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Study on the effect of adding co-solvent (n-alkoxyethanol) to sulfolane on the toluene extraction

Khalid Farhod Chasib[*]

Department of Chemical Engineering, University of Technology, Baghdad, P.O. Box 18310, Iraq.

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UNIFAC.

Abstract. Liquid-liquid equilibrium data, both binodal and tie lines are presented for the pseudo-ternary systems: (sulfolane + n-Alkoxyethanol) + octane + toluene at 293.15 K. The experimental liquid-liquid equilibrium data have been correlated using the nonrandom two liquid (NRTL), UNIQUAC and UNIFAC models to predict the phase composition of the systems studied here, and the binary interaction parameters of these components have been calculated. The correlated tie lines have been compared with the experimental data. The comparisons indicate that the calculation based on both NRTL and UNIQUAC models gave a good representation of the equilibrium compositions data for all systems studied. Also Othmer, Tobias and Hand methods satisfactorily correlated tie-line data of the studied systems. The agreement between the correlated and experimental results was very good. The solvent (25% sulfolane+75% 2-ethoxyethanol) shows a high capacity for toluene (a distribution coefficient around unity), and for this reason, it can be used for higher recovery of aromatics at lower solvent to feed ratios and temperatures.

1. Introduction

Solvent extraction is one of the most important methods to produce high-purity aromatic extracts from catalytic reformates. The selection of a solvent for extraction study depends on the solvent power measured by the solute distribution coefficient and also on its selectivity. In the case of recovery of aromatics from reformats, a solvent with largest possible capacity and highest selectivity toward aromatics is preferred.

The efficient separation of aromatic from catalytic reformates is an important concept in the chemical industry where many solvents have been tested to improve such recovery. Sometimes it may be desirable to use a low-boiling solvent that has to be distilled for a recycling process. Three major factors have been found to influence the equilibrium characteristics of solvent extraction of aromatic from catalytic reformates (i.e. the nature of solute, the concentration of solute, and the type of organic solvent). Simultaneously, the impact of additional controlling factors, such as the third-phase formation and the swing effect of a mixed solvent, can also modify the equilibrium. Process considerations dealing with the physical extraction of aromatic through hydrogen bonding or dipole-dipole interaction still remain a challenging problem, because such systems show extremely nonideal behavior.

Regarding the technical and economic merits of low boiling solvents during regeneration by distillation, the selection of Sulfolane as extracting agents from various classes of polar, protic, or nonprotic compounds was made.

In recent years, *Sulfolane* has been employed more and more in new or improved extraction processes. It is an important industrial solvent having the ability to extract aromatic hydrocarbons from petroleum products and to purify natural gas. This process is still widely used in refineries and petrochemical industry. Because sulfolane is one of the most efficient industrial

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[*] *Tel.: +964 790 2 89 80 18*
E-mail address: khalid_farhod@uotechnology.edu.iq

solvents for purifying aromatics, the process operates at a relatively low solvent-to-feed ratio, making sulfolane relatively cost-effective, compared to similar-purpose solvents. In addition, it is selective in a range that complements distillation, where sulfolane cannot separate two compounds, distillation easily can and vice versa, keep sulfolane units useful for a wide range of compounds with minimal additional cost. Sulfolane is highly stable and can therefore be reused many times. Therefore, it is necessary to have complete thermodynamic data for these systems [1].

Liquid-Liquid Equilibria (LLE) data on a number of ternary mixtures containing sulfolane have been extensively studied [2-7]. Few papers in the literature deal with quaternary liquid-liquid equilibrium data, which include sulfolane [8-12]. In this paper, we present a new experimental quaternary liquid-liquid equilibrium data for toluene + octane + sulfolane + n-Alkoxyethanol at 293.15 K. There is no literature data on the quaternary systems studied. There are also no references to earlier published work about aromatics extraction from aliphatic components. This quaternary system is treated as a pseudo ternary system; component 1 is (sulfolane + n-Alkoxyethanol) and two components are kept the same (octane and toluene), where n-Alkoxyethanol means 2-methoxyethanol or 2-ethoxyethanol. The mass fractions of n-Alkoxyethanol in sulfolane were (5 to 75)%. Furthermore, the LLE data were correlated using the NRTL [13], UNIQUAC [14] and UNIFAC [15] activity coefficient models to obtain the binary interaction parameters of these pairs of components. The experimental data for all studied systems were also correlated by using equation proposed by Hand [16], Othmer and Tobias [17].

2. Experimental section

2.1. Chemicals

Sulfolane (> 99.5%, GC), octane (> 99.8%, GC), toluene (> 99.9%, GC), 2-methoxyethanol (> 99.8%, GC) and 2-ethoxyethanol (> 99.8%, GC) were supplied by Fluka, these chemicals were presented in Table 1 with their purities. Physical properties such as density of these materials used in this study were measured experimentally, and compared with values in the literature [18,19]. All chemicals were used without further purification, but were kept over freshly activated molecular sieves of type 4A (Union Carbide) for several days and filtered before use. Mass fractions of impurities detectable by GC were found to be < 0.0020. Deionized and redistilled water was used throughout all experiments. Refractive indices were measured through an Abbe-Hilger refractometer with an uncertainty of $\pm 5 \times 10^{-4}$. Densities were measured using an Anton Paar DMA 4500 density meter. The estimated uncertainty in the density was $\pm 10^{-4}$ g/cm^3. The measured densities and refractive indices of the pure solvents used in this work agreed well with those values published in the literature [18,19].

2.2. Apparatus and procedures

The binodal (solubility) curves were determined by the cloud-point titration method, in an equilibrium glass cell with a water jacket, to maintain isothermal conditions as described by Hadded and Edmister [20]. The temperature in the cell was measured by a certified Fischer thermometer with an accuracy of ±0.1 K, and was kept constant by circulating water from a water bath equipped with a temperature controller.

The major central part of the solubility curves was obtained by titrating heterogeneous mixtures of octane + toluene with sulfolane until the turbidity had disappeared. For the octane side and solvent side limited regions in which the curve and the sides of the triangle are close and exhibit similar slopes, binary mixtures of either (octane + sulfolane) or (toluene + sulfolane) were titrated against the third component until the transition from homogeneity to cloudiness was observed. All mixtures were prepared by weight with a Mettler scale, accurate within $\pm 10^{-4}$ g. The transition point between the homogeneous and heterogeneous regions was determined visually. The reliability of the method depends on the precision of the Metrohm microburet with an uncertainty of ± 0.005 cm^3, and is limited by the visual inspection of the transition across the apparatus. Concentration determinations were

Table 1. Physical properties of chemicals used at 25°C.

Component	M. wt. g/mol	Density ρ^{25} g/cm^3		Refractive index n_D^{25}		Boiling point °C
		Exp.	Lit.	Exp.	Lit.	
Sulfolane	120.17	1.2654	1.2646	1.4819	1.4816	285.2
Octane	114.23	0.7027	0.7031	1.3952	1.3956	125.7
Toluene	92.14	0.8575	0.8577	1.4930	1.4935	110.6
2-methoxyethanol	76.09	0.9642	0.9651	1.4013	1.4026	124.4
2-ethoxyethanol	90.12	0.9313	0.9305	1.4096	1.4082	135.1

made with a mass fraction uncertainty of ±0.002. Endpoint determinations of the tie lines were based upon the independent analysis of the conjugate phases that were regarded as being in equilibrium. The tie-lines were determined using the refractive index method; the experimental procedures were described by Briggs and Comings [21]. Plait points were determined using the method outlined by Treybal et al. [22].

3. Results and discussion

3.1. Liquid-liquid equilibria of the systems (sulfolane +2-methoxyethanol)+n-octane + toluene

The liquid-liquid equilibria of the following systems have been studied at 293.15 K:

1. sulfolane + n-octane + toluene.
2. [sulfolane + 2-methoxyethanol (mass fraction 0.95: 0.05)] + n-octane + toluene.
3. [sulfolane + 2-methoxyethanol (mass fraction 0.75: 0.25)] + n-octane + toluene.
4. [sulfolane + 2-methoxyethanol (mass fraction 0.50: 0.50)] + n-octane + toluene.
5. [sulfolane + 2-methoxyethanol (mass fraction 0.25: 0.75)] + n-octane + toluene.

3.1.1. Mutual solubility

The compositions of mixtures on the binodal curve of the above five systems at 293.15 K are represented as triangular diagrams in Figures 1-5.

For comparison purpose, binodal curves of the five systems are included in Figure 6. Binodal curve of the pure sulfolane + n-octane + toluene at 293.15K are also included in this diagram for comparison.

Figure 1 shows that the two-phase region for the system containing only sulfolane as a solvent is large, indicating a large range of separation compositions.

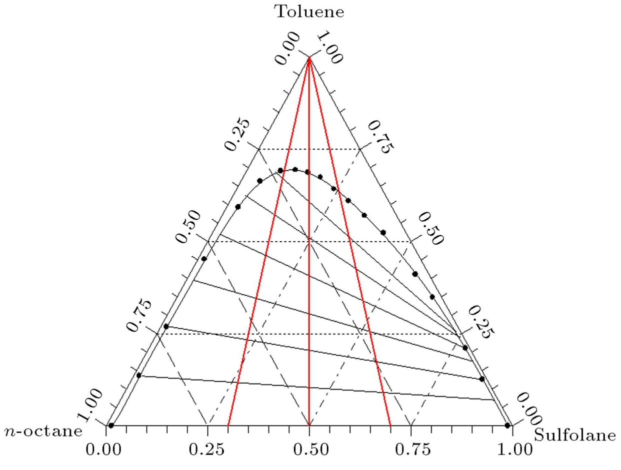

Figure 1. Binodal curve and tie lines for pure sulfolane + n-octane + toluene at 293.15K.

The relative solubility of toluene in an n-octane or in solvent mixture is evident from the tie lines. The slopes of the tie lines presented here (Figures 2-5) show that toluene is more soluble in the n-octane than in solvent mixture, with a skewing toward the

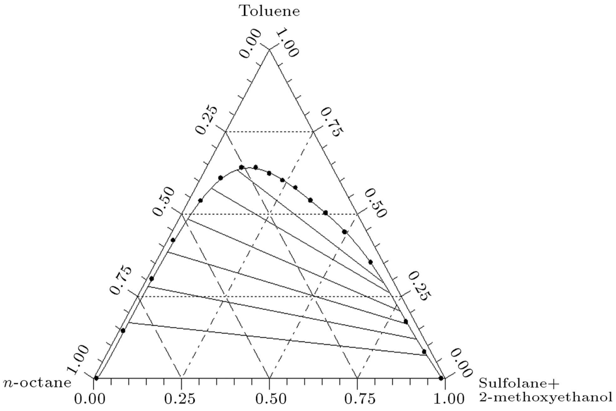

Figure 2. Binodal curve and tie lines for (sulfolane + 2-methoxy ethanol (mass fraction 0.95: 0.05)) + n-octane + toluene at 293.15K.

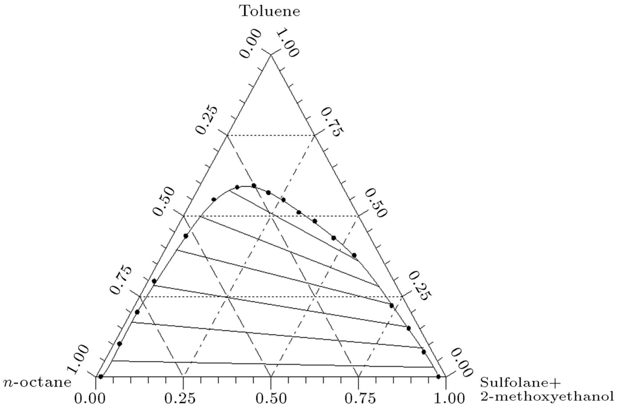

Figure 3. Binodal curve and tie lines for (sulfolane + 2-methoxy ethanol (mass fraction 0.75: 0.25)) + n-octane + toluene at 293.15 K.

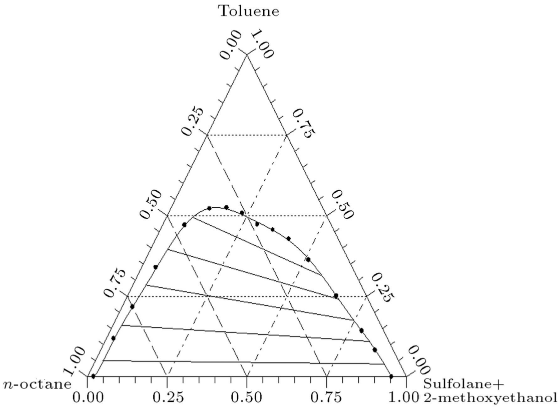

Figure 4. Binodal curve and tie lines for (sulfolane + 2-methoxy ethanol (mass fraction 0.50: 0.50)) + n-octane + toluene at 293.15 K.

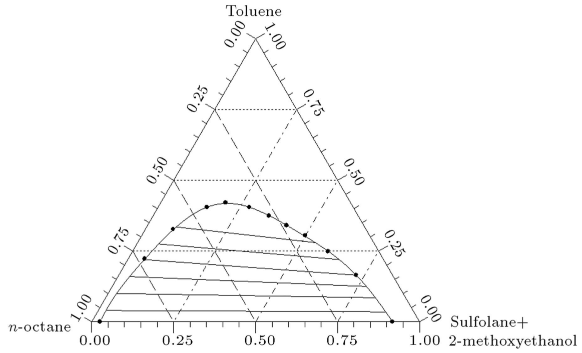

Figure 5. Binodal curve and tie lines for (sulfolane + 2-methoxy ethanol (mass fraction 0.25: 0.75)) + n-octane + toluene at 293.15 K.

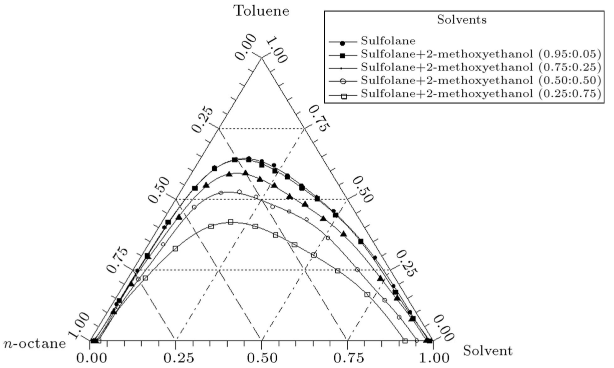

Figure 6. Comparison of the phase-equilibrium diagram for solvent + n-octane + toluene at 293.15 K.

solvent mixture axis. This skewing decreases with the increase of the 2-methoxyethanol content in the solvent mixture.

Figure 6 shows that the area of the two-phase region increases in the order pure sulfolane > sulfolane : 2-methoxyethanol (0.95: 0.05) > (0.75: 0.25) > (0.50 : 0.50) > (0.25 : 0.75).

The maximum solubility of n-octane in solvent mixture (sulfolane + 2-methoxyethanol) (0.95: 0.05), (0.75: 0.25), (0.50: 0.50), and (0.25: 0.75) is 0.010, 0.020, 0.046, and 0.082 mass fraction, respectively, and the solubility of solvent mixture in n-octane is 0.010, 0.016, 0.020, and 0.026 mass fraction, respectively, at 293.15 K.

The increase in the 2-methoxyethanol content in the solvent mixture results in a decrease in the two-phase area, and reflects the increase in solubility of n-octane in the solvent mixture.

3.1.2. Tie line data

Tie line data for the five systems at 293.15 K are plotted on triangular diagrams, according to a method of Francies [23] (Figures 1-5). The tie line data indicate the composition of two phases (solvent-rich phase and n-octane-rich phase). These data are observed to fit well in the smoothed binodal curves, indicating the accuracy of the experimental tie line data. From the slope of the tie lines, it can be seen that, in all cases, toluene is more soluble in n-octane-rich phase than in solvent-rich phase, with a large skewing toward the solvent axis, but the selectivity is greater than 1; thus, the extraction is possible.

3.1.2.1. Evaluation of the consistency of the experimental tie lines

The accuracy of the experimental data for the four pseudo-ternary systems at 293.15K were checked by the Bachman, Othmer-Tobias, Hand, and selectivity methods [16,17,21]:

Bachman method:

$$w_{11} = a_1 + b_1 \left(\frac{w_{11}}{w_{22}} \right). \tag{1}$$

Othmer-Tobias method:

$$\log \left(\frac{1 - w_{11}}{w_{11}} \right) = a_2 + b_2 \log \left(\frac{1 - w_{22}}{w_{22}} \right). \tag{2}$$

Hand method:

$$\log \left(\frac{w_{31}}{w_{11}} \right) = a_3 + b_3 \log \left(\frac{w_{32}}{w_{22}} \right). \tag{3}$$

Selectivity method:

$$\log \left(\frac{w_{32}.w_{11}}{w_{12}.w_{31}} \right) = a_4 + b_4 \log \left(\frac{w_{11}.w_{22}}{w_{21}.w_{12}} \right). \tag{4}$$

The tie line data of the mixture (sulfolane + 2-methoxyethanol) + n-octane + toluene were correlated by the Bachman, Othmer-Tobias, Hand and selectivity methods to ascertain the reliability of the experimental results for each system.

The parameters a_j and b_j ($j = 1 - 4$) of Eqs. (1)-(4) are obtained by using *maximum likelihood principle* method [24,25]. The parameters and the correlation coefficients, R_j, are given in Table 2. Since the data show little scattering from a straight line, they are considered acceptable on an empirical basis, indicating internal consistency of the experimental data. The estimation of plait points for the systems is presented by the use of Treybal's method [21,22].

As can be seen from Table 2, all methods gave good correlation for the equilibrium distribution data, the largest correlation coefficient (R) being found for all systems with selectivity method.

The values of the coefficient of correlation (R) are close to unity. The goodness of the fit confirms the reliability of the results.

Table 2. Results of the maximum likelihood principle method for (sulfolane + 2-methoxyethaonl) + n-octane + toluene at 293.15 K.

Solvent	**Correlation**					
Sulfolane:	**Bachman**			**Othmer - Tobias**		
2-methoxyethaonl (mass fraction)	a_1	b_1	R_1	a_2	b_2	R_2
(0.95: 0.05)	-0.3070	1.2404	0.9946	0.7097	-0.5284	0.9966
(0.75: 0.25)	-0.6635	1.6111	0.9895	0.8160	-0.3665	0.9975
(0.50: 0.50)	-0.7652	1.6199	0.9862	0.6840	-0.2494	0.9978
(0.25: 0.75)	-1.0847	1.8321	0.9803	0.7390	-0.0385	0.9957
Sulfolane:	**Hand**			**Selectivity**		
2-methoxyethaonl (mass fraction)	a_3	b_3	R_3	a_4	b_4	R_4
(0.95: 0.05)	0.7239	-0.5827	0.9856	0.6107	0.1824	0.9990
(0.75: 0.25)	0.8623	-0.4008	0.9987	0.5712	0.1735	0.9998
(0.50: 0.50)	0.8079	-0.3251	0.9995	0.4277	0.5070	0.9991
(0.25: 0.75)	0.9581	-0.0990	0.9949	0.5825	0.1152	0.9990

$$k_1 = \frac{\text{Toluene mole fraction (or mass fraction) in solvent layer}}{\text{Toluene mole fraction (or mass fraction) in } n\text{-octane layer}} = \frac{w_{31}}{w_{32}}, \tag{5}$$

$$k_2 = \frac{n\text{-Octane mole fraction (or mass fraction) in solvent layer}}{n\text{-Octane mole fraction (or mass fraction) in n-octane layer}} = \frac{w_{21}}{w_{22}}. \tag{6}$$

Box I.

3.1.3. *Distribution coefficient and selectivity*

The effectiveness of the solvent for the extraction can be expressed in terms of the distribution coefficient (k_1) and (k_2) of the toluene and n-octane, respectively, and the selectivity (S) of the solvent.

Distribution coefficients of toluene and n-octane are represented in Eqs. (5)-(6) shown in Box I.

The selectivity (S) which is a measure of the ability of solvent to separate toluene from n-octane is given by the formula:

$$S = \frac{k_1}{k_2}. \tag{7}$$

Figure 7 shows the comparison of distribution coefficients of toluene, and Figure 8, the selectivity of solvents.

As can be seen from the distribution and selectivity curves, Figures 7 and 8, the selectivity and capacity vary in the following order:

Sulfolane:

Selecvtivity ←

2-methoxyethanol(0.75:0.25)>(0.95:0.05)>(0.5:0.5)>(0.25:0.75)

Capacity →

Similar conclusions can be drawn from Figure 6; increase in the heterogeneous area in the ternary diagram results in an increase in selectivity and a decrease in capacity.

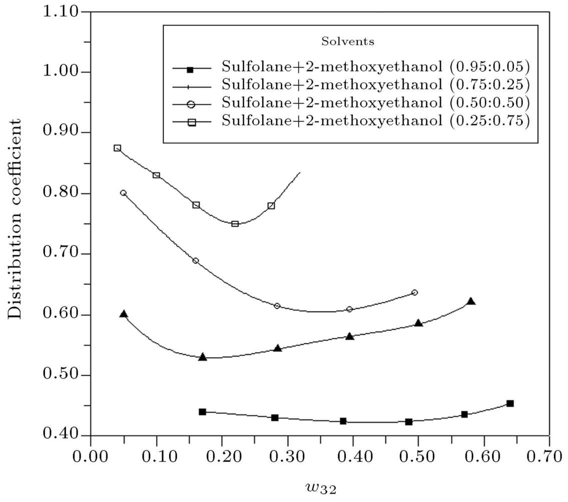

Figure 7. Distribution curves for solvent (1) + n-octane (2) + toluene (3) at 293.15K.

Combination solvent systems (sulfolane + 2-methoxyethanol), although less selective, have higher capactiy compared to that of pure sulfolane.

High selectivity for a desired capacity or solvent power is the primary requirement for a good solvent.

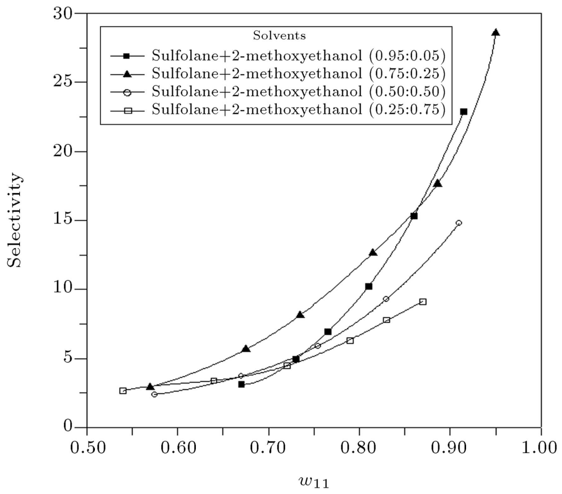

Figure 8. Selectivity curves for solvent (1) + *n*-octane (2) + toluene (3) at 293.15K.

However, an increase in the capacity of a solvent leads to a decrease in its selectivity or vice versa. To choose the optimum values of selectivity and capacity is therefore a compromise between the two values, which can be adjusted here by the amount of 2-methoxyethanol being added to sulfolane.

3.1.4. Estimation of the plait point

The compositions of the plait points as determined by construction and Treybal methods [21,22] for the systems (sulfolane + 2-methoxyethanol) (1) + *n*-octane (2) + toluene (3) at 293.15 K are listed in Table 3, as mass fraction.

It is apparent from Table 3 that the plait point concentration changes from a solvent-rich composition to *n*-octane-rich composition, as the 2-methoxyethanol content increases in the solvent mixture.

3.2. Liquid-liquid equilibria of the systems (sulfolane + 2-ethoxyethanol) + n-octane + toluene

The phase equilibria (LLE) of the following systems have been studied at 293.15 K:

(6) [sulfolane + 2-ethoxyethanol (mass fraction 0.95: 0.05)] + *n*-octane + toluene.

(7) [sulfolane + 2-ethoxyethanol (mass fraction 0.75: 0.25)] + *n*-octane + toluene.

(8) [sulfolane + 2-ethoxyethanol (mass fraction 0.50: 0.50)] + *n*-octane + toluene.

(9) [sulfolane + 2-ethoxyethanol (mass fraction 0.25: 0.75)] + *n*-octane + toluene.

3.2.1. Mutual solubility

The experimental data for the binodal curve at 293.15 K are represented as triangular diagrams in Figures 9-12.

The binodal curves of the sulfolane + *n*-octane

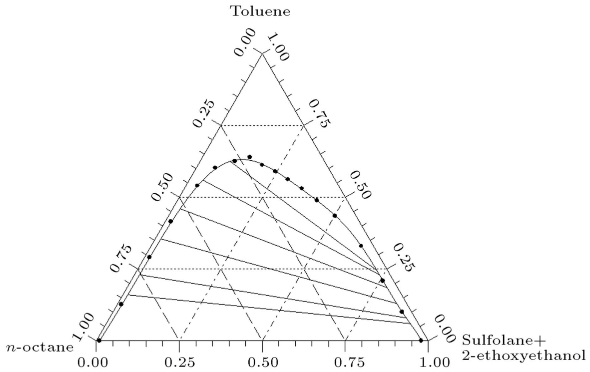

Figure 9. Binodal curve and tie lines for [sulfolane + 2-ethoxyethanol (mass fraction 0.95: 0.05)] + *n*-octane + toluene at 293.15 K.

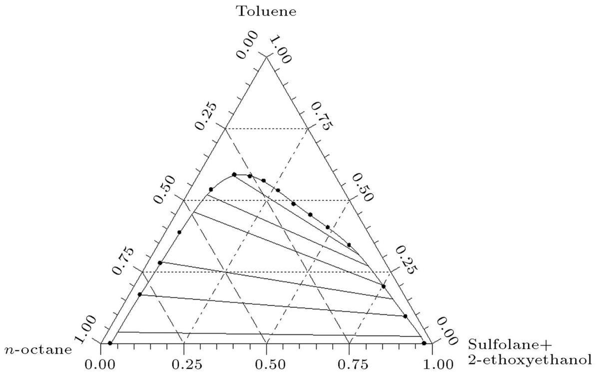

Figure 10. Binodal curve and tie lines for [sulfolane + 2-ethoxyethanol (mass fraction 0.75: 0.25)] + *n*-octane + toluene at 293.15 K.

Table 3. Compositions of the plait points for solvent (1) + *n*-octane (2) + toluene (3) at 293.15K.

Solvent	**Construction method**			**Treybal method**		
Sulfolane + 2-methoxy ethanol (mass fraction)	w_1	w_2	w_3	w_1	w_2	w_3
(0.95: 0.05)	0.400	0.088	0.512	0.397	0.086	0.517
(0.75: 0.25)	0.320	0.160	0.520	0.322	0.163	0.515
(0.50: 0.50)	0.300	0.220	0.480	0.307	0.223	0.470
(0.25: 0.75)	0.280	0.316	0.404	0.283	0.318	0.399

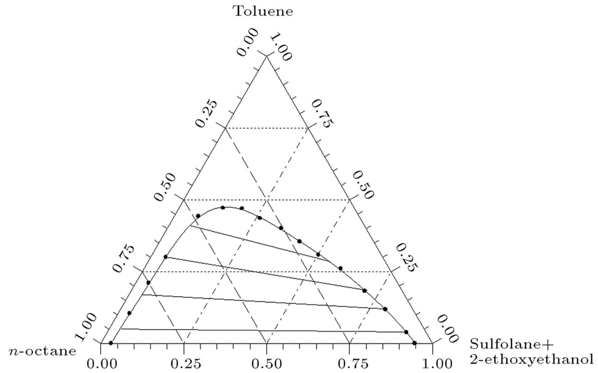

Figure 11. Binodal curve and tie lines for [sulfolane + 2-ethoxyethanol (mass fraction 0.50: 0.50)] + n-octane + toluene at 293.15 K.

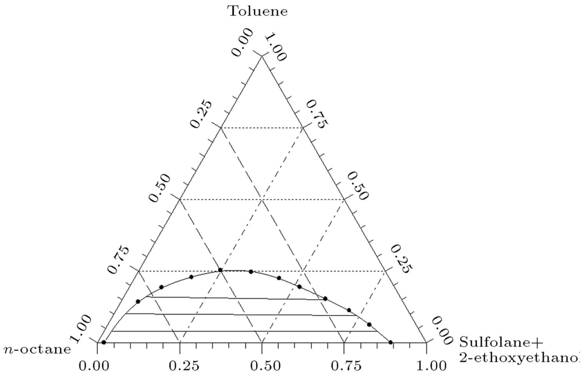

Figure 12. Binodal curve and tie lines for [sulfolane + 2-ethoxyethanol (mass fraction 0.25: 0.75)] + n-octane + toluene at 293.15 K.

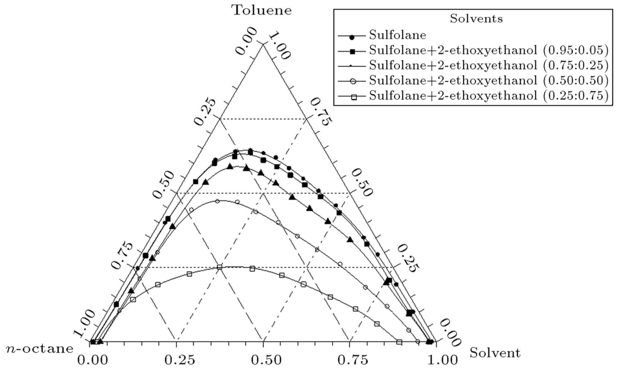

Figure 13. Comparison of the phase equilibrium diagram for solvent + n-octane + toluene at 293.15 K.

+ toluene and the above four systems are included in Figure 13 for comparison.

From the binodal curves data shown in Figure 13, it can be seen that an increase in the 2-ethoxyethanol content in solvent mixture (from 0.05 to 0.75 mass fraction) results in a decrease in the area of two-phase region, i.e. the mutual solubility of the components are increased (the maximum solubility of n-octane in solvent mixture is 0.020, 0.022, 0.052, and 0.107 mass fraction, respectively, and the solubility of solvent mixture in n-octane is 0.010, 0.030, 0.032, and 0.040 mass fraction, respectively). This implies that the existence of more hydrogen bonding interaction between sulfolane and 2-ethoxyethanol results in a decrease in the area of the two-phase region.

3.2.2. Tie line data

3.2.2.1. Evaluation of the consistency of the experimental tie lines

From the slope of the tie lines, Figures 9-12, it can be clearly seen that the toluene is slightly more soluble in the n-octane-rich phase than in solvent mixture-rich phase.

It can also be seen from tie line data that as the content of 2-ethoxyethanol increases in the solvent mixture, the solubility of toluene in the solvent-rich phase increases, and, correspondingly, decreases in the n-octane-rich phase.

The consistency of the data was tested by the Bachman, Othmer-Tobias, Hand, and selectivity methods [16,17,21]. All methods gave good correlation for the equilibrium data. The results of the maximum likelihood principle method [24,25] are presented in Table 4. The values of the coefficient of correlation (R) are close to unity. The goodness of the fit confirms the reliability of the results.

The distribution coefficient and selectivity of solvents are presented in Figures 14 and 15.

3.2.3. Distribution coefficient and selectivity

The dissolving ability, i.e. the distribution coefficient, k_1, is defined as the ratio of the mass fraction of toluene, in the solvent rich phase, to that in octane-rich phase. The effectiveness of the extraction of toluene (3) by a solvent is indicated by its separation factor (selectivity, S), that is used as a measure of the ability of solvent (sulfolane + 2-ethoxyethanol) (1) to separate toluene (3) from octane (2).

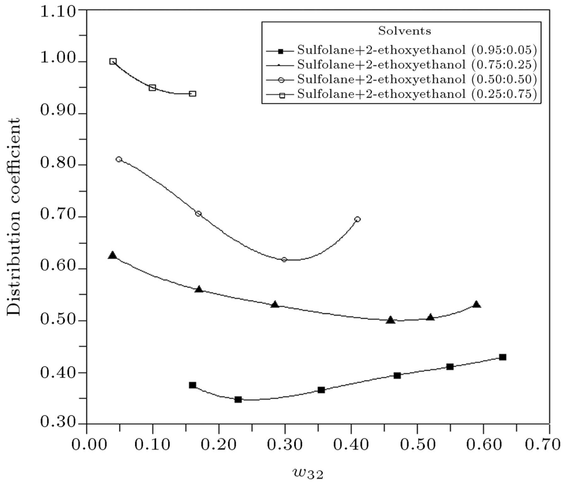

Figure 14. Distribution curves for solvent (1) + n-octane (2) + toluene (3) at 293.15 K.

Table 4. Results of the maximum likelihood principle method for (sulfolane + 2-ethoxyethaonl) + n-octane + toluene at 293.15K.

Solvent	**Correlation**					
Sulfolane: 2-ethoxyethaonl (mass fraction)	**Bachman**			**Othmer - Tobias**		
	a_1	b_1	R_1	a_2	b_2	R_2
(0.95: 0.05)	-0.2552	1.2023	0.9976	0.7291	-0.5722	0.9977
(0.75: 0.25)	-0.5289	1.4805	0.9963	0.8241	-0.3844	0.9985
(0.50: 0.50)	-1.0761	1.9462	0.9936	0.8679	-0.0748	0.9969
(0.25: 0.75)	-1.6929	2.3134	0.9999	0.8297	0.2081	0.9992
Sulfolane: 2-ethoxyethaonl (mass fraction)	**Hand**			**Selectivity**		
	a_3	b_3	R_3	a_4	b_4	R_4
(0.95: 0.05)	0.7326	-0.6468	0.9781	0.6207	0.2094	0.9992
(0.75: 0.25)	0.7904	-0.4658	0.9939	0.4041	0.5236	0.9974
(0.50: 0.50)	0.8935	-0.2323	0.9930	0.2428	0.8861	0.9959
(0.25: 0.75)	1.0245	0.0745	0.9996	0.5608	0.1407	0.9995

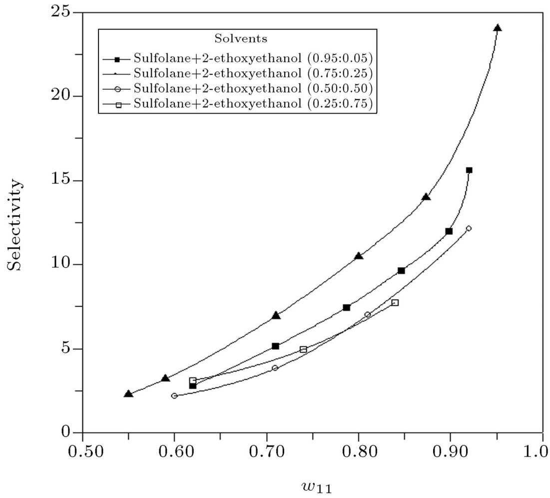

Figure 15. Selectivity curves for solvent (1) + n-octane (2) + toluene (3) at 293.15 K.

From Figures 14-15, the distribution coefficients increases with increasing 2-ethoxyethanol concentration (from 0.05 to 0.75 mass fraction), and the reverse is true for selectivities, but at lower concentrations of toluene, the solvent with 0.25 mass fraction 2-ethoxyethanol shows higher selectivities than that with 0.05 mass fraction 2-ethoxyethanol as shown in Figure 15.

The slope of the tie lines (k_1 values) shows that toluene is more soluble in the octane phase than in the solvent phase for all of the percentage mass composition of the solvent studied, except for (sulfolane + 75% 2-ethoxyethanol) composition yielding k_1 of about 1. Selectivity, S, is an important factor in examining the efficiency of solvent extraction processes. The measured selectivity of solvent for the extraction of toluene is greater than 1, and this means that extraction is possible. Furthermore, selectivity is decreased by more addition of co-solvent 2-ethoxyethanol, which reflects the strong molecular interaction between sulfolane and 2-ethoxyethanol.

The solvent [sulfolane + 2-ethoxyethanol (0.25: 0.75)] shows higher capacity for toluene ($k_1 \approx 1.00$) compared to pure sulfolane, and for this reason, it can be used for higher recovery of aromtics at lower solvent to feed ratios and temperatures.

The effect of addition of 2-ethoxyethanol to the sulfolane on the selectivity of solvent for extraction of toluene from (toluene + octane) mixture is shown in Figure 15. It is shown that increase of 2-ethoxyethanol percentage decreases the selectivity of sulfolane (selectivity of pure sulfolane is 37). At lower concentration of toluene, the solvent with 0.25 mass fraction 2-ethoxyethanol shows higher selectivity than that with 0.05 mass fraction 2-ethoxyethanol, as shown in Figure 15.

3.2.4. Estimation of the plait point

Compositions of plait points for the systems (sulfolane + 2-ethoxyethanol) (1) + n-octane (2) + toluene (3) at 293.15 k are listed in Table 5, as mass fraction.

As shown in Table 5, the plait points moved from region of high solvent concentration to a region of high n-octane concentration as the 2-ethoxyethanol increases in the solvent mixture.

3.3. General discussion

Selection of a solvent for extraction study depends on the solvent power measured by the solute distribution

Table 5. Compositions of the plait points for (sulfolane + 2-ethoxyethanol) (1) + n-octane (2) + toluene (3) at 293.15 K.

Solvent	**Construction method**			**Treybal method**		
Sulfolane: 2-ethoxyethanol (mass fraction)	w_1	w_2	w_3	w_1	w_2	w_3
(0.95: 0.05)	0.388	0.100	0.512	0.385	0.101	0.514
(0.75: 0.25)	0.310	0.170	0.520	0.314	0.164	0.522
(0.50: 0.50)	0.260	0.300	0.440	0.261	0.304	0.435
(0.25: 0.75)	0.290	0.460	0.250	0.288	0.463	0.249

coefficient and also on its selectivity. In the case of recovery of aromatics from reformats, a solvent with largest possible capacity and highest selectivity toward aromatics is preferred. Sulfolane is an important industrial solvent having the ability to extract monocyclic aromatic hydrocarbons from petroleum products. Thus this combination solvent system appears to be attractive for extraction of aromatics from naphtha reformate.

Polarity difference between the (sulfolane + co-solvent) molecules and the aromatic compound increases as the polarity of the co-solvent increases.

In the aromatic series, benzene, toluene, and xylene (ortho and meta) polarity increases as the molecular weight of the aromatic member increases [18], due to the greater amount of π electrons, which are subject to electromeric shifts within the ring (inductive effect of the methyl groups). Rawat [26] found that the solvent power for many extractive solvents was always greater for benzene than for toluene or xylene. Other factors such as smaller molecular size and lower molecular weight also help in the association of the benzene with the solvent molecule, making benzene more effectively extracted. The polarity difference between the solvent and an aromatic compound should not be too high for effective extraction. A low polarity difference between the solvent and the aromatic compound results in attractive forces between different molecules, and as a result, the aromatic molecules are preferentially pulled toward the solvent [19].

Combination solvent systems (sulfolane + 2-methoxyethanol and sulfolane + 2-ethoxyethanol), although less selective, have higher capacity compared to that of pure sulfolane. This may be attributed to the greater dipole moments of n-alkoxyethanols and to smaller intermolecular self-association. The existence of intramolecular H-bonds in n-alkoxyethanols may enhance the dipolar interactions between n-alkoxyethanols and hydrocarbons, leading to an increase of the capacity and a decrease in selectivity. Consequently, such interaction is also stronger in mixtures with 2-methoxyethanol than in systems with 2-ethoxyethanol. Figure 16 shows the comparison of experimental selectivity data for the (sulfolane +mass% 2-ethoxyethanol) with those for the (sulfolane + mass% 2-methoxyethanol).

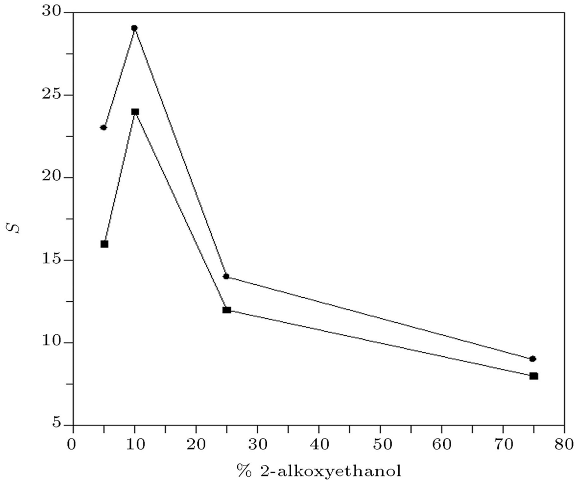

Figure 16. Experimental selectivity data for (●) sulfolane + 25% 2-methoxyethanol and (■) sulfolane + 25% 2-ethoxyetanol in {(sulfolane + 25% 2-alkoxyethanol) (1) + octane (2) + toluene (3)} system at 293.15 K.

3.3.1. Prediction and correlation of experimental data
If a liquid mixture of a given composition at a known temperature is separated into two phases (i.e. in equilibrium), the composition of the two phases can be calculated from the following equations:

$$\gamma_i^{\mathrm{I}} x_i^{\mathrm{I}} = \gamma_i^{\mathrm{II}} x_i^{\mathrm{II}}, \tag{8}$$

$$z_i = z_i^{\mathrm{I}} + z_i^{\mathrm{II}}, \tag{9}$$

where z_i, z_i^{I} and z_i^{II} are the number of moles of component i in the system and in phases I and II, respectively, and γ_i^{I} and γ_i^{II} are the corresponding activity coefficients of component i in phases I and II, as calculated from the equilibrium equations, NRTL and UNIQUAC. The generated binary and ternary component equilibria data are used to determine interaction parameters between paraffinic/aromatic hydrocarbons and solvent; these in turn are used to estimate the activity coefficients from the NRTL and the UNIQUAC equations. In a similar fashion, the interaction parameters between parffinic/aromatic hydrocarbon groups and solvent groups were used to predict the activity coefficients form the UNIFAC model. Interaction parameters between certain group pairs have already been reported in the literature [15], and these values have been used where required.

The R_i and Q_i values for the UNIFAC groups and the r_i and q_i for the UNIQUAC compounds are shown in Table 6. Eqs. (8) and (9) were solved for the mole fraction (or mass fraction) x_i of component i in each liquid phase.

Optimal interaction parameters between compounds for NRTL and UNIQUAC and between functional groups for UNIFAC were found by using an optimized computer program, using maximum likelihood principle method developed by Sorensen [24] and Anderson [25]. The objective function (F) in this case was minimized by minimizing the square of the difference between the mole fractions (or mass fractions) predicted by the respective method and these experimentally measured.

$$F = \sum_{i=1}^{n} \min \sum_{j=1}^{3} \sum_{L=1}^{2} \left[x_{jL}(\text{exptl}, i) - x_{jL}(\text{caled}, i)\right]^2, \tag{10}$$

where $x_{jL}(\text{exptl}, i)$ is the experimental mole fraction and $x_{jL}(\text{caled}, i)$ is the calculated mole fraction. The subscripts and superscripts are i for the tie lines $(1, 2, \cdots, n)$, j for the components $(1, 2, 3)$, and L for the phase (I,II).

Values of the parameters that minimized this objective function were sought, using both the UNIQUAC model and the NRTL model. The values of the six parameters for the UNIQUAC model:

$$U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, U_{33} \quad (\text{J mol}^{-1}),$$

were calculated.

The values of the nine parameters for the NRTL model:

$$g_{11}, g_{22}, g_{33}, g_{12}, g_{13}, g_{23}, \alpha_{11}, \alpha_{12}, \alpha_{13},$$

for the ternary systems were calculated by using maximum likelihood principle method [25]. The parameters calculated in this way are shown in Tables 7 and 8.

The Root Mean Square Deviation (RMSD) is calculated from the results of each method, according to the following equation:

$$\text{RMSD}=\left[\sum_{i=1}^{n}\sum_{j=1}^{3}\sum_{L=1}^{2}\frac{\left(x_{jL}(\text{exptl}, i)-x_{jL}(\text{calcd}, i)\right)^2}{6n}\right]^{\frac{1}{2}}. \tag{11}$$

Table 6. The R_i/r_i and Q_i/q_i values for the groups/components resent in the systems.

UNIFAC Model [15]			**UNIQUAC Model [14]**		
Group	R_i	Q_i	**Component**	r_i	q_i
Sulfolane	3.7220	2.936	Toluene	3.922	2.968
CH_3	0.9011	0.848	n-octane	5.847	4.936
CH_2	0.6744	0.540	Sulfolane	4.034	3.200
CH_3O	1.1450	1.088	2-methoxyethanol	3.026	2.752
CH_2O	0.9183	0.780	2-ethoxyethanol	3.698	3.292
ACH	0.5313	0.400			
$ACCH_3$	1.2663	0.968			

Table 7. NRTL parameters (g_{ij} (J mol^{-1})) and (α_{ij}) for the systems solvent (1) + n-alkane (2) + aromatic hydrocarbons (3) at 293.15 K.

System no.	g_{11}	g_{22}	g_{33}	g_{12}	g_{13}	g_{23}	α_{12}	α_{13}	α_{23}
1	1065.240	802.562	1859.220	5550.930	8735.760	9602.010	0.289	0.408	0.397
2	1052.370	694.712	158.667	4987.620	2073.060	1453.320	0.343	0.328	0.455
3	2065.140	447.993	406.901	5526.180	7874.460	11137.500	0.211	0.382	0.339
4	1684.980	279.689	7123.050	5304.420	8432.820	9248.580	0.272	0.302	0.310
5	2737.350	535.393	6802.290	5227.200	9786.150	9563.400	0.292	0.363	0.256
6	2755.170	615.049	4994.550	4824.270	10157.400	9659.430	0.328	0.272	0.318
7	1479.060	799.422	2105.730	5645.970	7860.600	5858.820	0.258	0.351	0.301
8	195.517	128.102	7085.430	7857.630	7501.230	8897.130	0.455	0.303	0.411
9	671.033	1782.990	2344.320	7099.290	11919.600	11503.800	0.391	0.451	0.455

Table 8. UNIQUAC parameters (U_{ij} (J.mol^{-1})) for the systems solvent (1) + n-alkane (2) + aromatic hydrocarbons (3) at 293.15 K.

System no.	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
1	888.593	1201.860	257.087	2813.580	1937.430	1465.200
2	573.380	2226.510	2664.090	3446.190	490.404	1105.830
3	1550.340	903.869	9382.230	2071.080	735.754	598.002
4	1074.150	1131.570	5911.290	2710.620	1755.270	1172.160
5	534.681	589.191	2347.290	2017.620	969.954	381.979
6	1123.650	719.878	4729.230	2307.690	1706.760	994.950
7	292.298	5482.620	1137.510	1294.920	1344.420	312.462
8	1386.990	868.199	1242.450	2458.170	2792.790	1770.120
9	78.605	4433.220	13355.100	1204.830	450.286	2735.370

RMSD is a measure of the agreement between the experimental data and the calculated data.

The calculated tie lines using the three models for systems studied are compared with the experimental data in Figures 17-19.

The average RMSD values for the three methods for all system studied are 0.165, 0.491 and 1.304 for NRTL, UNIQUAC and UNIFAC, respectively. The calculations based on both the UNIQUAC and NRTL models gave a good representation of the tie line data. However, the NRTL model, fitted to the experimental data, is more accurate than the UNIQUAC model. The UNIFAC model has also predicted the overall composition with a reasonable error, though its average RMSD value is higher than those of the NRTL and UNIQUAC models, as would be expected. It is therefore considered to be less accurate than the NRTL and UNIQUAC models in correlating the phase equilibria of the studied systems.

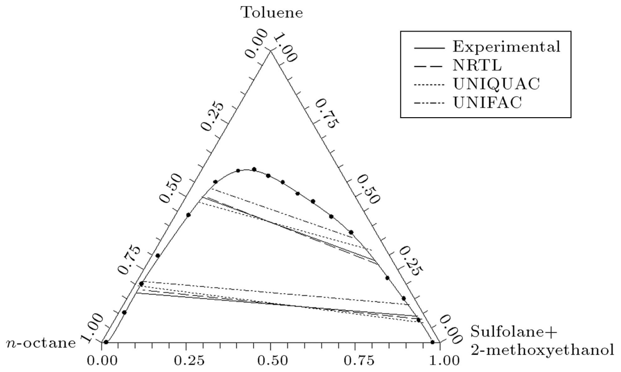

Figure 17. Experimental and calculated tie lines for the system [sulfolane + 2-methoxyethanol (mass fraction 0.75: 0.25)] + n-octane + toluene at 293.15 K.

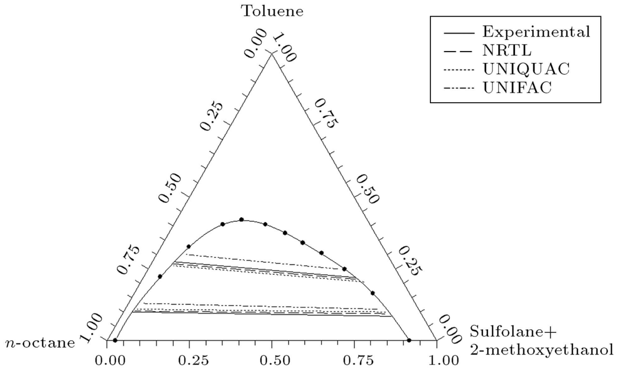

Figure 18. Experimental and calculated tie lines for the system [sulfolane + 2-methoxyethanol (mass fraction 0.25: 0.75)] + n-octane + toluene at 293.15 K.

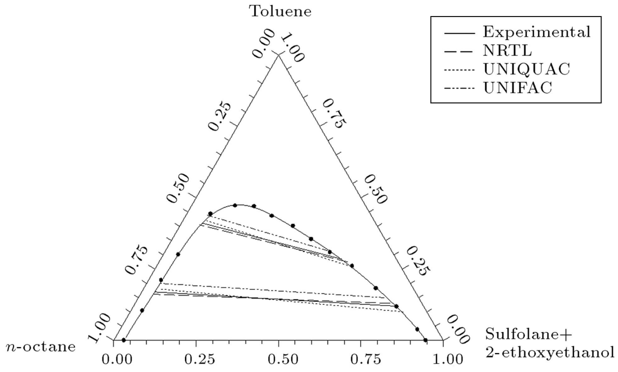

Figure 19. Experimental and calculated tie lines for the system sulfolane + 2-ethoxyethanol (mass fraction 0.50: 0.50) + n-octane + toluene at 293.15 K.

4. Conclusions

From the results of this work, it can be concluded that:

1. As a result of phase diagrams produced, the addition of n-alkoxyethanol to sulfalone in (n-octane+ toluene) mixture leads to a decrease in the two-phase area, and reflects the increase in the solubility of n-octane in the solvent mixture.
2. In multistage, counter current extraction (using sulfolane) of toluene from the (n-octane + toluene) mixture, the extract purity can evidently be in-

creased to any desired level by using a modified solvent.

3. Combination solvent systems (sulfolane+2-methoxyethanol and sulfolane + 2-ethoxyethanol), although less selective, have higher capacity compared to that of pure sulfolane. Moreover, viscosities of the combination solvent systems are very low in relation to the viscosity of pure sulfolane, which should improve the extraction efficiency.
4. The solvent (25% sulfolane+75% 2-ethoxyethanol) shows a distribution coefficient around unity for toluene, and for this reason, it can be used for higher recovery of aromatics at lower solvent to feed ratios and temperatures.
5. The consistency of the data was tested by the Bachman, Othmer-Tobias, Hand, and selectivity methods. All methods gave good correlations for the equilibrium distribution data.
6. The NRTL, UNIQUAC, and UNIFAC models were used to correlate the experimental data and to predict the phase compositions of the ternary systems. Agreement between the predicted and experimental results was good with the three models. However, the calculated values based on the NRTL model are found to be better than those based on the UNIQUAC and UNIFAC models.
7. From the selectivity values, the separation of toluene from octane by extraction with (sulfolane + 2- ethoxyethanol) is feasible. The comparison between experimental selectivity data of (sulfolane + 2-ethoxyethanol) with that of (sulfolane + 2-methoxyethanol) for the extraction of toluene from (toluene + octane) mixture at 293.15 K indicate that the latter is more efficient than former.

Nomenclature

Abbreviations

LLE	Liquid-Liquid Equilibrium
NRTL	Non-Random Two Liquid activity coefficient model
RMSD	Root Mean Square Deviation
UNIFAC	UNIQUAC Functional Group Activity Coefficients model
UNIQUAC	Universal Quasi-Chemical Activity Coefficient model

Symbols

a_1, b_1	Parameters of Bachman equation (Eq. (1))
a_2, b_2	Parameters of Othmer-Tobias equation (Eq. (2))
a_3, b_3	Parameters of Hand equation (Eq. (3))
a_4, b_4	Parameters of selectivity equation (Eq. (4))
F	Objective function
g_{ij}	Parameters of the NRTL model (J mol^{-1})
k_i	Distribution coefficient
n	No. of experimental points
q_i	Surface area parameter of the UNIQUAC model
Q_i	Surface area parameter of the UNIFAC model
r_i	Volume parameter of the UNIQUAC model
R_i	Volume parameter of the UNIFAC model
R_j	Correlation coefficient
S	Selectivity
U_{ij}	Parameters of the UNIQUAC model (J mol^{-1})
w	Mass fraction
x_i^{I}	Mole fraction of component i in phase I
x_i^{II}	Mole fraction of component i in phase II
Z_i	Number of mole of component i in the system

Greek litters

α_{ij}	Non-randomness parameters of the NRTL model
γ	Activity coefficient

Superscript

caled	Calculated value
exptl	Experimental value
I	Phase I
II	Phase II

Subscript

i	Component i
j	Component j
11	Solvent in the solvent phase
12	Solvent in the octane phase
21	Octane in the solvent phase
22	Octane in the octane phase
31	Toluene in the solvent phase
32	Toluene in the octane phase

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Biography

Khalid Farhod obtained his PhD degree in Chemical Engineering in 2002. Since then he has worked in different projects in the field of Thermodynamics, Vapor-Liquid Equilibrium, Liquid-Liquid Equilibrium. Currently, he is working at Chemical Engineering Department, Oil & Gas refinery engineering branch, University of Technology, Baghdad, Iraq. He published two books under the following titles "Vapor-Liquid Equilibrium of Ternary Systems" and "Gasoline Additives (Gasoline Oxygenates)".