RECOVERY OF AROMATIC AND BICYCLIC AROMATIC COMPOUNDS

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
INTEGRATED DUAL DEGREE
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(With Specialization in Hydrocarbon Engineering)

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DECLARATION

I hereby declare that the work being presented in the dissertation entitled "Recovery Of Bicyclic Aromatic Compounds " in partial fulfillment of the requirements for the award of the degree of Integrated Dual Degree (B. Tech with Specialization in Hydrocarbon Engineering) and submitted in the Department of Chemical Engineering of Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during the period from May 2012 to July 2013 under the supervision of Dr. I. D. Mall, Department Of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India. The matter presented in this report has not been submitted by me for the award of any other degree of this or any other institute.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

Light cycle oil (LCO), which is a product of the catalytic cracking of the vacuum gas oil in the FCCU, contains a good percentage of aromatics, monocyclic and polycyclic. These compounds need to be separated from the streams, as these are not very suitable in the further conversion units or can add value to the specialized streams. In this study, liquid-liquid extraction has been used to recover the aromatics (p-xylene) and bicyclic aromatics (naphthalene) from model oil. The efficacies of various solvents have been tested for recovery of aromatics and bicyclic aromatics. Equilibrium data have been presented for compound p-xylene and naphthalene using the solvents: dimethyl sulfoxide (DMSO), N-methyl pyrrolidone (NMP) and dimethyl formamide (DMF). Phase diagrams have been plotted for all these systems at the normal temperature of industrial separation which are very much important in the industries. Regression of the experimental points is done by NRTL and UNIQUAC equations. Qualitative analysis is done on the basis of distribution coefficients and separation factors and graphs are produced for the same. DMF was found to be very good solvent for recovery of p-xylene and naphthalene. Various solvents are tested for their suitability for the recovery of aromatics. Quaternary systems are studied for NMP and DMF systems and their efficiency for the recovery of bicyclic aromatic compounds is studied. NMP was found to have a very good separation factor and distribution coefficient for naphthalene. LSER model has been used to correlate the various physiochemical properties of the solvents to the distribution coefficients and separation factors.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Cyclic and bicyclic aromatic compounds are one of the important chemical intermediaries and also used in manufacture of many chemicals. Bicyclic aromatic compounds like naphthalene are used for medical purposes (Alajbeg et al., 2001). Naphthalene is used in the manufacture of plastics, resins, fuels, and dyes. It is also used as a fumigant insecticide that works by turning directly from a solid into a toxic vapor (NPIChttp://npic.orst.edu/ingred/naphth.html). Paraxylene is primarily consumed in the manufacture of terephthalic acid and dimethyl terephthalate that are used in the production of polyester polymers. Light Cycle Oil, which is major source of cyclic aromatic compounds, is a product stream from catalytic cracking unit. It is mainly used as a fuel. But this fraction contains also many raw materials like 2, 6-dimethylnaphthalene (2,6 -DMNA) which can be used as raw materials for engineering plastic (PEN plastic), polymer liquid crystal, etc. The raffinate from the LCO can be used as diesel fuel if we can improve the cetane number of the light cycle oil by dearomatizing the fraction. Aromatic organic hydrocarbons and heterocycles are a source for almost a large part of one-third of all industrially produced organic basic raw materials. Aromatics compounds such as benzene, phenol, naphthalene, anthracene, and their homologues, are derived from raw materials which have their source from the refinery aromatic feedstock. Another main source of cyclic aromatic compounds in the petrochemical refinery is reformate from the catalytic reforming process. In industries, separation is done by solvent extraction from the streams.

1.2 Aromatics in the Refinery

The fuels for the three dominant transportation means: cars, trucks or trains, and airplanes- are gasoline, diesel fuel, and jet fuel, respectively. Diesel oil is the prime mover of all the vehicles on the road. Saturated and aromatic hydrocarbons are the main constituents of diesel fuels. Saturated hydrocarbons are dominant diesel components that include n-paraffins, isoparaffins, and cycloparaffins (naphthenes). N-paraffins are good for combustion as they have a good cetane number and so are desirable in diesel oil. However paraffins with higher b.p, if present in large amounts cause cold flow problems. Benzenes, indanes, indenes, naphthalenes, biphenyls, acenaphthenes, phenenthrenes, anthracenes and the naphthenophenantherenes constitute the majority of aromatic compounds. Diesel has a good amount of diaromatic hydrocarbons. A small amounts of polycyclic aromatic hydrocarbons (3+ring aromatic HCs) such as chrysenes, pyrenes, benzanthracenes and perylenes can also be present. A typical specification of diesel oil is given in the Table 1.1.

Table1.1: Typical Fuel specifications for a class A2 diesel fuel (analysis performed by Shell Global Solutions)

Analysis	Method	Standard A2 Diesel
Carbon (wt %)	Flash combustion	87±0.8
Hydrogen (wt %)	Flash combustion	12.1±0.6
Sculpture (wt %)	IP373	0.125
Aromatic content	IP391/mod	
Monoaromatic (wt %)		20.7
Diaromatic (wt %)		11.0
Triaromatic (wt %)		2.3
Total (wt %)		34.0
Cetane no.	ASTM D613	46.3, 46.5, 47.6
Average Cetane no.		46.8
Viscosity at 40 °C (cSt)	IP71/ASTM D445	3.510
Density at 15 °C (kg m^{-3})	IP365	862.4

1.2.1 Meeting diesel fuel requirements*:*

Various methods of satisfying the norms of diesel fuel in the refinery. Fractionating the fraction, addition of improvers and treating them with more complex hydrocarbon processing options are some of the techniques. Modern techniques can help to change low-grade blend stocks, such product from cracker or catalytic cracking unit to good diesel precursors.

1.2.2 Increasing cetane value:

One of the ways to increase the cetane number is to use a suitable chemical addition such as alkyl nitrates to upgrade the ignition. Paraffins have a high cetane value and also these react effectively to chemical additives. Multiple ring-aromatics, however have a low cetane value have and give a poor response. Figure1.1 shows the relationship between hydrocarbons with their cetane number. We can see that naphthalene have lowest of cetane numbers and paraffins have very good cetane efficiency.

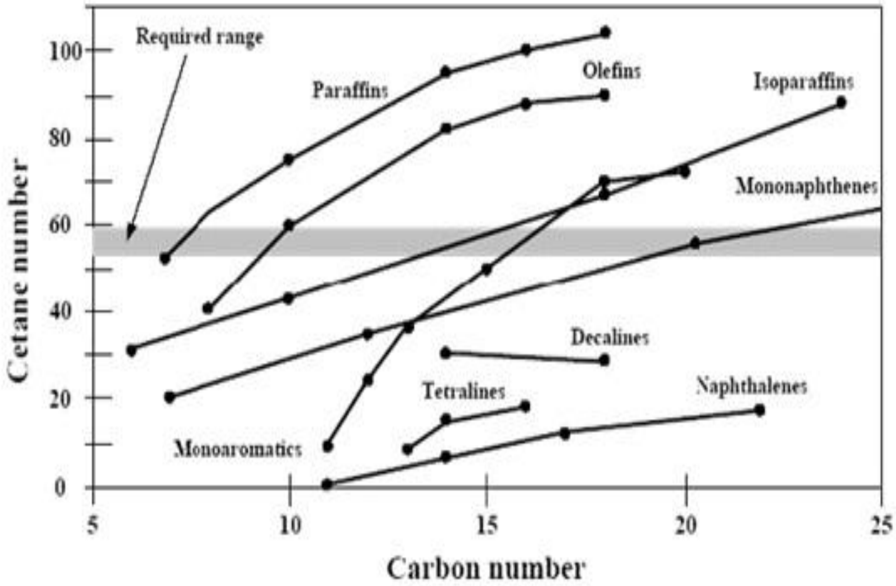


Fig 1.1 Cetane Number corresponding to various molecular types (Naszer et al., 2012)

1.2.3 Fluid Catalytic Cracking

FCC is one of the vital units of conversion in the petrochemical unit. It is used to convert heavy gas oils, namely, vacuum distillates into more valuable products such as LPG gasoline, cycle oils, olefin rich light HCs that may be further processed to even more valuable products and fuel oils. The decant oil can be used as feedstock for carbon black and needle coke manufacture. FCC is a low pressure, intermediate to high temperature process. This process may be designed and operated to achieve either of the processing objectives, either to maximization of middle distillates or maximization of gasoline and LPG. In the former case the catalytic cracker essentially functions as a tiebreaker. The transition from one from to another can be made rapidly without expensive revamps and turn around. This process can accept a wide variety of feedstock's thereby enhancing the total refinery flexibility.

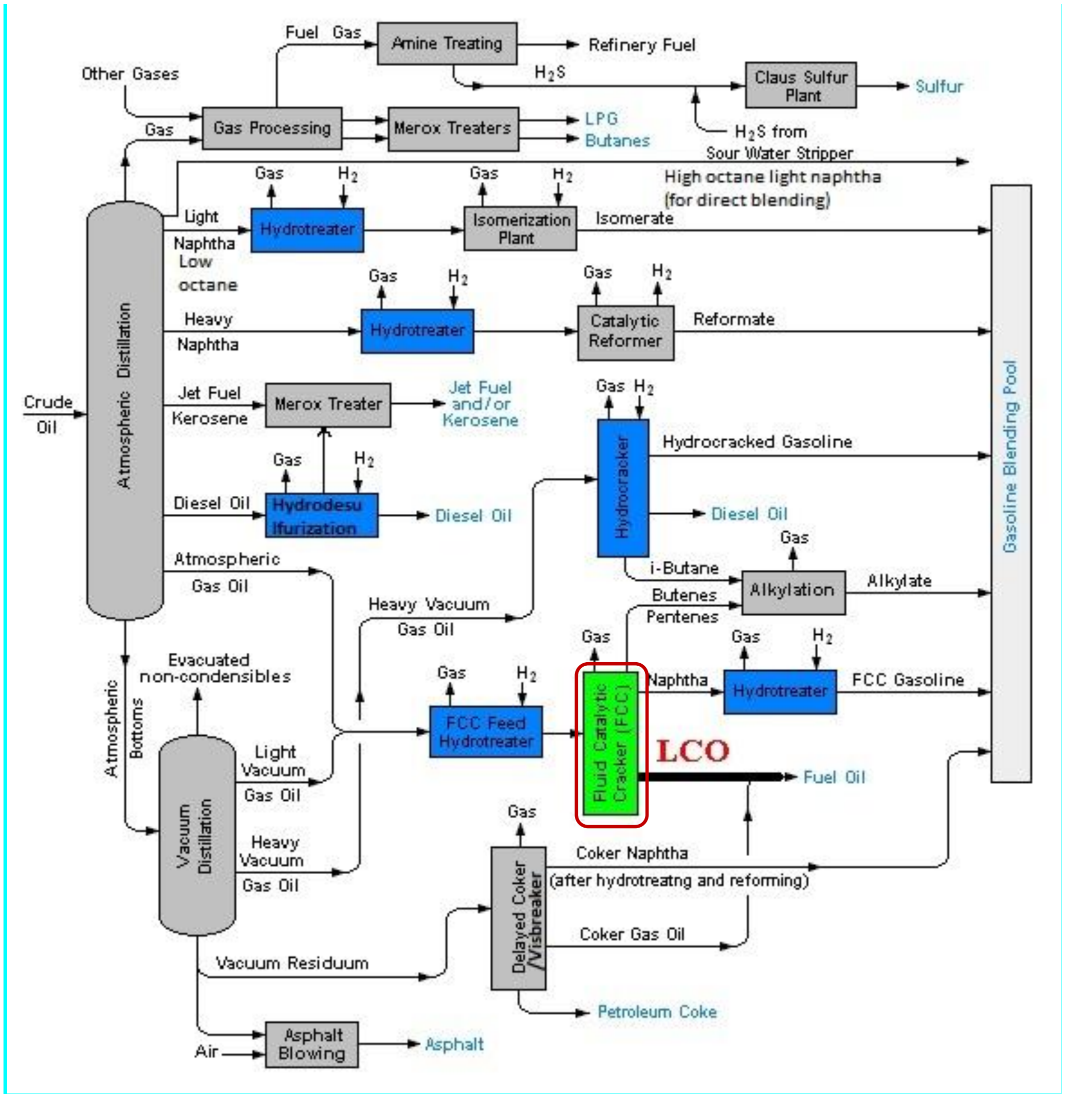


Figure 1.2 Schematic of a refinery

A catalyst for FCC usually consists of an active substance (which determined the course of desirable reactions) applied onto a carrier substance (mostly alumina) having a largely extended surface. In some cases, some other substances (promoters) are added to improve the characteristics of catalytic conversion processes. The particles (granules) of a catalyst possess an enormous porosity and therefore a very large internal surface area. The activity of a catalyst is due mainly to the surface of pores rather than to their external surface. The name of a catalyst depends upon the process where it is used, for instance, reforming catalysts, cracking catalysts, etc.

Vacuum gas oils in the boiling range of 350 – 550 °C are used as feedstock in FCC process. These are obtained by distillation of atmospheric residue under vacuum. The cut point of VGO is controlled to the limit the concentration of sulphur, nitrogen and metals in the FCC feed which deactivate catalyst to reduce yield and cause pollution problems due to SO_x and NO_x emissions. Asphaltenes in the feedstock increase the yield coke yield and may result in higher regenerator temperatures.

1.2 Light Cycle Oil

Table : 1.3 Light Cycle Oil

Trade Name	Light Cycle Oil (LCO)
CAS Number	64741-59-9
Product Family	Petroleum Hydrocarbon Middle Distillate
Synonyms	LCO, FCCU LCO, FCCU Light Cycle Oil, Middle Distillate Cutter Oil, Untreated Diesel Fuel Blending Component, Light Catalytic Cracked Distillate (Petroleum), C9-C25 Petroleum Hydrocarbons.

1.3.1 Characterization of LCO (Light Cycle Oil)

The total international installed FCC capability is about 15 million barrels per stream day, which amounts to a total production of 3.1 million barrels per stream day of Light Cycle Oil. The bulk of catalytic cracking facility is in N. America, closely trailed by Asia and Europe. Operating parameters vary which rely on the demand. Physical and chemical properties of LCO are given in the Table 1.4.

Light cycle oil and streams form the coking unit have lesser cetane numbers(16-24) as compared to the streams directly from the crude sources(~50). LCO has a .2 to 2.5 % sulphur content. A large part of the sulphur is in DBT. A LCO fraction can have at times as much as eighty percent of aromatics which is quite high as compared to other streams.

Table 1.3: Physical and Chemical properties of Light Cycle Oil

Physical State	Liquid
Color	Transparent, slightly yellow to amber
Odor	Characteristic, Kerosene like
Specific Gravity	0.94 to 0.95 at 60° F
Ph	Not applicable
Vapor Density	AP 50 (Air = 1 at 70°F)
Boiling Point/Range	150° to 415°C (302° to780°F) (ASTM D-2887)
Melting/Freezing Point	LT - 12°C (10°F) (ASTM D-97)
Vapor Presure	0.8 to 1.8 mm Hg at 20° C (68°F) or LT 0.1 Reid-psia at 38° C (100°F)
Viscosity (cSt @ 40 °C)	3 to 7.5 (ASTM D-445)
Solubility in Water	Negligible to slightly soluble in cold water (LT 0.005 to 0.04 %)
Volatile Characteristics	Volatile Organic Compounds (VOCs) Content = 30% below 400°F

A distribution of the aromatics, bicyclic aromatics and the 3 ring aromatics is given in the Figure 1.2. More than seventy percent of all the aromatics present in the LCO is bicyclic whereas the remaining is almost equally distributed between 1 ring and three ring aromatics. Bicyclic and tricyclic aromatics have poor combustion efficiency. These have a smaller cetane value and result in poorer blending ability of the fraction. So it requires desaturating and opening the components to upgrade the fraction. This makes it possible for the light cycle oil to be treated as better diesel oil.

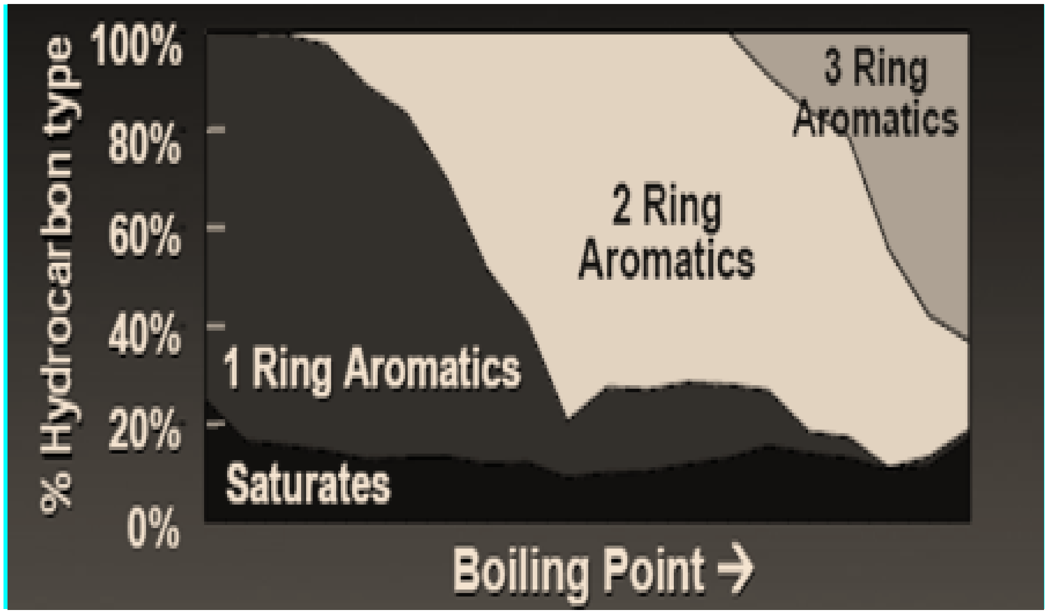


Figure 1.3 Hydrocarbon Distribution of LCO

(Source: http://www.aiche.org/uploadedFiles/Conferences/DepartmentUploads/PDF/2008_ Midwest_Regional_Frey_High_Value_Xylenes.pdf. Accessed on 20/7/2012.)

1.3.2 LCO in the clean Fuels Refinery

The removal of aromatics is very much wanted to increase the cetane number of the LCO fraction. This is required so that it can be used as a blending stock for the diesel oil. Major parameters which affect the quality of FCC product are the quality of feed, type of catalyst, and operational conditions of the unit. Stricter rules and environmental regulations make the refineries to follow healthy practices. These include the resulting parameters of the fuels like diesel and gasoline. Many of these restrictions focus upon reducing the density, increasing the cetane numbers and reducing the levels of poly-nuclear aromatic compounds apart from reducing sulphur concentrations.

1.4 Other Sources of Aromatics in Refinery:

The manufacture of aromatics feed-stock originates from the catalytic reformer of a petrochemical stream of heavy naphtha range (say 110°C – 410°C) and loaded in naphthelenes. Table 1.2 shows a typical composition of a cut from catalytic reforming. A typical stream that meets the criterion is the naphtha stream from a hydrocracker unit. Thus to meet the requirement of this stream, a hydrocracker synthesizing section of a fuel refinery design is necessary. Production of naptha is maximized by operating this unit at optimum conditions. This is achieved by running reactor with smaller space velocity and a larger recycle rate. A very good source of naphthenic feed which can be fed into catalytic reformer is the cracked naphtha from the catalytic hydrotreater. A cracker or a steam cracker in the petrochemical unit produces naphtha which when hydrotreated can yield high naphthenic reformer feed-stock.

Table 1.4 Typical composition of a C_6-C_8 cut from catalytic reforming.

	Component	Content in % wt
Aromatics	Benzene	1 to 8
	Toluene	8 to 24
	Xylenes	30 to 50
	C_{9+} (including mesitylene)	0.1 to 6
Paraffins	C_5	0.6 to 6
	C_6	1.5 to 11
	C_7	1 to 7
	C_8	0.5 to 2
	C_9	0 to 1
Naphthenes+olefins		0.5 to 2

Source : Wauquier, 2000.

A thorough inspection of how impurity is scattered according to the no. of carbon atoms, shows that their concentration decrease significantly moving from C_6 to C_8. Several current reforming units generate effluents from which a C_8 cut can be secluded by easy refinement. The fraction is prepared of xylenes which, after a clay finish-treatment to get rid of olefins, are of the preferred purity.

Using highly rich naphtha with napthenes in catalytic reformers produces aromatics with a little of linear alkanes and alkenes. The operation and capital investment for separation of aromatics at the downstream is very high. So the need of BTX compounds is very demanding and they are to be separated from the non aromatic compounds as much as possible. An additional process of a LLE extraction plant is added to the refinery arrangement to selectively clean up the aromatic stream. This is a very suitable method to separate the paraffins and BTX compounds by LLE extraction. The aromatic compounds are then separated in the respective units where benzene and o-xylene are separated by distillation and crystals of p-xylene are separated. Meta-xylene is made from its isomers to separate it from the streams rather than by distillation.

The removal of aromatic compounds present in the feed for the cracking unit in the refinery will be very much beneficial. Not only do they engage a huge part of the efficiency of the furnaces but also they put additional duty on the separation section for the C5+-aliphatic compounds and the presence of aromatic compounds in the feed to the cracking unit decreases the thermal efficiency. Furthermore, the traces of aromatic compounds in the feed is very much harmful for the radiation zones as they foul the zones by aggravating the coking of the coils and also for the Transfer line Exchangers (Meindersma et al., 2005).

1.5 Liquid-liquid extraction in Refineries

Processes of extraction, extractive and azeotropic rectification, absorption, and extractive crystallization, which use selective solvents, are widely used in petroleum processing and petrochemistry. As far back as 1950s–1960s, effective agents were suggested for separation and purification of petroleum products: sulfolane, N-formylmorpholine, and N-methylpyrrolidone.

The recovery of aromatic compounds (benzene, toluene, ethyl benzene and xylenes) from a mixture of C_4 to C_{10} aliphatic hydrocarbons mixtures is not easy because these hydrocarbons have close boiling points and often these compositions form very difficult to separate azeotropes. The usual processes for the recovery of these aromatic and aliphatic hydrocarbon mixtures are

Aromatic content (wt %)	**Process most suitable**
20-65	Liquid liquid extraction
65-90	Extractive distillation
> 90	Azeotropic distillation

Liquid-liquid extraction is one of the vital industrial techniques, especially in petroleum processing, where it is used for the recovery of various compounds. Aromatics are mainly found in the naptha feed from the reformer. As per Weissermel and Arpe (2003), no practicable processes are in use for the separation of aromatic and aliphatic hydrocarbons below twenty percent of aromatics in the feed mixture. This study focuses on the separation of aromatic hydrocarbons from the feed stream of naphtha crackers, which may contain up to 25% aromatics. Separating pure components by distillation is a very strenuous process and at times mixtures form azeotropes, solvent extraction proves to be a very useful process for the recovery of aromatics (Ahmad et al., 2004).

Refineries all over the world nowadays prefer to extract the aromatics from the reformate rather than blend them into gasoline. The reasons for this are the first is to meet the ever-growing demand of BTX and other aromatics by the petrochemical and other chemical industry. The second is the stringent restrictions on how much aromatic gasoline can contain due to the various environmental norms and policies, and guidelines issued by the various governments. For these two reasons, the current tendency is to take apart the various aromatics in the reformate into product streams rather than blend them into gasoline.

In liquid-liquid extraction, solvent properties play a very important role in the recovery of desired products and equilibrium characteristics. Investigation are carried out on recovery of aromatics from various feed stocks using different solvents (Bendebane et al., 2010; Hansmeier et al., 2010).

Typical solvents used for the process of LLE are polar compounds such as Dimethyl Formamide (DMF), n-methyl pyrrolidone (NMP), n-formyl morpholine (NFM), diethylene glycols, sulfolane, propylene carbonate. Sulfolane and DEG are used in extraction processes. These help to separate aromatic compounds from low boiling point fractions like naptha or gasoline.After the process, these compounds are difficult to recover by only using the distillation nprecess as these have a very close boiling temperatures of the solvent and the extracted component. So, there are very few studies regarding the recovery of compounds from high b. point compounds like light cycle oil.

Benham et al (1967) studied the removal of aromatics from light cycle oil using the liquid extraction process. Water along with furfural was used to recover aromatics from the light cycle oil. Then he used a mixture of naphtha and xylene to extract again the compounds from the solvent in the extract phase. This process was called as redex process. Using this technique, the raffinate oil's cetane improved a lot. However experiments on the use of re-extraction techniques for the recovery of aromatic compounds were not upto satisfaction. Recovery of expensive bycyclic-aromatics from light cycle oil using LLE was reported by Kim et al (2003). The efficiency of the solvents like sulfolane, dimetyll solfoxide, diethylene glycol and dimethyl formamide was tested to ascertain the suitability of extraction towards bicyclic aromatic components. For dearomatization of light cycle oil , it was found that dimethyl sulfoxide to be a good solvent. In addition to this, the consequence of parameters on recovering bicyclic-aromatic compounds was studied by LLE extraction using dimethyl sulfoxide. The effect of water in the feed was also discussed. It was also shown that distribution coefficient of bicyclic aromatic components was reduced with increasing water content and the selectivity in reference to *n*-nonane was also increased. Also the effect of temperature was reported on the distribution coefficient and selectivity.

Many works have been done by different researchers for recovery of aromatics by LLE using different solvents (Kim et al., 2008; Radwan et al.,1997; Kumar et al., 2011; Jin et al., 2003; Heidari et al., 2012). Dimethylformamide (DMF) is aprotic polar solvent widely used in various chemical processes (Prasad et al.,2008). N-methyl-2-pyrrolidone (NMP) is a dipolar aprotic solvent used in aromatic extraction for it has a high selectivity towards aromatics (Alkhaldi et al, 2009). Dimethyl sulfoxide (DMSO) is a polar aprotic solvent soluble in both, aqueous and organic media (Andreattaa et al, 2007). All these are organic solvents that can be used for recovery of the aromatic and bicyclic aromatic compounds. Recently many works have been done to ascertain the feasibility of these solvents in liquid liquid extraction. (Chen et al., 2013; Mohsen-Nia et al., 2005; Modarress et al., 2005; Al-Jimaz et al., 2006; Alkhaldi et al.,2009).

In this study p xylene is taken as a representative of cyclic aromatic compound and naphthalene as a representative of bicyclic aromatic compounds. Extraction of p xylene and naphthalene is studied from a mixture of 2,2,4-Trimethylpentane(isooctane) using various solvents – Dimethylformamide (DMF), Dimethyl Sulfoxide (DMSO) and N-Methyl-2-pyrrolidone(NMP).

1.6 Objective

The present study deals with removal of p-xylene and naphthalene from model oil. Following aims have been set for the present study:

- To study the recovery of naphthalene and p-xylene from model oil (isooctane) with the solvents namely DMF, DMSO and NMP, and to prepare the liquid-liquid phase diagrams at 30°C and atmospheric pressure.
- To model the experimental data with the help of UNIQUAC and NRTL models.
- To correlate the efficiency of various solvents to their physicochemical properties with the help of LSER model
- To study the quaternary systems for solvents DMF and NMP and make a qualitative analysis on the recovery of aromatics and bicyclic aromatics.

CHAPTER 2

LITERATURE REVIEW

2.1 Review on Aromatic Extraction

In past, aromatic extraction from different systems has been carried out using different processes. Table 2.1 provides a brief review of research work in this area. It can be observed that appreciable work has been carried out in the field of aromatic extraction. However, the system analysed are majorly naphtha reformate, lube oil etc. Also, many papers related to extraction of aromatic compounds from vacuum distillates and lubricating oil has been published.

In this field, significant work has been done by **Kim et al.** (2003). In this paper, they investigated the separation and recovery of valuable aromatic components (bicyclic aromatic components: carbon number 10–12) in LCO by solvent extraction method. They estimated the distribution equilibrium of certain industrial solvents - Sulfolane, dimethylsulfoxide (DMSO), diethyleneglycol, and dimethylformamide. **Kim et al**. (2003) also examined the process of separation and recovery for dimethylnaphthalene (DMNA) mixture with 10 structural isomers in LCO using experimental results of the previous work and that of equilibrium re-extraction.

Further, it can be observed that many people are working on the field of extraction of poly aromatic hydrocarbons from marine sands and other sand samples. These research works mainly concentrate on the study of effect on extraction efficiency by extraction cycles and hold up time. (**Marian et al., 2002; Librando et al., 2004; Agnieszka et al., 2010**).

Supercritical extraction is also a popular research topic. Many papers have been published in which carbon dioxide, water and other compounds in supercritical state have been used for extraction of aromatics. However, most of these research concentrate on poly-aromatic hydrocarbons and generally they are limited to solid extraction. Usually, the study of effect of temperature, pressure and solvent polarity forms the major part of the research work. **(Agnieszka, 2010; Librando et al., 2004)**

Table 2. 1 Major research papers in the field of aromatics extraction

Author	**System**	**Brief Description**	**Operating conditions**
1. Solvents			
1.1 Sulfolane			
Kao et al., 1999	Alkane(C10–C14) octyl benzene using sulfolane	UNIQUAC , NRTL parameters estimated	323.15, 348.15 373.15 (K)
Chen et al., 2000	Six ternary systems : Mixture of n-hexane with benzene/ toluene/ xylene recovered with the help of sulfolane. Mixture of n-octane with benzene/toluene/xylene recovered with the help of sulfolane. Three quaternary systems of n-hexane, n-octane, benzene, xylene taken three at a time and recovered with the help of sulfolane One quinary system : Mixture of n-hexane, n-octane, benzene, toluene with the help of sulfolane	LLE data of all the mentioned systems was used to calculate NRTL coefficients. They used this data to predict the LLE data of ternary systems.	298.15. K Atmospheric pressure
Rappel et al., 2002	Mixture of p- xylene/toluene/n-hexane taken two at a time recovered with sulfolane	NRTL and UNIQUAC activity coefficient models were estimated	310.15 K and 320.15 K

Kim et al., 2003	Light cycle oil using SUL, DMSO, DEG & DMF	Effect of temperature and moisture content was studied	30 – 52 (^oC)
Nia et al., 2007	n-hexane, toluene, m-xylene, propanol, and water using sulfolane	Phase diagrams were constructed for the systems. Determined interaction parameters for NRTL and UNIQUAC models	303.15 K
Santiago et al., 2007	nonane+undecane+(benzene or toluene or m-xylene using sulfolane	Studied 3 ternary systems. used NRTL and UNIFAC-LLE models	298.15 K and 313.15 K
1.2 Furfural			
Grieken et al., 2008	Lubricating oil using furfural	Extraction of aromatics from lubricating oil using furfural has been studied. Emphasis has been given in identifying a suitable thermodynamic model for the system.	-
Hoseini et al., 2009	Lube oil using furfural	Different co-solvent to feed volume ratios (ranging from 0.0 to 0.5). and optimum temperature was determined	323.15K to 343.15K
1.3 DMSO			
Su Jin Kim et al., 2003	Light cycle oil using SUL, DMSO, DEG & DMF	Effect of temperature and moisture content. DMSO asserted as a good solvent for recovery of aromatic compounds and selectivity for nonane.	30 – 52 (^oC)
1.4 Carbonates			
Ali et al., 2003	Naptha reformate using propylene carbonate	Phase equilibrium of the extraction of aromatics from naptha reformate with propylene carbonate has been studied	303-333 K
Nia et al., 2006	Mixture of benzene/BTX with ethyl carbonate	The liquid–liquid equilibrium data were correlated with	313.5 K

	with cyclohexane as co solvent	the UNIQUAC and NRTL activity coefficient models.	
Nia et al., 2010	toluene or m-xylene with co solvent hepatne using ethyl carbonate	The partition coefficients and the selectivity factor of the solvents using NRTL and UNIQUAC	298.25- 313.15 K
Fazlali et al., 2012	Petrochemical naphtha reformate using a mixture solvent of 1-cyclohexyl-2-pyrrolidone and ethylene carbonate	Phase equilibria data was given and regressed using the UNIFAC group contribution method.	300 - 330 K
2. OTHERS			
Radwan et al., 1997	naphtha reformate (b.p. 60–135°C) using a mixed solvent of dimethylformamide (DMF) and ethylene glycol (EG)	The phase equilibria for the extraction of aromatics from naphtha reformate in a mixed solvent of dimethyl formamide (DMF) and ethylene glycol (EG) have been correlated using the UNIFAC group contribution model. The extraction runs were carried out at different temperatures, solvent compositions and solvent-to-feed ratios and optimum found out.	25 – 45 ^{o}C at solvent to feed ratios 1:1, 2:1, 3:1
Gfrerer et al., 2002	Contaminated soil samples using acetone and n-hexane	A comparison of Soxhlet extraction and a new extraction technique, fluidized-bed extraction, has been conducted. The extraction of polycyclic aromatic hydrocarbons (PAHs) on variation of the number of extraction cycles and the holding time was studied	-
Librando et al., 2003	Marine sediments and soil samples using super-critical CO_2	Effect of Temperature (50 to 80°C), Pressure (230-600 bar) and three organig modifiers (methane, *n*-hexane and toluene), added at 5 %/vol on the extraction of polycyclic	50 to 80°C 230-600 bar

		aromatics hydrocarbons was studied. Using methanol as a co-solvent increased yield and higher temperaures decreased yield.	
Yu et al., 2003	Water sample using β-Cyclodextrin epichlorohydrin copolymer	12 aromatic compounds as model compounds and GC-MS and UV spectrophotometry for detection. It was found that the optimum range for pH for extraction of aromatic compounds is 2.5 – 5.0. The method has high extraction efficiency with recoveries of 90% at .02 - 1.67ppm levels.	-
Meindersma et al., 2005	Heptanes, toluene mixture using ionic liquids	Various ionic liquids were tested and best one found for aromatic extraction	40 – 75 ^{o}C
Agnieszka et al., 2010	contaminated soil samples using subcritical water	A rapid sequential subcritical (superheated) water extraction method for polycyclic aromatic hydrocarbons (PAHs) in contaminated soil and sediment is presented. The effect of polarity of water, temperature and pressure was studied.	50 – 200 (^{o}C)

Librando et al. (2004) have used supercritical fluid extraction (SFE) to recover polycyclic aromatic hydrocarbons (PAH). They recovered PAH from samples of marine sediment organic pollutants that were there in tad amounts. They extracted at different temperatures and pressures using CO_2 at a very high temperature and the effect of three organic modifiers (methanol, n-hexane and toluene), added at 5%/vol, at the same temperature and pressure conditions, were then considered.

Similarly, Agnieszka et al. (2010) used superheated steam for the extraction of polycyclic aromatic hydrocarbons (PAHs) in contaminated soils and sediments. They tried to increase the selectivity and by decreasing the polarity of water by rapid increase of extraction temperature from 45-50^{o}C to 200-210^{o}C at the moderate pressure (≈10 MPa).

Recently interest has been generated in the use of ionic liquids. Many ionic liquids, (mebup)BF_4, (mebupy)CH_3SO_4, (bmim)BF_4 (50 °C) and (emim) tosylate (75 °C) have been used (Meindersma et al., 2005). Meindersma et al., found the selectivity of toluene/ heptane the above mentioned solvents are a higherby a factor of 1/2 compared to those obtained with sulfolane (Stol/hept =30.9, Dtol =0.31 at 40 -C), which is the most industrially used solvent for the extraction of aromatic hydrocarbons from a mixed aromatic/aliphatic hydrocarbon stream. Even though these solvents give a commendable performance, economic constraints make them industrially unsuitable (Wytze et al., 2005).

Apart from the above mentioned categories there is a variety of other research related to extraction of aromatics. Extraction of carcinogenic aromatic amines using calixarenes and extraction using β-Cyclodextrin epichlorohydrin copolymer can be suggested as few examples in this category (Serkan et al., 2009).

An addition to the studies on LCO is done by Pasadkis et al. Pasadakis et al. (2011) carried out the LLE of the LCO fraction and studied the process using acetonitrile and its mixtures with methanol and water at around 50°C and 1:1.5 solvent-to-feed ratio. The yield of raffinate was found to increase with increased moisture content in the solvent, while it was unaffected in the presence of MeOH. Detailed composition study of the LCO feed stock and its extraction products using FTIR and GCMS techniques, revealed characteristic distribution patterns of individual saturated and aromatic hydrocarbons in the raffinate and extract fractions. The developed analytical protocol provides detailed compositional information of the extraction products and can be used efficiently in future studies dealing with the upgrading of the LCO.

Significant recent developments have taken place in the field of LLE using carbonates. Mainly propylene carbonate (Ali et al., 2003) and ethyl carbonate (Nia et al., 2006; Nia et al., 2010; Fazlali et al., 2012) are used for extraction. Ali et al. (2003) developed the LLE phase diagram whereas Nia et al. (2006, 2010) and Fazlali et al. (2012) estimated the UNIQUAC and UNIFAC parameters.

As indicated in Table 2.1, there has been appreciable work on equilibrium data for various ternary and quaternary chemical systems. In most of the cases various thermodynamic models like NRTL, UNIQUAC, Wilson equation etc were tested for the equilibrium data obtained. The best model for each system was ascertained.

In another set of research works, investigators have attempted to modify the existing models like NRTL, Wilson equation so that they can be better predictors of the system. The modifications were based on comprehensive consideration of the molecular physics of the system. These modified models were later tested on equilibrium data of various ternary and quaternary systems to prove their superiority (Nagata et al., 1991; Feng et al., 1994).

2.2 Review on Modeling and LSER Theory

Recent works in the field of LLE data generation for different compounds include the use of various correlations for the consistency of data like Othmer Tobias, Hand's and Bachman's correlation. Again the activity and physical properties as well as the efficiency of solvents used for liquid liquid extraction have been correlated using various strategies. The most important and contemporary among them is the use of LSER theory which takes into account the physical properties of the solvents. The researchers in this field try to correlate various physiochemical parameters of generally used solvents to the various molecular properties of the solvents. Significant work in this regard has been done by Ghanadzadeh et al. (2012, 2013), Uslu et al. (2009, 2010), etc. The various works are presented in Table 2.2.

Table 2.2: Major contemporary works in the field of LLE data generation and correlation of solvents

Author	System	Brief Description	Operating conditions
Ghanadzadeh et al., 2012	water + phosphoric acid + 1-octanol	Othmer Tobias and Hand's plot used for consistency. Katritzky LSER model used to correlate distribution coefficient and separation factors.	Normal pressure and temperature from 298.2-318.2K
Uslu et al., 2010	Water + malic acid + diluents	Separation factor and Extraction efficiency reported and correlated by LSER model	1 atm pressure and 303.2 K
Uslu et al., 2009	Water + leuvilinic acid + solvents	Distribution factor and Extraction efficiency reported. Also Freundlich, Langmuir and LSER model parameters regressed.	1 atm pressure and 298.15 K
Hasan et al., 2009	Organic solvents used to recover tripropylamine withlactic acid	LSER modelling of reactive extraction at different loading ratio of solvent.	1 atm pressure and 298.5 K
Senol et al., 2012	Alcohol used to extract pyruvic acid from water	LLE diagrams produced along with optimizing the conditions for efficient extraction of acid.	Normal pressure and temperature.
İnci et al., 2012	**T**ridodecylamine used to recover succinic acid	LSER model used on reactive extraction process. Equilibrium and kinetic studies are performed.	298.15 K and 1 atm pressure.

CHAPTER 3

EXPERIMENTAL AND THEORY

3.1 Experimental

3.1.1 Materials

Analytical grade compounds Isooctane and P-xylene have been used with a minimum assay of 99.5 % and 99 % respectively, procured from SD fine chemicals. Naphthalene procured form Himedia Laboratories Limited with a minimum assay of 99% has been used. Solvents DMSO, NMP and DMF are procured from MERCK with mass fraction purity not less than 0.99. All materials were used without further purification. Model oil used in the study was prepared by mixing 10 ml of isooctane (sp. gr. =0.688 at 20^{o}C) with para-xylene (sp. gr. =0.866 at 20^{o}C) or naphthalene to make the feed. To obtain other desired paraffinic content in the model oil as suggested by the experimental design, appropriate amount of isooctane was added. Amount of solvent to be added was calculated by the experimental requirement. Solvents tested in this study are NMP, DMF and DMSO.

3.1.2 Apparatus and procedure

In the first part of the experiment, solubility of solvent in isooctane and vice versa is determined. The switch to the two-phase region can be observed as appearance of another layer in the stirred solution. This gives the first two points in the phase diagram that lie along the horizontal axis.

In the second part, the solubility data was obtained by cloud point method in a glass cell (Peschke et al., 1995). The points defining the arc will be determined by starting from the two-phase region and adding xylene until the system switches into one phase. Known mixtures of prescribed composition of isooctane and solvent were prepared in the glass cell and p-xylene was added drop by drop till the two layers merge into one single layer. The amount of p-xylene added was noted. Whole of this time temperature was maintained using water jacket within an accuracy of ± 0.1 K. For naphthalene, naphthalene was added till naphthalene remains soluble in the two phase region. Final weight of naphthalene added was noted. All the readings were taken three times and average was taken to be the final reading. This transition can be observed by disappearance of the layers in the stirred solution.

In the third part, tie lines are determined experimentally. This will be done by choosing a point from the two-phase region and determining the compositions of the two phases formed. Tie line data was measured by preparing ternary mixtures of the compounds in 250 ml flasks. The flasks were put in temperature controlled shaking incubator for 8 hrs to mix the mixture thoroughly The experiments were done in an orbital shaker maintained at a constant temperature, in this case, at 30^{o} C. The mixture of solvent and model oil was agitated in a temperature-controlled orbital shaker regulated by a precision ±0.1 K at a constant speed of 150 rpm for required time period. For thermodynamic studies of the system, the system has to reach equilibrium. Thus, the solution was kept in the shaker for 8-10hrs, as was estimated from the literatures the required time for attainment of equilibrium. Then the mixture was allowed to settle in small diameter glass vessel for 4 hrs to separate it into two phases. Formation of well defined interface occurred within a minute of transferring the mixture to small diameter tube. However, solutions were kept for 4 h in the small diameter tubes so as to ensure clear distinction between the split liquid phases. The phases are separated using separating funnel. Both the phases are weighed accurately and analyzed for their compositions. To cover the entire range of two phase region, mixtures were made by keeping the isooctane and solvent fixed and gradually increasing the amount of third component. The conical flasks were filled as much as possible to avoid the diffusion of liquids into vapor phase.

3.1.3 Analytical Measurements

The liquid samples are analyzed using gas chromatograph (GC) with FID. Detector temperatures are kept at 250^{o}C. Injection temperature at 80^{o}C with a ramp rate of 10^{o}C was used. A capillary column of length 30 m and ID 0.53 mm (film thickness 0.88µm) was used for the analysis by GC. High purity nitrogen is used as the carrier gas at a flow rate of $40cm^{3}$/min. The GC response factor for each component in the sample mixtures were obtained by calibration .Standard mixtures were used as calibration solution. All weighing measurements were made with analytical balance within an accuracy of ± 0.001g. For each reading, a 0.4 µl of sample was taken and injected into GC. The compositions of standard samples were obtained by mass.

3.2 Liquid- liquid extraction

3.2.1 Process

Liquid-liquid extraction is a separation technique that takes advantage of the differences in solubility between the components of a homogeneous liquid feed in an appropriate solvent. Adding a partially miscible solvent to the feed causes a second liquid phase to appear and the more soluble components are selectively transferred toward it.

In the figure 3.1, a feed is brought in contact with another liquid solvent which is not miscible. The object is to recover the solute. This results in two fractions: the extract contains the preferred extracted solute rich in solvent and the raffinate which is the residual feed solution containing small amount of solute.

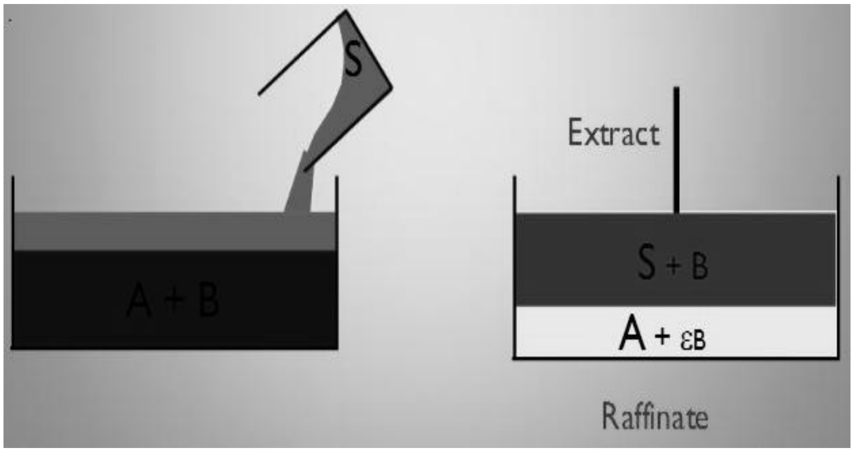


Figure 3.1 : Formation of Extract and Raffinate phases in Liquid-Liquid Extraction

(Source: http://www.scribd.com/doc/22381091/Liquid-Liquid-Extraction. Accessed on 20/7/2012)

Selection of the solvent, conditions prevailing while operating the unit, Operation mode, types of extraction column used and various criteria used while designing are some of the parameters which should be taken care of while designing the extraction operations.

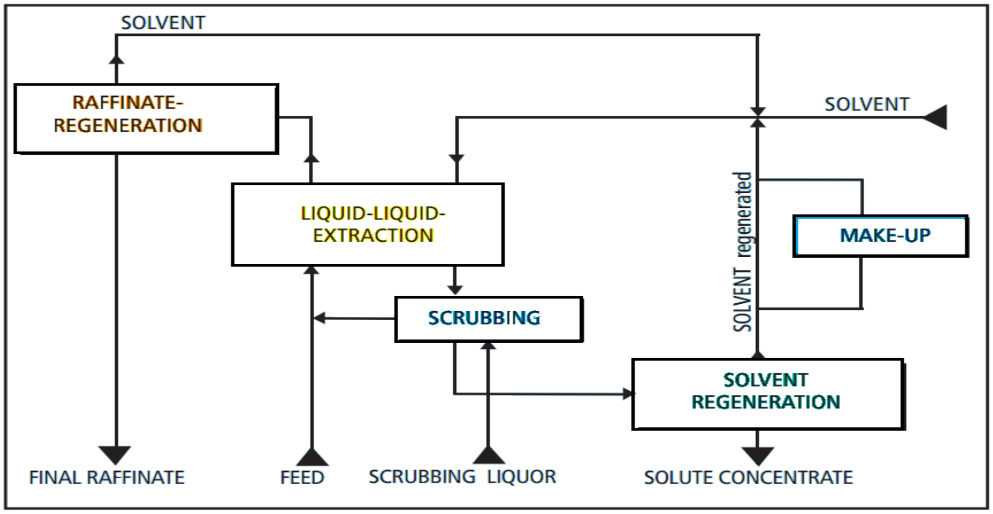


Figure 3.2 Block diagram of liquid- liquid extraction

(Source:http://www.schulzpartner.com/prospekte/extraktion-en.pdf. Accessed on 20/7/2012.)

3.2.2 Solvent Properties:

Generally solvents used in refinery applications are either glycols: di-, tri- and tetra-ethyleneglycols (abbreviated to DEG, TEG and TETRA respectively); amides: N-methylpyrrolidone (NMP), N-formylmorpholine (NFM); or oxygenated derivatives of sulfur-bearing molecules such as dimethylsulfoxide (DMSO) or tetramethylenesulfone (sulfolane) or dimethylformamide (DMF). They certainly have the general properties possessed by industrial solvents: these are stable thermally and chemically, non-toxic and less corrosive, easily available and economic in cost.

3.2.3 Physical Properties:

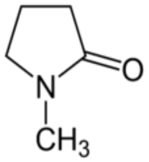
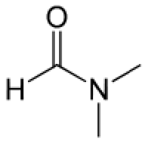
In addition to the above mentioned properties, all the solvents have:

- A sufficiently low crystallization temperature so that they can be implemented without elaborate equipment. At the most, solvents such as sulfolane, DMSO and NFM, which have the highest crystallization temperatures, require steam tracing on some storage tanks and lines.

- A boiling temperature much higher than that of xylene (= 140 °C) which is generally the least volatile of the aromatics to be extracted. The solvent can therefore be regenerated from the extract by easy, and consequently economical, distillation.
- A specific gravity close to or greater than 1.1, thereby ensuring a gravity differential with the hydrocarbons in the feed (density at 20°C between 0.660 and 0.880 g/cm^3) which promotes proper phase settling and extractor operation.
- A viscosity that may be high at ordinary temperature, especially for glycols, but which is always lower than 2.5 mPa.s at the operating temperature in the extractor and consequently favorable to rapid mass transfer kinetics.

A brief overview of the physical properties of some major solvents used for aromatics extraction is given in Table 3.1

Table 3.1: Physical properties of the major aromatics extraction solvents.

Pure solvent	**Developed formula**	**M (kg/kmol)**	**T_f (°C)**	**T_b (760 mmHg)(°C)**	**ρ (kg/m^3) (at 20°C)**	**μ (mPa.s)/ Θ (°C)**
Diethyleneglycol (DEG)	$H(OCH_2\text{—}CH_2)_2OH$	106.1	-8	245	1 116	35.7/20 0.97/140
Triethyleneglycol (TEG)	$H(OCH_2\text{—}CH_2)_3OH$	150.2	-7	288	1 123	49/20 0.70/140
Tetraethylene-glycol (TETRA)	$H(OCH_2\text{—}CH_2)_4OH$	194.2	-4	291 (300 mmHg)	1 125	61.9/20 1.8/150
Sulfolane		120.2	27.6	287	1 266 (at 30 °C)	10.3/30 2.5/100
N-methylpyrro-lidone (NMP)		99.1	-24.4	202	1 027	1.65/25 1.3/30
Dimethylsulfoxide (DMSO)	$CH_3\text{—} SO\text{—}CH_3$	78.1	18.5	189	1 080	1.99/25 1.6/35
Dimethyl formmamide (DMF)		99.13	-24	204	1028	.92/20

3.3 Yield & Selectivity

The main variables which can quantize extraction are yield and selectivity of the desired compound to be separated. In the following paragraphs both these concepts have been explained:

The distribution coefficient (D_i) is defined as the ratio of composition of component i in extract to that in raffinate and is given as:

$$D_i = \frac{y_i}{x_i} \tag{3.1}$$

where, y_i and $x_{i,}$ respectively denote the mass fraction of component i in the extract phase and that in the raffinate phase after a run.

Yield of component i (Y_i) is defined as:

$$Y_i = Ey_i/R_o x_{i,o} \tag{3.2}$$

where, $x_{i,o}$ denotes the mass fraction of component i in the feed. E refers to the mass of the extract phase after a run and R_o denotes the mass of the feed.

Selectivity of component i ($\beta_{i,j}$) is the ratio of the distribution coefficient for component i to that for component j. It is calculated by following expression:

$$S_{i,j} = d_i/d_j \tag{3.3}$$

Selectivity gives a measure of the ability of a solvent to differentiate between the alkanes and the aromatics. For an efficient separation, it is necessary that the aromatic content in solvent should be high and the alkane content should be less. In other words, selectivity should be high for efficient separation.

Mass balance of component i is given by:

$$R_o x_{i,o} + E_o y_{i,o} = R x_i + E y_i \tag{3.4}$$

where, E_o and R_o, respectively, denote the initial mass of extract phase and that of raffinate phase after a run.

In general, solvent properties for extraction are dependent on many other factors. Some of these are moisture content, the temperature of extraction, etc. The effect of these two factors is mentioned below,

- Addition of water: Addition of water to a solvent, selectivity is increased and capacity is decreased.
- Temperature variation: Increasing the temperature enhances solvent capacity at the cost of its selectivity.

In the extraction course, the temperature and moisture content of the solvent are two influential parameters for the extraction step, but also have an influence on downstream units. Therefore, they are optimized for every method taking into account all the units that create it.

3.3 Thermodynamic Modeling of LLE Equilibria

Traditionally, the models which permit the reproduction of the solute-solvent interactions are classified into three groups [*Tomasim J and Persico, (1994]*). Those based on the simulation of liquids by means of computers, those of continuum, those of the super molecule type. In the models classifiable into the first group, the system analyzed is represented by means of a group of interacting particles and the statistical distribution of any property is calculated as the average over the different configurations generated in the simulation.

Especially notable among these models are those of Molecular Dynamics and those of the Monte Carlo type. The continuum models center their attention on a microscopic description of the solute molecules, whilst the solvent is globally represented by means of its macroscopic properties, such as its density, its refractive index, or its dielectric constant. Finally, the super molecule type models restrict the analysis to the interaction among just a few molecules described at a quantum level which leads to a rigorous treatment of their interactions but does not allow us to have exact information about the global effect of the solvent on the solute molecules, which usually is a very long range effect.

Several parameters affect the equilibrium between two liquids. Some of these are the properties of the components, compositions in both the phases, and temperature of analysis. An estimation of the distribution is done by following a suitable equilibrium model. In this study, universal quasi-chemical model (UNIQUAC) is used to regress the experimental points of the equilibrium.

In this theory, optimized interaction parameters between each pair of components are taken into account, which can be obtained by experiments. The UNIQUAC model is solved to the experimental compositions by optimizing the interaction parameter (a_{ij} and a_{ji}). The optimized interaction parameters can also be correlated with temperature. Apart from this model, the NRTL model has been very successful in modeling numerous systems. The theory behind these models is discussed below:

3.3.1 UNIQUAC

Universal Quasi Chemical (UNIQUAC) is a model which takes into consideration activity coefficient and is used to describe liquid-liquid equilibriums. This model is based theoretical on lattice -theory and considers a first order approximation of interacting molecule surfaces in statistical thermodynamics to come to the results. The model uses a two liquid mixture approach. So it is not fully satisfied and consistent. This model uses the concept that the local gradient around one molecule does not depend upon the local concentration around other type of molecules. This has been experimentally proven that this assumption has very little effect on the activity coefficients used in the model (McDermott et al., 1976).

Equations

UNIQUAC model describes the activity coefficients of component i of a binary mixture by a combinatorial and a residual contribution to the equation

$$\ln(\gamma_i) = \ln\left(\gamma_i^C\right) + \ln(\gamma_i^R) \qquad (3.5)$$

First term is a deviation term which gives the effect of molecular shape in departure from ideal solubility. And the second term is a correction term for the enthalpy which is due to interaction of varying molecules on mixing.

Combinatorial contribution:

This term takes into account the molecular shape of different molecules and changes the mixture's entropy. The excess entropy γ^C is determined from the properties of the compounds, which uses Van-der Waals volume-r_i and surface areas-q_i of the the compounds in pure state.

$$\ln\left(\gamma_i^C\right) = 1 - V_i + lnV_i - \frac{z}{2}q_i\left(1 - \frac{V_i}{F_i} + ln\frac{V_i}{F_i}\right) \qquad (3.6)$$

Volume fraction is defined as

$$V_i = \frac{r_i}{\sum_j r_j x_j} \qquad (3.7)$$

Surface area fraction given by F_i

$$F_i = \frac{q_i}{\sum_j q_j x_j} \qquad (3.8)$$

Z is taken to be the coordinate no. which denoted the effectively surrounding molecules. It takes a vale of ten generally. This value is determined by taking into account both the factors of average value of cubic =6 and hexagoalpacking of z=12 that are considered to be round balls.

At dilution taken to infinity, the combinatorial contribution of a two liquid mixture becomes

$$\begin{cases} \ln\gamma_i^{C,\infty} = 1 - \frac{r_1}{r_2} + ln\frac{r_1}{r_2} - \frac{z}{2}q_1\left(1 - \frac{r_1q_2}{r_2q_1} + ln\frac{r_1q_2}{r_2q_1}\right) \\ \ln\gamma_2^{C,\infty} = 1 - \frac{r_2}{r_1} + ln\frac{r_2}{r_1} - \frac{z}{2}q_2\left(1 - \frac{r_2q_1}{r_1q_2} + ln\frac{r_2q_1}{r_1q_2}\right) \end{cases} \qquad (3.9)$$

This implies that same sized and shaped atoms that is having same value for r and q parameters, the equation is reduced to

$$\gamma_1^{C,\infty} = \gamma_2^{C,\infty} = 1 \qquad (3.10)$$

Residual contribution:

The next term is expressed by empirical parameters that are to be estimated by doing experiments or by calculating the activity coefficients. The equation is given as

$$ln\,\gamma_i^R = q_i\left(1 - ln\frac{\sum_j q_j x_j \tau_{ji}}{\sum_j q_j x_j} - \sum_j \frac{q_j x_j \tau_{ij}}{\sum_k q_k x_k \tau_{kj}}\right) \qquad (3.11)$$

Where

$$\tau_{ji} = e^{-\Delta u_{ij}/RT} \qquad (3.12)$$

Δu_{ij} (J/mol) is the binary interaction energy parameter. Theory defines $\Delta u_{ij} = u_{ij} - u_{ii}$, and $\Delta u_{ji} = u_{ji} - u_{jj}$, where u_{ij} is the energy of interacting molecules i and j.

Usually $\Delta u_{ij} \neq \Delta u_{ji}$, as the energy required for evaporating the componet (i.e. u_{ii}), is different in mist of the cases, however interacting energy is equal form either way, and so $u_{ij}=u_{ji}$. So, if either pair of molecules contribute same to the pair of molecules than mixing has no additional energy effect upon the mixture, $\Delta u_{ij} = \Delta u_{ji} = 0$ and thus $\gamma_i^R = 1$

Alternatively, in some process simulation software τ_{ij} can be expressed as follows:

$$\ln(\tau_{ij}) = A_{ij} + B_{ij}/T + C_{ij} \times \ln(T) + D_{ij} \times T^2 + E_{ij}/T^2 \qquad (3.13)$$

Here A, B, C, D are coefficients to be regressed.

Applications

Models like UNIQUAC are used to assess the equilibrium data and physical properties. Also these can be used to calculate compostions in the multicomponent system. Also engineers use these models to calculate the flow volumes in a process flow chart.

Parameters:

UNIQUAC model is based on 2 determining factors

Constants for chemicals like volume fractions and relative surface area are retrieved from literature or estimated for the newer components using the Bondi method.

Another factor is a parameter that explains the behaviour between the molecules. This is assumed to be available for all the two component mixtures. For a four component mixture, the number of such parameters are six and the number of such parameters for higher number of components increases drastically.

To calculate the parameters, LLE diagrams are used from which activity coefficients can be estimated or are estimated from experiments for activity coefficients. An alternative way can be to estimate these parameters by using a model like UNIFAC and using these values to regress the objective equations of UNIQUAC. This is rather faster method than directly computing the activity coefficients.

3.3.2 Recent Advancements

UNIQUAC model is one of the advancements is the UNIFAC method. In this method, we can estimate the volume and surface parameter along with the interaction parameters. This refrains the use of experimental data for the calculation of UNIQUAC parameters. Other advancements include :

- Extensions to the evaluation of activity coefficients for electrolytes.
- Extensions in better relating the dependence of γ n temperatures.
- Solutions for explicit molecular arrangements.

3.3.3 Non-Random Two Liquid Model (NRTL)

Non-Random Two Liquid model (NRTL) is one of the other models which are used to correlate the activity coefficients. It relates this value to the component's mole fraction in both the phases. This is used many times like Prausnitz et al. for LLE calculations in chemical and process engineering. The notion of NRTL is built upon the theory that the immediate concentration to a molecule in a solution is quite different from the concentration in bulk part of the fluid. This is based on the propositions proposed by Wilson. This difference in energy of interacting molecules is different for different kind of molecules because of the difference interaction energy of the components. This also has effect on the randomness at the molecular level. As a result of this, randomness decreases. So, NRTL is one of the local composition models. One disadvantage with these type of models is that these are thermodynamically inconsistent as local composition is quite dependent on the bulk composition as showed by Flemmer (1976). (McDermott et al., 1976)

Equations:

The following equations are given for a binary mixture:

$$\begin{cases} ln\gamma_1 = x_2^2\left[\tau_{21}\left(\dfrac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \dfrac{\tau_{21}G_{12}}{(x_2 + x_1G_{12})^2}\right] \\ ln\gamma_2 = x_1^2\left[\tau_{12}\left(\dfrac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \dfrac{\tau_{12}G_{21}}{(x_1 + x_2G_{21})^2}\right] \end{cases} \tag{3.13}$$

where

$$\begin{cases} ln\ G_{12} = -\alpha_{12}\tau_{12} \\ ln\ G_{21} = -\alpha_{21}\tau_{21} \end{cases} \tag{3.14}$$

where τ_{12} & τ_{21} are the interaction parameters and are dimensionless. These parameters are expressed in terms of interaction energy parameters Δg_{12} and Δg_{21} by:

$$\begin{cases} \tau_{12} = \frac{\Delta g_{12}}{RT} = \frac{U_{12}-U_{22}}{RT} \\ \tau_{21} = \frac{\Delta g_{21}}{RT} = \frac{U_{21}-U_{11}}{RT} \end{cases} \tag{3.15}$$

R= Universal gas constant

T=absolute temperature

$\alpha_{12} \approx \alpha_{21}$ are the non randomness parameters.

In the liquid phase, in which all the composition are homogeneous everywhere,

α_{12} becomes equal to zero.

This condition can be represented by Margules activity model with one-parameter

$$\begin{cases} ln\ \gamma_1 = x_2^2[\tau_{21} + \tau_{12}] = Ax_2^2 \\ ln\ \gamma_2 = x_1^2[\tau_{21} + \tau_{12}] = Ax_1^2 \end{cases} \tag{3.16}$$

Generally while calculation, α_{12} made equal to almost 0.2, 0.3 or 0.48. Systems with water in it often use the value of 0.5. This is due to presence of Hydrogen bonds which give a much arranged structure. In the other cases, a initial assumption of -1 is taken to better fit the regression but this is impractical as it makes the system more random than a completely random system. The activity coefficients at infinity dilution is given by

$$\begin{cases} ln\gamma_1^\infty = [\tau_{21} + \tau_{12}\exp\ (-\alpha_{12}\tau_{12})] \\ ln\gamma_2^\infty = [\tau_{12} + \tau_{21}\exp\ (-\alpha_{12}\tau_{21})] \end{cases} \tag{3.17}$$

In this equation, making $\alpha_{12} = 0$, the activity at infinity dilution becomes equal for both the components. This is a situation we encounter when molecules are of same size and the polarities are varied.

Temperature dependent parameters:

The NRTL equation can be modified to include the effect of temperature of a rabge of temperatures. A relation between temperature and the interaction parameters is given by the Antoine equation.

$$\tau_{ij} = f(T) = a_{ij} + \frac{b_{ij}}{T} + c_{ij}\ln(T) + d_{ij}T \qquad (3.18)$$

The terms inside log are specifically used to describe the LLE solubility gap.

Another equation that can be used is

$$\Delta g_{ij} = f(T) = a_{ij} + b_{ij}T + c_{ij}T^2 \qquad (3.19)$$

Parameter determination:

For determination of NRTL parameters, experiments are done to calculate the activity coefficients. Compositions of LLE data and heat duty of mixing are determined through the experiments or may be literatures. It can also be procured by using models like UNIFAC. Also NRTL parameters may be different for same group of compound as it is dependent upon the phase. For example, it is different for gas-liquid equilibrium or for a gas in real or ideal state. To describe a Azeotropic state, precise measurements in VP values are required. Generally, gas fugacities are taken equal to one but one needs a real equation of state before one could describe it perfectly.

3.4 Consistency Plots:

Certain empirical equations are used to verify the data obtained by the experiments. Othmer Tobias (**Othmer et al., 1942**) used a correlation to ascertain the veracity of experimental LLE points. They used a graphical method for applying the lever rule, which increased the accuracy of manual method of generating the tie lines. The equation is given by:

$$\ln\left(\frac{1-w_{33}}{w_{33}}\right) = A + B\ \ln\left(\frac{1-w_{11}}{w_{11}}\right) \tag{3.20}$$

Similarly, Hand gave certain modifications in the equation. The equation is of the form

$$\ln\left(\frac{w_{21}}{w_{11}}\right) = A' + B' \ln\left(\frac{w_{23}}{w_{33}}\right) \tag{3.21}$$

Another correlation that can be used for the verification of experimental data is the Bachman correlation. The equation is given by

$$w_{23} = a + b\ \frac{w_{23}}{w_{11}} \tag{3.22}$$

In all these equations, w represents the mass fraction and the first letter of two letter subscript in w represents the compound (1 for isooctane, 2 for p-xylene or naphthalene, and 3 for the solvents) and second letter in the subscript represents either 1 for iso-octane rich phase or 3 for solvent-rich phase. Thus, w_{33} refers to the mass fraction of solvent in solvent rich phase, and $w_{11,}$ mass fraction of isooctane in the feed. w_{21} and w_{23} are the mass fraction of naphthalene or p xylene (in the respective cases) in feed and solvent rich phase, respectively.

For all these equations, the regressed parameters are found out by fitting straight line in the given equations and the value of R^2 is calculated. The linearity of the graph and a close to unity value of R^2 implies a very high accuracy of experimental results.

3.5 Linear Solvation Energy Relationships (LSER theory):

LSER theory is useful method to compute, show a relationship between many interacting solvent-effects on various types of physical and chemical properties and reactivity parameters of liquids in interaction with each other. The π^* scale is an indicator of solvent dipolarity / polarizability, which is a measure of the capability of solvent to stabilize a charge or a dipole by property of its dielectricity. π^* for various solvents, nonchlorinated-nonprotonic aliphatic compounds with a one dominating bond dipole, is proportional to μ, the dipole moment. The α parameter of solvent's HBD (hydrogenbond donating) acidity explains the propensity of a solvent to contribute a H^+ ion in a solvent- -solute hydrogen bond. The β parameter of HBA (hydrogen-bond acceptor) basicity gives an assessment of the solvent's propensity to admit an H^+ ion (or donate an e^- pair) in a solute-solvent H- bond. The β scale is also used to assess hydrogen- bond-accepting strengths of Hydrogen-bond accepting bases which are particularly made to dissolve in non-Hydrogen-bond accepting solvents.

The solvatochromic parameters are to be used for linear salvation energy relationships (LSER) or, in the case of solute to solute interactions, linear complex energy relationships in the generalized form of the equation 3.23:

$$\boldsymbol{XYZ = XYZ_O + s\,(\,\pi^* + d\delta\,) + b\,\beta + a\,\alpha + h\,\delta_H + e\,\xi} \tag{3.23}$$

δ is a correction for the polarizability and is equal to zero for nonchlorinated aliphatic solvents, half for polychlorinated aliphatics, and one for aromatic solvents. The δ implies that generally variations in solvent polarizability are considerably larger between these different types of solvents than within the classes.

δ_H term in eq 3.23 is called Hildebrand solubility parameter, which is a gauge of the solvent-solvent interactions that are broken up in the creation of a a cavity for the solute (the cavity term), and is significant when working with free energies or enthalpies of solution or of transfer between different solvents, or with gas-liquid chromatographic partition coefficients. The ξ term measures coordinate covalency and is equal to -.20 for P=O bases, 0 for C=O,S=O, and N=O bases, 0.20 for single-bonded oxygen bases, 0.60 for pyridine bases, and 1.00 for sp^3-hybridized amine bases, and predicts the base properties. For the current study, the modification of LSER equation used by Uslu et al. (2008) is used. The equations used for the study are

$$\ln d_2 = \ln d_2^o + v[s(\pi * + d\delta) + b\beta + a\alpha] \tag{3.24}$$

$$\ln S = \ln S^o + v[s(\pi * + d\delta) + b\beta + a\alpha] \tag{3.25}$$

For comparison, SSE values are taken into consideration. SSE is given by the equation 3.26

$$SSE = \sum_{i=1}^{n} (x_i - \hat{x}_i)^2 \tag{3.26}$$

CHAPTER 4

RESULTS AND DISCUSSIONS

The experiments were performed as mentioned in previous chapter. The LLE data for the recovery of p-xylene and naphthalene was evaluated at the experimental conditions and corresponding thermodynamic analysis has been done and presented in this part of the thesis.

The solubility data for the system has been determined using the method as described in the last chapter. The experiments are performed at normal atmospheric pressure and at temperature of 303.2 K which is the normal temperature of industrial separation.

4.1 LLE extraction data for ternary systems of p-xylene

4.1.1 Isooctane - p-xylene - DMSO system

For the isooctane – p-xylene – DMSO system, the solubility data has been determined by adding p-xylene drop by drop to a solution of isooctane and DMSO in two layers. Accurate volume and weight measurements were made as of when the two phases disappeared and a single homogenous mixture was formed. An average of three readings was taken for the final data. The solubility data is produced for the system is produced in Table 4.1.

Table 4.1 Solubility data for Isooctane – p-xylene – DMSO system (all in mass fraction)

	Isooctane	Xylene	DMSO
1	0.113	0.542	0.345
2	0.151	0.610	0.240
3	0.177	0.645	0.177
4	0.340	0.612	0.048

Experimental liquid liquid equilibrium data has been determined for the system by analyzing both the phases of liquids using GC calibration data. Weight of both the phases is determined and calculation were made for the mass fraction of components n both the phases. Experimental LLE data is produced below in Table 4.2.

Table 4.2 Experimental data for the Isooctane – p-xylene – DMSO system (all in mass fraction):

Isooctane phase			DMSO rich phase		
w_{11} (IO)	w_{21} (p-xylene)	w_{31} (DMSO)	w_{13} (IO)	w_{23} (p-xylene)	w_{33} (DMSO)
0.2170	0.6504	0.1326	0.0438	0.4005	0.5557
0.3515	0.6034	0.0451	0.0249	0.2673	0.7077
0.5105	0.4615	0.0280	0.0200	0.1874	0.7926
0.5294	0.4439	0.0267	0.0187	0.1754	0.8059
0.8545	0.1378	0.0078	0.0101	0.0506	0.9393

The experimental data has been correlated using UNIQUAC and NRTL models. The correlated tie line data has been produced in Table 4.3.

Table 4.3 NRTL and UNIQUAC tie line data for the Isooctane – p-xylene – DMSO system

Isooctane phase						DMSO rich phase					
w_{11} (IO)		w_{21} (p-xylene)		w_{31} (DMSO)		w_{13} (IO)		w_{23} (p-xylene)		w_{33} (DMSO)	
NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC
0.2043	0.2350	0.6763	0.6398	0.1194	0.1252	0.0427	0.0475	0.4234	0.4191	0.5340	0.5335
0.3880	0.3881	0.5618	0.5631	0.0502	0.0488	0.0248	0.0234	0.2589	0.2762	0.7163	0.7004
0.5166	0.4953	0.4510	0.4711	0.0324	0.0336	0.0202	0.0189	0.1902	0.1899	0.7896	0.7912
0.5390	0.5176	0.4314	0.4522	0.0295	0.0302	0.0190	0.0178	0.1783	0.1772	0.8027	0.8050
0.8508	0.8540	0.1416	0.1384	0.0076	0.0076	0.0100	0.0108	0.0498	0.0501	0.9402	0.9391

The phase diagrams for the LLE experimental points are shown in Figure 4.1. In this figure solubility points are also shown.

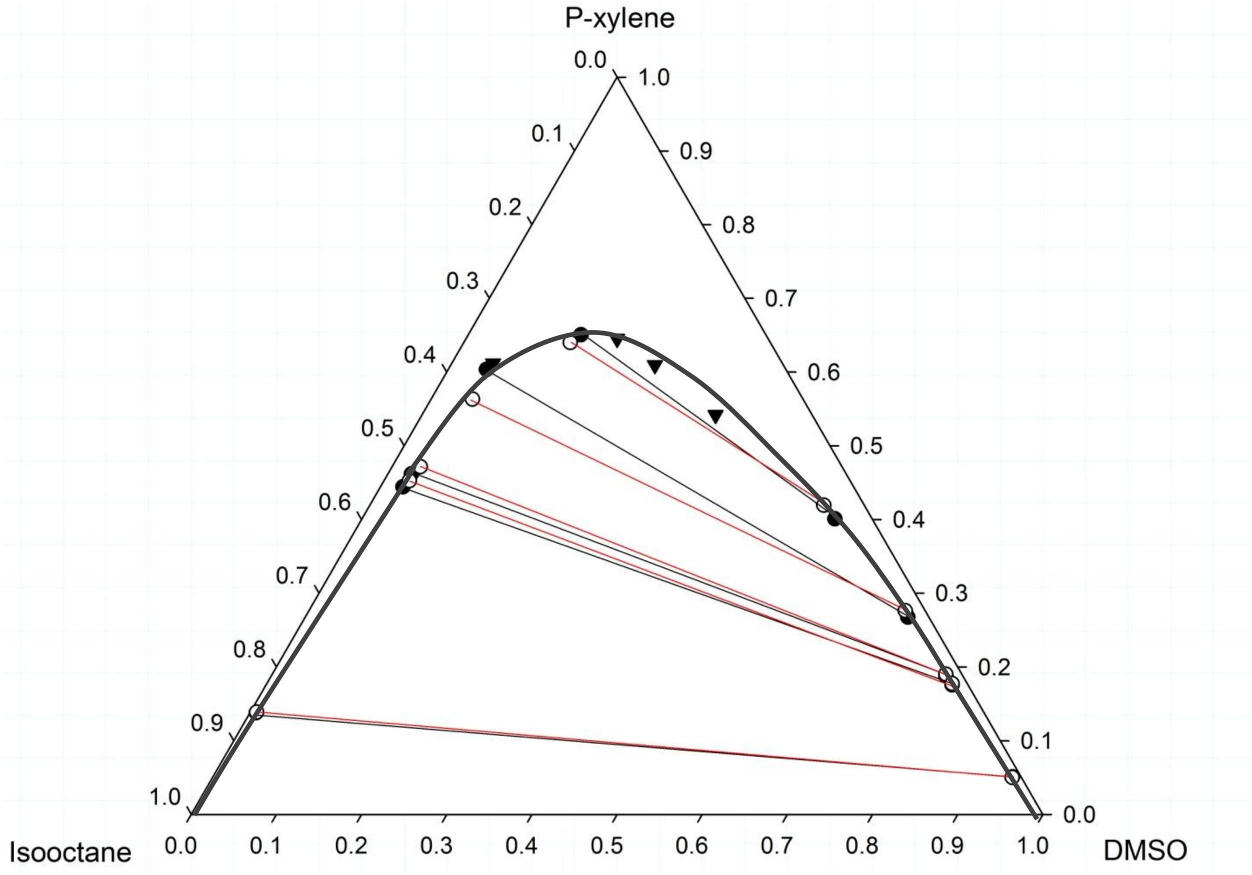
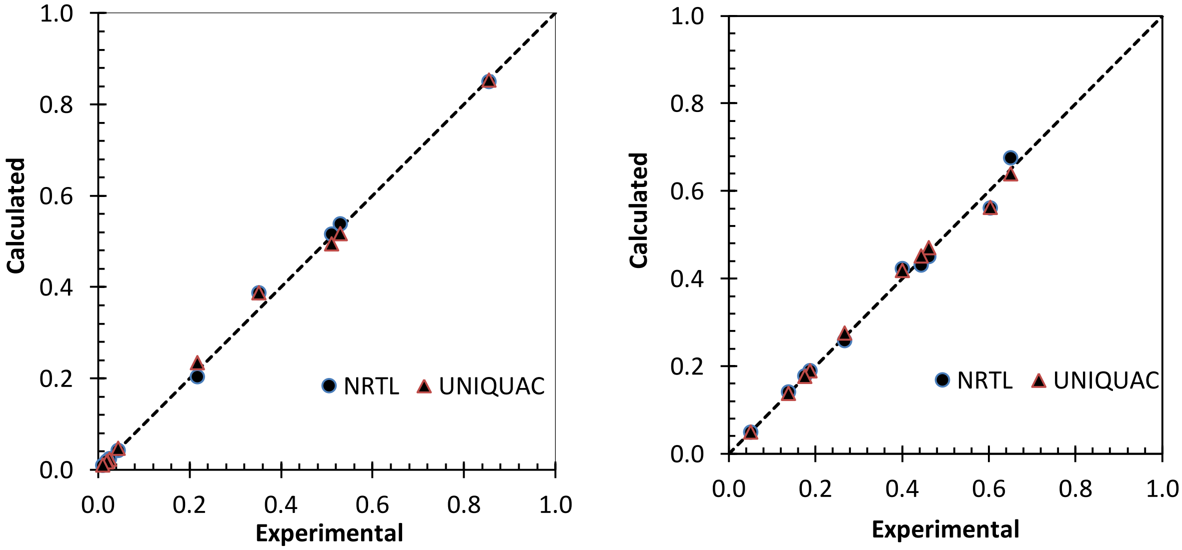


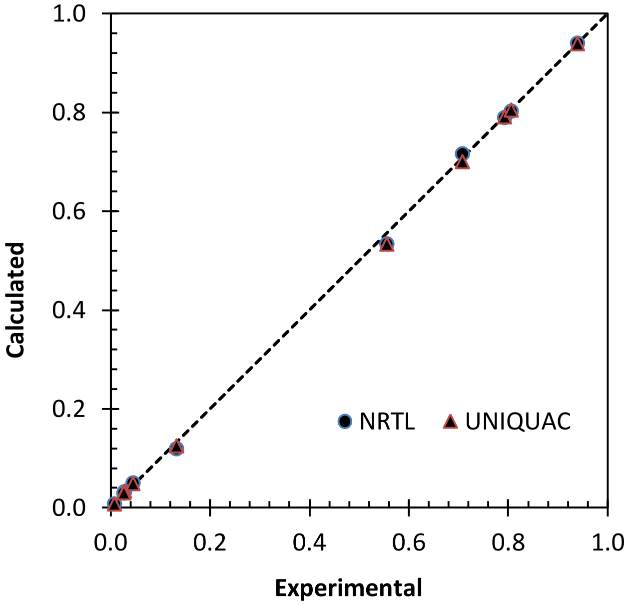
Figure 4.1 LLE diagram for the Isooctane – p-xylene – DMSO system {((•)Experimental tie line data, (o) UNIQUAC calculated tie line data, and (▼) solubility data points)}

A large area under the two phase region shows that DMSO is an appropriate solvent for recovery of p-xylene as the solvent is quite insoluble with the feed solvent. It takes a good amount of DMSO to make both the phases a homogeneous layer. The feed point is on the tie line. To estimate the solubility of only solvents i.e. isooctane and DMSO in this case, one has to study the composition on the base line. In Figure 4.1, the closeness of the phase diagram to the isooctane and the DMSO axes implies that the solvents are very less soluble with each other.

A comparison between the actual experimental points and the calculated points by the equations NRTL and UNQUAC is presented in the parity plots in Figure 4.2. In the parity plots, a closeness of a point to the y=x line shows the validation of results of experimental and the theoretical points.



(a) (b)



(c)

Figure 4.2 Parity plots for Isooctane – p-xylene – DMSO system (a) Isooctane parity plot (b) p-xylene parity plot (c) DMSO parity plot

The interaction parameters for a mixture of Isooctane – p-xylene – DMSO for both the models of UNIQUAC and NRTL is present in Table 4.4.

Table 4.4 Interaction Parameters in UNIQUAC and NRTL model for Isooctane – p-xylene – DMSO system

Component i	Component j	Value (SI units)	
		UNIQUAC	NRTL
Isooctane	p-xylene	-78.25	-130.91801
p-xylene	Isooctane	-3530.32	153.161659
Isooctane	DMSO	-574.39	1332.98116
DMSO	Isooctane	-69.86	1311.94972
p-xylene	DMSO	-310.33	518.244124
DMSO	p-xylene	-322.87	154.73143

4.1.2 Isooctane - p-xylene - NMP system

For the isooctane – p-xylene – NMP system, the solubility data has been determined by adding p-xylene drop by drop to a solution of isooctane and NMP in two layers. Accurate volume and weight measurements were made as of when the two phases disappeared and a single homogenous mixture was formed. An average of three readings was taken for the final data. The solubility data is produced for the system in Table 4.5.

Table 4.5 Solubility data for Isooctane – p-xylene – NMP system (all in mass fraction)

	Isooctane	Xylene	NMP
1	0.233	0.270	0.497
2	0.352	0.275	0.374
3	0.422	0.256	0.322
4	0.538	0.242	0.220

Experimental liquid liquid equilibrium data has been determined as mentioned above for all the data in Table 4.6.

Table 4.6 Experimental data for the Isooctane – p-xylene – NMP system (all in mass fraction):

Isooctane phase			**NMP rich phase**		
w_{11} **(IO)**	w_{21} **(p-xylene)**	w_{31} **(NMP)**	w_{13} **(IO)**	w_{23} **(p-xylene)**	w_{33} **(NMP)**
0.4740	0.2570	0.2690	0.2546	0.2620	0.4833
0.5805	0.2172	0.2023	0.1978	0.2279	0.5743
0.6891	0.1752	0.1357	0.1533	0.1773	0.6694
0.7715	0.0947	0.1338	0.1521	0.1004	0.7475
0.8100	0.0490	0.1410	0.1393	0.0511	0.8096

The experimental data has been correlated using UNIQUAC and NRTL models. The correlated tie line data has been produced in the Table 4.7.

Table 4.7 NRTL and UNIQUAC tie line data for the Isooctane – p-xylene – NMP system

Isooctane phase						**NMP rich phase**					
w_{11} (IO)		**w_{21} (p-xylene)**		**w_{31} (NMP)**		**w_{13} (IO)**		**w_{23} (p-xylene)**		**w_{33} (NMP)**	
NRTL	**UNIQUAC**	**NRTL**	**UNIQUAC**	**NRTL**	**UNIQUAC**	**NRTL**	**UNIQUAC**	**NRTL**	**UNIQUAC**	**NRTL**	**UNIQUAC**
0.5030	0.5000	0.2763	0.2757	0.2207	0.2243	0.2406	0.2401	0.2806	0.2807	0.4788	0.4792
0.5967	0.5946	0.2213	0.2211	0.1820	0.1843	0.1988	0.1981	0.2267	0.2270	0.5744	0.5749
0.6783	0.6776	0.1647	0.1645	0.1569	0.1579	0.1709	0.1704	0.1703	0.1700	0.6588	0.6596
0.7676	0.7691	0.0956	0.0944	0.1368	0.1364	0.1478	0.1482	0.0998	0.1010	0.7524	0.7509
0.8247	0.8250	0.0490	0.0493	0.1263	0.1257	0.1353	0.1359	0.0516	0.0513	0.8131	0.8128

The values of solubility data and the experimental points along with the UNIQUAC modeled parameters are plotted in the phase diagram of Figure 4.3. It has a comparatively lower 2 phase region as compared to the DMSO solvent. So, it implies that it has a lower solubility for p-xylene than DMSO.

The parity plots for the given system are presented in the Figure 4.4. Which show a very good agreement between the experimental points and the modeled points with NRTL and UNIQUAC.

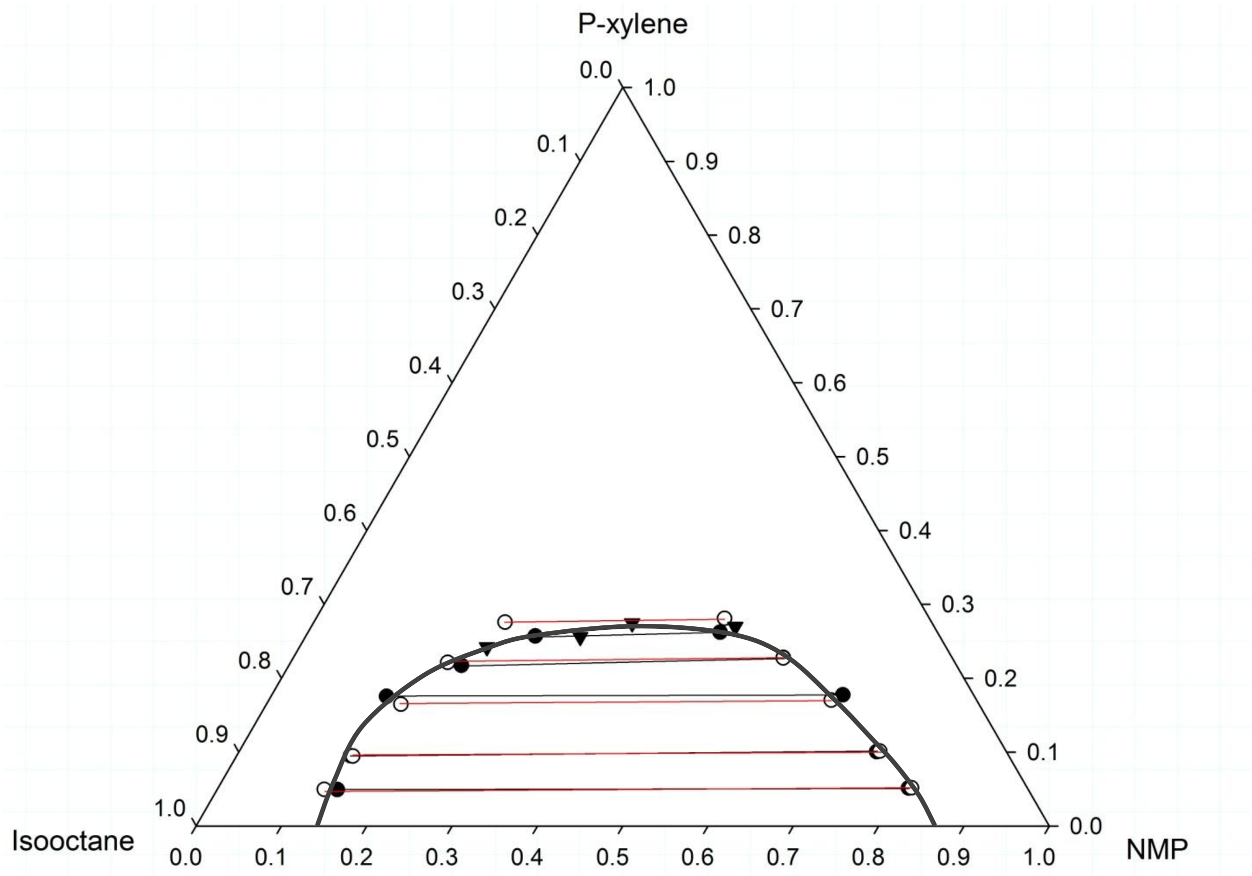
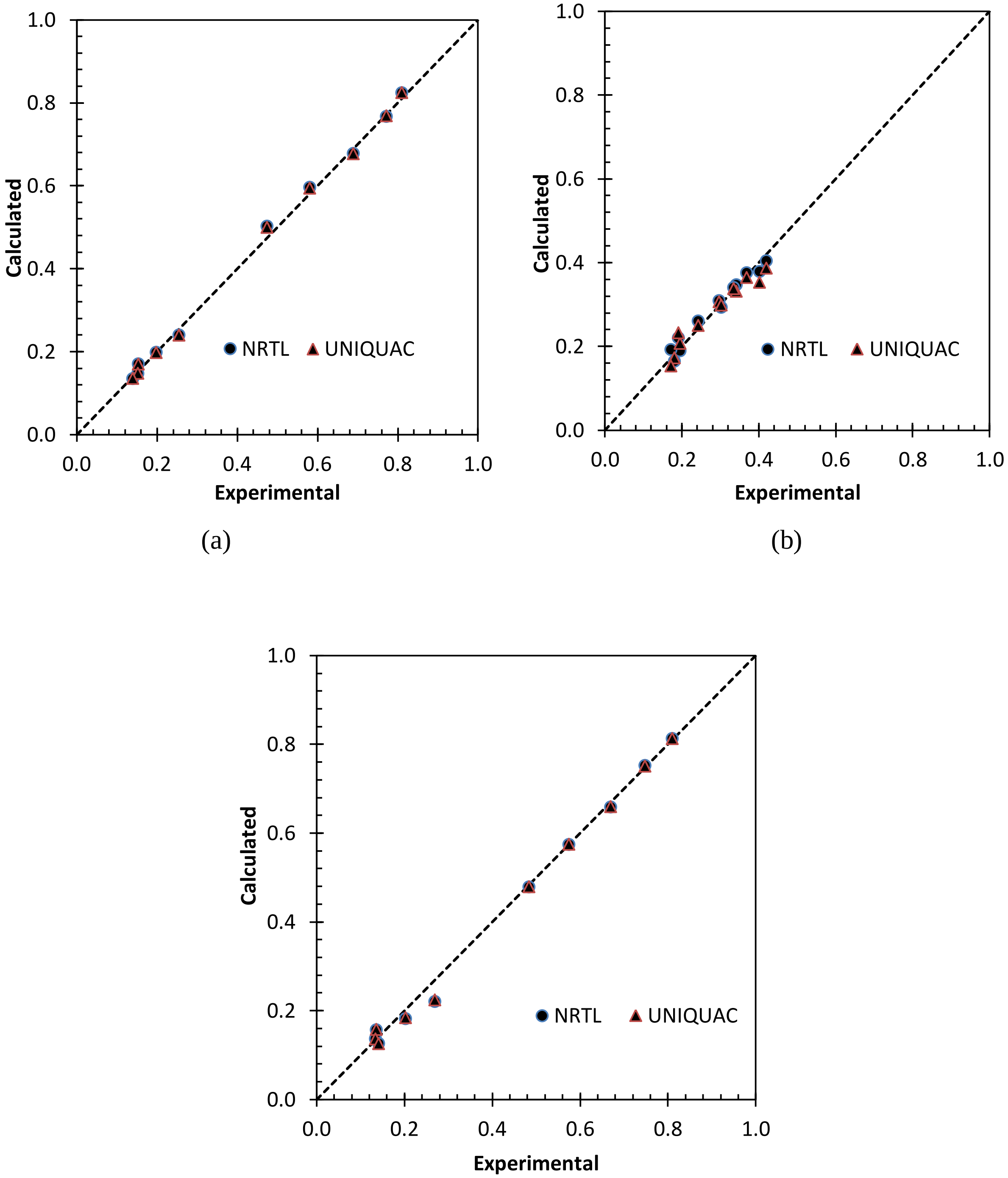


Figure 4.3 LLE diagram for the Isooctane – p-xylene – NMP system {((•)Experimental tie line data, (o) UNIQUAC calculated tie line data, and (▼) solubility data points)}



(a)

(b)

(c)

Figure 4.4 Parity plots for Isooctane – p-xylene – NMP system (a) Isooctane parity plot (b) p-xylene parity plot (c) NMP parity plot

The interaction parameters for the given system is given in the Table 4.8

Table 4.8 Interaction Parameters in UNIQUAC and NRTL model for Isooctane – p-xylene – NMP system

Component i	**Component j**	**Value (SI units)**	
		UNIQUAC	**NRTL**
Isooctane	P-Xylene	708.09	-335.50912
P-Xylene	Isooctane	-2563.41	284.609181
Isooctane	NMP	-246.29	417.488139
NMP	Isooctane	1.28	518.262231
P-Xylene	NMP	-263.15	505.893706
NMP	P-Xylene	576.93	-405.7812

4.1.3 Isooctane - p-xylene - DMF system

Solubility data are generated in the same way as for the other data. The solubility data is produced for the system in Table 4.9.

Table 4.9 Solubility data for Isooctane – p-xylene – DMF system (all in mass fraction)

	Isooctane	Xylene	DMF
1	0.103	0.500	0.397
2	0.124	0.534	0.342
3	0.197	0.596	0.208
4	0.332	0.527	0.140

Experimental liquid liquid equilibrium data has been determined as mentioned above for all the data and given in Table 4.10.

Table 4.10 Experimental data for the Isooctane – p-xylene – DMF system (all in mass fraction):

Isooctane phase			DMF rich phase		
w_{11} (IO)	w_{21} (p-xylene)	w_{31} (DMF)	w_{13} (IO)	w_{23} (p-xylene)	w_{33} (DMF)
0.5011	0.4191	0.0797	0.0513	0.4014	0.5473
0.5752	0.3679	0.0569	0.0469	0.3410	0.6121
0.6116	0.3341	0.0544	0.0394	0.2962	0.6644
0.6532	0.3018	0.0450	0.0241	0.2420	0.7339
0.7819	0.1905	0.0275	0.0169	0.1948	0.7883
0.8187	0.1710	0.0104	0.0114	0.1800	0.8087

The experimental data has been correlated using UNIQUAC and NRTL models. The correlated tie line data has been produced as below.

Table 4.11 NRTL and UNIQUAC tie line data for the Isooctane – p-xylene – DMF system

Isooctane phase						NMP rich phase					
w_{11} (IO)		w_{21} (p-xylene)		w_{31} (DMF)		w_{13} (IO)		w_{23} (p-xylene)		w_{33} (DMF)	
NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC
0.4973	0.5204	0.4048	0.3872	0.0980	0.0924	0.0532	0.0564	0.3793	0.3534	0.5675	0.5901
0.5477	0.5581	0.3762	0.3649	0.0761	0.0771	0.0450	0.0472	0.3475	0.3320	0.6075	0.6208
0.6023	0.5993	0.3409	0.3384	0.0568	0.0623	0.0360	0.0382	0.3096	0.3069	0.6543	0.6549
0.6665	0.6556	0.2936	0.2992	0.0398	0.0452	0.0263	0.0236	0.2611	0.2503	0.7126	0.7261
0.7508	0.7418	0.2207	0.2330	0.0285	0.0252	0.0155	0.0162	0.1898	0.2077	0.7946	0.7761
0.7976	0.8355	0.1928	0.1536	0.0096	0.0109	0.0126	0.0117	0.1650	0.1731	0.8224	0.8152

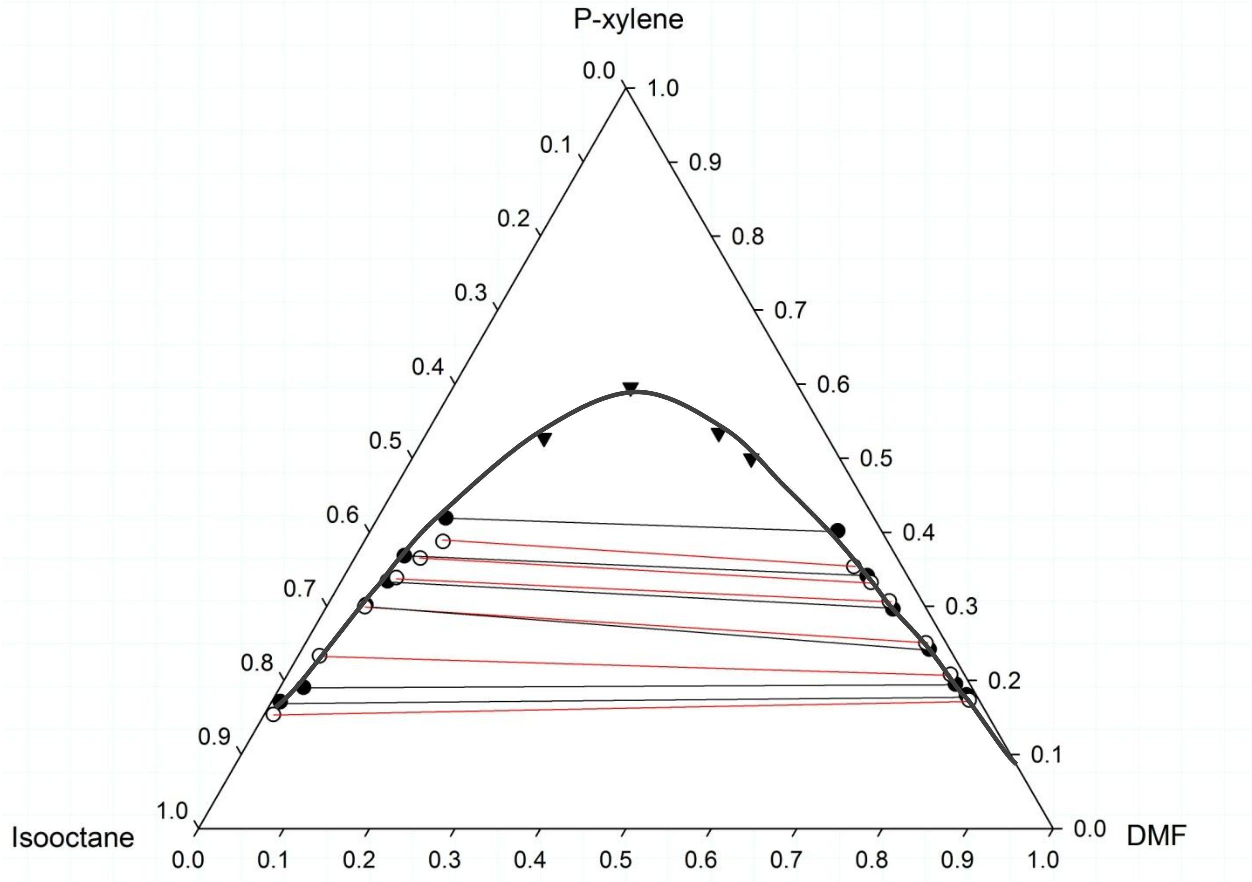
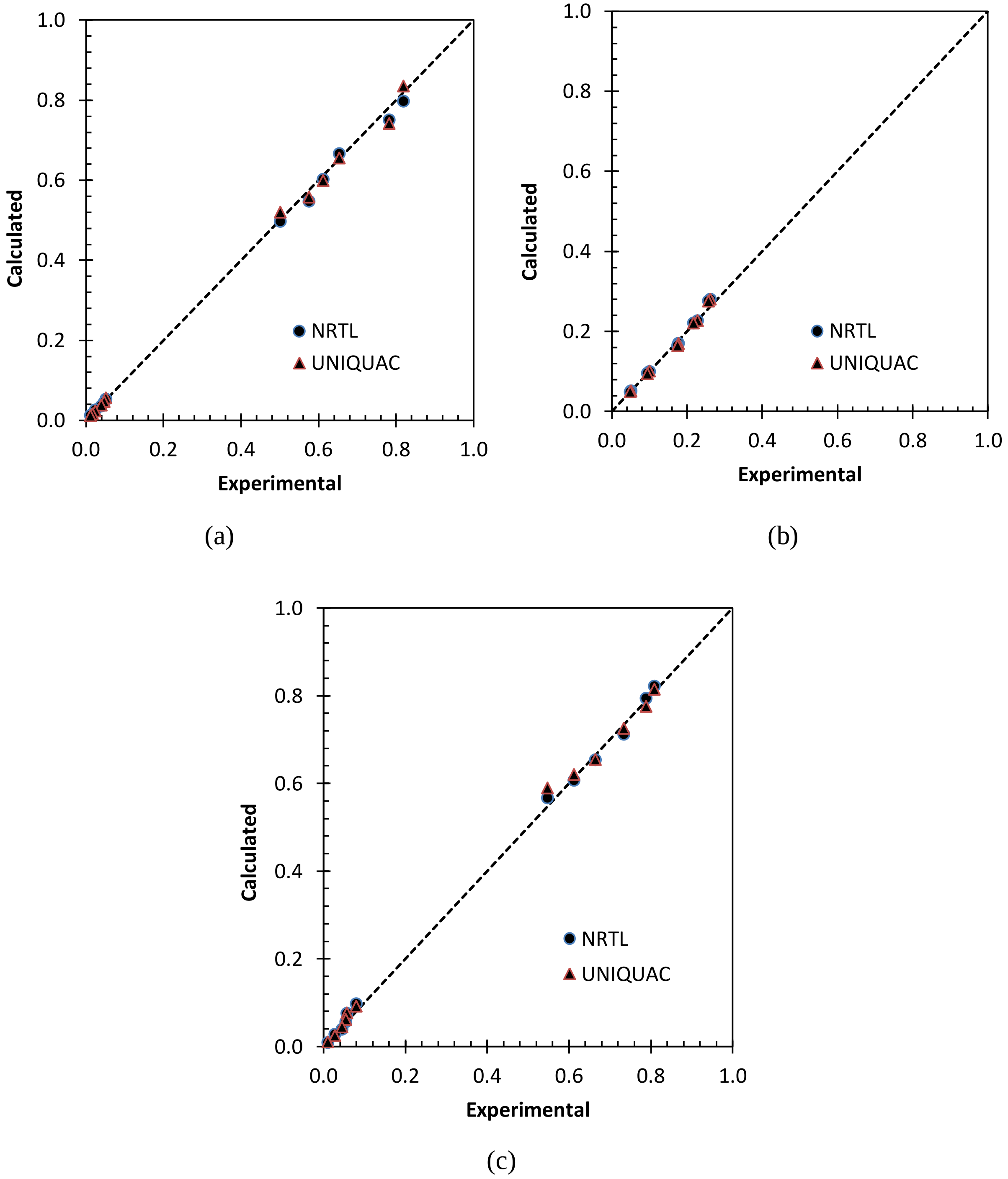


Figure 4.5 LLE diagram for the Isooctane – p-xylene – DMF system {((•)Experimental tie line data, (o) UNIQUAC calculated tie line data, and (▼) solubility data points)}



(a)

(b)

(c)

Figure 4.6 Parity plots for Isooctane – p-xylene – DMF system (a) Isooctane parity plot (b) p-xylene parity plot (c) DMF parity plot

Table 4.12 Interaction Parameters in UNIQUAC and NRTL model for Isooctane – p-xylene – DMF system

Component i	Component j	Value (SI units)	
		UNIQUAC	NRTL
Isooctane	P-Xylene	-458.85	-803.122
P-Xylene	Isooctane	244.25	616.2662
Isooctane	DMF	-690.86	4229.304
DMF	Isooctane	-180.94	1860.278
P-Xylene	DMF	132.90	912.5228
DMF	P-Xylene	-198.41	-780.489

4.1.4 Analysis of Isooctane - P-Xylene – Solvent system:

The consistency of experimental data can be verified by certain correlations. In this study, the relationships used to determine the veracity of the data are using Othmer Tobias (Othmer et al., 1942), Bachman (Bachman et al., 1940) and Hand’s correlations (Othmer et al., 1942).

The values are plotted for the y values against the x values of the respective equations. The plots are presented in the the following figures. (Othmer-Tobias’ plot Figure 4.7, Hand’s plot Figure 4.8, Bachman’s plot Figure 4.9)

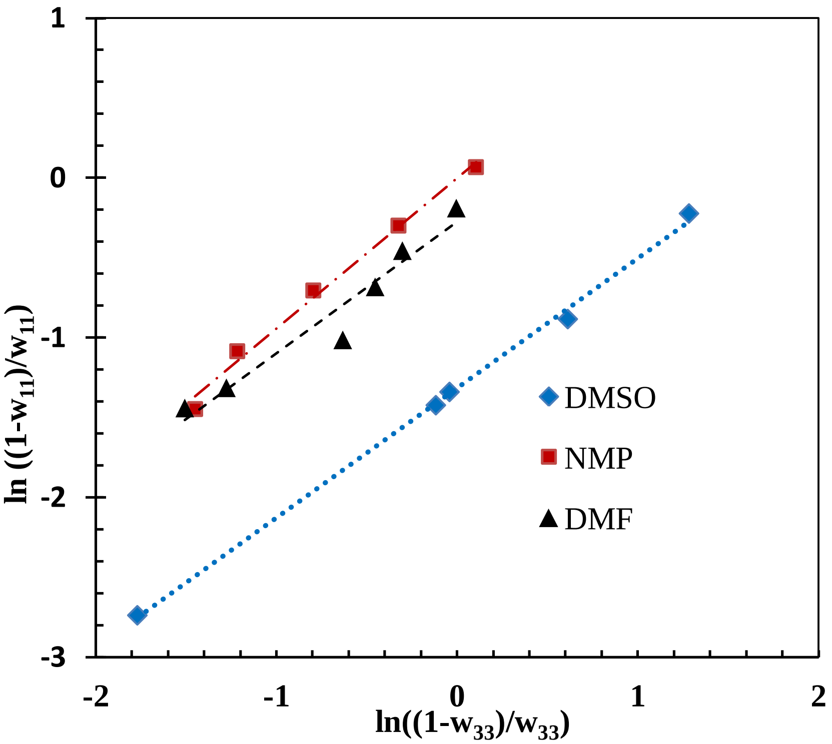


Figure 4.7 Othmer-Tobias' plot

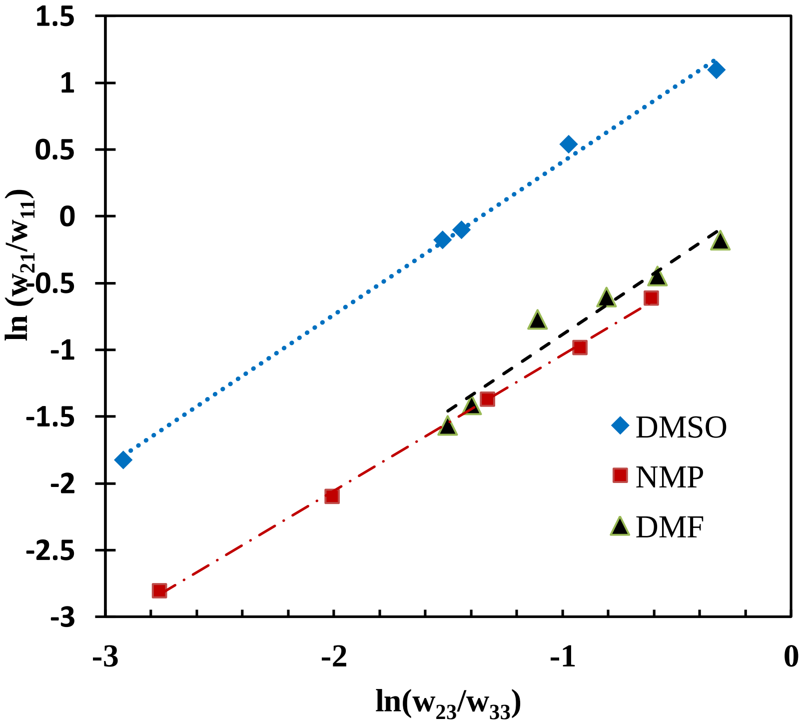


Figure 4.8 Hand's plot

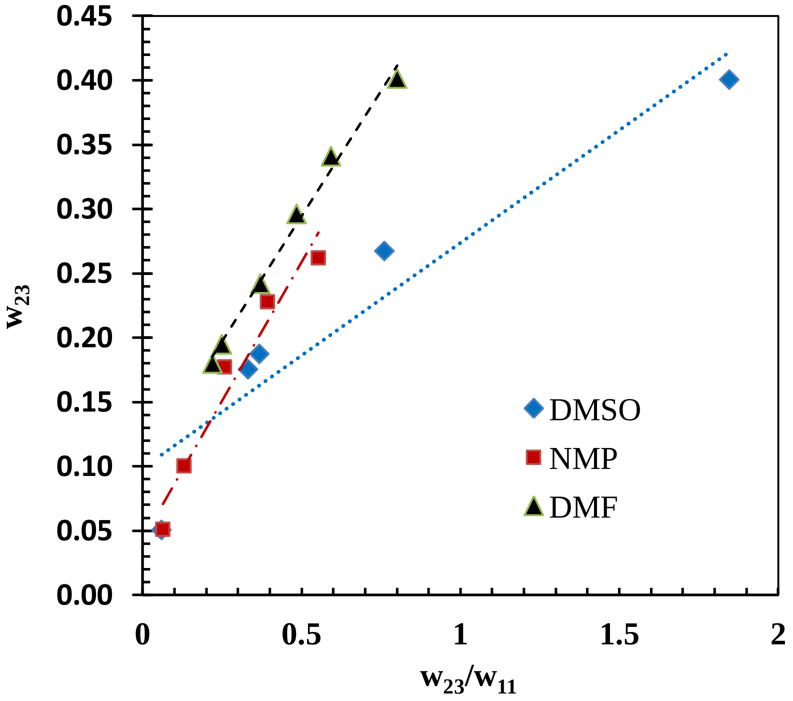


Figure 4.9 Bachman's Plot

The tie line data points showed a very good degree of fitting on a straight line with the correlations. The constants of the correlation equations are determined by fitting straight line and finding the slope and intercept for the given equations. R^2 values are determined for the correlations and are presented in Table 4.13.

Table 4.13 Othmer Tobias, Hand's and Bachman correlation constants and correlation factor R^2 for the p-xylene at 30° C.

Solvent	Othmer Tobias			Hand's			Bachman		
	A	B	R^2	A'	B'	R^2	a	b	R^2
p-xylene									
DMSO	-1.3166	0.812	0.9979	1.5557	1.1466	0.9962	0.0984	0.1751	0.9086
NMP	0.0011	0.9436	0.9908	-0.0203	1.0171	0.9989	0.0435	0.4306	0.9501
DMF	-0.2711	0.8226	0.9445	0.255	1.1695	0.9435	0.0996	0.3892	0.9917

From the above table, it can be noted that both DMSO and NMP gave a high R^2 with Othmer Tobias and Hand's correlations whereas DMF gave a very near unity R^2 with Bachman correlation for p-xylene.

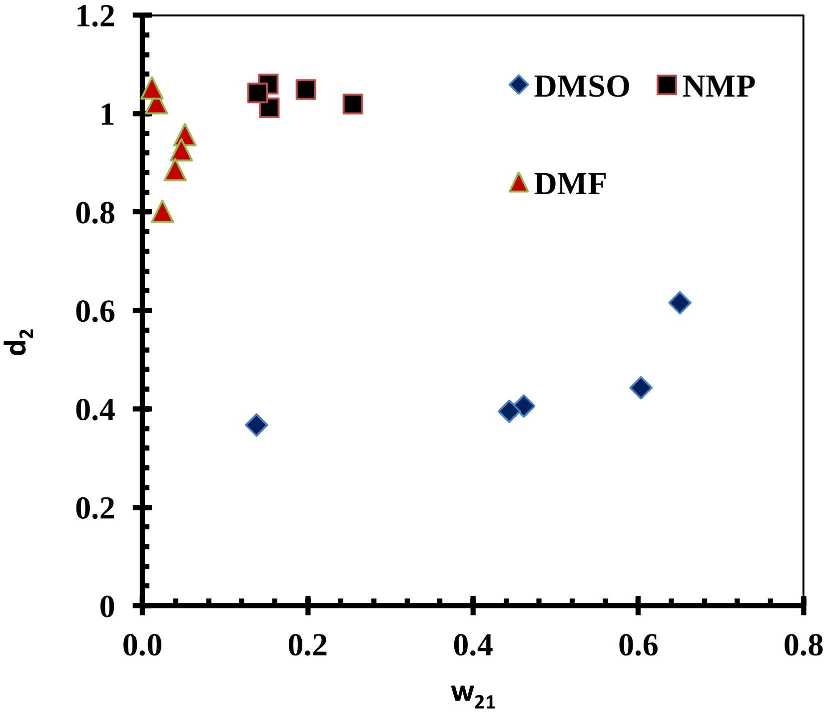


Figure 4.10 Distribution coefficient for P xylene

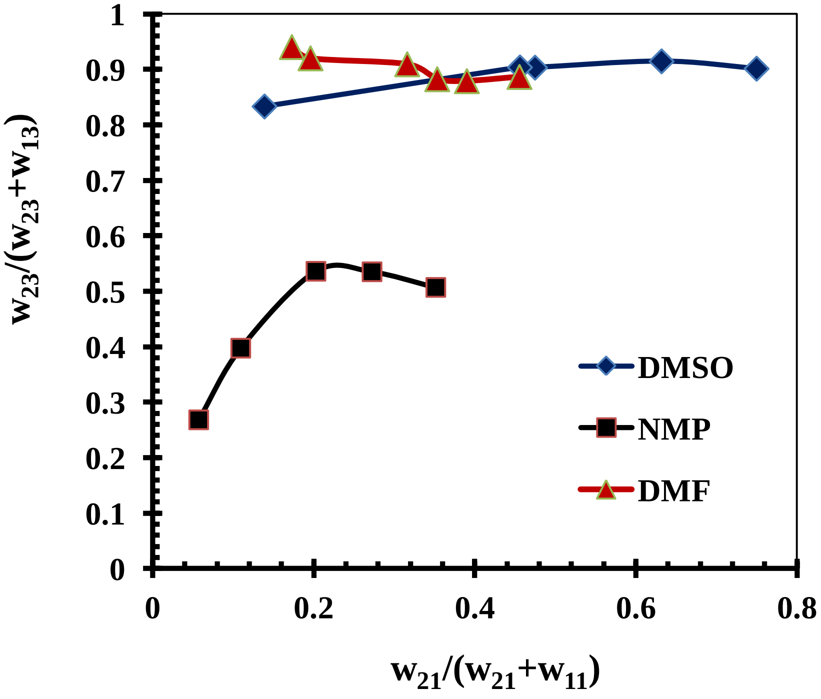


Figure 4.11 Selectivity Chart for P xylene

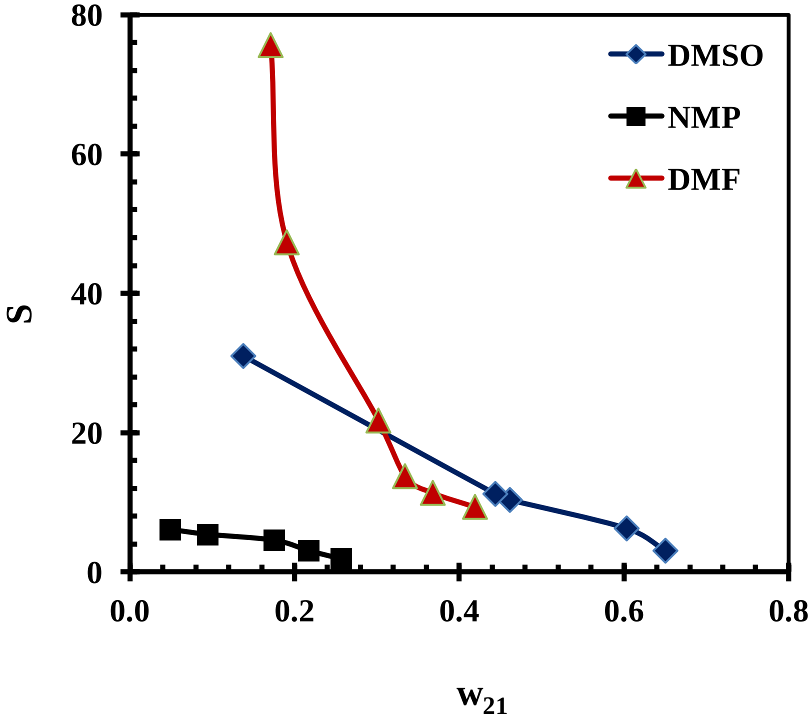


Figure 4.12 Separation factor S plotted against mass fraction of P-xylene in model oil

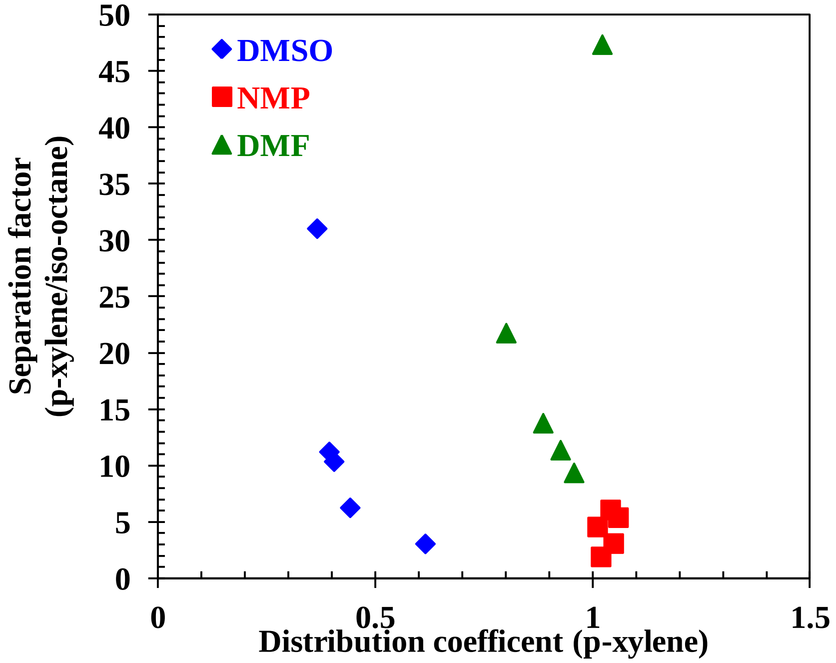


Figure 4.13 P-xylene/isooctane separations against distribution coefficients using DMSO, NMP and DMF for various feed conditions experimental data.

4.2 LLE extraction data for ternary systems of naphthalene

4.2.1 Isooctane - Naphthalene - DMSO system

For the isooctane – naphthalene – DMSO system, the solubility data has been determined by adding weighed quantity of naphthalene in small amounts to a solution of isooctane and DMSO in two layers. Naphthalene was added till no more dissolves in the given quantity of solution. An average of three readings was taken for the final data. The solubility data is produced for the system in Table 4.14.

Table 4.14 Solubility data for Isooctane – naphthalene – DMSO system (all in mass fraction)

	Isooctane	Xylene	DMSO
1	0.222	0.233	0.545
2	0.338	0.247	0.415
3	0.376	0.245	0.379
4	0.626	0.204	0.170

Experimental liquid liquid equilibrium data has been determined for the system by analyzing both the phases of liquids using GC calibration data and presented in Table 4.15.

Table 4.15 Experimental data for the Isooctane – naphthalene – DMSO system (all in mass fraction):

Isooctane phase			DMSO rich phase		
w_{11} (IO)	w_{21} (naphthalene)	w_{31} (DMSO)	w_{13} (IO)	w_{23} (naphthalene)	w_{33} (DMSO)
0.6248	0.1899	0.1853	0.0449	0.2209	0.7342
0.7504	0.1168	0.1328	0.0130	0.1636	0.8233
0.7815	0.0845	0.1340	0.0102	0.0573	0.9325
0.8094	0.0570	0.1336	0.0075	0.0497	0.9428
0.8552	0.0232	0.1216	0.0073	0.0286	0.9642

The experimental data has been correlated using UNIQUAC and NRTL models. The correlated tie line data has been produced in Table 4.16.

Table 4.16 NRTL and UNIQUAC tie line data for the Isooctane – naphthalene – DMSO system

Isooctane phase						DMSO rich phase					
w_{11} (IO)		w_{21} (naphthalene)		w_{31} (DMSO)		w_{13} (IO)		w_{23} (naphthalene)		w_{33} (DMSO)	
NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC
0.5790	0.6279	0.2369	0.1994	0.1841	0.1727	0.0390	0.0440	0.2592	0.2171	0.7017	0.7389
0.7468	0.7647	0.1119	0.1036	0.1414	0.1317	0.0162	0.0129	0.1384	0.1683	0.8453	0.8188
0.7824	0.7820	0.0839	0.0860	0.1338	0.1320	0.0089	0.0098	0.0596	0.0558	0.9315	0.9344
0.8204	0.8196	0.0533	0.0556	0.1264	0.1248	0.0083	0.0077	0.0522	0.0516	0.9395	0.9407
0.8550	0.8540	0.0250	0.0242	0.1200	0.1218	0.0068	0.0075	0.0269	0.0281	0.9663	0.9644

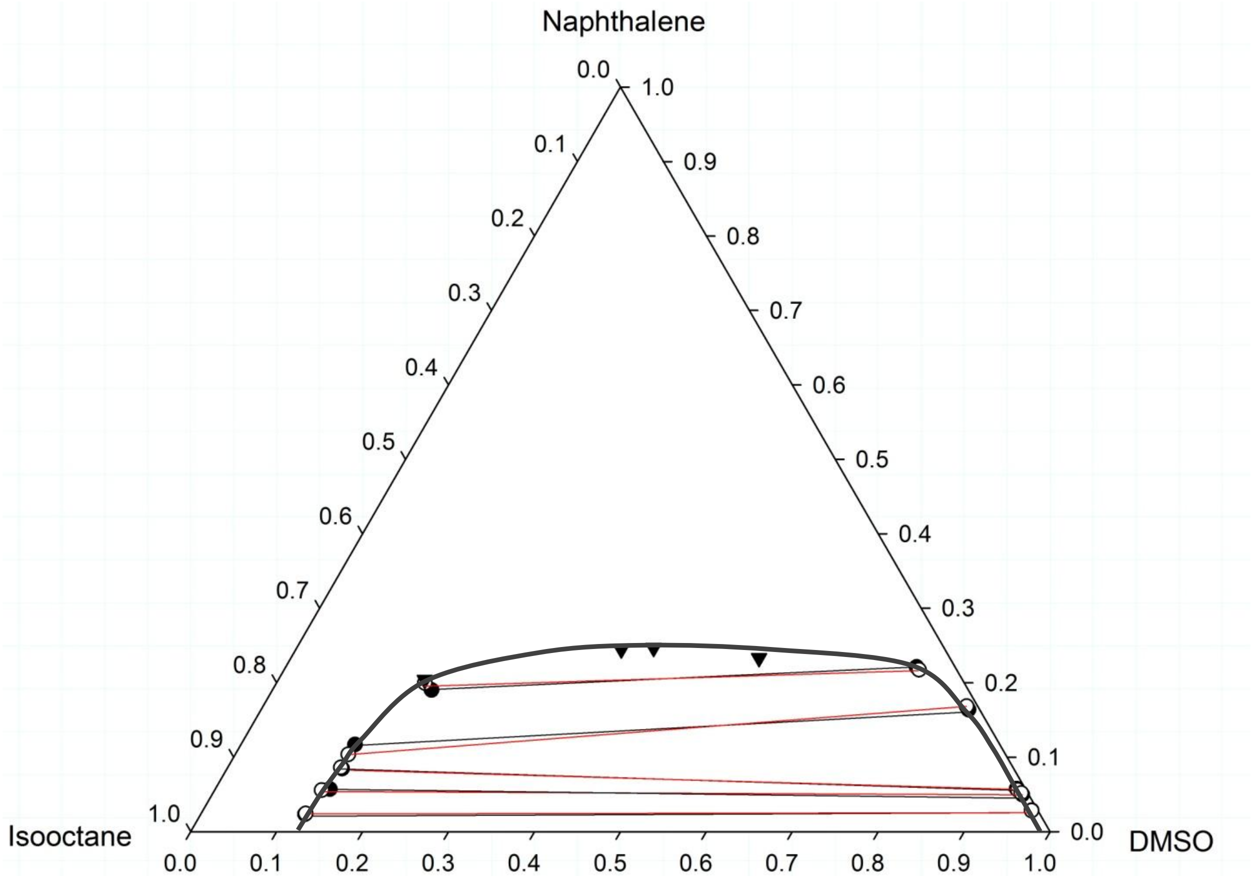
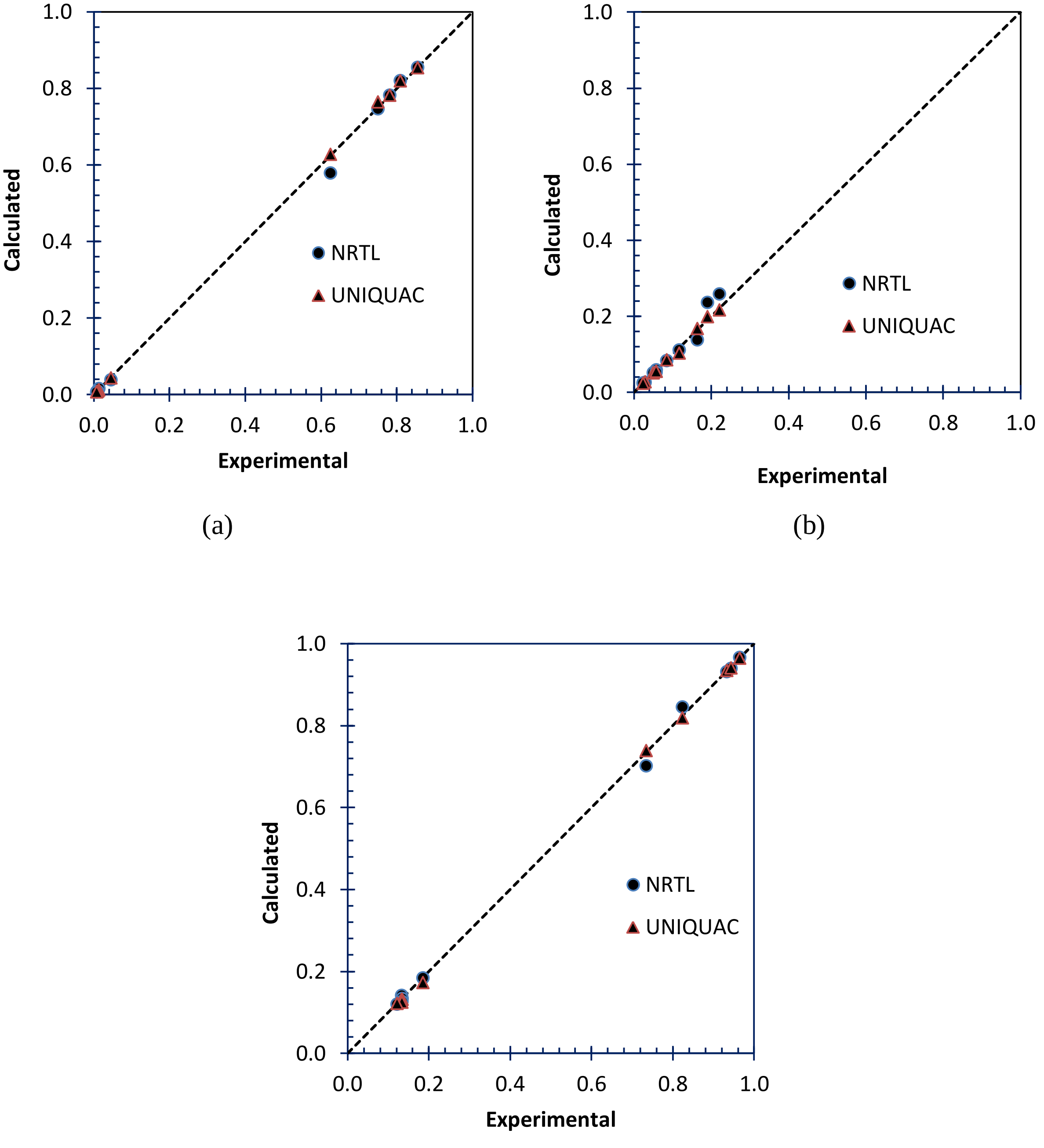


Figure 4.14 LLE diagram for the Isooctane – naphthalene – DMSO system {((•)Experimental tie line data, (o) UNIQUAC calculated tie line data, and (▼) solubility data points)}



(a)

(b)

(c)

Figure 4.15 Parity plots for Isooctane – naphthalene – DMSO system (a) Isooctane parity plot (b) naphthalene parity plot (c) DMSO parity plot

Table 4.17 Interaction Parameters in UNIQUAC and NRTL model for Isooctane – naphthalene – DMSO system

Component i	Component j	Value (SI units)	
		UNIQUAC	NRTL
Isooctane	DMSO	-110.41	391.06712
DMSO	Isooctane	-263.24	1438.70021
Isooctane	Naphthalene	-546.78	1095.76354
Naphthalene	Isooctane	78.98	226.991579
DMSO	Naphthalene	-396.44	1222.43397
Naphthalene	DMSO	-78.26	46.8386028

4.2.2 Isooctane - Naphthalene - NMP system

The solubility data is produced for the system in Table 4.18.

Table 4.18 Solubility data for Isooctane – naphthalene – NMP system (all in mass fraction)

	Isooctane	Xylene	NMP
1	0.473	0.279	0.249
2	0.554	0.237	0.209
3	0.307	0.256	0.437
4	0.231	0.225	0.544

Experimental liquid liquid equilibrium data has been determined as mentioned above for all the data in Table 4.19

Table 4.19 Experimental data for the Isooctane – naphthalene – NMP system (all in mass fraction):

Isooctane phase			NMP rich phase		
w_{11} (IO)	w_{21} (naphthalene)	w_{31} (NMP)	w_{13} (IO)	w_{23} (naphthalene)	w_{33} (NMP)
0.6823	0.1689	0.1488	0.3086	0.2308	0.4606
0.8973	0.0568	0.0460	0.1260	0.1118	0.7622
0.9107	0.0347	0.0545	0.1417	0.0520	0.8063
0.9201	0.0518	0.0281	0.1330	0.1029	0.7641
0.9222	0.0310	0.0468	0.1477	0.0487	0.8036

The experimental data has been correlated using UNIQUAC and NRTL models. The correlated tie line data has been produced in Table 4.20.

Table 4.20 NRTL and UNIQUAC tie line data for the Isooctane – naphthalene – NMP system

Isooctane phase						NMP rich phase					
w_{11} (IO)		w_{21} (naphthalene)		w_{31} (NMP)		w_{13} (IO)		w_{23} (naphthalene)		w_{33} (NMP)	
NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC
0.6742	0.6739	0.1927	0.1931	0.1330	0.1330	0.3119	0.3093	0.2405	0.2417	0.4476	0.4490
0.8930	0.8929	0.0584	0.0583	0.0486	0.0488	0.1503	0.1506	0.0976	0.0975	0.7521	0.7519
0.9256	0.9257	0.0336	0.0336	0.0408	0.0407	0.1302	0.1302	0.0593	0.0594	0.8106	0.8104
0.9048	0.9049	0.0498	0.0497	0.0453	0.0454	0.1425	0.1430	0.0850	0.0847	0.7725	0.7723
0.9302	0.9302	0.0302	0.0302	0.0397	0.0396	0.1273	0.1274	0.0537	0.0537	0.8190	0.8189

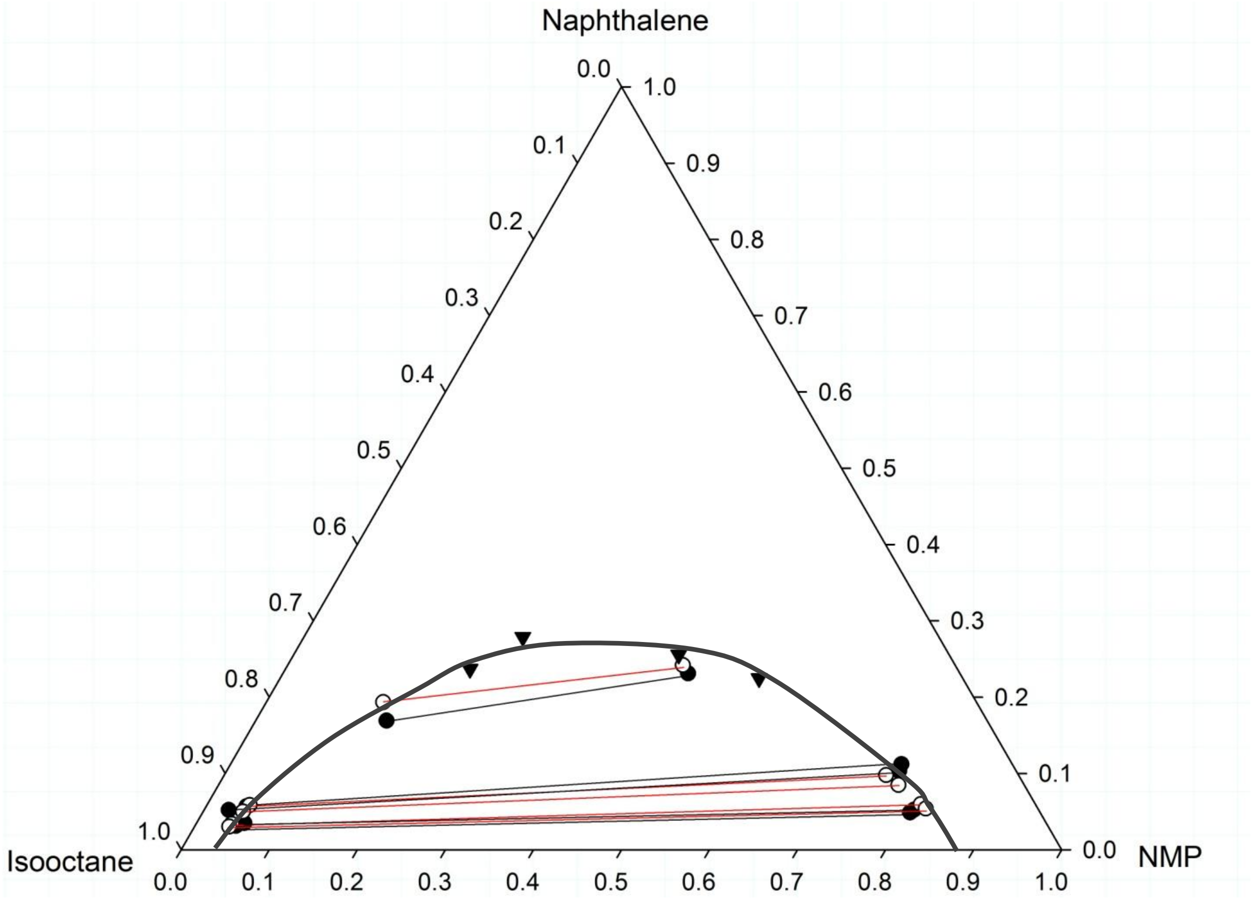
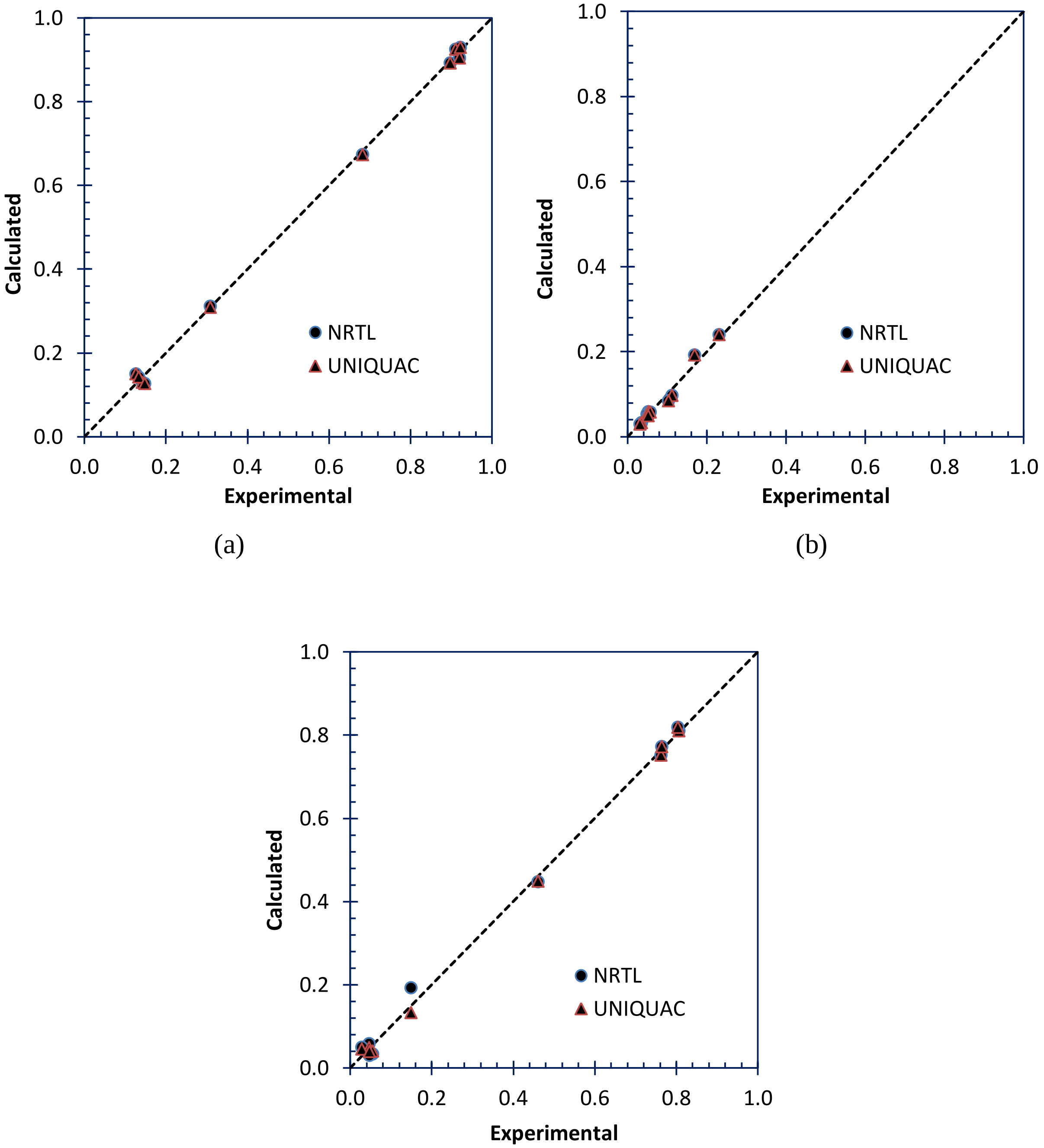


Figure 4.16 LLE diagram for the Isooctane – naphthalene – NMP system {((•)Experimental tie line data, (o) UNIQUAC calculated tie line data, and (▼) solubility data points)}



(a)

(b)

(c)

Figure 4.17 Parity plots for Isooctane – naphthalene – NMP system (a) Isooctane parity plot (b) naphthalene parity plot (c) NMP parity plot

Binary interaction parameters are given for the system in Table 4.21.

Table 4.21 Interaction Parameters in UNIQUAC and NRTL model for Isooctane – naphthalene – NMP system

Component i	**Component j**	**Value (SI units)**	
		UNIQUAC	**NRTL**
Isooctane	Naphthalene	-72.032173	-37.161723
Naphthalene	Isooctane	80.396438	113.158802
Isooctane	NMP	-432.08975	868.142926
NMP	Isooctane	67.1692507	322.780555
Naphthalene	NMP	83.1338691	-199.9437
NMP	Naphthalene	-41.592147	121.195052

4.2.3 Isooctane - Naphthalene - DMF system

Solubility data are generated in the same way as for the other data. The solubility data is produced for the system.

Table 4.22 Solubility data for Isooctane – naphthalene – DMF system (all in mass fraction)

	Isooctane	**Xylene**	**DMF**
1	0.311	0.205	0.484
2	0.143	0.214	0.643
3	0.423	0.187	0.390
4	0.590	0.144	0.266

Experimental liquid liquid equilibrium data has been determined as mentioned above for all the data and presented in Table 4.23.

Table 4.23 Experimental data for the Isooctane – naphthalene – DMF system (all in mass fraction):

Isooctane phase			DMF rich phase		
w_{11} (IO)	w_{21} (naphthalene)	w_{31} (DMF)	w_{13} (IO)	w_{23} (naphthalene)	w_{33} (DMF)
0.5413	0.1533	0.3054	0.0807	0.1779	0.7414
0.8803	0.0599	0.0599	0.0488	0.1427	0.8086
0.9053	0.0473	0.0473	0.0412	0.1207	0.8380
0.9271	0.0391	0.0338	0.0351	0.0953	0.8696
0.9480	0.0343	0.0177	0.0156	0.0885	0.8959
0.9811	0.0177	0.0012	0.0033	0.0741	0.9226

The experimental data has been correlated using UNIQUAC and NRTL models. The correlated tie line data has been produced as below.

Table 4.24 NRTL and UNIQUAC tie line data for the Isooctane – naphthalene – DMF system

Isooctane phase						NMP rich phase					
w_{11} (IO)		w_{21} (naphthalene)		w_{31} (DMF)		w_{13} (IO)		w_{23} (naphthalene)		w_{33} (DMF)	
NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC
0.1854	0.6771	0.2183	0.1133	0.5963	0.2096	0.1342	0.1094	0.2250	0.1420	0.6408	0.7486
0.9154	0.8678	0.0432	0.0664	0.0414	0.0658	0.0504	0.0418	0.1344	0.1194	0.8152	0.8388
0.9163	0.8938	0.0437	0.0579	0.0400	0.0484	0.0411	0.0348	0.1314	0.1150	0.8275	0.8502
0.9176	0.9172	0.0443	0.0495	0.0382	0.0333	0.0317	0.0287	0.1246	0.1106	0.8437	0.8607
0.9243	0.9481	0.0469	0.0367	0.0288	0.0152	0.0126	0.0203	0.0897	0.1030	0.8977	0.8768
0.9817	0.9832	0.0171	0.0155	0.0012	0.0013	0.0044	0.0033	0.0497	0.0730	0.9460	0.9237

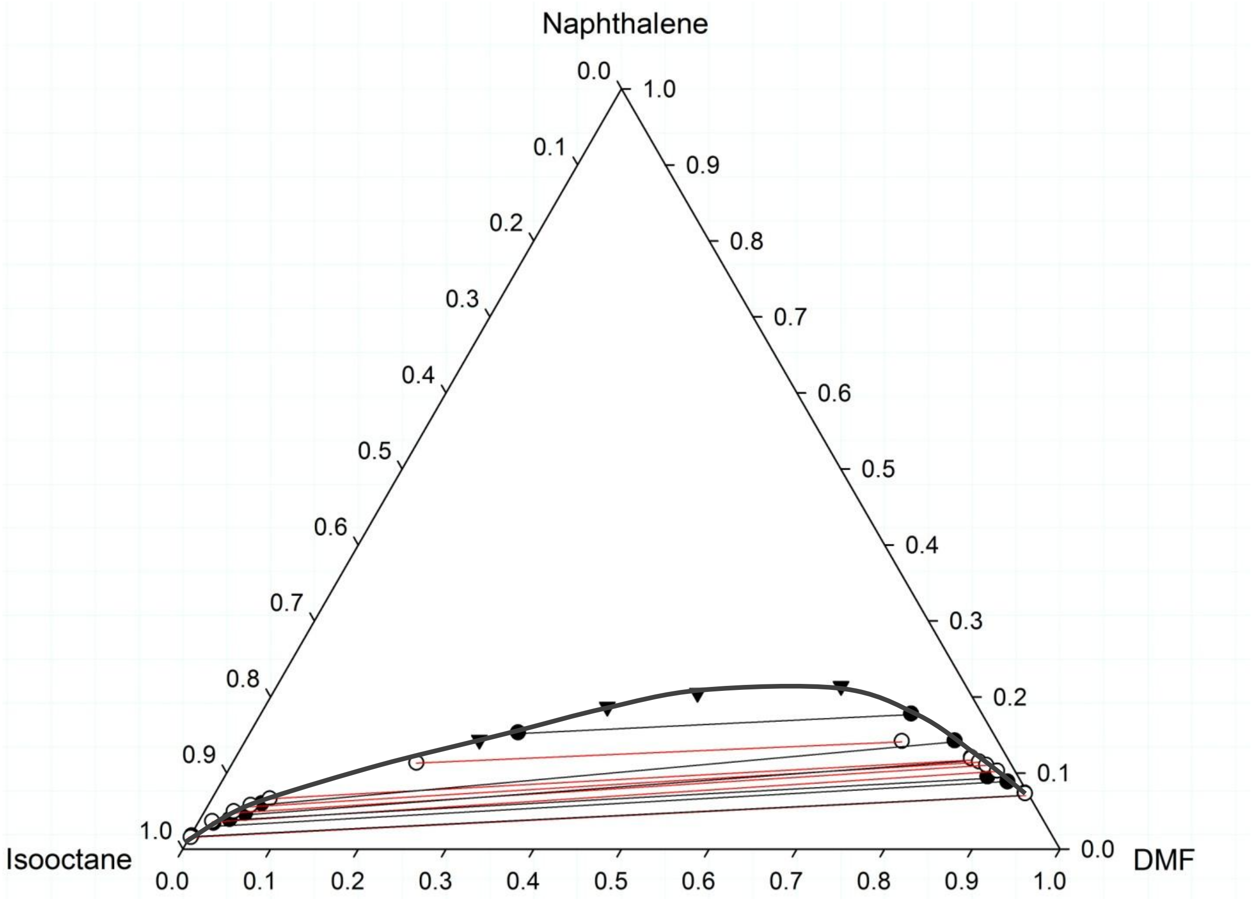
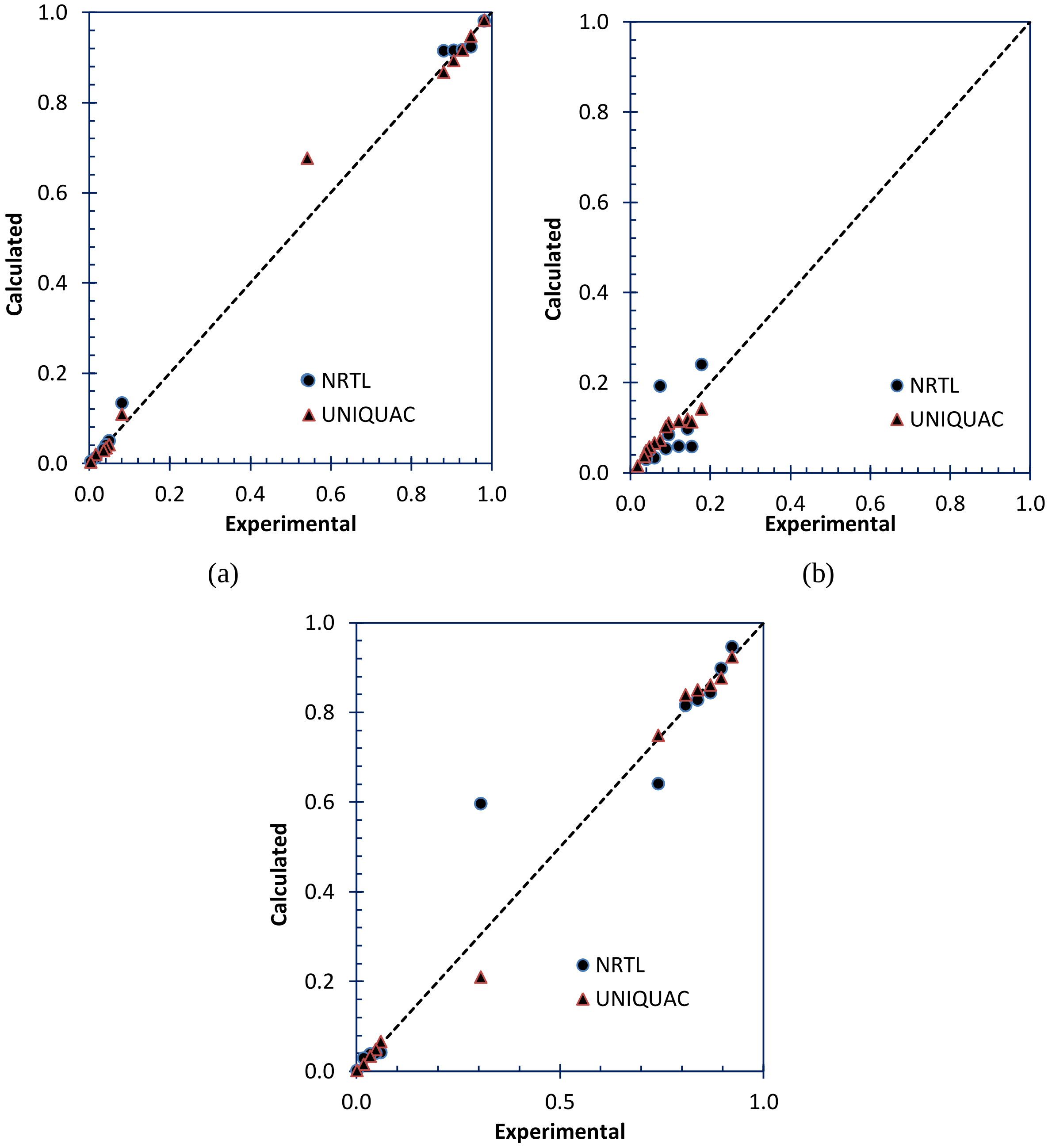


Figure 4.18 LLE diagram for the Isooctane – naphthalene – DMF system {((•)Experimental tie line data, (o) UNIQUAC calculated tie line data, and (▼) solubility data points)}



(a)

(b)

(c)

Figure 4.19 Parity plots for Isooctane – naphthalene – DMF system (a) Isooctane parity plot (b) naphthalene parity plot (c) DMF parity plot

The experimental data against the theoretical data is given in the Figure 4.19 for all the components. The parity plots showed a very good extent of correlation with the experimental points. The interactionparameters for the system Isooctane – naphthalene – DMF is given in the Table 4.25

Table 4.25 Interaction Parameters in UNIQUAC and NRTL model for Isooctane – naphthalene – DMF system

Component i	**Component j**	**Value (SI units)**	
		UNIQUAC	**NRTL**
Isooctane	Naphthalene	3149.57	723.587973
Naphthalene	Isooctane	808.82	75.0683157
Isooctane	DMF	-1057.64	2203.54092
DMF	Isooctane	-2114.23	2070.80413
Naphthalene	DMF	984.03	-543.02851
DMF	Naphthalene	4182.02	2356.40378

4.2.4Analysis of Isooctane - Naphthalene – Solvent system:

The consistency of experimental data can be verified the correlations as done before. Same relationships of Othmer Tobias ,Bachman and Hand's correlations are used.

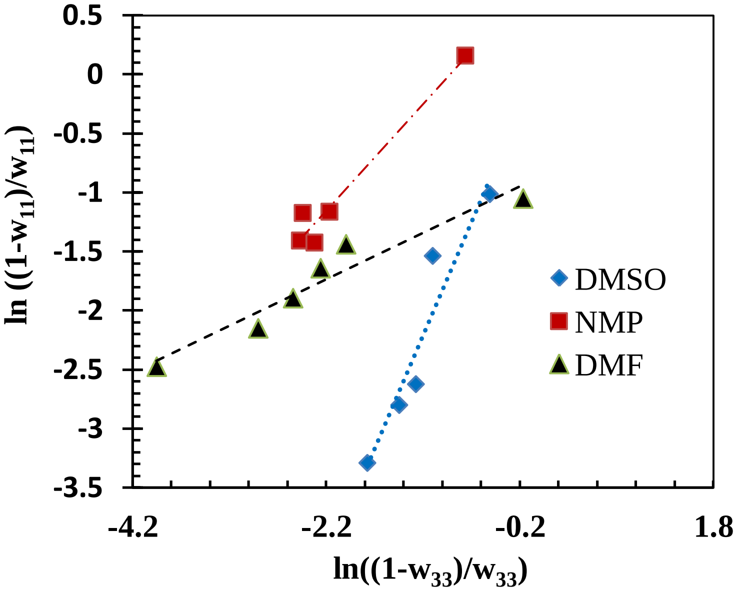


Figure 4.20 Othmer-Tobias' plot

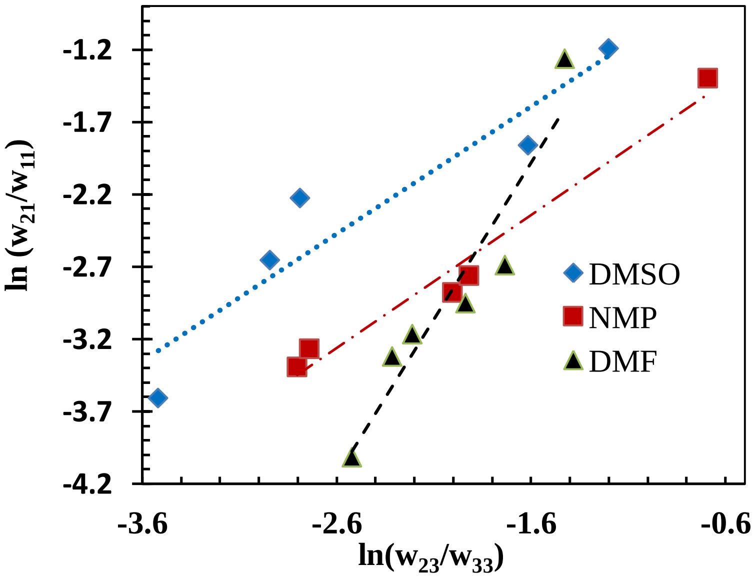


Figure 4.21 Hand's plot

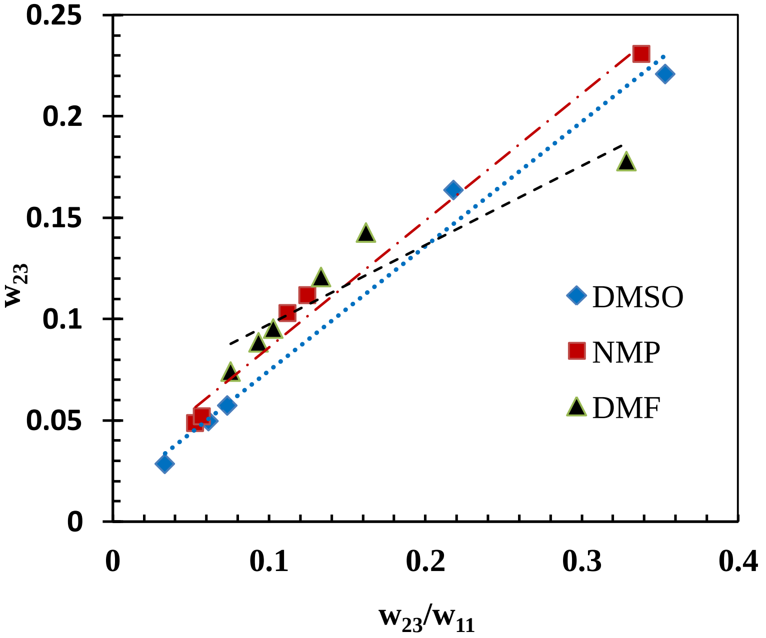


Figure 4.22 Bachman's Plot

The tie line data points showed a very good degree of fitting on a straight line with the correlations. The constants of the correlation equations are determined by fitting straight line and finding the slope and intercept for the given equations. R^2 values are determined for the correlations**.**

Table 4.26 Othmer Tobias, Hand's and Bachman correlation constants and correlation factor R^2 for the naphthalene at 30° C.

Solvent	**Othmer Tobias**			**Hand's**			**Bachman**		
	A	**B**	**R^2**	**A'**	**B'**	**R^2**	**a**	**b**	**R^2**
Naphthalene									
DMSO	0.0814	1.913	0.9056	-0.1835	0.8799	0.89	0.0132	0.6139	0.9861
NMP	0.8276	0.9001	0.9614	-0.8727	0.9182	0.971	0.0236	0.625	0.9849
DMF	-0.8724	0.3931	0.926	1.4771	2.1628	0.9021	0.0581	0.3916	0.8848

From the above table, it can be noted that both DMSO and NMP gave a high R^2 with Bachman correlations whereas DMF gives a very good fitting with Othmer Tobias plot.

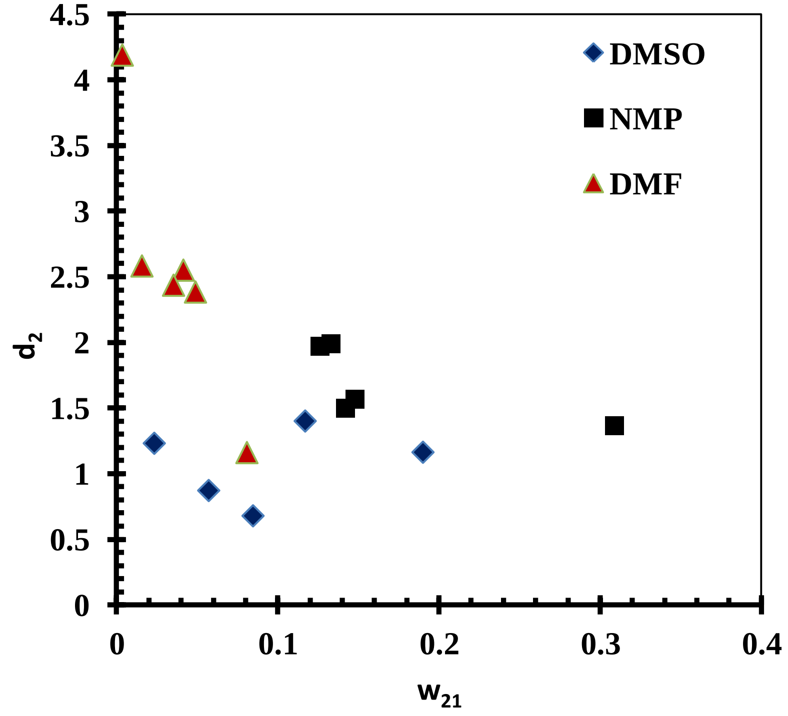


Figure 4.23 Distribution coefficient for naphthalene

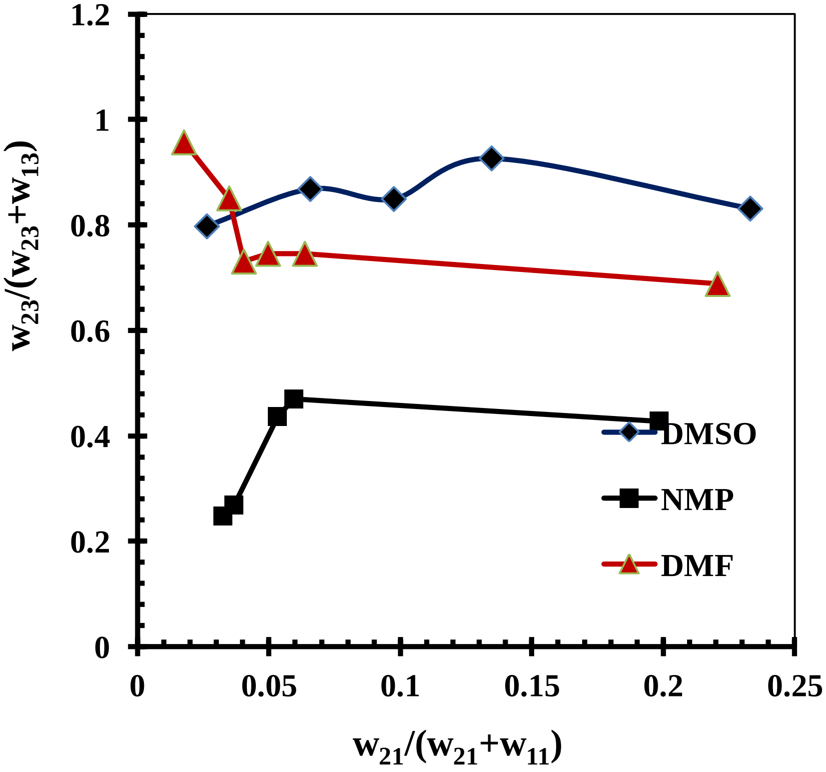


Figure 4.24 Selectivity Chart for naphthalene

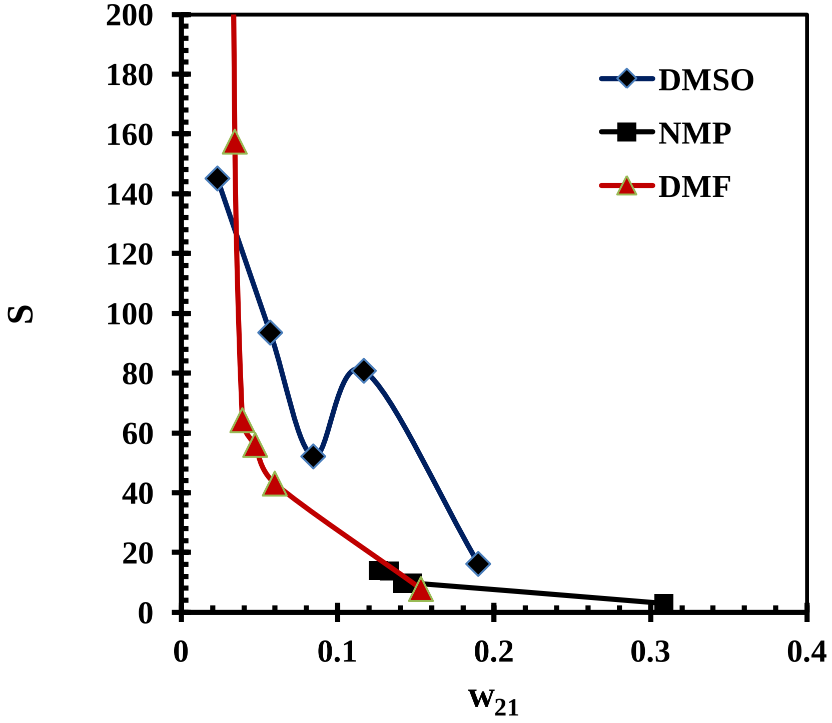


Figure 4.25 Separation factor S plotted against mass fraction of Naphthalene

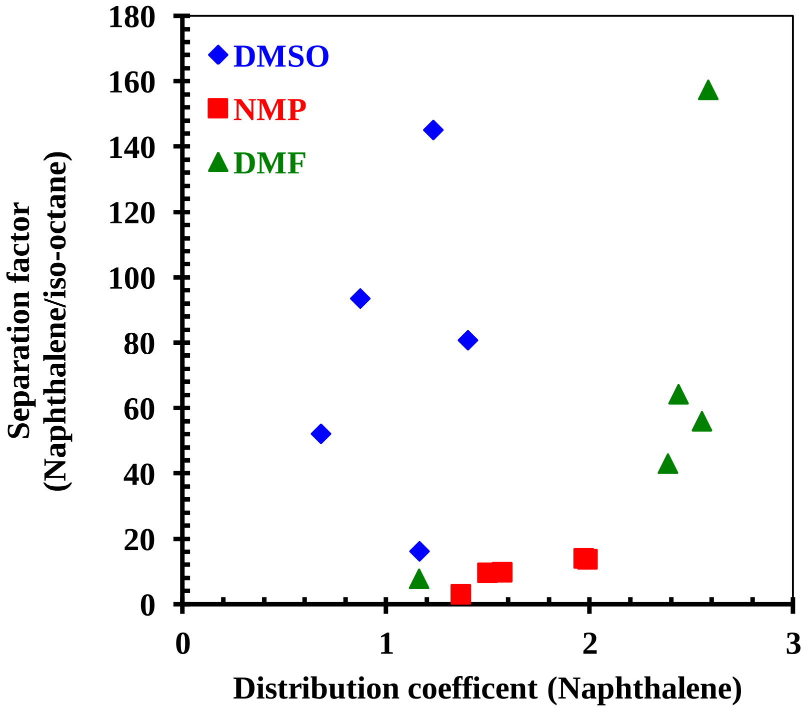


Figure 4.26 P-xylene/isooctane separation against distribution coefficients using DMSO, NMP and DMF for various feed conditions experimental data.

4.3 LSER analysis of Solvents

As mentioned in theory, LSER analysis was performed on the solvents used in the experiments. The solvatochromic parameters were retrieved form literature **(Kamlet et al., 1983)**. The parameters for the solvents are presented in the Table 4.27. As all the solvents are non aromatic, the δ value for all the solvents is zero. Also α value, which is the hydrogen bond donor capacity for a solvent, was found to be zero for all the solvents. Other values are mentioned as below.

Table 4.27 LSER solvatochromic parameters for the solvents (Kamlet et al., 1983).

	δ	**π***	**α**	**β**
DMSO	0	1	0	0.76
NMP	0	0.92	0	0.77
DMF	0	0.88	0	0.69

These solvatochromic parameters are used to regress the distribution coefficient and separation factor for p-xylene and naphthalene. The following equations are used to regress the parameters.

$$\ln D_2 = \ln D_2^o + s(\nu \pi^* + \nu d \delta) + b \nu \beta + a \nu \alpha \quad (4.1)$$

$$\ln S = \ln S^o + s(\nu \pi^* + \nu d \delta) + b \nu \beta + a \nu \alpha \quad (4.2)$$

The predicted LSER properties and the experimental values for D_2 and S are presented in Table 4.28 for p-xylene.

Table 4.28 Comparison of data between observed and predicted (LSER) for distribution coefficients (d_2) and separation factor (S) for p-xylene.

P-xylene				
V (volume fraction)	**Ln D_2, LSER**	**Ln D_2, exp**	**Ln S LSER**	**Ln S, exp**
DMSO				
0.74	-0.7	-0.9	3.03	2.34
0.76	-0.72	-0.93	3.09	2.42
0.65	-0.57	-0.81	2.63	1.83
0.49	-0.37	-0.48	1.94	1.12
0.92	-0.92	-1	3.77	3.43

NMP				
0.41	0.18	0.02	1.17	0.64
0.6	0.14	0.01	1.78	1.51
0.68	0.13	0.06	2.03	1.68
0.75	0.11	0.04	2.24	1.8
0.5	0.16	0.05	1.46	1.12
DMF				
0.52	-0.17	-0.04	1.69	2.24
0.58	-0.23	-0.08	1.92	2.43
0.64	-0.27	-0.12	2.11	2.62
0.71	-0.33	-0.22	2.37	3.08
0.77	-0.38	0.02	2.57	3.86
0.79	-0.4	0.05	2.65	4.33

The predicted values show a closed resemblance with the experimental values. So, we can say that LSER model can predict the activity of the solvents to a great extent. The values of regressed parameters for the group of solvents are present in the Table 4.29.

Table 4.29 Results of regression coefficient for LSER equation

Coefficients	**ln D_2 or ln S**	**s**	**d**	**b**	**a**	**SSE**
P-xylene						
Distribution coefficients	0.261	-11.832	0.000	13.879	0.000	0.67
Separation factors	0.262	11.799	0.000	-11.230	0.000	3.61

The SSE values for distribution coefficient are very small, which implies that it gives a good correlation whereas for separation factors, the correlation needs inclusion of certain more parameters may be.

Similarly the values for naphthalene and group of solvents is given in Table 4.30

Table 4.30 Comparison of data between observed and predicted (LSER) for distribution coefficients (d_2) and separation factor (S) for naphthalene.

Naphthalene				
V (volume fraction)	**Ln $D_{2,\ LSER}$**	**Ln $D_{2,\ exp}$**	**Ln S_{LSER}**	**Ln S_{exp}**
DMSO				
0.96	0.33	0.21	0.29	0.25
0.94	0.33	0.14	0.32	0.08
0.93	0.33	0.39	0.33	0.31
0.82	0.32	0.34	0.49	0.53
0.72	0.32	0.15	0.64	0.48
NMP				
0.75	0.75	0.45	1.01	0.73
0.76	0.75	0.40	1.00	0.68
0.72	0.73	0.69	1.03	1.01
0.72	0.73	0.68	1.03	1.00
0.41	0.54	0.31	1.32	1.21
DMF				
0.81	0.46	0.87	0.75	1.07
0.84	0.46	0.94	0.72	1.11
0.87	0.47	0.89	0.68	1.03
0.90	0.48	0.95	0.65	1.05
0.93	0.48	1.43	0.61	1.50
0.74	0.44	0.15	0.83	0.45

In case of naphthalene, LSER model shows a good degree of prediction for the group of solvents. Hence LSER model can also be used here to predict the distribution coefficient D and the separation factors. The regressed values for the group of solvents is given in Table 4.31.

Table 4.31 Results of regression coefficient for LSER equation for naphthalene

Coefficients	**ln D_2 or ln S**	**s**	**d**	**b**	**a**	**SSE**
Distribution coefficients	4.414	-9.993	0.000	6.253	0.000	.214
Separation factors	13.955	7.730	0.000	-25.602	0.000	7.292

The SSE values show a good fitting of LSER model for distribution coefficient and also with the separation factors.

4.4 Quaternary Systems

4.4.1 Using DMF

In this study, a mixture of p-xylene and naphthalene together is put in isooctane and recovered using solvent. The both the phases are separated and analyzed for composition of constituents. The extraction with the help of DMF is given in the Table 4.32. The calculated points with the help of UNIQUAC and NRTL parameters are given in the Table 4.33. The interaction parameters for the system is given in the Table 4.37

4.4.2 Using NMP

Here both p-xylene and naphthalene are recovered from isooctane mixture with the help of solvent NMP. The compositions are calculated and presented in the Table 4.34. The correlated points with the help of UNIQUAC and NRTL equations are presented in Table 4.35. Interaction parameters are given in the Table 4.38.

The distribution coefficients d_2 and d_3 are calculated for both p-xylene and naphthalene in the quaternary system. Separation factor for naphthalene over p-xylene is calculated for both DMF and NMP and are given in Table 4.36. These readings are for various feed conditions.

Table 4.32 Experimental data for the Isooctane – naphthalene – p-xylene – DMF system (all in mass fraction):

Isooctane phase				DMF rich phase			
w_{11} (IO)	w_{21} (p xylene)	W_{31} (naphthalene)	W_{41} (DMSO)	w_{14} (IO)	w_{24} (p xylene)	W_{34} (naphthalene)	W_{44} (DMF)
0.8163	0.0810	0.0623	0.0404	0.0971	0.0911	0.1145	0.6973
0.6011	0.1876	0.1588	0.0525	0.1243	0.1923	0.2241	0.4593
0.5821	0.2874	0.0833	0.0472	0.1298	0.3000	0.1001	0.4701
0.5562	0.3601	0.0399	0.0438	0.1222	0.3312	0.0447	0.5019
0.4791	0.2389	0.2100	0.0720	0.1345	0.2560	0.2298	0.3797
0.5177	0.3345	0.0899	0.0579	0.1412	0.3145	0.1108	0.4335
0.4231	0.1924	0.2444	0.1401	0.1551	0.1978	0.2459	0.4012
0.4991	0.4014	0.0873	0.0122	0.1492	0.3820	0.0954	0.3734

Table 4.33 Table 4.35 NRTL and UNIQUAC tie line data for Isooctane – naphthalene – p-xylene – DMF (all in mass fraction):

Iso octane phase								Solvent-rich phase (organic phase)							
w_1 (IO)		w_2 (p xylene)		w_3 (naphthalene)		w_4 (solvent)		w_1 (IO)		w_2 (p xylene)		w_3 (naphthalene)		w_4 (solvent)	
NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC
0.8160	0.8160	0.0809	0.0813	0.0622	0.0624	0.0409	0.0403	0.0958	0.0970	0.0915	0.0908	0.1149	0.1144	0.6978	0.6978
0.5835	0.5976	0.1875	0.1849	0.1710	0.1601	0.0580	0.0574	0.1270	0.1292	0.1899	0.1915	0.2056	0.2186	0.4775	0.4608
0.5679	0.5647	0.2932	0.2917	0.0839	0.0835	0.0549	0.0600	0.1290	0.1269	0.2926	0.2959	0.0999	0.1008	0.4785	0.4765
0.5655	0.5615	0.3458	0.3413	0.0387	0.0387	0.0500	0.0585	0.1243	0.1246	0.3439	0.3450	0.0459	0.0460	0.4859	0.4845
0.4797	0.4775	0.2454	0.2426	0.2064	0.2057	0.0685	0.0743	0.1412	0.1451	0.2444	0.2445	0.2295	0.2276	0.3849	0.3829
0.5178	0.5134	0.3276	0.3252	0.0934	0.0939	0.0612	0.0676	0.1381	0.1358	0.3228	0.3251	0.1070	0.1069	0.4321	0.4322
0.4800	0.4485	0.2009	0.2027	0.2401	0.2561	0.0789	0.0927	0.1550	0.1507	0.2009	0.1975	0.2676	0.2493	0.3766	0.4026
0.4592	0.4565	0.3871	0.3820	0.0877	0.0884	0.0659	0.0731	0.1438	0.1432	0.3766	0.3802	0.0967	0.0960	0.3829	0.3806

Table 4.34 Experimental data for the Isooctane – naphthalene – p-xylene – NMP system (all in mass fraction):

Isooctane phase				DMF rich phase			
w_{11} (IO)	w_{21} (p xylene)	w_{21} (naphthalene)	w_{31} (NMP)	w_{13} (IO)	w_{21} (p xylene)	w_{23} (naphthalene)	w_{33} (NMP)
0.5831	0.1033	0.0892	0.2244	0.2333	0.0912	0.1134	0.5621
0.5332	0.1345	0.0232	0.3091	0.2562	0.1412	0.0512	0.5514
0.5623	0.1043	0.0753	0.2581	0.2241	0.1341	0.0824	0.5594
0.5401	0.1223	0.0721	0.2655	0.2792	0.1234	0.0713	0.5261
0.4677	0.1984	0.0276	0.3063	0.2930	0.1819	0.0291	0.4960

Table 4.35 NRTL and UNIQUAC tie line data for Isooctane – naphthalene – p-xylene – NMP (all in mass fraction):

Isooctane phase								Solvent-rich phase (organic phase)							
x1 (IO)		x2 (P xylene)		naphthalene		x3 (solvent)		x1 (IO)		x2 (p xylene)		naphthalene		x3 (solvent)	
NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC
0.5645	0.5540	0.0951	0.1029	0.0941	0.0942	0.2463	0.2489	0.2300	0.2308	0.0999	0.0908	0.1087	0.1069	0.5614	0.5715
0.5576	0.5516	0.1353	0.1373	0.0231	0.0230	0.2839	0.2881	0.2627	0.2613	0.1418	0.1386	0.0514	0.0515	0.5441	0.5487
0.5704	0.5820	0.1139	0.1050	0.0739	0.0755	0.2418	0.2376	0.2279	0.2344	0.1193	0.1330	0.0834	0.0820	0.5694	0.5506
0.5257	0.5274	0.1220	0.1211	0.0690	0.0684	0.2833	0.2831	0.2708	0.2699	0.1237	0.1262	0.0738	0.0755	0.5318	0.5284
0.4668	0.4625	0.1959	0.1940	0.0273	0.0276	0.3101	0.3159	0.2941	0.2886	0.1861	0.1854	0.0295	0.0291	0.4903	0.4968

Table 4.36 Experimental distribution coefficients and selectivity for p-xylene and naphthalene in quaternary systems using solvents DMF and NMP.

	d_2	d_3	$S_3=d_3/d_2$
DMF			
	1.1247	1.8379	1.6341
	1.0251	1.4112	1.3767
	1.0438	1.2017	1.1512
	0.9197	1.1203	1.2181
	1.0716	1.0943	1.0212
	0.9402	1.2325	1.3109
	1.0061	1.0281	1.0219
	0.9517	1.0928	1.1483
NMP			
	0.8829	1.2713	1.4400
	1.0498	2.2069	2.1022
	1.0943	1.2857	1.1749
	0.9889	1.0090	1.0203
	0.9168	1.0550	1.1507

A plot between separation factor of naphthalene vs distribution coefficient of naphthalene is given in Figure 4.27. Separation factor for naphthalene is calculated by using the relation $S_3=d_3/d_2$.

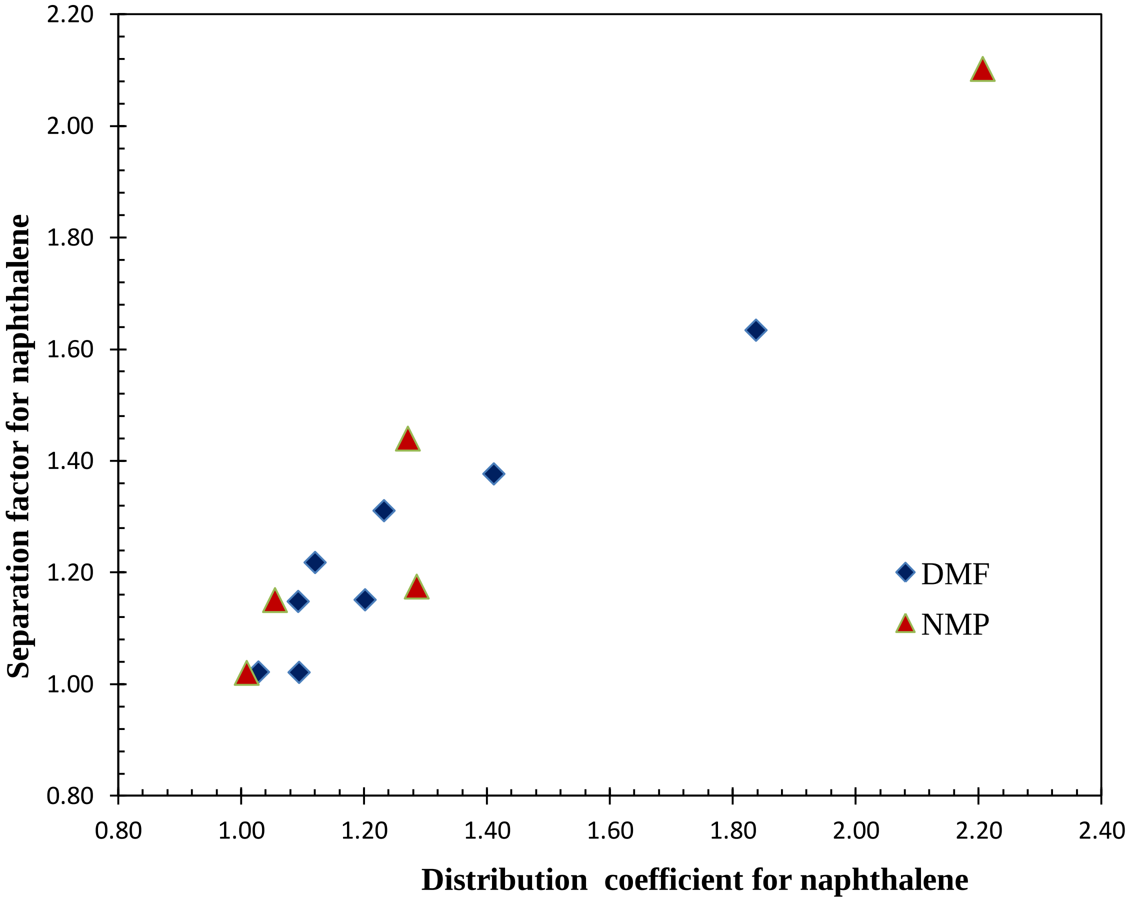


Figure 4.27 Naphthalene separations against distribution coefficients using NMP and DMF for various feed conditions experimental data in quaternary system.

From the separation factor-distribution coefficient diagram, a qualitative analysis of the efficiency of the solvents can be made. Both the solvents show a separation factor value of greater than unity. This implies that both these can be used to separate naphthalene from other aromatic solvents. Also, the distribution coefficient values for both the solvents are similar and significant. However, for the given set of experiments, NMP showed a greater selectivity as well as capacity for the recovery of naphthalene.

Table 4.37 Interaction Parameters in UNIQUAC and NRTL model for Isooctane – p-xylene - naphthalene – DMF system

Component i	Component j	Value (SI units)	
		UNIQUAC	NRTL
Isooctane	P-xylene	-9.10103	-195.475
P-xylene	Isooctane	38.59024	230.6684
Isooctane	Naphthalene	-312.077	1627.083
Naphthalene	Isooctane	35.00318	367.3231
Isooctane	DMF	-391.833	661.3402
DMF	Isooctane	5.885953	685.1015
P-xylene	Naphthalene	40.33712	-3283.91
Naphthalene	P-xylene	-112.947	9998.39
P-xylene	DMF	-777.616	1018.184
DMF	P-xylene	289.3535	-300.362
Naphthalene	DMF	-314.754	471.0954
DMF	Naphthalene	-36.4791	3711.623

Table 4.38 Interaction Parameters in UNIQUAC and NRTL model for Isooctane – p-xylene - naphthalene – NMP system

Component i	Component j	Value (SI units)	
		UNIQUAC	NRTL
Isooctane	P-xylene	-230.089	563.3194
P-xylene	Isooctane	-213.031	341.3634
Isooctane	Naphthalene	-694.115	1884.687
Naphthalene	Isooctane	-151.386	2599.633
Isooctane	NMP	-208.254	289.3444
NMP	Isooctane	0.9900	502.5481
P-xylene	Naphthalene	-9999.91	912.3731
Naphthalene	P-xylene	-244.103	1529.702
P-xylene	NMP	-299.043	1417.362
NMP	P-xylene	-240.369	332.0028
Naphthalene	NMP	-9937.14	2332.883
NMP	Naphthalene	-525.181	1514.044

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

On the basis of the present studies, the following conclusions are drawn

- The recovery of aromatic compound (represented by p-xylene) and bicyclic aromatic compound (represented by naphthalene) was studied by various solvents at the normal atmospheric pressure and 30°C. The solvents used for extraction are DMSO, DMF and NMP. Liquid-liquid equilibrium diagrams were made for each case showing the tie-lines and solubility data. In the diagrams, one phase region and two phase region can be clearly seen. A larger area under the two phase region demarcates a higher miscibility of the solute in the solvent. The veracity of experimental data was verified with the empirical correlations of Othmer-Tobias, Bachman and Hand.
- For naphthalene, DMF showed a very high distribution coefficient which means it has a greater capacity to recover naphthalene from the feed. But it is distributed only over a narrow range of solute mass fraction in the feed. Whereas, NMP covered a good range of mass fraction of solute and also had a considerable degree of capacity to recover the amount of naphthalene. Considering the separation factor which is the efficiency of a solvent to effectively separate one compound from another, DMSO has a higher value compared to other two solvents. However from analyzing both distribution coefficient and the separation factor, DMF can be said to be a good solvent.
- NMP and DMF both show a good degree of capacity towards recovery of p-xylene. Whereas considering the separating efficiency, DMF has very good efficacy. So we can say that DMF is very good solvent for the recovery of bicyclic aromatic compounds like p-xylene.
- Also quaternary extraction for the recovery of naphthalene and p-xylene was made with the help of DMSO and NMP. The efficiency of solvents are reported for the simultaneous removal of aromatics and bicyclic aromatics from the feed. Selectivity versus distribution factor chart was made for the removal of naphthalene using the solvents. NMP and DMF

show similar removal efficiency for naphthalene with NMP showing a little better performance than DMF.

- Thermodynamic models of NRTL and UNIQUAC were used to fit the data by regression and find the interaction parameters for the extractions with different. The tie-line points were calculated using these models. The various RMSD values for the results is as shown below:

System	**UNIQUAC**	**NRTL**
	100 × RMSD	
Ternary systems		
Isooctane + p-xylene + DMSO	1.29	1.38
Isooctane + p-xylene + NMP	1.39	1.47
Isooctane + p-xylene + DMF	1.79	1.45
Isooctane + naphthalene + DMSO	0.56	1.67
Isooctane + naphthalene + NMP	1.23	1.23
Isooctane + naphthalene + DMF	3.11	8.11
Quaternary systems		
Isooctane + p-xylene + naphthalene + NMP	1.02	0.38
Isooctane + p-xylene + naphthalene +DMF	1.34	1.58

The values of RMSD show a good degree of fitting for UNIQUAC model as compared to NRTL model though both of them show an accurate regression.

- LSER model was used to correlate the various solvents efficacy in extraction to their physical properties like hydrogen bond accepting and donating ability and their dipole moment. Predicted distribution coefficients and separation factors are compared with the experimental results and the SSE values are reported.

5.2 Recommendations:

- More work needs to be done in the field of simultaneous extraction of aromatic compounds with the help of newer solvents.
- Attention should be given to recovery of solvents after the separation.
- Several new ionic solvents may be correlated with LSER model so that the distribution coefficient can be studied and predicted.

CHAPTER 6

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