LIQUID-LIQUID EQUILIBRIA OF QUATERNARY SYSTEMS INCLUDING SULFOLANE AT 293.15 K

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ABSTRACT

Liquid – liquid equilibrium data were measured at 293.15 K for three quaternary systems sulfolane + methanol + n-octane + toluene, sulfolane + ethanol + n-octane + toluene and sulfolane + 1-propanol + n-octane + toluene. Tie-line data were satisfactorily correlated by the Othmer and Tobias method. The non-random two-liquid (NRTL) model was used to correlate the experimental results and to calculate the phase compositions of the quaternary systems. Good quantitative agreement was obtained

INTRODUCTION

Sulfolane has been widely used as a solvent in the recovery of high purity monocyclic aromatic hydrocarbons, such as benzene, toluene and xylenes from naphtha and hydrogenated pyrolysis gasoline. Many investigators have studied the liquid-liquid equilibria for ternary systems containing sulfolane (Lee and Kim, 1995; Letcher et al., 1996; lee and Kim, 1998; De Fre and Vehoeye, 1976; Hassan et al., 1988; Cassell et al., 1989). An alternate approach is to use a combination of solvents to balance the selectivity and solvency functions (Muller and Hochfeld, 1967; Nagpal and Rawat, 1981). Such a combination of solvents is reported to give the advantages of lower consumption of energy and lower solvent –to- feed ratio, with an effect on the dimensions of the column of extraction. To our knowledge, liquid-liquid equilibrium data on n-octane + toluene + (sulfolane + methanol or ethanol or 1-propanol) combination solvent systems have not been published so far in the literature.

In the present investigation, liquid-liquid equilibrium data of n-octane- toluene hydrocarbon systems have been reported with sulfolane + 1-alkanol (mass ratio 95: 05) at 298.15 K.

EXPERIMENTAL WORK

Materials

n–octane, toluene, sulfolane, methanol, ethanol and 1 – propanol (> 99.5 mol %) were obtained from Fluka Chemie AG. All solvents were used without further purification but kept over freshly activated molecular sieve of type 4A0 before use. The purity of solvents was checked by gas liquid chromatography analysis.

Procedure

The binodal curves were determined using cloud point titration method (Hadded and Edmister, 1972). The accuracy of this technique was greater than 0.005 mass fraction. Tie-lines data were determined using the refractive index method (Briggs and Comings, 1968). The precision of this method was better than 0.01 mass fraction.

RESULTS AND DISCUSSION

Liquid – liquid equilibrium data for different n–octane + toluene + sulfolane + 1-alkanols at 293.15 K are illustrated in Figures (1-3). The experimental tie-line data for the systems are given in Tables 1-3, and fit well on the binodal curves. The accuracy of the experimental data for quaternary systems studied here at 293.15 K were checked Othmer-Tobias correlation (Othmer and Tobias, 1941).

$$\log(\frac{1-x_{11}}{x_{11}}) = a + b\log(\frac{1-x_{22}}{x_{232}}) \qquad (1)$$

plotting $\log((1-x_{22})/x_{22})$ versus $\log((1-x_{11})/x_{11})$ gave all linear correlations for all the systems, Table 4 and the results agreed with the binodal curve data within ± 0.01 mol %, thus confirming the soundness of the present experimental determinations.

The effectiveness of the solvent for the extraction can be expressed in terms of the distribution coefficient (k1) and (k2) 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:

$$k_1 = \frac{x_{31}}{x32} \qquad (2)$$

$$k_2 = \frac{x_{21}}{x_{22}} \qquad (3)$$

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

$$s = \frac{k_1}{k_2} \qquad (4)$$

The obtained results of the distribution coefficient and selectivity are included in Tables (1-3), as calculated from the experimental tie lines using equations (2), (3), and (4) respectively. As can be seen from Tables (1-3), the selectively vary in the following order : sulfolane + 5 % MeOH > sulfolane + 5% EtOH > sulfolane + 5% 1-PrOH and capacity in the order sulfolane + 5% EtOH > sulfolane + 5% 1-PrOH > sulfolane + 5% MeOH.

The compositions of the plait points as determined by construction and Treybal methods (Hand, 1930 and Treybal et al., 1946) for the three systems are listed in Table 5.

It is apparent that the plait points are located in the region of mixtures containing more solvent. 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 1. Tie-line data, Distribution coefficient, and selectivity for (Sulfolane + 5% MeOH) (1) + n-octane (2) + toluene (3) at 293.15 K.

Solvent – rich phase			n-Octane – rich phase			Toluene k_1	n-Octane k_2	S= k_1/k_2
x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}			
0.920	0.010	0.070	0.012	0.868	0.120	0.583	0.012	48.583
0.860	0.010	0.130	0.015	0.735	0.250	0.520	0.014	37.143
0.805	0.010	0.185	0.020	0.590	0.390	0.474	0.017	27.882
0.750	0.015	0.235	0.020	0.470	0.510	0.461	0.032	14.406
0.680	0.020	0.300	0.035	0.350	0.615	0.488	0.057	8.561
0.653	0.022	0.325	0.080	0.230	0.690	0.471	0.096	4.906

Table 2. Tie-line data, Distribution coefficient, and selectivity for (Sulfolane + 5% EtOH) (1) + n-octane (2) + toluene (3) at 293.15 K.

Solvent – rich phase			n-Octane – rich phase			Toluene k_1	n-Octane k_2	S= k_1/k_2
x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}			
0.900	0.020	0.080	0.016	0.854	0.130	0.615	0.023	26.739
0.828	0.022	0.150	0.018	0.732	0.250	0.600	0.030	20.000
0.757	0.023	0.220	0.020	0.605	0.375	0.587	0.038	15.447
0.701	0.024	0.275	0.030	0.465	0.505	0.545	0.052	10.481
0.660	0.025	0.315	0.040	0.345	0.615	0.512	0.072	7.111
0.610	0.030	0.360	0.085	0.225	0.690	0.522	0.133	3.925

Table 3. Tie-line data, Distribution coefficient, and selectivity for (Sulfolane + 5% 1-PrOH) (1) + n-octane (2) + toluene (3) at 293.15 K.

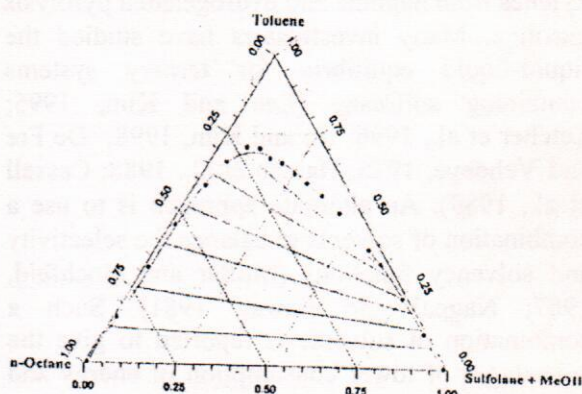| Solvent – rich phase			n-Octane – rich phase			Toluene k_1	n-Octane k_2	S= k_1/k_2
x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}			
0.910	0.020	0.070	0.015	0.855	0.130	0.538	0.023	23.391
0.840	0.025	0.135	0.015	0.715	0.270	0.500	0.035	14.286
0.775	0.030	0.195	0.020	0.580	0.400	0.488	0.052	9.385
0.695	0.035	0.270	0.025	0.460	0.515	0.524	0.076	6.895
0.635	0.040	0.325	0.040	0.335	0.625	0.520	0.119	4.370
0.600	0.040	0.360	0.095	0.220	0.685	0.526	0.182	2.890

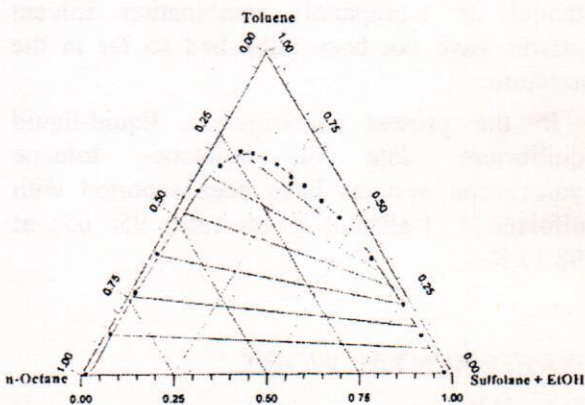Fig. (1) Binodal curve and tie lines for (sulfolane+5%MeOH)+n-octane+toluene

Fig. (2) Binodal curve and tie lines for (sulfolane+5%ETOH)+n-octane+toluene
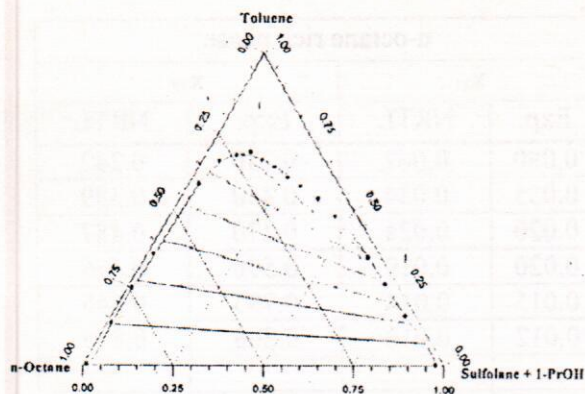
Fig. (3) Binodal curve and tie lines for (sulfolane+5% 1-PrOHETOH)+n-octane+toluene

Table 4. Results of the least squares analysis using Othmer-Tobias correlation for solvent + n-octane + toluene at 293.15 K.

Solvent	a	b	R
Sulfolane + methanol	0.5222	-0.5282	0.9987
Sulfolane + ethanol	0.5289	-0.4367	0.9976
Sulfolane + 1-propanol	0.7134	-0.4427	0.9982

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

Solvent	Construction method			Treybal method		
	x_1	x_2	x_3	x_1	x_2	x_3
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

Data correlation and Prediction

The NRTL model was used to predict the LLE data in the present work. The multicomponent form of the NRTL equation is given by (Renon and Prausnitz, 1968):

$$g^E = \sum_{i=1}^{M} x_i \frac{\sum_{j=1}^{M} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{M} G_{ki} x_j} \qquad (5)$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \qquad (6)$$

and

$$G_{ij} = \exp\left(-\infty_{ji} \tau_{ji}\right) \qquad (7)$$

Where gE is the molar excess Gibbs energy, gij is the energy parameter in the NRTL equation, M is the number of components, R is the gas constant, τ is the temperature (K), xi is the mole fraction of component i , and $\propto$ji is the nonrandomness parameter. The value of the nonrandomness parameter is taken as 0.2 as recommended by Renon and Prausnitz. The objective function, F was used to minimize the difference between the experimental and calculated mole fractions.

$$F = \sum_{i=1}^{n} \min \sum_{j=1}^{3} \sum_{l=1}^{2} (x_{jl} \exp(i) - x_{jl} cal(i))^2 \qquad (8)$$

Where xjl exp(i) is the experimental mole fraction, xjl cal(i) is the calculated mole fraction, and n is the number of experimental tie-lines.

The values of the parameters that minimized this objective function were sought, using the NRTL model. Applying the direct search method of (Hooke and Jeeves, 1961), the values of g11, g12, $\propto$12, $\propto$13 and $\propto$23 were set, and the values of the five parameters of the NRTL model g22, g33, g12, g13, g23 (J.mol-1) were calculated.

The parameters calculated in this was are given in Table 6. Also included in the table, the root-mean-square deviation (RMSD) :

$$RMSD = 100 \left(\sum_{i=1}^{n} \min \sum_{j=1}^{3} \sum_{l=1}^{2} \frac{(x_{ji} \exp(i) - x_{jl} cal(i))^2}{6M} \right)^{1/2} \qquad (9)$$

Where x is the mole fraction, i is the number of components, j is the number of phases, k is the number of tie-line points, n is the total number of components and M is the total number of LLE sets. RMSD may be regarded as a measure of the precision of the correlation. The calculations based on NRTL model gave a good representation of the tie-line data for all systems studied, Table 7.

Table-6: NRTL parameters (gij(J.mol-1)) and (αij) for the systems Solvent (1) + n-octane (2) + toluene (3) at 293.15 K

System	g_{11}	g_{22}	g_{33}	g_{12}	g_{13}	g_{23}	α_{12}	α_{13}	α_{23}	RMSD
Sulf + 5 % methanol	776.118	189.003	3075	5604	7895	6176	0.266	0.402	0.336	0.237
Sulf + 5 % ethanol	1634	75	1196	5468	7716	7716	0.302	0.425	0.426	0.013
Sulf + 5 % 1-propanol	1745	15	4543	5465	6872	6872	0.290	0.310	0.460	0.145

Table 7. Comparing experimental and predicted LLE data for the systems solvent (1) + n-octane (2) + toluene (3) t 293.15 K

Solvent	Solvent rich phase				n-octane rich phase			
	x_{11}		x_{12}		x_{21}		x_{22}	
	Exp.	NRTL	Exp.	NRTL	Exp.	NRTL	Exp.	NRTL
Sulfolane + MeOH	0.653	0.845	0.022	0.021	0.080	0.062	0.230	0.242
	0.680	0.689	0.020	0.018	0.035	0.034	0.350	0.389
	0.75	0.624	0.015	0.015	0.020	0.024	0.470	0.487
	0.805	0.848	0.010	0.012	0.020	0.019	0.590	0.476
	0.860	0.945	0.010	0.011	0.015	0.014	0.735	0.645
	0.92	0.928	0.010	0.011	0.012	0.010	0.868	0.815
Sulfolane + EtOH	0.610	0.653	0.030	0.029	0.085	0.079	0.225	0.227
	0.660	0.635	0.025	0.025	0.040	0.042	0.345	0.343
	0.701	0.718	0.025	0.024	0.030	0.029	0.465	0.464
	0.757	0.721	0.023	0.023	0.020	0.021	0.605	0.602
	0.828	0.845	0.022	0.022	0.018	0.017	0.732	0.736
	0.900	0.917	0.020	0.020	0.016	0.016	0.854	0.837
Sulfolane + 1-PrOH	0.600	0.689	0.040	0.040	0.095	0.083	0.220	0.219
	0.635	0.616	0.040	0.035	0.040	0.041	0.335	0.386
	0.695	0.636	0.035	0.031	0.025	0.027	0.460	0.525
	0.775	0.720	0.030	0.026	0.020	0.022	0.580	0.657
	0.840	0.720	0.025	0.023	0.015	0.017	0.715	0.757
	0.910	0.895	0.020	0.021	0.015	0.015	0.855	0.817

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