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!!Al-Khwarizmi
!!!Engineering
!!Journal

! !Al-Khwarizmi Engineering Journal, Vol. 6, No. 3, PP 1-13 (2010)

Extraction of Monocyclic Aromatic Hydrocarbons From Petroleum Products Using Sulfolane as Industrial Solvent

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(Received 26 Sebtember 2009 ; Accepted 22 September 2010)

Abstract

Liquid – liquid equilibria data were measured at 293.15 K for the pseudo ternary system (sulfolane + alkanol) + octane + toluene. It is observed that the selectivity of pure sulfolane increases with cosolvent methanol but decreases with increasing the chain length of hydrocarbon in 1-alkanol. The nonrandom two liquid (NRTL) model, UNIQUAC model and UNIFAC model were used to correlate the experimental data and to predict the phase composition of the systems studied. The calculation based on NRTL model gave a good representation of the experimental tie-line data for all systems studied. The agreement between the correlated and the experimental results was very good.

Keywords: *Liquid -liquid equilibria, extraction of aromatic, activity coefficient, sulfolane*

1. Introduction

Solvent extraction is one of the most important methods to produce high-purity aromatic extracts from catalytic reformates. In recent years, sulfolane or tetraethylene glycol has been employed more and more in new or improved extraction processes. Therefore, it is necessary to have complete thermodynamic data for these systems.

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. Sulfolane is an important industrial solvent having the ability to extract monocyclic aromatic hydrocarbons from petroleum products. The efficient separation of ring containing compounds (e.g., cyclic ethers, cyclic alcohols, or hydrocarbons) from petroleum products 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 cyclic aromatic from petroleum products (i.e., the nature of the solute, the concentration of the solute, and the type of organic solvent).

Liquid-liquid equilibria (LLE) data and thermophysical properties of mixtures containing an aromatic and sulfolane with other solvents have been reported by several authors [1-3]. The quaternary system sulfolane + alkanol + octane + toluene is treated as pseudo ternary system, component 1 is (sulfolane + methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 1-butanol (1-BuOH) or 1-pentanol (PeOH)).

2. Experimental Section

2.1. Materials

Sulfolane (> 99.5%, GC), octane (> 99.8%, GC), toluene (> 99.0%, GC), methanol (> 99.5%, GC), ethanol (> 99.8%, GC), 1-propanol (> 99.5%, GC), 1-butanol (> 99.5%, GC), 1-pentanol (> 99.0%, GC), were supplied by Fluka. 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 $\pm 5\times10^{-4}$. Densities were measured using an Anton Paar DMA 4500 density meter. The estimated uncertainty in the density was $\pm10^{-4}$ g/cm^3.

2.2. Procedure

The binodal (solubility) curves were determined by the cloud-point method in an equilibrium glass cell with a water jacket to maintain isothermal conditions. The temperature in the cell was measured by a certified Fischer thermometer within 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 to within $\pm10^{-4}$ 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 made with a mass fraction uncertainty of ±0.002. End-point 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 are described by Briggs and Comings [4].

3. Results & Discussion

3.1. Liquid-Liquid Equilibria of the ternary systems sulfolane/co-solvent +n-Octane + Toluene

Liquid – liquid equilibrium for the ternary systems

1. sulfolane + n-octane + toluene
2. (sulfolane+ 5% water)+ n – octane + toluene.
3. (sulfolane+5% methanol)+n–octane+toluene.
4. (sulfolane+ 5% ethanol)+ n–octane+ toluene.
5. (sulfolane+5% 1-propanol)+n–octane+toluene.
6. (sulfolane+5% 1-butanol)+n–octane+toluene.
7. (sulfolane+5% 1-pentanol)+n–octane+toluene.

were studied at 293.15 K.

3.2. Mutual Solubility

The compositions of mixtures on the binodal curve for the above seven systems at 293.15 K are plotted as triangular diagrams, Figures 1-7. The minimum concentration (in mole fraction) for the solubility of toluene, over the whole composition range, in the mixture (n- octane + solvent), was found to be 0.693, 0.703, 0.702, 0.691, 0.687, 0.679, and 0.680 for sulfolane, sulfolane + 5% water, sulfolane + 5% methanol, sulfolane + 5% ethanol, sulfolane + 5% 1- propanol, sulfolane + 5% 1-butanol, and sulfolane + 5% 1-pentanol, respectively. This reflects the magnitude of the area of the two- phase region. The two-phase region increases in the order sulfolane + 5% water > sulfolane + 5% methanol > pure sulfolane > sulfolane + 5% ethanol > sulfolane + 5% 1-propanol > sulfolane + 5% 1- butanol ≈ sulfolane + 5% 1- pentanol.

The maximum solubility of sulfolane, sulfolane + water or sulfolane + alcohols in n-octane is less than 0.014 mole fraction, and the maximum solubility of n- octane in sulfolane, sulfolane + water or sulfolane + alcohol is less than 0.020 mole fraction at 293.15K.

It was observed that, the two-phase area decreases as the chain length of alcohol increases, this reflects the increase in the solubility of n-octane in sulfolane + alcohols (maximum solubility of n-octane in sulfolane + alcohols is 0.008, 0.018, 0.020, and 0.028 mole fraction for sulfolane + methanol + ethanol, + 1- propanol, and + 1- pentanol, respectively). Therefore, less n-octane miscible in solvent or solvent- co- solvent, these solvents is selective for toluene. In addition the area of the two- phase region is large, it is therefore expected that one mixture containing large proportions of toluene + n-octane extracted with sulfolane, sulfolane + water or sulfolane + alcohols, toluene will be selectively extracted by these solvents.

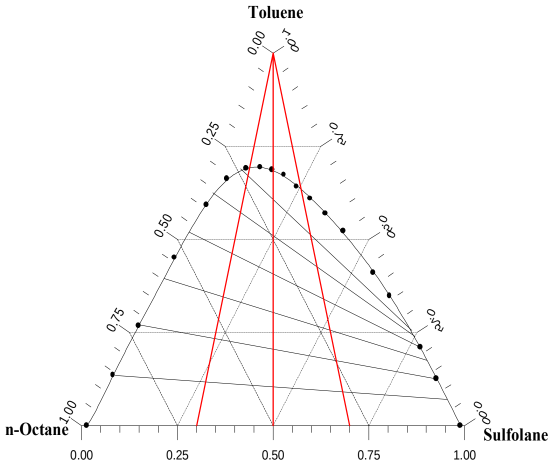

Fig.1. Binodal Curve and Tie Lines for Pure Sulfolane + n- octane + Toluene at 293.15 K.

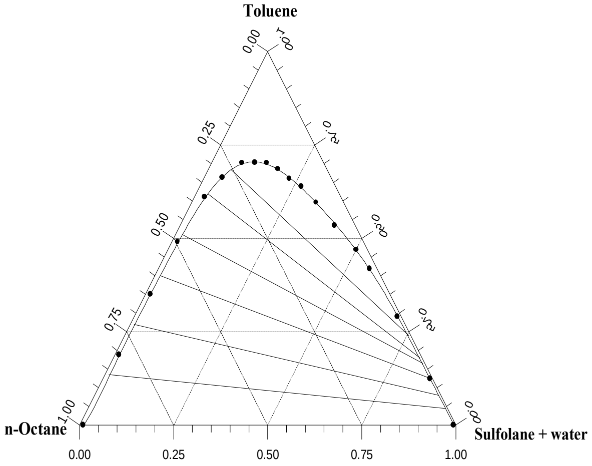

Fig.2. Binodal Curve and Tie Lines for (Sulfolane + 5% Water) + n- octane + Toluene at 293.15K.

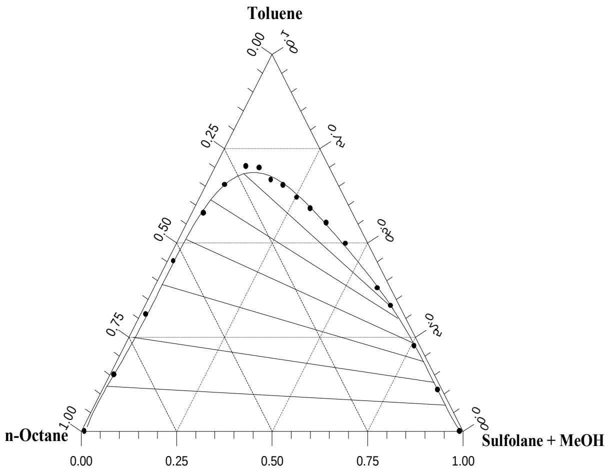

Fig.3. Binodal Curve and Tie Lines for (Sulfolane + 5% MeOH) + n- octane + Toluene at 293.15K.

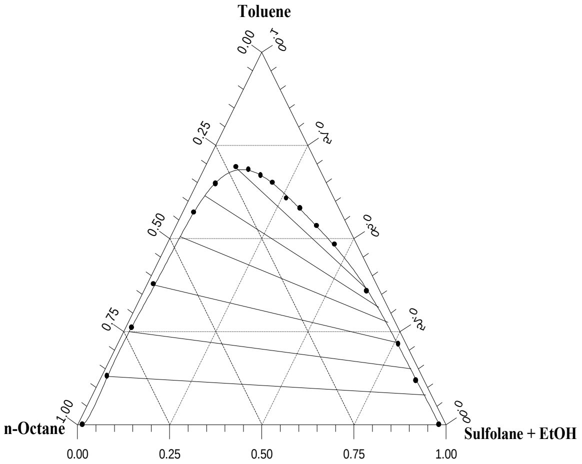

Fig.4. Binodal Curve and Tie Lines for (Sulfolane + 5% EtOH) + n- octane + Toluene at 293.15K.

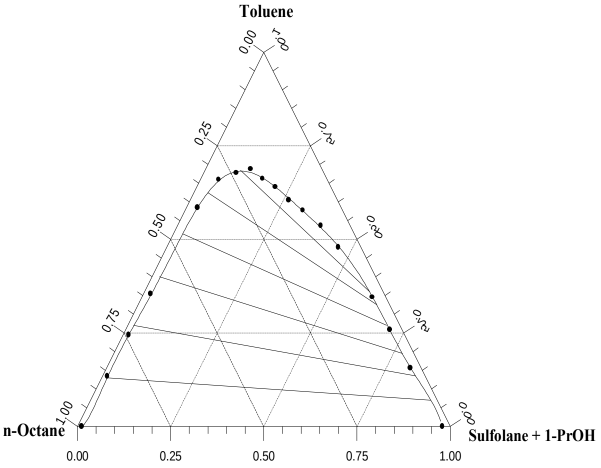

Fig.5. Binodal Curve and Tie Lines for (Sulfolane + 5% 1- PrOH) + n- octane + Toluene at 293.15K.

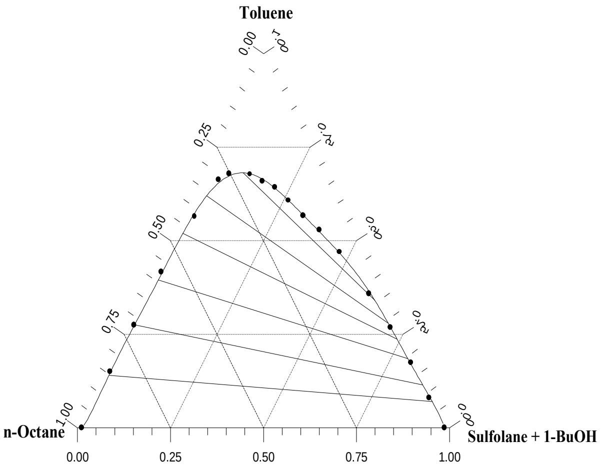

Fig.6. Binodal Curve and Tie Lines for (sulfolane + 5% 1- BuOH) + n- octane + Toluene at 293.15K.

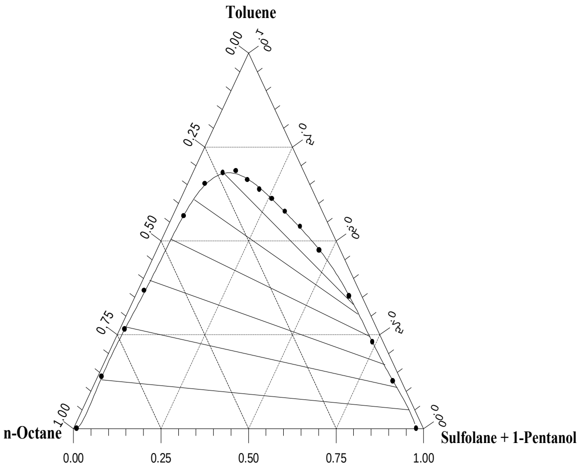

Fig.7. Binodal Curve and tie Lines for (sulfolane + 5% 1-Pentanol) + n- octane + Toluene at 293.15K.

3.3. Tie Line Data

Tie line data for the seven systems at 293.15K are plotted on triangular diagrams according to a method of Francies [5], Figures 1-7. The tie line data indicating the composition of the 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.

3.4. Evaluation of the Consistency of the Experimental Tie Lines

The accuracy of the experimental data for the seven ternary systems at 293.15K were checked by the Bachman, Othmer-Tobias, Hand, and selectivity methods [4].

Bachman method

$$x_{11} = a_1 + b_1\left(\frac{x_{11}}{x_{22}}\right) \qquad \ldots(1)$$

Othmer- Tobias method

$$\log\left(\frac{1-x_{11}}{x_{11}}\right) = a_2 + b_2 \log\left(\frac{1-x_{22}}{x_{22}}\right) \qquad \ldots(2)$$

Hand method

$$\log\left(\frac{x_{31}}{x_{11}}\right) = a_3 + b_3 \log\left(\frac{x_{32}}{x_{22}}\right) \qquad \ldots(3)$$

Selectivity method

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

Experimental data are plotted using these coordinates, and the plots are shown in Figures 8-11. The parameters a_j and b_j (j= 1-4) of Eqs 1-4 are obtained by using *maximum likelihood principle* method. The parameters and the correlation coefficients, R_j, are given in Table 1. Since the data show little scattering from a straight line, they are judged acceptable on an empirical basis, indicating internal consistency of the experimental data. The estimation of plait points for the systems is also presented in Figure 10 by the use of Treybal's method.

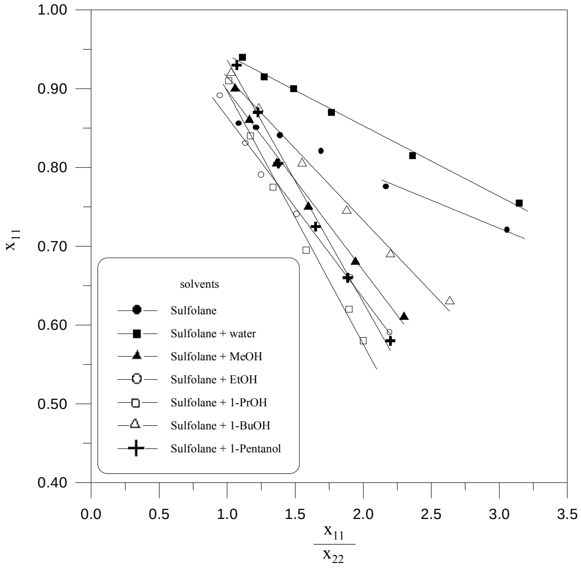

Fig.8. Bachman Correlation for Solvent (1) + n-Octane (2) + Toluene (3) at 293.15K.

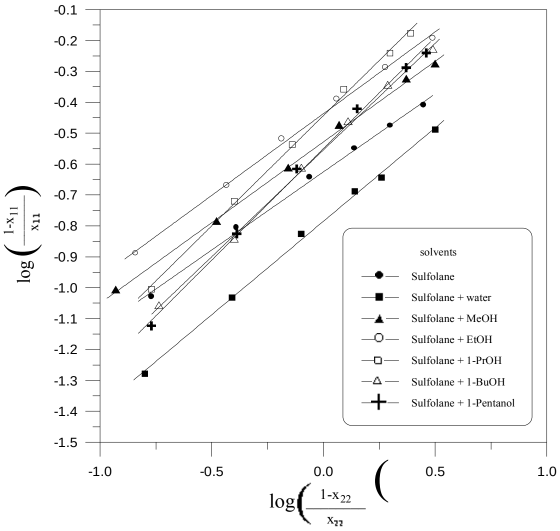

Fig.9. Othmer- Tobias Correlation for Solvent (1) + n- octane (2) + Toluene (3) at 293.15 K.

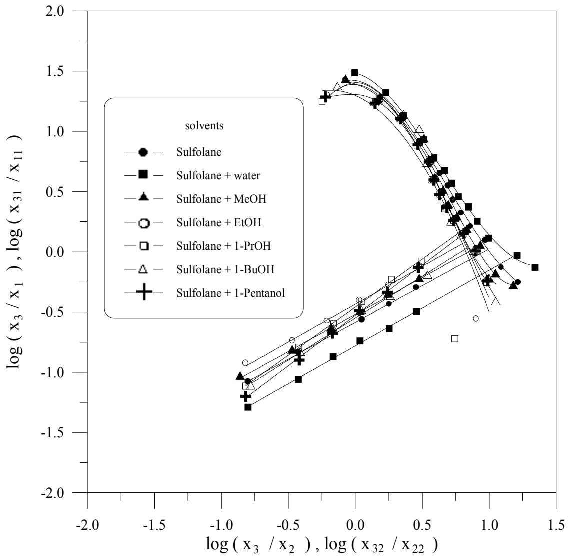

Fig.10. Hand Correlation and plait Point Determination for Solvent (1)+ n-octane (2) + Toluene (3) at 293.15 K.

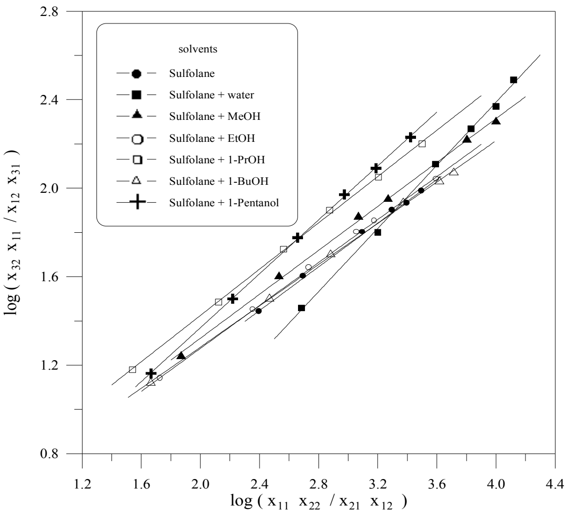

Fig.11. Selectivity Correlation for Solvent (1) + n-octane (2) + Toluene (3) at 293.15K.

As can be seen from Table 1 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 1,
Results of the Maximum Likelihood Principle Method for Solvent + n- Octane + Toluene at 293.15K.

Solvent	Correlation					
	Bachman			Othmer - Tobias		
	a_1	b_1	R_1	a_2	b_2	R_2
Sulfolane	-0.0710	0.9358	0.9937	0.5050	-0.6252	0.9970
Sulfolane + water	-0.0897	1.0325	0.9944	0.6045	-0.7850	0.9977
Sulfolane + Me OH	-0.2285	1.1264	0.9908	0.5222	-0.5282	0.9987
Sulfolane + EtOH	-0.2299	1.0939	0.9914	0.5289	-0.4367	0.9976
Sulfolane + 1-PrOH	-0.3210	1.2177	0.9897	0.7134	-0.4427	0.9982
Sulfolane + 1-BuOH	-0.1818	1.0965	0.9915	0.6903	-0.5542	0.9985
Sulfolane + 1-pentanol	-0.3072	1.2439	0.9908	0.7215	-0.5497	0.9971

Solvent	Hand			Selectivity		
	a_3	b_3	R_3	a_4	b_4	R_4
Sulfolane	0.6103	-0.5869	0.9975	0.4934	0.2625	0.9984
Sulfolane + water	0.6284	-0.7816	0.9975	0.7134	-0.4650	0.9985
Sulfolane + Me OH	0.6147	-0.5208	0.9989	0.4963	0.3291	0.9987
Sulfolane + EtOH	0.6281	-0.4354	0.9981	0.4852	0.3054	0.9994
Sulfolane + 1-PrOH	0.7970	-0.4597	0.9991	0.5231	0.3784	0.9993
Sulfolane + 1-BuOH	0.6966	-0.5508	0.9945	0.4660	0.3496	0.9994
Sulfolane + 1-pentanol	0.8350	-0.5289	0.9990	0.6092	0.1508	0.9998

3.5. 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 by the formula:

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

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

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

$$S = \frac{k_1}{k_2} \quad \ldots(7)$$

Figure 12 shows the comparison of distribution coefficients of toluene and Figure 13 the selectivity of solvents. As can be seen from Figures 12 and 13, The selectively vary in the following order: sulfolane + 5% water > sulfolane + 5% MeOH > pure sulfolane > sulfolane + 5% 1-BuOH > sulfolane + 5% EtOH > sulfolane + 5% 1-PrOH > sulfolane + 5% 1-Pentanol, and capacity in the order sulfolane + 5% EtOH > sulfolane + 5% 1-PrOH > sulfolane + 5% MeOH > Sulfolane + 5% 1-BuOH > sulfolane + 5% 1-Pentanol > pure sulfolane > sulfolane + 5% water. This indicates the solvent power (capacity) and its selectivity.

It is apparent that increasing the water content in the modified solvent increases the selectivity and reduces the hydrocarbon solubility, while increasing the alcohol content reduces selectivity and increases the hydrocarbon solubility. In multistage, countercurrent extraction (using sulfolane) of toluene from n-octane + toluene mixture the extract purity can evidently be increased to any desired level by using a water-modified solvent. This is achieved at the expense of some increase in the solvent throughput owing to the reduced hydrocarbon solubility in the extract solvent.

High selectivity for a desired capacity or solvent power is the primary requirement for a good solvent. However, an increase in the solvent 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 co-solvent being added to sulfolane .

On balance, considering both capacity and selectivity of solvents, with the systems studied better results were obtained for sulfolane + methanol as compared with pure sulfolane or sulfolane + water, for this reason it can be used for higher recovery of aromtics at lower solvent to feed ratios and temperatures.

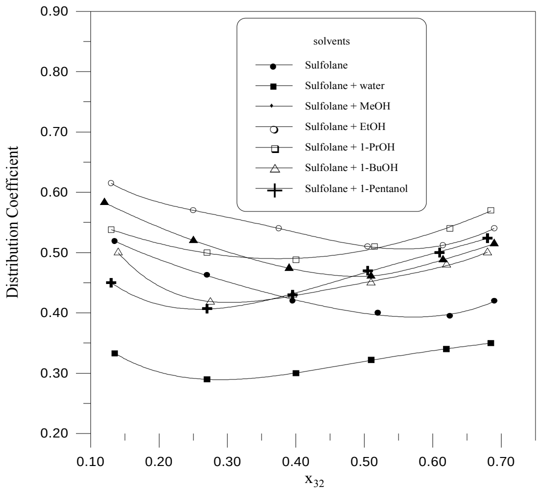

Fig.12. Comparison of Distribution Coefficient of Toluene with Solvents -n-octane Systems at 293.15K.

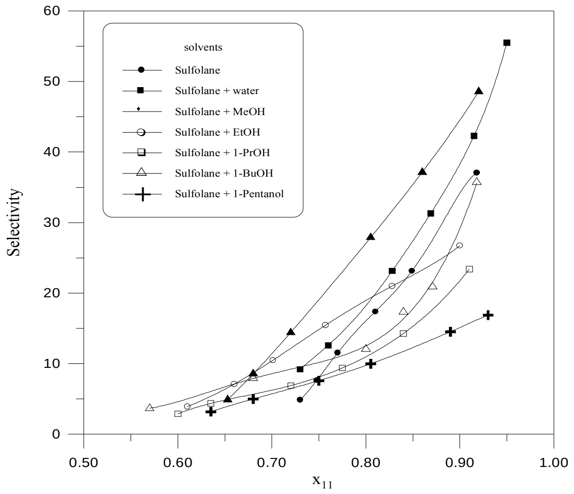

Fig.13. Selectivity Curves for Solvent (1) + n- octane (2) + Toluene (3) at 293.15K.

3.6. Estimation of the Plait Point

The compositions of the plait points as determined by construction and Treybal methods for the seven systems are listed in Table 2.

It is apparent that the plait points are located in the region of mixtures containing more solvent. Although sulfolane + water have higher selectivity and plait point composition but its capacity is very poor. On the other hand, sulfolane + methanol have higher selectivity, capacity and plait point composition compared with the solvents studied. Thus, sulfolane + methanol can be considered to be one of the most powerful solvents for the toluene extraction.

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

Solvent	Construction method			Treybal method		
	x_1	x_2	x_3	x_1	x_2	x_3
Sulfolane	0.394	0.070	0.536	0.391	0.076	0.533
Sulfolane + water	0.312	0.078	0.610	0.315	0.077	0.608
Sulfolane + MeOH	0.327	0.091	0.582	0.324	0.090	0.586
Sulfolane + EtOH	0.355	0.090	0.555	0.352	0.091	0.557
Sulfolane + 1- PrOH	0.360	0.090	0.550	0.363	0.092	0.545
Sulfolane + 1- BuOH	0.374	0.084	0.542	0.376	0.080	0.544
Sulfolane + 1- pentanol	0.382	0.078	0.540	0.385	0.073	0.542

4. General Discussion

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. Combinations of sulfolane + MeOH solvent have higher capacity, selectivity, and plait point compositions compared with pure sulfolane or sulfolane + water solvent systems. Thus, sulfolane + MeOH can be considered to be one of the most powerful solvents for the toluene extraction. Moreover, viscosity of the combination of sulfolane + MeOH system is very low relative to the viscosity of pure sulfolane ($\eta_{\text{sulfolane}}$ = 10.286 cP, η_{MeOH} = 0.538 at 30°C), which should improve the extraction efficiency. Thus this combination solvent system appears to be attractive for extraction of aromatics from naphtha reformate.

It is worth while to mention that, the liquid-liquid equilibria in the presence of water and alcohols are determined by intermolecular forces, predominantly hydrogen bonds. The addition of water or alcohols as co-solvent to sulfolane enhances the formation of hydrogen bonded system, which a result of greater dipole-dipole interactions between sulfolane and the co-solvent molecules. The 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 [6] due to the greater amount of π electrons which are subject to electromeric shifts within the ring (inductive effect of the methyl groups). Rawat [7] 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 [8]. A low polarity difference between the solvent and the aromatic compound results in attractive forces between the different molecules, and as a result the aromatic molecules are preferentially pulled toward the solvent [7].

The selectivity of (sulfolane + co-solvent) decreases in the order sulfolane + H_2O > sulfolane + MeOH > sulfolane + EtOH > sulfolane + 1-PrOH > sulfolane + 1-pentanol. Indeed the hydrogen bonds system formation and the polarity difference between the solvent and the aromatic compound decreasing in the same order, supporting the above arguments.

5. Prediction and Correlation of Experimental Data

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

$$\gamma_i^{I} x_i^{I} = \gamma_i^{II} x_i^{II} \qquad \ldots(8)$$

$$z_i = z_i^{I} + z_i^{II} \qquad \ldots(9)$$

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 groups pairs have already been reported in the literature [9], 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 3. Equations 8 and 9 were solved for the mole fraction (or mass fraction) x_i of component i in each liquid phase.

Table 3,
The Ri /ri and Qi/qi Values for the Groups/Components Resent in the Systems.

UNIFAC Model [10]			UNIQUAC Model [9]		
Group	**R_i**	**Q_i**	**Component**	**r_i**	**q_i**
Sulfolane	3.7220	2.936	Water	3.190	2.400
H_2O	0.9200	1.400	Toluene	3.922	2.968
CH_3OH	1.4311	1.432	Methanol	4.502	3.856
CH_3CH_2OH	2.1055	1.972	Ethanol	5.175	4.396
CH_2CH_2OH	1.8788	1.664	n-Octane	5.847	4.936
CH_3	0.9011	0.848	Sulfolane	4.034	3.200
CH_2	0.6744	0.540	1-Propanol	3.026	2.752
CH_3O	1.1450	1.088	1-Butanol	3.698	3.292
CH_2O	0.9183	0.780	1-Pentanol	3.471	3.638
ACH	0.5313	0.400			
$ACCH_3$	1.2663	0.968			

Optimal interaction parameters between compounds for NRTL and UNIQUAC and between functional groups for the UNIFAC were found by using optimized computer program using *maximum likelihood principle* method developed by Sorensen [10]. 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.

$$F = \sum_{i=1}^{n} \min \sum_{j=1}^{3} \sum_{L=1}^{2} [x_{jL}(\exp tl, i) - x_{jL}(caled, i)]^2 \qquad \ldots(10)$$

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

The 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_{23} (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} , α_{11} , α_{12} , α_{13}

for the ternary systems were calculated by using *maximum likelihood principle* method [11]. The parameters calculated in this way are shown in Tables 4 and 5.

The root mean square deviation (RMSD) are calculated from the results of each method according to the following equation

$$RMSD = \left[\sum_{i=1}^{n} \sum_{j=1}^{3} \sum_{L=1}^{2} \frac{\left(x_{jL}(\exp tl, i) - x_{jL}(calcd, i)\right)^2}{6n} \right]^{\frac{1}{2}} \qquad \ldots(11)$$

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

The calculated tie lines using the three models for all systems studied are compared with the experimental data in Figures 14-15.

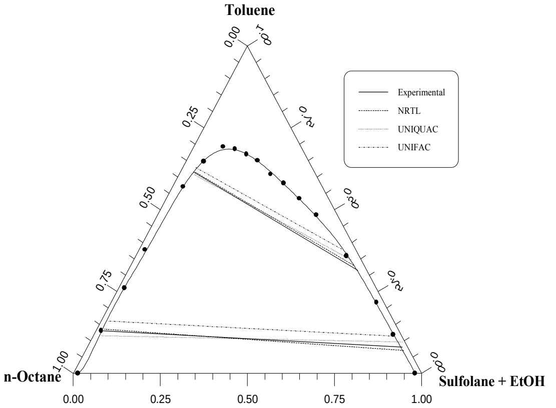

Fig.14. Experimental and Calculated Tie Lines for the System (Sulfolane + 5% EtOH) + n-octane + Toluene at 293.15 K.

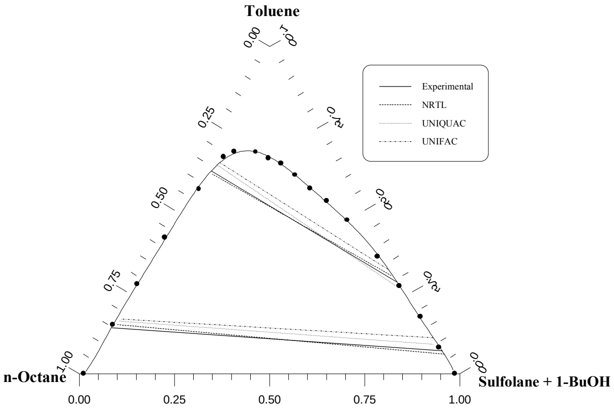

Fig.15. Experimental and Calculated Tie Lines for the System (Sulfolane + 5% 1-BuOH) + n-octane + Toluene at 293.15 K.

Table 4,
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	1076.000	810.669	1878.000	5607.000	8824.000	9699.000	0.292	0.412	0.401
2	1077.000	1117.000	4676.000	5547.000	7220.000	5026.000	0.367	0.332	0.345
3	776.118	189.003	3075.000	5604.000	7895.000	6176.000	0.266	0.402	0.336
4	1634.000	74.661	1196.000	5468.000	7716.000	7712.000	0.302	0.425	0.426
5	1745.000	14.885	4543.000	5465.000	6872.000	7940.000	0.290	0.310	0.460
6	1188.000	961.639	418.311	5598.000	8461.000	9525.000	0.206	0.392	0.359
7	1878.000	76.276	2431.000	5401.000	7798.000	6068.000	0.261	0.411	0.435

Table 5,
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	897.569	1214.000	259.684	2842.000	1957.000	1480.000
2	1294.000	1741.000	4654.000	3571.000	1855.000	1423.000
3	1718.000	1765.000	938.861	2632.000	2746.000	2167.000
4	827.113	837.306	724.378	2519.000	2040.000	1395.000
5	955.544	1797.000	176.807	3122.000	1886.000	1674.000
6	1226.000	1569.000	210.087	3222.000	1977.000	1529.000
7	769.481	1225.000	310.311	2664.000	1808.000	1289.000

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 model and the NRTL model 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 the UNIQUAC models in correlating the phase equilibria of the studied systems.

6. Conclusions

From the results of the present study, it can be concluded that:

1) In combination solvent systems (sulfolane + water or + alcohols), water acts as an antisolvent, increasing the size of the two-phase region. Conversely, alcohols decrease the size of the two-phase region and may be described as prosolvents.
2) On balance, considering both capacity and selectivity of (sulfolane + water or +alcohols), with the systems studied better results were obtained with sulfolane+ methanol as compared with pure sulfolane.
3) As a result of phase diagrams produced, the addition of alcohol 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.
4) In multistage, counter current extraction (using sulfolane) of toluene from the (n-octane + toluene) mixture, the extract purity can evidently be increased to any desired level by using a water-modified solvent.
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. The agreement between the predicted and the 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 the UNIFAC models.

Abbreviations

GC	Gas chromatography
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

F	Objective function
K_i	Distribution coefficient
S	Selectivity
Z_i^I	number of mole of component *i* in the system in the I phase
Z_i^{II}	number of mole of component *i* in the system in the II phase

Greek Litters

γ	Activity coefficient

Superscript

I	Phase I
II	Phase II

Subscript

i	component *i*
j	component *j*

7. References

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أستخلاص الهيدروكاربونات الأروماتية ذات الحلقة الأحادية من المنتجات النفطية بأستخدام السلفولين كمذيب صناعي

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*** قسم تقنيات الأشعة/ كلية التقنيات الطبية و الصحية*

الخلاصة

بيانات إتزان سائل – سائل قد تم قياسها عند درجة حرارة ٢٩٣.١٥ كلفن للنظام الثلاثي الكاذب (pseudo ternary system) (سلفولين + الكانول) + اوكتان + تلوين. لقد تم ملاحظة ان الأنتقائية للسلفولين النقي تزداد مع المذيب المساعد (cosolvent) (الكانول) ولكن تقل مع زيادة طول السلسلة (chain length) للهيدروكاربونات في المركب الكانول. الموديل الرياضي لـ (The nonrandom two liquid (NRTL)) و الموديل الرياضي لـ (UNIQUAC) و الموديل الرياضي لـ (UNIFAC) تم استخدامهم لربطهم بعلاقات مع البيانات العملية و للتنبؤ بتراكيز الأطوار للانظمة المدروسة. الحسابات المبنية على الموديل الرياضي لـ (NRTL) تعطي تمثيل جيد للبيانات العملية (experimental tie-line data) لكل الأنظمة المدروسة. التوافق بين النتائج المستحصلة من العلاقات الرياضية والبيانات العملية كان جيداً جداً.

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