230	1.0000	0.0000	0.0000
0.5543	-1.2336	0.0300			
Sulfolane (1) + 2-Butanol (2)					
0.0000	0.0000	0.0000	0.4751	-1.3390	-0.0210
0.0588	-0.1382	-0.0200	0.5243	-1.3430	0.0120
0.0821	-0.2351	0.0640	0.5818	-1.2929	-0.0280
0.1064	-0.3585	-0.0400	0.6169	-1.1993	0.0220
0.1552	-0.4658	-0.0390	0.6724	-1.0839	0.0220
0.1850	-0.5247	0.0050	0.7170	-0.9674	-0.0220
0.2533	-0.7839	0.0280	0.7822	-0.7454	0.0120
0.2935	-0.9302	0.0060	0.8179	-0.5372	0.0400
0.3414	-1.1010	0.0300	0.9109	-0.2136	-0.0580
0.3644	-1.1812	-0.0070	1.0000	0.0000	0.0000
0.4140	-1.2838	-0.0290			

Table 5.36 Continued

x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^3.mol^{-1})	x_1	V_m^E (cm^3.mol^{-1})	δV_m^E (cm^{3}mol^{-1})
		Sulfolane (1) + 2- Methyl-1-propanol (2)			
0.0000	0.0000	0.0000	0.5133	-1.3430	-0.0080
0.0577	-0.4028	-0.0210	0.6161	-1.1420	0.0040
0.0991	-0.6381	-0.0260	0.6709	-0.9434	0.0080
0.1572	-0.8812	-0.0003	0.7167	-0.8378	0.0070
0.2049	-0.9997	0.0150	0.7324	-0.6102	0.0100
0.2541	-1.1852	0.0210	0.7935	-0.4876	0.0380
0.2830	-1.2546	0.0210	0.8334	-0.3156	-0.0360
0.3487	-1.4072	-0.0090	0.8918	-0.1888	-0.0180
0.3856	-1.4257	-0.0040	0.9309	-0.0620	-0.0010
0.4444	-1.4277	-0.0260	1.0000	0.0000	0.0000
0.4965	-1.3850	-0.0070			
		Sulfolane (1) + 2- Methyl-2-propanol (2)			
0.0000	0.0000	0.0000	0.6259	-1.1970	-0.0420
0.0598	-0.1340	-0.0880	0.6259	-1.0857	0.0190
0.0911	-0.1879	-0.0070	0.6826	-0.8640	0.0020
0.1435	-0.3478	0.0190	0.7114	-0.7596	0.0110
0.1912	-0.4909	0.0670	0.7523	-0.5836	0.0440
0.2254	-0.6438	-0.0220	0.7815	-0.4898	0.0330
0.2854	-0.8521	-0.0140	0.8347	-0.3528	-0.0160
0.3154	-0.9696	0.0760	0.8921	-0.1947	-0.0320
0.3785	-1.1425	-0.0059	0.9281	-0.1087	-0.0300
0.4047	-1.2192	-0.0050	1.0000	0.0000	0.0000
0.4951	-1.3244	-0.0280			

Table 5.37 Coefficients, A_r and standard deviations from equation for the excess molar volumes of systems [Sulfolane (1) + Alcohol (2)] at T = 308.15 K.

	A_0	A_1	A_2	A_3	σ
	T = 308.15 K				
Methanol	-5.023	-0.915	3.333	0.456	0.036
Ethanol	-9.227	-2.550	2.322	2.300	0.060
1-Propanol	-5.193	0.454	4.385	1.180	0.065
2-Propanol	-7.242	7.038	2.220	-5.771	0.043
1-Butanol	-5.075	0.101	0.107	-0.980	0.023
2-Butanol	-5.231	2.491	1.407	-3.463	0.030
2-Methyl-1-Propanol	-5.584	-2.176	1.914	1.465	0.019
2-Methyl-2-Propanol	-4.855	-0.614	5.088	0.918	0.042

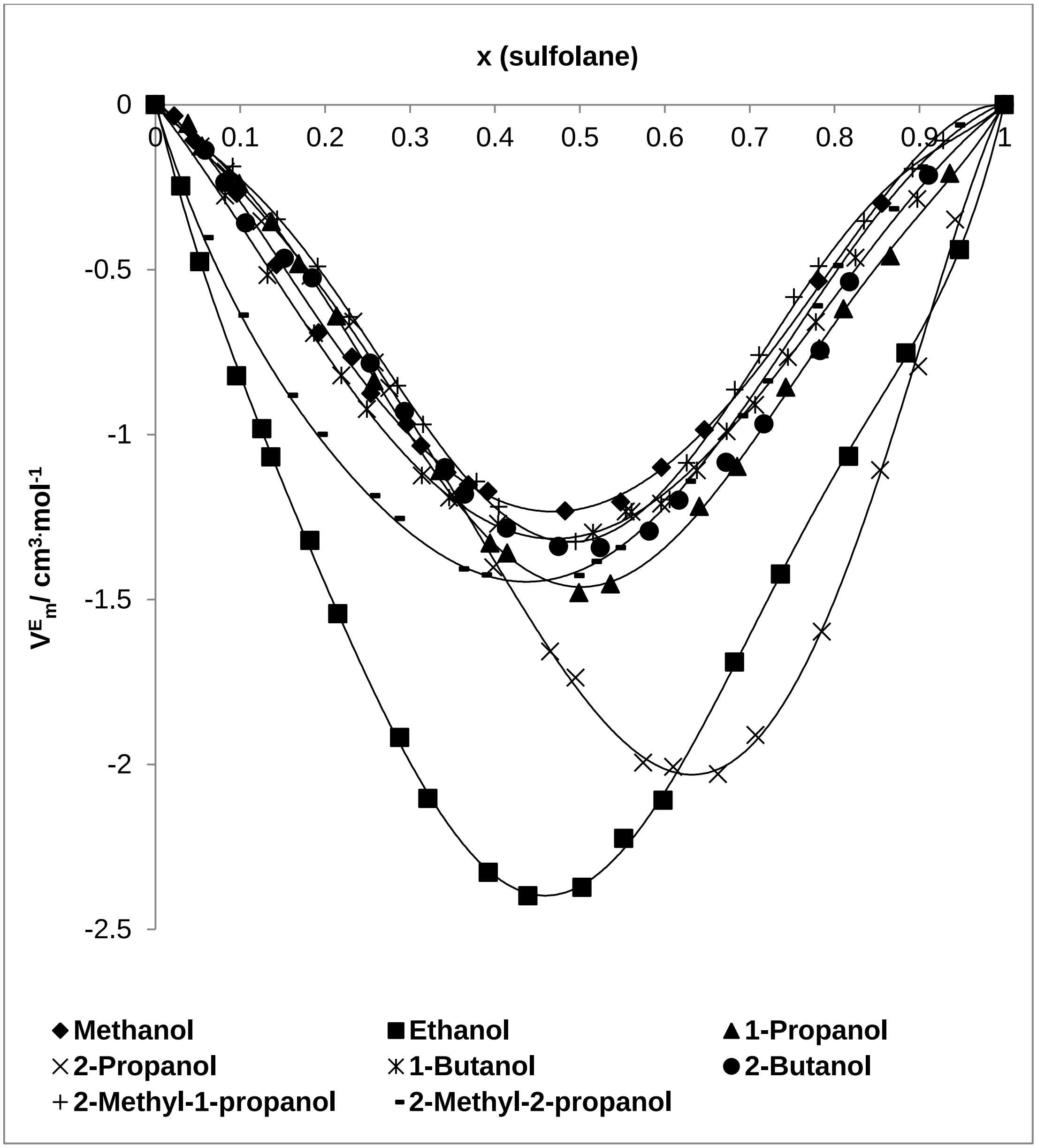


Figure 5.63 Plot of excess molar volume, V_{m}^{E}, for binary mixtures of [sulfolane(1) + methanol (2)], [sulfolane (1) + ethanol (2)], [sulfolane (1) + (1-propanol (2)], [sulfolane (1) +2-propanol (2)], [sulfolane (1) +1-butanol (2)], [sulfolane (1) + 2-butanol (2)], [sulfolane (1) + 2-methyl-1-propanol (2)], [sulfolane (1) +2-methyl-2-propanol (2)] at T= 308.15 K, as a function of mole fraction x (sulfolane)

CHAPTER 6

DISCUSSION

6.1 LIQUID- LIQUID EQULIBRIA (LLE)

6.1.1 Ternary systems involving sulfolane (1) + carboxylic acid (2) + heptane (3) at T = 303.15 K

Previous Work

Mohsen-Nia *et al*. (2005) studied the ternary mixtures of (solvent + aromatic hydrocarbon + alkane) at different temperatures from T = 298.15 K to T = 313.15 K. The aromatic hydrocarbon was (toluene or *m*-xylene) and the alkane was (*n*-heptane or n-octane or cyclohexane) whilst the solvent was (sulfolane or dimethyl sulfoxide or ethylene carbonate). It was reported that the size of the two phase region decreased with increase in temperature. The selectivity and distribution coefficient of the solvents used were compared in the study. It was also found that in the extraction of aromatics from non aromatics, the solvent with higher selectivity and distribution coefficient was preferred, and based on calculated partition coefficient and selectivity factor values the superiority of ethylene carbonate and dimethyl sulfoxide was evident. It was concluded based on the very strong and bad odour as well as recovery difficulties of dimethyl sulfoxide, ethylene carbonate was more favourable than dimethylsulfoxide.

This work

This work presents new LLE data for the ternary system (sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + heptane) at T = 303.15 K.

In binodal curves in figures 5.1-5.6, it can be observed that the solubility of heptane in (sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) is dependent on the type of carboxylic acid. In the ternary systems investigated, the partitioning of carboxylic acid between heptane and sulfolane is shown to be dependent on both the length and the structure of the carboxylic acid.

The size of the two phase region decreases with an increase in alkyl group chain length of the carboxylic acid. Acetic acid has the largest area of the two phase region as it has shorter carboxylic acid chain length and pentanoic acid or 3-methylbutanoic acid has the smallest area of the two phase region as it has most number of carbon atoms, of all the investigated carboxylic acids. The solubility of carboxylic acid in heptane is also inversely related to the size of the two phase region. In the ternary system investigated, heptane is most soluble in the systems containing 3-methylbutanoic acid, pentanoic acid, 2-methylpropanoic acid and butanoic acid.

The single phase homogenous region increases as the carbon chain length of the carboxylic acid is increased. It can be observed that heptane is most soluble in the carboxylic acid mixtures with long carbon chains, viz., (3-methylbutanoic acid + sulfolane) or (pentanoic acid + sulfolane) and least soluble in the carboxylic acid with short carbon chain (acetic acid + sulfolane).

The area of the two phase heterogeneous region for the carboxylic acid mixtures decrease as the number of carbons in the carboxylic acid chain length progressively increases. The decreases observed follow the order: acetic acid > propanoic acid > butanoic acid ~ 2-methylpropanoic acid > pentanoic acid ~3-methylbutanoic acid.

The mutual solubility of carboxylic acid in sulfolane is dependent on the length and structure of the carbon chains of the carboxylic acid. Acetic acid, with two carbons is too short to act as suitable bridging agent between the sulfolane and heptane. Mutual solubility of the carboxylic acids progressively increases with an increase in the length of the alkyl chain of the carboxylic acids.

Branching of the carbon chain of carboxylic acid improves the mutual solubility effect, and both 2-methylpropanoic acid and 3-methylbutanoic acid showed similar solubility to their corresponding straight chains anologues inspite of their non-linear structures.

The slope of the tie lines obtained in this investigation showed that all acids investigated are more soluble in heptane-rich layer than sulfolane- rich layer. The partitioning of carboxylic acids between the heptane-rich and sulfolane rich layers for all the systems studied show that all the carboxylic acids are more soluble in heptane than sulfolane mixtures (Figure 14).

The relatively large two phase region for (the sulfolane + acetic acid + heptane) system suggested that the entrainer sulfolane has high capacity or loading of solute per mole fraction of the solvent (sulfolane), that is small quantities of it would be needed for efficient separation.

The effectiveness of extraction of the carboxylic acid by sulfolane is given by its selectivity (ω), which is measure of the ability of sulfolane to separate carboxylic acid from heptane.

$$\text{Selectivity} = \frac{\text{distribution coefficient of carboxylic acids}}{\text{distribution coefficient of heptane}}$$

$$\omega = \frac{(x_2/x_3)_{\text{sulfolane-rich phase}}}{(x_2/x_3)_{\text{heptane-rich phase}}}$$

where x_2 refers to the mole fraction of the carboxylic acid, and x_3 the mole fraction of heptane.

Table 5.7 gives representative values of the selectivity for the middle of the area of the measured tie lines for the separation of the carboxylic acids from heptane using sulfolane. From the selectivity data, it can be observed that the values of selectivity are all more than 1. Separation of all carboxylic acids from heptane by extraction therefore feasible. Sulfolane is a good component for separation of mixtures of heptane and 2-methylpropanoic acid or heptane and 3-methylbutanoic acid.

The modified Hlavatý, beta (β) and log γ equations were fitted to the experimental binodal data. Table 5.1.5 presents the results of fitting of modified Hlavatý, beta (β) and log γ equations, Hlavatý function gave the best overall fit as compare to beta (β) and log γ function. The NRTL and UNIQUAC models were used to correlate the experimental tie-lines and to calculate the phase compositions of the ternary systems. It was found that the NRTL equation fitted the experimental data significantly better than the UNIQUAC equation.

6.1.2 Ternary systems involving sulfolane (1) + carboxylic acid (2) + cyclohexane at T = 303.15 K

Previous Work

Rappell *et al*. (2002) studied the ternary systems of (sulfolane + *p*-xylene + cyclohexane), (sulfolane + *p*-xylene + *n*-hexane) and (sulfolane + toluene + n-hexane) at T = 308.15 K and T = 323.15 K.

The systems were compared at different temperatures and the results showed that the two-phase region was enlarged as the temperature was increased indicating that at higher temperature, sulfolane is more selective solvent for aromatic compounds. The experimental data were fitted to the NRTL and UNIQUAC models and NTRL model fitted slightly better than the UNIQUAC model.

This work

This work presents new LLE data for the ternary system (sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + cyclohexane) at T = 303.15 K.

The composition of the mixtures on the binodal curve and mutual solubilities of sulfolane, carboxylic acid and cyclohexane are given in figure 5.15-5.20. It can be observed that the solubility of cyclohexane in (sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid) is again dependent on the type of carboxylic acid. The partitioning of carboxylic acid between cyclohexane and sulfolane is also shown to be dependent on both the length and the structure of the carboxylic acid.

The solubility of carboxylic acid in (cyclohexane + sulfolane) is dependent on the alkyl chain length of carboxylic acid. The size of the area of the two phase region decreases with the increase in the alkyl chain length of carboxylic acid. It can be observed that acetic acid is observed to have the largest two phase region are, than all the other carboxylic acids. The single phase homogeneous region increases as the alkyl group length of the carboxylic acid is increased, and it can be observed that cyclohexane is most soluble in the carboxylic acid with long carbon chain (3-methylbutanoic acid + sulfolane) or (pentanoic acid + sulfolane) and least soluble in the carboxylic acid with short carbon chain (acetic acid + sulfolane).

The area of the two phase heterogeneous region for the carboxylic acid mixtures decrease as the number of carbons in the carboxylic acid increases. The decrease is observed to follow this order: acetic acid > propanoic acid > butanoic acid ~ 2-methylpropanoic acid > pentanoic acid ~ 3-methylbutanoic acid.

Mutual solubility of cyclohexane in (sulfolane + carboxylic acid) mixtures is dependent in the length and structure of the carbon chains of the carboxylic acid. Acetic acid, with two carbons is too short to act as a suitable bridging agent between the sulfolane and heptane. Mutual solubility of the carboxylic acids progressively increases with an increase in the length of the alkyl chain of the carboxylic acids.

The slope of the tie lines is very important when investigating phase separation effects. The relative solubility of carboxylic acid in the sulfolane or the alkane is evident from the tie lines. The gradient of the tie lines obtained in this study show that all the carboxylic acids investigated are more soluble in cyclohexane than sulfolane mixtures, as represented on figure 5.21 (a)-(f). From 5.21 (a)-(f) , it can also be observed that all carboxylic acids with longer alkyl chain than acetic acid that were investigated, are more soluble in the cyclohexane rich layer.

Branching of the carbon chain affects the mutual solubility of both 2-methylpropanoic acid and 3-methylbutanoic acid. Both showed similar solubility to their corresponding straight chains anologues inspite of their non-linear structures. The relatively large two phase region for the (sulfolane + acetic acid + cyclohexane) system suggests that the entrainer sulfolane has high capacity or loading of solute per mole fraction of the solvent (sulfolane), that is small quantities of it would be needed for efficient separation.

Comparing the ternary diagrams for all systems [sulfolane (1) + carboxylic acid (2) + cylohexane (3)] discussed presently, with the ternary diagrams for [sulfolane (1) + carboxylic acid (2) + heptane (3)], it was found that replacing heptane with cyclohexane resulted in a corresponding decrease in the area of the two-phase heterogeneous region as well as a corresponding decrease in the slope of tie-lines. This implies that the solvent sulfolane has a higher solubility, but lower capacity for (carboxylic acid + cyclohexane) mixtures, at the same temperature. Sulfolane is thus a better solvent for extracting carboxylic acid from heptane than from cyclohexane.

Table 5.2.5 presents the results of fitting of modified Hlavatý, beta (β) and log γ equations to the binodal curves. The Hlavatý function gave the best overall fit as compare to beta (β) and log γ function. The NRTL and UNIQUAC models were used to correlate the experimental tie-lines and to calculate the phase compositions of the ternary systems. It was found that the NRTL equation fitted the experimental data significantly better than the UNIQUAC equation.

6.1.3. Ternary systems involving sulfolane (1) + carboxylic acid (2) + dodecane (3) at T = 303.15 K

Previous Work

Chen-Feng and Wen-Churng (1999) studied the ternary liquid-liquid equilibria of [alkane (C10/C11/C12/C14) + 1.4 disopropylbenzene + sulfolane] at T = 322.15 K, T = 348.15 K and T = 373.15 K. It was reported that addition of 1.4, diisopropylbenzene to sulfolane increased the solubility of alkanes in the order of n-decane > n-dodecane > n-tetradecane, and that the relative mutual solubility of 1.4-diisopropylbenzene is higher in (n-decane + sulfolane) than in the (n-dodecane + sulfolane) or (n-tetradecane + sulfolane) mixtures.

It was also reported that the size of the two phase region decreased with an increase in temperature, and from the selectivity data, it can be concluded that the separation of 1.4-diisopropylbenzene from n-decane, n-dodecane or n-tetradecane is feasible with sulfolane as a solvent.

This Work

In this work new LLE data have been obtained for (sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + dodecane) at T = 303.15 K.

The amount of hydrocarbon that is miscible with (sulfolane + carboxylic acid) mixture is dependent on the carbon number and type of carboxylic acid. In the ternary systems, illustrated in figures 5.29-5.34 it can be observed that dodecane is most soluble in the systems containing in pentanoic acid or 3-methylpropanoic acid. It is found that for a particularly carboxylic acid, the solubility of dodecane in sulfolane is inversely related to the area of the two phase region.Solubility of (sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid + dodecane) is dependent on the type of carboxylic acid.

In the ternary systems investigated, the partitioning of carboxylic acid between dodecane and sulfolane is shown to be dependent on both the alkyl group chain length and the structure of the carboxylic acid. In all carboxylic acids the single phase homogenous region increases as the carbon chain length of the carboxylic acid is increased, and it is found that dodecane is most soluble in the carboxylic acid with the long carbon chain (pentanoic acid + sulfolane) mixtures or (3-methylbutanoic acid + sulfolane) mixtures, and least soluble in the carboxylic acid with short carbon chain (acetic acid + sulfolane). All carboxylic acids are more soluble in the dodecane-rich layer than sulfolane-rich layer.

Branching of the carbon chain affects the solubility for both 2-methylpropanoic acid and 3-methylbutanoic acid resulting in both components showing similar solubilities to their corresponding straight chain anologues.

The shapes of the binodal curves for (sulfolane + carboxylic acid + dodecane) system show more skewing towards the dodecane axis than that of the (sulfolane + carboxylic acid + heptane) system. The area of the two phase heterogeneous region for carboxylic acid mixtures is observed to follow this order: acetic acid > propanoic acid > butanoic acid ~ 2-methylpropanoic acid > pentanoic acid ~ 3-methylbutanoic acid.

The relative solubility of an acid in the sulfolane-rich mixture or the alkane- rich is evident from the tie lines. The gradient of the tie lines obtained in this study show that all the carboxylic acids are more soluble in dodecane –rich mixture than in sulfolane-rich mixture. The relatively large two phase region for the (sulfolane + acetic acid + dodecane) system suggest that the entrainer sulfolane has a high capacity or loading of solute per mole fraction of the solvent (sulfolane), that is small quantities of it would be needed for efficient separation.

The mutual solubility of dodecane in sulfolane and carboxylic acids mixtures is dependent on the length and structure of the carbon chains of the carboxylic acid. Mutual solubility of the carboxylic acids progressively increases with an increase in the length of the alkyl chain of the carboxylic acids. Figure 5.42 shows the plot of relative solubilities of carboxylic acid in sulfolane–rich and dodecane-rich layers. In the ternary systems investigated, all the carboxylic acids are more soluble in the dodecane-rich layers than sulfolane-rich layers.

The effectiveness of extraction of the carboxylic acids by sulfolane is given by its selectivity, which is measure of the ability of sulfolane to separate carboxylic acid from dodecane. The selectivity values obtained are 6 for acetic acid, 2 for propanoic acid, 6 for butanoic acid, 16 for 2-methylpropanoic acid, 6 for pentanoic acid and 6 for 3-methylbutanoic acid respectively. From the selectivity data, it can be observed that the separation of all carboxylic acids from dodecane by extraction is feasible, and sulfolane is a good solvent for the separation of mixtures of (3-methylbutanoic acid and dodecane).

Comparing the ternary diagrams for all systems [sulfolane (1) + carboxylic acid (2) + dodecane (3)] discussed presently, with the ternary diagrams for [sulfolane (1) + carboxylic acid (2) + heptane (3)], it was found that for all the ternary systems, replacing heptane with dodecane always results in an increase of the heterogenous (or 2-phase) region. This implies that the solvent sulfolane has higher solubility, but lower solvent capacity for (carboxylic acid + heptane) mixtures at the same temperature and pressure. Sulfolane is thus a better solvent for extracting carboxylic acids from dodecane , than from heptanes, whilst sulfolane shows more selectivity for ternary systems with heptanes than dodecane.

Table 5.19 presents the results of fitting the modified Hlavatý, beta (β) and log γ equations to the bimodal curves. The Hlavatý function gave the best overall fit as compare to beta (β) and log γ function.

The NRTL and UNIQUAC models were used to correlate the experimental tie-lines and to calculate the phase compositions of the ternary systems. It was again found that the NRTL equation fitted the experimental data significantly better than the UNIQUAC equation.

6.1.4 Ternary systems involving sulfolane (1) + alcohol (2) + heptane (3) at T = 303.15 K

Previous Work

Awwad *et al*. (2008) presented liquid-liquid equilibria for pseudo-ternary systems [(sulfolane + 2-ethyoxyethanol) (1) + octane (2) + toluene (3)] at T = 293.15 K. It was found that the area of the two-phase heterogeneous region decreases with increase mass fraction of 2-ethoxyethanol in solvent component, that implies that the existence of more hydrogen bonding interaction between sulfolane and 2-ethoxyethanol resuts in decrease in the area of two-phase region.

It was concluded from the selectivity values that the separation of toluene from octane by extraction with (sulfolane + mass % 2-ethyoxyethanol) was feasible. The comparison between experimental selectivity data of (sulfolane + mass % 2-ethyoxyethanol) with that of (sulfolane + 2-methoxyethanol) for the extraction of toluene from (toluene + octane) mixture at T = 293.15 K was more efficient using (sulfolane + mass % 2-methoxyethanol).

This work

Liquid- liquid equilibrium data of a new ternary system of (sulfolane + methanol or ethanol or 1-propanol or 2-propanol or 1-butanol or 2-butanol, or 2-methyl-1-propanol or 2-methyl-2-propanol + heptane) at T= 303.15 K have been investigated. The amount of hydrocarbon that is miscible with the (sulfolane + alcohol) mixture is dependent on the carbon number and type of alcohol. The ternary diagrams are illustrated on figure 5.43-5.50.

It can be observed that heptane is most soluble in the systems containing (2-methyl-1-propanol and 2-methyl-2-propanol.

It is evident that the amount of hydrocarbon that is miscible with the alcohols is very much dependent on the alkyl chain of the alcohol and the location of the hydroxyl group (-OH) of the alcohol.

It is found that for particular alcohols the solubility of heptane in sulfolane is inversely related to the area of the two phase region. Solubility of alcohols investigated is dependent on the type of alcohol, the partitioning of alcohol between heptane and sulfolane is shown to be also dependent on both the length and the structure of the alcohol. The single phase homogenous region increases as the alkyl chain length of the alcohol is increased, and it is found that heptane is most soluble in the alcohol with long carbon chain(2-methyl-1-propanol + sulfolane) or (2-methyl-2-propanol + sulfolane) and least soluble in the alcohol with short carbon chain (methanol + sulfolane).

Figure 5.60 shows a plot of the relative solubities of the alcohols in the sulfolane-rich and heptane-rich layers. All the alcohols are more soluble in the heptane layer than sulfolane layer. In case of methanol and ethanol, the hydrogen bonding with sulfolane is stronger since these alcohols are completely miscible with sulfolane. However, propanol and butanol alcohols are partially miscible with sulfolane because the hydrocarbon part of these alcohol molecules show diminished interaction with sulfolane even though sulfolane molecule form strong hydrogen bonds (Hwang *et al*.,2008)

From Figure 5.51, the area of the two phase heterogeneous region for alcohol mixtures increase is observed to follow this order: 2-methyl-1-propanol ~ 2-methyl-2-propanol < 1-butanol ~ 2-butanol < ethanol < 1-propanol ~ 2-propanol < methanol.

The relative solubility of an alcohol in the sulfolane or the alkane is evident from the tie lines. The gradient of the tie lines obtained in this study show that all the alcohols are more soluble in sulfolane than heptane mixture. The relatively large two phase region for the sulfolane + methanol + heptane system suggest that the entrainer sulfolane has high capacity or loading of solute per mole fraction of the solvent (sulfolane), that is small quantities of it would be needed for efficient separation.

Mutual solubility of heptane in sulfolane is dependent in the length and structure of the carbon chains of the alcohol. Mutual solubility of the alcohols progressively increases with an increase in the length of the alkyl chain of the acids but it is shown that branching does not increase solubility appreciably.

The effectiveness of extraction of the carboxylic by sulfolane is given by its selectivity, which is measure of the ability of sulfolane to separate alcohol from heptane. The selectivity values obtained are 5 for methanol, 8 for ethanol, 3 for 1-propanol, 6 for 2-propanol, 11 for 1-butanol, 5 for 2-butanol, 8 for 2-methyl-1-propanol and 9 for 2-methyl-2-propanol respectively. From the selectivity data, it can be observed that the separation of all alcohols from heptane by extraction is feasible. Sulfolane is a good solvent for the separation of the mixtures of alcohols from heptane.

Comparing the ternary diagrams for all systems [sulfolane (1) + alcohol (2) + heptane (3)] discussed presently, with the ternary diagrams for [sulfolane (1) + carboxylic acid (2) + heptane (3), there was an increase in two-phase heterogeneous region as well the slope of tie-linesfrom the former systems. This implies that the solvent sulfolane has a higher solubility, but lower solvent power or capacity for (carboxylic acid + heptane) mixtures, at the same temperature and pressure. Sulfolane is thus a better solvent for extracting alcohols from heptane than carboxylic acids from heptane.

Table 5.26 presents the results of fitting of modified Hlavatý, beta (β) and log γ equations, Hlavatý function gave the best overall fit as compare to beta (β) and log γ function. The NRTL and UNIQUAC models were used to correlate the experimental tie-lines and to calculate the phase compositions of the ternary systems. It was found that overall the NRTL equation fitted the experimental data significantly better than the UNIQUAC equation.

6.2 EXCESS MOLAR VOLUMES

6.2.1 Mixtures of (sulfolane + alcohols) at T = 298.15 K

Previous work

Chen *et al*. (2005) presented viscosities and densities for binary mixtures of *n*-methylpiperazine with methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol and isobutanol at T = 293.15 K, T = 298.15 K and T = 303.15 K and atmospheric pressure. It was found that all the investigated systems exhibited very large positive values of viscosity deviation and excess Gibbs energy, and that excess molar volumes were negative over the entire composition range. It was reported that the deviations were attributed to the strong cross association between the alkanol and *n*-methylpiperazine molecules through the hydrogen bond of O-H-N. It was also reported the temperature had significant effect on of viscosity deviation and relatively slight effect on the excess molar volumes and excess Gibbs energy.

This work

Excess molar volumes for eight binary mixture of (sulfolane + methanol or ethanol or 1-propanol or 2-propanol or 1-butanol or 2-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol) at T = 298.15 K have been determined. The aim of the investigation was to determine the influence the increasing carbon chain length of the alcohols on the excess molar volumes ($\mathrm{V_m^E}$)

The excess molar volumes are the results of the intermolecular interactions that are due to the difference between the real and ideal molar volumes. Positive excess molar volumes are the result of the intermolecular dissociation effect resulting in bond breaking of the pure solvents. The negative excess molar volumes are due to association between the solutes molecules and packing.

Table 5.30 show that the excess molar volume values are negative over the entire mole fraction range for all the binary mixtures studied in present work. The negative excess molar volumes indicate that the packing degree in these mixed liquids is higher than in the pure species and in their idealized mixtures. Negative values of excess molar volume suggest a more efficient packing or attractive interaction occurred when sulfolane and alcohol molecular liquids were mixed.

The negative excess molar volumes can be also explained in terms of two opposing effects, expansion in volume due to mutual loss of dipolar association as well as the difference in the size and shape of component molecules and contraction in volume comes from dipole-induced dipole dipole-dipole interactions and donor-acceptor interactions between unlike molecule (Yang-Xin *et al*.,1998).

Assuming that the energy associated with orientational order for all pure alcohols is the same order, the variation in excess molar volume of these mixtures will be due to the variation in magnitude of specific energy in these mixtures. There are specific electron donor interactions between sulfolane and alcohols (Yang-Xin *et al*., 1998).

A negative excess molar volume could be due to an association of the species involved, bringing the molecules closer together, resulting in decrease or contraction of volume, or it could be due to the sympathetic packing effect of the molecule. Packing effects could also contribute either positively or negatively to the excess volumes.The negative excess molar results obtained are due to both the intermolecular effects as well as packing effect (Redhi, 2003). The excess molar volumes curves have a minima ranging from between -0.6257 $cm^3.mol^{-1}$ to -2.2357 $cm^3.mol^{-1}$ at T = 298.15 K.

The excess molar volume at equimolar composition for the binary systems (sulfolane + methanol or ethanol or 1- propanol or 2-propanol or 1-butanol or 2 -butanol or 2- methyl-1-propanol or 2-methyl-2-propanol) at T = 298.15 K, T = 303.15 K and T= 308.15 K is tabulated on Table 6.1.

The excess molar volume is most negative in the case of ethanol and 2-propanol at all the temperatures investigated. The magnitude of excess volumes of alcohols decreases in the following order ethanol > 2propanol > 2-methy-1-propanol > 1-butanol > 2-methyl-2-propanol > methanol > 2-butanol >1-propanol at T = 298.15 K.

From figure 5.62, it can be observed that most of the curves of the alcohols are skewing towards the region of high mole fraction of sulfolane or low mole fraction of the alcohol. The same trend is observed on most of alcohols investigated.

The interaction between the unlike molecules seems to be stronger than the intra-molecular interactions, leading to negative values of excess molar volumes. The kinetic energy of the molecules increases when the temperature increases, and this lead to a decrease of their interaction as the contraction in volume decreases that is excess molar volumes increases (Wang *et al,* 2004). The resulting differences in energies of the molecules and packing effects disrupts the ordered structure of pure component during the formation of the mixture leading to negative effect observed on excess molar volume when as order formation in the mixture leading to negative contribution to the excess molar volume (Iloukhani *et al.,* 2006).

For each binary mixture, excess molar volume data were fitted to the Redlich–Kister equation to correlate the composition dependence of the excess property using equation 4.10. The parameters A_0, A_1, A_2, A_3 and the standard deviations for each binary mixture are shown on table 5.31.

6.2.2 Mixtures of (sulfolane + alcohols) at T = 303.15 K

Previous work

Kinart *et al*., (2007) presented densities and relative permittivities of the binary mixtures of sulfolane with ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol as has been measured as function of composition at T = 303.15 K.

It was reported that the excess molar volumes were negative over the composition range for all systems, the value of molar excess volume became more negative as the number of oxyethylene groups in the glycols increased.

It was concluded that the globular molecules of sulfolane had no significant intermolecular hydrogen bonding capability in pure liquid, and that molecules of glycols are self-associated liquids though inter- and intramolecular hydrogen bonding. It was found that formation of intramolecular hydrogen bonds in the liquid ethylene glycols was more favourable when the molecules of these solvents are in the gauche formations.

This work

Excess molar volumes for binary mixture of sulfolane and alcohols (methanol or ethanol or 1-propanol or 2-propanol or 1-butanol or 2-butanol or 2-methyl-2-propanol or 2-methyl-1-propanol) at T = 303.15 K have been investigated. Table 5.33 shows that the excess molar volume values are negative over the entire mole fractions range, for all the binary mixtures studied in present work. Negative values of excess molar volume suggest that a more efficient packing or attractive interaction occurred when sulfolane and alcohol molecular liquids were mixed. The results are graphically represented in figure 5.62.

The negative excess molar volumes indicate that the packing degree in these mixed liquids is higher than in the pure species and in their idealized mixtures, suggesting that the specific intermolecular interaction such as hydrogen bonding and dipolar interactions of any kind are effective among these chemical species (Kinart *et al.,* 2007). The molecular interactions between the mixing species mainly depend upon the composition, the different molecular sizes and the shapes of the components and experimental temperature.

The globular molecules of sulfolane have no significant intermolecular hydrogen bonding capability in pure liquid, on the other hand, the molecules of alcohols are self-associated liquids through inter and intermolecular hydrogen bonding.

The free sulfolane and alcohol molecules may interact by dipole-dipole forces and or intermolecular hydrogen bonds forming the mixed intermolecular complexes. Similar structural effects have been observed in binary of sulfolane + aliphatic alcohol (normal and branched chain) (Kinart *et al.*, 2007).

From Table 6.1, it is found that the excess molar volumes curves of sulfolane and alcohols have a minima ranging from -1.1461 $cm^3.mol^{-1}$ to -2.1016 $cm^3.mol^{-1}$ at T = 303.15 K. The excess molar volume values are most negative in the case of ethanol and 2- propanol. The magnitude of excess molar volumes of alcohols decreases in the following order ethanol > 2-propanol > 1-propanol > 2-methyl-1-propanol > 1-butanol > methanol > 2-butanol at T = 303.15 K.

For each binary mixture, excess molar volume data were fitted to the Redlich–Kister equation to correlate the composition dependence of the excess property using equation 4.10. The parameters A_0, A_1, A_2, A_3 and the standard deviations for each binary mixture are shown on table 5.34.

6.2.3 Mixtures of (sulfolane + alcohols) at T = 308.15 K

Previous work

Wang *et al*, (2004) presented the excess molar of (cyclohexanone + benzene or toluene or ethylbenzene or styrene) were obtained from the densities over the composition range at temperature T = (293.15 K, 303.15 K, 313.15 K, 323.15 K, 333.15 K, 343.15 K and 353.15 K) and atmospheric pressure.

It was found that the excess molar volumes had shifted in a regular way with the increasing temperature from T = 293.15 K to 313.15 K. It was reported that in each system, a slight decrease in excess molar volumes over the whole mole fraction range was noticeable with increasing temperature.

From the comparison of the minimum values of excess molar volumes for the three mixtures containing an aromatic hydrocarbon at the same temperature. It was concluded styrene was the most favourable one to form close packing with cylohexanone.

This work

Excess molar volumes for binary mixtures of (sulfolane + methanol or ethanol or 1-propanol or 2-propanol or 1-butanol or 2-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol) at T = 308.15 K have been determined.

Table 5.36 show that the excess molar volume values are negative over the entire mole fraction range for all the binary mixtures studied in the present work. The negative excess molar volumes indicate that the packing degree in these mixed liquids is higher than in the pure species and in their idealized mixtures. Negative values of excess molar volume suggest a more efficient packing or attractive interaction occurred when sulfolane and alcohol molecular liquids were mixed.

From figure 5.63 it can be observed that most of the curves of the alcohols are slightly skewed towards the region of high mole fraction of sulfolane or low mole fraction of the alcohol. The interaction between the unlike molecules seems to be stronger than the intramolecular interactions, leading to negative values of excess molar volumes. The kinetic energy of the molecules increases when the temperature increases, that lead to decrease of their interaction as the contraction in volume decreases, that is the excess molar volumes increases (Wang *et al*., 2004).

The excess molar volumes curves have a minima ranging from -1.2016 $cm^3.mol^{-1}$ to - 2.3983 $cm^3.mol^{-1}$ at T = 308.15 K.

The magnitude of excess molar volume of alcohols decreases in the following order ethanol > 2-propanol > 2-methyl-1-propanol >1-propanol >2-butanol > methyl-2-propanol > 1-butanol > methanol.

The excess molar volume at equimolar composition for binary systems (sulfolane + methanol or ethanol or 1- propanol or 2-propanol or 1-butanol or 2 -butanol or 2- methyl-1-propanol or 2-methyl-2-propanol) at T = 298.15 K, T = 303.15 K and T= 308.15 K is tabulated on Table 6.1. The excess molar volume at equimolar composition for binary systems at T = 298.15 K, T = 303.15 K and T = 308.15 K are graphically represented in figure 6.1.

For each binary mixture, excess molar volume data were fitted to the Redlich–Kister equation to correlate the composition dependence of the excess property using equation 4.10. The parameters A_0, A_1, A_2, A_3 and the standard deviations for each binary mixture are shown on table 5.37.

Table 6.1: V_{m}^{E} at equimolar composition for binary systems (sulfolane + Methanol or Ethanol or 1- propanol or 2-propanol or 1-butanol or 2-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol at T = 298.15 K, T = 303. 15 K and T = 308.15

Alcohol	V_{m}^{E} ($cm^3.mol^{-1}$) T = 298.15 K	V_{m}^{E} ($cm^3.mol^{-1}$) T = 303.15 K	V_{m}^{E} ($cm^3.mol^{-1}$) T=308.15 K
Methanol	-1.1016	-1.1165	-1.2046
Ethanol	-2.1403	-2.1658	-2.3983
1-Propanol	-0.6257	-1.4290	-1.4307
2-Propanol	-2.0552	-2.0556	-2.0591
1-Butanol	-1.1803	-1.2846	-1.2347
2-Butanol	-0.8299	-1.1461	-1.3745
2-Methyl-1-propanol	-1.3921	-1.3982	-1.4277
2-Methyl-2-propanol	-1.1109	-1.2409	-1.2443

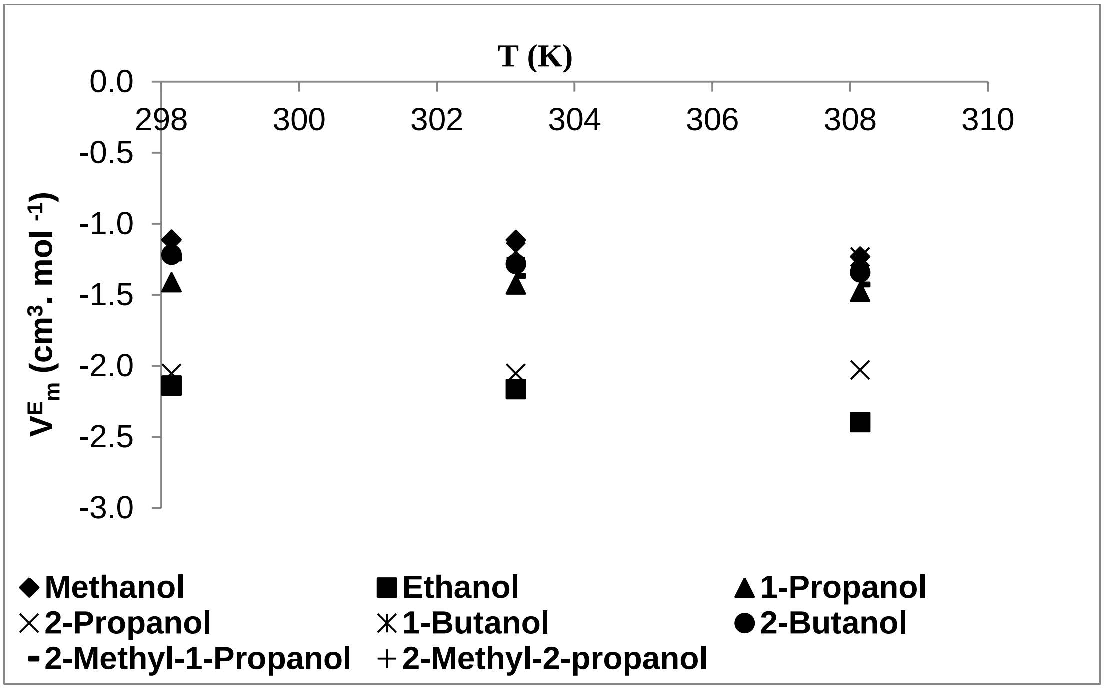


Figure 6.1: V_{m}^{E} for equimolar composition of binary systems (Sulfolane + Methanol or Ethanol or 1-Propanol or 2-Propanol or 1- Butanol or 2-Butanol or 2- Methyl-2-propanol or 2-Methyl-1-propanol at T = (298.15 K, 303.15 K, 308.15 K)

CHAPTER 7

CONCLUSIONS

In this chapter, the experimental work presented in chapter 5 is summarized.

7.1 TERNARY SYSTEM LIQUID-LIQUID EQUILIBRIA

Precise new liquid- liquid equilibria data are presented for the following systems at 303.15 K.

- Sulfolane (1) + Carboxylic Acid (2) + Heptane (3) at T = 303.15 K
- Sulfolane (1) + Carboxylic Acid (2) + Cyclohexane (3) at T = 303.15 K
- Sulfolane (1) + Carboxylic Acid (2) + Dodecane (3) at T = 303.15 K
- Sulfolane (1) + Alcohol (2) + Heptane (3) at T = 303.15 K

7.1.1 Liquid- liquid equilibria for mixtures of sulfolane (1) + carboxylic acid (2) + heptane (3)

Liquid-liquid equilibria for the ternary system (sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or butanoic acid or 3-methylbutanoic acid + heptane) were investigated at T = 303.15 K.

The solubility of carboxylic acid in (heptane + sulfolane) mixtures is inversely related to the size of the two phase region. The area of the two phase heterogeneous region for the carboxylic acid mixtures decrease as the number of carbon in the carboxylic acid increases. The decrease is observed to follow the order: acetic acid > propanoic acid > butanoic acid ~ 2-methylpropanoic acid > pentanoic acid ~3-methylbutanoic acid.

The slope of the tie lines obtained in this investigation showed that all acids are more soluble in heptane-rich layers than in sulfolane-rich layers. The partitioning of carboxylic acids between the heptane-rich and sulfolane rich layers for all the systems studied show that all the carboxylic acids are more soluble in heptane than in sulfolane.

The separation of a carboxylic acid from heptane by extraction with sulfolane is feasible, as can be ascertained from the selectivity data in table 5.1.7. The selectivity values are all greater than 1. Sulfolane has the highest solvent capacity for the extraction of acetic acid, than any of the other carboxylic acids.

The modified Hlavatý, beta (β) and log γ equations were fitted to the experimental binodal data. The Hlavatý function gave the best overall fit when compare to the beta (β) and log γ function.

It was found that the NRTL equation fitted the experimental data significantly better than the UNIQUAC equation.

7.1.2 Liquid- liquid equilibria for mixtures of sulfolane (1) + carboxylic acid (2) + cyclohexane (3)

Liquid-liquid equilibria for the ternary system (sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or butanoic acid or 3-methylbutanoic acid + cyclohexane) was investigated at T = 303.15 K.

The relative solubility of carboxylic acid in the sulfolane or the alkane mixture is evident from the tie lines. The gradient of the tie lines obtained in this study show that all the carboxylic acids investigated are more soluble in cyclohexane than sulfolane mixtures.

From figure 5.21 (a) - (f), it can be observed that the gradient of the tie-lines for 2-methylpropanoic is significantly greater that those for butanoic acid. This could be attributed to the solubilising effect of the two electron realising methyl groups on the terminal carbon of the 2-methylpropanoic acid as opposed to its straight chain isomer. A similar effect is noted for 3-methylbutanoic acid when compared to pentanoic acid.

The area of the two phase heterogeneous region for the carboxylic acid mixtures decrease as the number of carbon in the carboxylic acid increases. The decrease is observed to follow this order: 3-methylbutanoic acid < pentanoic acid< 2–methylpropanoic acid < butanoic acid < propanoic acid < acetic acid.

From the selectivity data, it can be concluded that the separation of all carboxylic acids from cyclohexane by extraction is feasible. It can also be concluded that sulfolane is a good component for separation of the mixtures of (cyclohexane and butanoic acid) and to a lesser extent or (cyclohexane pentanoic acid).

The modified Hlavatý, beta (β) and log γ equations were fitted to the experimental binodal data. The Hlavatý function again gave the best overall fit as compared to beta (β) and log γ function.

7.1.3 Liquid- liquid equilibria for mixtures of sulfolane (1) + carboxylic acid (2) + dodecane (3)

Liquid-liquid equilibria for the ternary system (sulfolane + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or butanoic acid or 3-methylbutanoic acid + dodecane) were investigated at T = 303.15 K.

Liquid-liquid equilibria for the ternary system: sulfolane + carboxylic acids (acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, butanoic acid and 3-methylbutanoic acid) + dodecane were investigated at T = 303.15 K. In the ternary systems investigated, the partitioning of carboxylic acid between dodecane and sulfolane is shown to be dependent on both the alkyl chain length and the structure of the carboxylic acid.

The single phase homogenous region increases as the carbon chain length of the carboxylic acid is increased, and it is found that dodecane is most soluble in the carboxylic acid with long carbon chain (pentanoic acid + sulfolane) or (3-methylpropanoic acid + sulfolane) and least soluble in the carboxylic acid with short carbon chain (acetic acid + sulfolane). All carboxylic acids are more soluble in dodecane layer than sulfolane layer.

Branching of the carbon chain improves the solubility of both 2-methylpropanoic acid and 3-methylbutanoic acid and they it show similar solubilities to their corresponding straight chains anologues. The area of the two phase heterogenous region for carboxylic acid mixtures increase in the order: acetic acid > propanoic acid > butanoic acid ~ 2-methylpropanoic acid > pentanoic acid ~ 3-methylbutanoic acid.

The effectiveness of extraction of the carboxylic by sulfolane is given by its selectivity, which is measure of the ability of sulfolane to separate carboxylic acid from dodecane. Table 5.21 shows that all the selectivity values are greater than 1, implying that separation is feasible in all cases and that sulfolane is an especially good component for separation of (dodecane and 2-methylpropanoic acid) mixtures.

The modified Hlavatý, beta (β) and log γ equations were fitted to the experimental binodal data. The Hlavatý function again gave the best overall fit as compare to beta (β) and log γ function.

It was found that the NRTL equation correlated the experimental tie line data significantly better than the UNIQUAC equation.

7.1.4 Liquid- liquid equilibria for mixtures of sulfolane (1) + alcohol (2) + heptane (3)

Liquid-liquid equilibria for the ternary system (sulfolane + methanol or ethanol or 1-propanol or 2-propanol or 1-butanol or 2-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol + heptane) were investigated at T = 303.15 K.

Solubility of heptane in (sulfolane + alcohol) mixtures is very much dependent on the carbon chain number and the type of the alcohol. The single phase homogenous region increases as the alkyl chain length of the alcohol is increased, and it is found that heptane is most soluble in the alcohol with long carbon chain (2-methyl-1-propanol + sulfolane) or (2-methyl-2-propanol + sulfolane) and least soluble in the alcohol with short carbon chain (methanol + sulfolane). All the alcohols are more soluble in heptane layer than sulfolane layer.

The gradient of the tie lines for 1-propanol and 2-propanol show considerable difference. This could be attributable to greater solubilizing effect of the secondary alcohol (2-propanol), as opposed to primary alcohol (1-propanol). Branching of the carbon chain improves the mutual solubility effect and 2-methyl-2-propanol and to a lesser extent 2-methyl-1-propanol serve as good bridging agents.

The effectiveness of extraction of the alcohols from heptane by sulfolane is given by its selectivity, which is measure of the ability of sulfolane to separate alcohols from heptane. Table 5.28 shows that the selectivity values are in all cases are greater than 1, and separation is therefore feasible. It can also be concluded that sulfolane is a good component for separation of (heptane + 1-butanol) mixtures.

The modified Hlavatý, beta (β) and log γ equations were fitted to the experimental binodal data. The Hlavatý function gave the best overall fit as compare to beta (β) and log γ function.

It was found that the NRTL equation correlated the experimental tie-line data significantly better than the UNIQUAC equation.

7.2 EXCESS MOLAR VOLUMES

The excess molar volumes for binary mixtures of (sulfolane + alcohol) have been determined. The systems are

- Binary mixtures of sulfolane and alcohols (methanol or ethanol or 1-propanol or 2-propanol or 1-butanol or 2-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol) at T = 298.15 K
- Binary mixtures of sulfolane and alcohols (methanol or ethanol or 1-propanol or 2-propanol or 1-butanol or 2-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol) at T = 303.15 K.

- Binary mixtures of sulfolane and alcohols (methanol or ethanol or 1-propanol or 2-propanol or 1-butanol or 2-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol) at T = 308.15 K.

7.2.1 Mixtures of (sulfolane + alcohols) at T = 298.15 K

Excess molar volume for the binary mixtures of sulfolane and alcohols (methanol or ethanol or 1-propanol or 2-propanol or 1-butanol or 2-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol) at T = 298.15 K has been determined.

The excess molar volume values are negative over the entire mole fraction range for all the binary mixtures studied in this work. Negative values of excess molar volume suggest a more efficient packing or attractive interaction occurred when sulfolane and alcohol molecular liquids were mixed. Negative excess molar volume could be due to an association of the species involved, bringing the molecules closer together, resulting in decrease or contraction of volume, or it could be due to the sympathetic packing effect of the molecule.

The excess molar volume is most negative in the case of ethanol and 2-propanol at all the temperatures investigated. At T = 298.15 K, the magnitude of excess volumes of alcohols decreases in the following order ethanol > 2-propanol > 1-propanol > 2-methyl-1-propanol > 2-butanol > 2-methyl-2-propanol > 1-butanol >methanol.

Figure 5.63 is the graphical representation of excess molar volume for the binary mixtures of (sulfolane + alcohol) at T = 298.15 K. It can be observed that most of the curves of the alcohols are skewing towards the region of high mole fraction of sulfolane or low mole fraction of the alcohol.

The excess molar volumes curves of sulfolane and alcohols have a minima ranging from -1.1121 cm^3.mol^{-1} to -2.1405 cm^3.mol^{-1} at T = 298.15 K . The excess molar volume values are most negative in the case of ethanol and 2-propanol. The free sulfolane and alcohol molecules may interact by dipole-dipole forces and intermolecular hydrogen bonds forming the mixed intermolecular complexes. Similar structural effects have been observed in binary mixtures of (sulfolane + aliphatic alcohol) involving normal and branched aliphatic chain.

7.2.2 Mixtures of (sulfolane + alcohols) at T = 303.15 K

The excess molar volumes of the binary mixtures of sulfolane and alcohols (methanol or ethanol or 1-propanol or 2-propanol or 1-butanol or 2-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol) at T = 303.15 K have been determined.

Table 5.33 show that the excess molar volume values are again negative over the entire mole fraction range for all the binary mixtures studied in the present work. Negative values of excess molar volume suggest a more efficient packing or attractive interaction occurred when sulfolane and alcohol molecular liquids were mixed. The results are graphically represented in figure 5.62.

The excess molar volumes curves of sulfolane and alcohols have a minima ranging from -1.1165 cm^3.mol^{-1} to -2.1658 cm^3.mol^{-1} at T = 303.15 K. The excess molar volume values are most negative in the case of ethanol and 2-propanol. The magnitude of excess molar volumes of alcohols decreases in the following order ethanol > 2-propanol > 1-propanol > 2-methyl-1-propanol > 2-butanol > 2-methyl-2-propanol > 1-butanol > methanol at T = 303.15 K.

Comparing the magnitude of excess molar volume minima for binary mixtures of (sulfolane + alcohol) at T = 298.15 K to the binary mixtures of (sulfolane + alcohol) at T = 303.15 K showed corresponding decrease in the excess molar volume minima over the entire range of mole fraction range with the increase in experimental temperature.

7.2.3 Mixtures of (sulfolane + alcohols) at T = 308.15 K

The excess molar volumes of the binary mixtures of sulfolane and alcohols (methanol or ethanol or 1-propanol or 2-propanol or 1-butanol or 2-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol) at T = 308.15 K have been determined.

The excess molar volume values are again negative over the entire mole fractions range for all the binary mixtures studied in the present work. Negative values of excess molar volume suggest a more efficient packing or attractive interaction occurred when sulfolane and alcohol molecular liquids were mixed. The results are graphically represented in figure 5.63.

The excess molar volumes curves have a minima ranging from -1.2319 $cm^3.mol^{-1}$ to - 2.3983 $cm^3.mol^{-1}$ at T = 308.15 K. The excess molar volume of alcohols decreases in the following order ethanol > 2-propanol > 1-propanol >2-methyl-1-propanol > 2-butanol > 2-methyl-2-propanol > 1-butanol > methanol.

Comparing the magnitude of excess molar volume minima for binary mixture of (sulfolane + alcohol) at T = 303.15 K to the binary mixture of (sulfolane + alcohol) at T = 308.15 K showed the decrease in the excess molar volume minima for the latter system at T = 303.15 K over the entire range of mole fraction range.

CHAPTER 8

REFERENCES

Abrams D., Prausnitz J.M., *AIChEJ*, **1975,** 21, 116.

Aguila-Hernandez J., Trejo A., Garcia F.B., Molnar R., *Fluid Phase Equlibria*, **2008**, 267, 172 -180.

Ahamd S.A., Tanwar R.S., Gupta R.K., Khanna A., *Fluid Phase Equilibria*, **2004**, 220, 189 -198.

Awwad A., Al-Dujaili A. H, Al-Haideri A. A., Essa Hatim M., *Fluid Phase Equilibria*, **2008**, 270, 10-14.

Ahmad A.B., Othham M. R., ScienceAsia, **2010**, 81-84.

Benoit R.L., Charbonneau J., *Canadian Journal of Chemistry*, **1969,** 47, 4195.

Bertleff W., Roeper M., Sava X., "Carbonylation" in Ullmann's Encyclopedia of Chemical Technology Wiley, **2003**, 217.

Bondi A., Physical Properties of Molecular Crystals, Liquid and Glasses,**1968** Wiley New York.

Bowen B. H., Irwin W. M., Coal Gasification & Fischer-Tropsch, Indiana Center for Coal Technology Research Report, **2006.**

Briggs S.W., Commings E.W., *In Eng. Chem*, **1943**, 35, 411.

British Colombia Ministry of Water, Land and Air Protection Report, Water Quality Guidelines for Sulfolane, **2003**, Komex International, Canada, USA, UK and Worldwide, 4 – 7.

Broughton, D.B.; Asselin B., George F., UOP Process Div., Universal Oil Prod. Co., Des Plaines, IL, USA. World Petrol. Congr., Proc.,**1968,** Meeting Data,*4,* 65-73.

Chen J., Duan L., Mi J., Fei W., Li Z., *Fluid Phase Equilibria*, **2000**, 173, 109– 119.

Chen S., Lei Q., Fang W., Fluid Phase Equilibrium, **2005**, 234, 22-33.

Chen-Feng K., Wen-Churng L, *Fluid Phase Equilibria*, **1999**, 163, 9-20

Chen-Feng K., Wen-Churng L, *Fluid Phase Equilibria*,**1999**, 165, 67-77.

Colin E. Webb, Julian D. C. Jones J, Handbook of Laser Technology and Applications, **2004**,Taylor & Francis ,1738-1740.

Derr E.L., Popapoules M.J., *Am Chem*. Soc, **1959**, 81, 2285.

Dibner J.J., Butin P., *J. Appl. Poultry Res*, **2002**, 11, 453-463.

Dunn, C. L., Freitas E. R.; Hill E. S.; Sheeler J. E. R., *Jr. Proc., Ann. Conv. Nat. Gas Processors Assoc. Am.,Tech. Papers* , **1965,** 44, 55-8.

Garguri I., Tasic A., *J Serb Chem Soc*, **2002**, 67, 5681-5686.

Gmehling J., Li J., Schiller M.A, *Ind Eng. Chem Res*.,**1993,** 32 (1), 178.

Goodenbour J. W.; Carlson G.J., (Shell International Research), **1962.**

Govender U. P., Thermodynamics of Liquid Mixtures: experimental and Theoretical Studies on the Thermochemical and Volumetric Behaviour of some Liquids and Liquid Mixtures, PhD Thesis, UKZN*, **1999***, 226.

Harding K. E, May L.M and Dick K. F, Organic. Chemistry, McGram Inc, **1975**,40, 1664-1665.

Ho S., Chen J., Li M., *Journal of the Chinese Institute of Chemical Engineers*, **2007**, 38, 349-354.

Hwang I.-C., Park S.-J., Choi J.-S., Fluid Phase Equilibria, **2008**, 269, 1-5.

Im J., Lee H., Lee S., Kim H., *Fluid Phase Equilibria*, **2006**, 246, 34-38.

Iloukhani H, Rezaei-Sameti M. Basari-Parsa J, *J. Chem Thermodynamics*, **2006**, 38, 975 -982.

Ivonar R.G., Aleksandar Z.T, Bojan D.D., Mirjana L.J.K., Slobodan P, S, *J. Serb.Chem.Soc*, **2002,** 67, 8-9.

Kinart C. M., Cwiklinska A., Maj M., Kinart W., *Fluid Phase Equilibria*, **2007**, 262, 244-250.

Khodakov, Wei C., Pascal F., “Advances in the Development of Novel Cobalt Fischer-Tropsch Catalysts for Synthesis of Long-Chain Hydrocarbons and Clean Fuels” Chemical Review 107, **2007**, 1692-1744.

Lal R K., Jagadamba B., Sodankoor G. T., Indian Petrochemicals Corp. Ltd., (India). Eur. Pat. Appl.,**1991**.

Langmuir I., The distribution and Orientation of molecules, Third Colloid symposium, Monograph, The chemical Catalogue Company,**1925**, Inc, New York.

Lee S., Kim H., *J. Chem Eng. Data*, **1995**, 40, 2, 499-503.

Letcher T.M., Moollan W.C., Nervines J.A., *J. Chem. Thermodynamics,* **2000**, 32, 579-586.

Letcher T.M., Redhi G.G., *J. Chem Thermodynamics*, **2001**, 33, 1643-1653.

Letcher T.M., Reddy P., *Fluid Phase Equilibria*, **2004**, 219, 107-112.

Letcher T.M., Reddy P., *Journal of Chemical Thermodynanics*, **2005**, 37, 5, 415- 421.

Letcher T.M., Chemical Thermodynamics for Industry, **2004**, Royal Society of Chemistry, 76-77 & 78-79.

Letcher T.M., and Reddy P., *Fluid Phase Equilibria*, **2004**, 219, 107-112.

Letcher T.M., Whitehead P.G., J. Chem. Thermodynamics, **1996**, 28, 843 - 849.

Maciuca A., Dimitru E., Fajula F., Hulea V., *Applied Catalysis A: General*, **2008**, 338, 1-8.

Mahmoudi J., Lotfollahi M. N., *J.Chem Thermodynamics*, **2010**, 42, 466-471.

Mohammad D.F.S., Mohsen-Nia M., Modarress H., *Journal of Chemical Thermodynamics*, **2006**, 38, 4, 405-412.

Mohsen-Nia M., Paikar I.,*The Journal of Chemical Thermodynamics*, **2007**, 39,1085 -1089.

Mohsen-Nia M., Modaress H., Doulabi F., Bagheri H., *J. Chem. Thermodynamics*, **2005**, 37, 1111-1118.

Morrison R.T, Boyd R.N, Organic Chemistry, **1992**, 6th Edition, Mc Gram Inc.

Naicker P. K, Thermodynamics of Liquid mixture, *PhD Thesis*, UKZN, **2000**, 110 -114.

Naicker P.K, Thermodynamics of Liquid mixtures containing N-methyl-2-Pyrrolidone, **1997**, Thesis, UKZN, 160 -165

Rappel R., de Gios L. M., Mattedi S., *Fluid Phase Equilibria*, **2002**, 263 -276.

Reddy P., Thermodynamic Properties of liquid Hydrocarbon mixtures Containing ionic liquids, **2003**, *Thesis*, UKZN, 150.

Redhi G.G., Liquid-Liquid Equilibria Related to the Fuel Industry, **1996,** *Thesis,* UKZN, 21-22, 69-70

Redhi G.G., Thermodynamics of liquid mixtures containing carboxylic acids, **2003**, Thesis, UKZN, 7, 104-112, 116.

Riddick J.A., Bunger W., Sakano T.K., Organic Solvents Physical Properties and Methods of Purification, **1986**, 4th Edition, John Wiley & Sons, New York.

Santiago R. S., Aznar M., *Fluid Phase Equilibria*, **2007**, 253, 137-141.

Santiago R.S., Aznar M., *Fluid Phase Equilibria*, **2007**, 259, 71-76.

Sen A, Srivasta M., Regression Analysis Theory, Method and Applications, **1990**, Springer Verlang, New York.

Senol A., *Fluid Phase Equilibria*, **2005**, 227, Issue 1, 87-96.

Senol A., *Journal of Chemical Thermodynamics*, **2004**, 36, 11, 1007-1014.

Senol A., Lutfullah S., *The Journal of Chemical Thermodynamics*, **2006**, 38, 5, 578-58.

Senol A., *Fluid Phase Equilibria*, 2005, 227, 1, 87-96.

Senol A., *J. Chemical Thermodynamics*, **2005**, 37, 1104-1110.

Šerbanović S. P., Kijevćanin M. L., Radović I.R., Djordjević B. D., *Fluid Phase* Equilibrium, **2006**, 239, 69-82.

Shaohui G., Wu Z.; Zhang M., Li W., Tao K., *Industrial & Engineering Chemistry* Research, **2006**, 45, 2229-2234.

Sharipov A., *Russian Journal of Applied Chemistry*, **2003**, 76, 1, 108-113.

Wang H., Lui W. J., *Chem Thermodynamics*, **2004**, 36, 936-946.

Wang H., Lui W., Wu Y., *J.Chem Thermodynamics*, **2004**, 36, 1079-1087.

Webb C. E., Jones J.D.C., Handbook of Laser Technology and Application, **2004**, Taylor and Francis Inc, 1738-1740.

Wen-Churng L., Nies-Hsin K., *J.Chem Eng. Data*, **2002**, 47, 4, 1007-1011.

Wilson G.M., Deal C.H., Ind. Eng. Chem Fundamentals, **1962**, 1, 20.

Yang C., Peisheng M.A.,Zhoung Q., Chinese, J. Chem. Eng., **2004**, 12, 4, 537-542.

Yang-Xin Y., Yi-Gui L., *Fluid Phase*, **1998**, 147, 207-213.

Yang-Xin Y., Lui J., Gao G., *J.Chem Data*, **2000**, 45, 570-574.

Yanwei Z., Haijun W., Kaishen D., *Journal of Chemical Thermodynamics*, **2007**, 39, 291-297.

Young, E. E., Shell International Research, **1962.**