Liquid−Liquid Equilibria for Sulfolane + 1-Alkanol (C_1 to C_5) + Octane + Toluene at 293.15 K

Amar H. Al-Dujaili,* Akl M. Awwad, Hatim M. Essa, and Abdulmuhasen A. Al-Haidri

Department of Chemistry, College of Education, Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq

Liquid−liquid equilibrium data were measured at 293.15 K for five different pseudo-ternary systems. Two components are kept the same (octane and toluene), but the other one, a pseudo-component, is made up of a mixture of sulfolane with a small amount of a 1-alkanol (methanol + ethanol, + 1-propanol, + 1-butanol, or + 1-pentanol). The nonrandom two liquid (NRTL) equation was used to correlate the experimental data and to predict the phase composition of the systems studied. The agreement between the correlated and the experimental results was good.

Introduction

The present paper is a continuation of our previous study[1] on the liquid−liquid equilibria of the quaternary systems containing sulfolane as a common solvent. Sulfolane is an important industrial solvent having the ability to extract monocyclic aromatic hydrocarbons from petroleum products. Liquid−liquid equilibrium (LLE) data and thermophysical properties of mixtures of sulfolane with other solvents have been reported by several authors.[2−4] In this paper, we present new experimental data for five different pseudo-ternary systems. Two components are kept the same (octane and toluene), but the other one, a pseudo-component, is made up of a mixture of sulfolane with a small amount of a 1-alkanol {methanol (MeOH), + ethanol (EtOH), + 1-propanol (1-PrOH), + 1-butanol (1-BuOH), or + 1-pentanol (1-PeOH)} at 293.15 K. The mass fraction of 1-alkanol in sulfolane was 5 %. Furthermore, the experimental quaternary results were correlated by fitting the nonrandom two-liquid (NRTL) equation.[5]

Experimental Section

Materials. The mole fraction purities of the materials were as follows: sulfolane (>99.5 %), octane (>99.8 %), toluene (>99.0 %), methanol (>99.5 %), ethanol (>99.8 %), 1-propanol (>99.5 %), 1-butanol (>99.5 %), and 1-pentanol (>99.0 %). They were obtained from Fluka Chemie AG. The purity of all solvents was checked by GLC analysis and 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. The measured densities (ρ) and refractive indices (n_D) of the pure solvents used in this study were found to be in a good agreement with those values published in the literature.[6]

Procedure. The binodal curves were determined by cloud point titration method as described previously in detail.[7] The uncertainty of this method was ± 0.005 mass fraction. The temperature fluctuation were limited to ± 0.01 K by using a constant temperature water bath (Schott-Gerate CT 1150) with a basic control unit. Tie-lines were determined using the refractive index method described by Briggs and Comings.[8] Refractive indices were measured using Abbe refractometer with an uncertainty of $\pm 4 \times 10^{-4}$. The uncertainty of the technique used to determine the tie lines was ± 0.01 mass fraction. The experimental procedures are described in detail in previous work.[7]

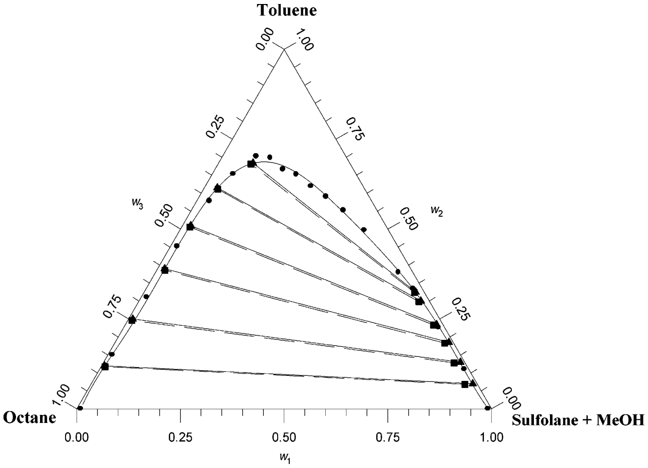

Figure 1. Liquid−liquid equilibria (mass fraction) for the system w_1 (sulfolane + MeOH) + w_2 (octane) + w_3 (toluene) at 298.15 K: ●, solubility (binodal curve) date; ▲, experimental tie lines (−); ■, NRTL-predicted end composition (− −).

Results and Discussion

Experimental Data. Liquid−liquid equilibrium data for the five pseudo-ternary systems studied here at 293.15 K are presented in Table 1 and illustrated in Figures 1 to 5. The experimental tie-line data for the systems are given in Table 2 and fit well on the binodal curves, indicating the accuracy of the experimental tie-line data. The distribution coefficients for toluene k_1 and octane k_2 in (sulfolane + 1-alkanol) and octane phases were calculated from the following formulas:

$$k_1 = \frac{w_{31}}{w_{32}} \quad \text{and} \quad k_2 = \frac{w_{21}}{w_{22}} \tag{1}$$

where w_{31} and w_{32} are toluene mass fraction in solvent and

---

* Correspondinag author. E-mail: ahdujaili@yahoo.com.

10.1021/je050096i CCC: $33.50

Table 1. Binodal Curve Compositions at 293.15 K for the Mixtures w_1 (Sulfolane + 0.05 1-Alkanol) + w_2 (Octane) + w_3 (Toluene)

w_1 (sulfolane + 0.05 MeOH)		w_1 (sulfolane + 0.05 EtOH)		w_1 (sulfolane + 0.05 1-PrOH)		w_1 (sulfolane + 0.05 1-BuOH)		w_1 (sulfolane + 0.05 1-PenOH)	
w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2
0.986	0.014	0.980	0.020	0.980	0.020	0.988	0.012	0.980	0.020
0.900	0.018	0.892	0.024	0.846	0.028	0.914	0.016	0.868	0.026
0.778	0.020	0.799	0.027	0.753	0.034	0.830	0.018	0.766	0.032
0.694	0.023	0.656	0.038	0.669	0.038	0.751	0.025	0.663	0.038
0.638	0.037	0.510	0.065	0.514	0.066	0.656	0.038	0.519	0.066
0.498	0.063	0.432	0.093	0.430	0.092	0.523	0.067	0.430	0.092
0.416	0.090	0.359	0.118	0.362	0.119	0.436	0.094	0.362	0.119
0.351	0.115	0.303	0.145	0.306	0.146	0.370	0.121	0.302	0.144
0.295	0.141	0.239	0.165	0.246	0.169	0.304	0.145	0.248	0.170
0.237	0.164	0.191	0.192	0.196	0.196	0.245	0.168	0.196	0.196
0.193	0.193	0.145	0.221	0.144	0.220	0.197	0.197	0.145	0.221
0.139	0.212	0.100	0.258	0.104	0.269	0.148	0.226	0.104	0.267
0.096	0.249	0.060	0.345	0.058	0.333	0.104	0.267	0.080	0.342
0.059	0.339	0.037	0.448	0.036	0.434	0.058	0.331	0.038	0.452
0.036	0.439	0.021	0.652	0.022	0.671	0.038	0.452	0.021	0.661
0.019	0.582	0.020	0.780	0.018	0.770	0.020	0.615	0.018	0.762
0.016	0.710	0.018	0.890	0.016	0.870	0.018	0.732	0.014	0.874
0.014	0.858	0.016	0.984	0.014	0.986	0.016	0.864	0.010	0.990
0.010	0.990					0.012	0.988		

Table 2. Tie-Line Data for w_1 (Sulfolane + 0.05 1-Alkanol) + w_2 (Octane) + w_3 (Toluene) at 293.15 K

solvent-rich phase			octane-rich phase		
w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
		w_1 (Sulfolane + 0.05 Methanol)			
0.920	0.010	0.070	0.012	0.868	0.120
0.860	0.010	0.130	0.015	0.735	0.250
0.805	0.010	0.185	0.020	0.590	0.390
0.750	0.015	0.235	0.020	0.470	0.510
0.680	0.020	0.300	0.035	0.350	0.615
0.653	0.022	0.325	0.080	0.230	0.690
		w_1 (Sulfolane + 0.05 Ethanol)			
0.900	0.020	0.080	0.016	0.854	0.130
0.828	0.022	0.150	0.018	0.732	0.250
0.757	0.023	0.220	0.020	0.605	0.375
0.701	0.024	0.275	0.030	0.465	0.505
0.660	0.025	0.315	0.040	0.345	0.615
0.610	0.030	0.360	0.085	0.225	0.690
		w_1 (Sulfolane + 0.05 1-Propanol)			
0.910	0.020	0.070	0.015	0.855	0.130
0.840	0.025	0.135	0.015	0.715	0.270
0.775	0.030	0.195	0.020	0.580	0.400
0.695	0.035	0.270	0.025	0.460	0.515
0.635	0.040	0.325	0.040	0.335	0.625
0.600	0.040	0.360	0.095	0.220	0.685
		w_1 (Sulfolane + 0.05 1-Butanol)			
0.918	0.014	0.068	0.015	0.802	0.183
0.871	0.014	0.115	0.015	0.710	0.275
0.799	0.016	0.185	0.020	0.585	0.395
0.742	0.018	0.240	0.030	0.460	0.510
0.690	0.020	0.290	0.040	0.340	0.620
0.630	0.030	0.340	0.100	0.220	0.680
		w_1 (Sulfolane + 0.05 1-Pentanol)			
0.930	0.020	0.050	0.015	0.855	0.130
0.870	0.020	0.110	0.020	0.710	0.270
0.805	0.025	0.170	0.020	0.585	0.395
0.725	0.030	0.245	0.025	0.470	0.505
0.660	0.035	0.305	0.040	0.350	0.610
0.635	0.035	0.330	0.090	0.230	0.680

octane layers, respectively; w_{21} and w_{22} are octane mass fraction in solvent and octane layers, respectively. The selectivity (S) of (sulfolane + 1-alkanol) solvent for toluene was calculated from the relation:

$$S = \frac{k_1}{k_2} \tag{2}$$

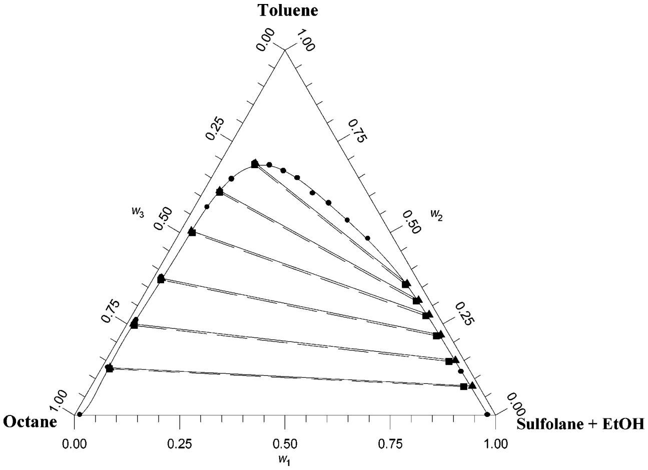

Figure 2. Liquid−liquid equilibria (mass fraction) for the system w_1 (sulfolane + EtOH) + w_2 (octane) + w_3 (toluene) at 298.15 K: ●, solubility (binodal curve) date; ▲, experimental tie lines (—); ■, NRTL-predicted end composition (− −).

It was found that the selectivity (S) in the following mass fractions of alcohol in order: sulfolane + 5 % methanol, $S = 48 >$ pure sulfolane, $S = 37$ from previous work[1] $>$ sulfolane + 5 % ethanol, $S = 27 >$ sulfolane + 5 % 1-propanol, $S = 23 >$ sulfolane + 5 % 1-butanol, $S = 21 >$ sulfolane 5 % 1-pentanol, $S = 17$. It is observed that the selectivity of (sulfolane + 5 % methanol) is higher than that of the pure sulfolane but decreases as the chain length of hydrocarbon in 1-alkanol increases.

Data Correlation. The NRTL model was used to correlate the LLE data in the present work. The multicomponent form of the NRTL equation is given by[5]

$$G^{\mathrm{E}} = \sum_{i=1}^{M} x_i \frac{\sum_{j-1}^{M} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{M} G_{k_1} x_k} \tag{3}$$

with $\tau_{ji} = \{(g_{ji} - g_{ii})\}/\{(RT)\}$ and $G_{ij} = \exp(-\alpha_{ji}\tau_{ji})$, where G^{E} is the molar excess Gibbs energy, g_{ij} is the energy parameter in the NRTL equation, M is the number of components, R is the gas constant, T is the absolute temperature, x_i is the mole

Table 3. NRTL Parameters and α_{ij} for the Systems w_1 (Sulfolane + 0.05 1-Alkanol) + w_2 (Octane) + w_3 (Toluene) at 293.15 K

	J·mol^{-1}									
1-alkanol	g_{11}	g_{22}	g_{33}	g_{12}	g_{13}	g_{23}	α_{12}	α_{13}	α_{23}	RMSD
MeOH	776	189	3075	3604	7895	6176	0.266	0.402	0.336	0.024
EtOH	1634	75	1196	5468	7716	7712	0.302	0.425	0.426	0.023
1-PrOH	1745	15	4543	5465	6872	7940	0.290	0.310	0.460	0.018
1-BuOH	1188	962	418	5598	8461	9525	0.206	0.392	0.359	0.019
1-PeOH	1878	76	2431	5401	7798	6068	0.261	0.411	0.435	0.094

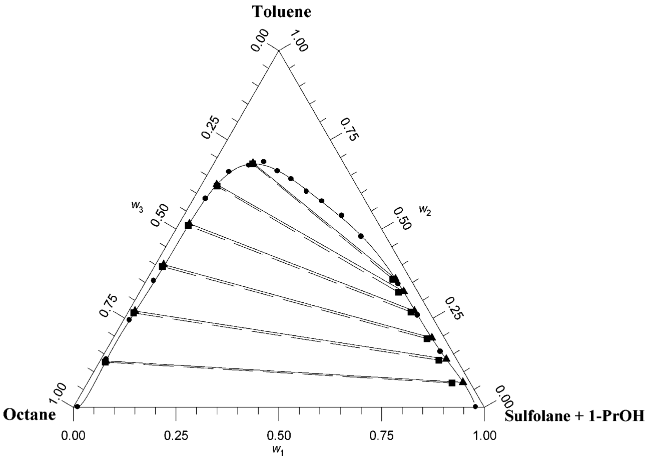

Figure 3. Liquid−liquid equilibria (mass fraction) for the system w_1 (sulfolane + 1-PrOH) + w_2 (octane) + w_3 (toluene) at 298.15 K: ●, solubility (binodal curve) date; ▲, experimental tie lines (—); ■, NRTL-predicted end composition (− −).

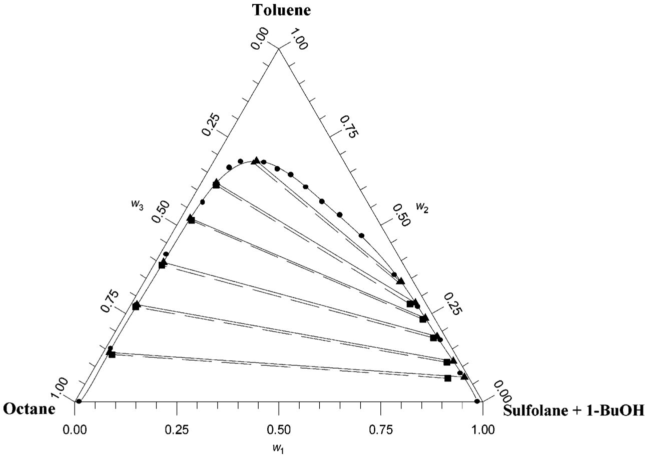

Figure 4. Liquid−liquid equilibria (mass fraction) for the system w_1 (sulfolane + 1-BuOH) + w_2 (octane) + w_3 (toluene) at 298.15 K: ●, solubility (binodal curve) date; ▲, experimental tie lines (—); ■, NRTL-predicted end composition (− −).

fraction of component i, and α_{ji} is the nonrandom parameter that can be set to a predetermined value ranging from 0.2 to 0.5 as recommended by Renon and Prausnitz.[5] The objective function (F) was used to minimize the difference between the experimental and the calculated mole fractions:

$$F = \sum_{i=1}^{n} \min \sum_{j=1}^{3} \sum_{i=1}^{2} \{x_{ji}^{\mathrm{exp}}(i) - x_{ji}^{\mathrm{cal}}(i)\}^2 \qquad (4)$$

where $x_{ji}^{\mathrm{exp}}(i)$ is the experimental mole fraction, $x_{ji}^{\mathrm{cal}}(i)$ is the calculated mole fraction, and n is the number of experimental tie-lines. The values of g_{11} could be chosen arbitrarily and fixed during the computation, and the values of the five parameters of the NRTL model g_{22}, g_{33}, g_{12}, g_{13}, and g_{23} were calculated by using Hooke and Jeeves direct search method.[9]

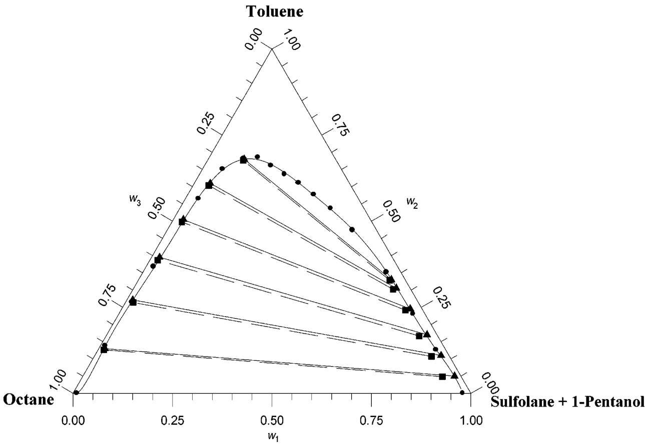

Figure 5. Liquid−liquid equilibria (mass fraction) for the system w_1 (sulfolane + 1-PenOH) + w_2 (octane) + w_3 (toluene) at 298.15 K: ●, solubility (binodal curve) date; ▲, experimental tie lines (—); ■, NRTL-predicted end composition (− −).

The parameters calculated in this way are given in Table 3. Also included in the table is the root-mean-square deviation (RMSD):

$$\mathrm{RMSD} = 100\left(\sum_{i=1}^{n} \min \sum_{j=1}^{3} \sum_{l=1}^{2} \frac{(x_{jl}^{\mathrm{exp}}(i) - x_{jl}^{\mathrm{cal}}(i)^2}{6n}\right)^{1/2} \qquad (5)$$

where x is the mole fraction, i is the number of component, j is the number of phases, l is the number of tie-line points, and n 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 experimental tie-line data for all systems studied.

Literature Cited

(1) Awwad, A. M.; Al-Dujaili, A. H.; Essa, M. H. Liquid−liquid equilibria for sulfolane + 2-methoxyethanol + octane + toluene at 293.15 K. *J. Chem. Eng. Data* **2005**, *50*, 788−791.

(2) Letcher, T. M.; Redhi, G. G.; Radloff, S. E.; Domanska, U. Liquid−liquid equilibria of the ternary mixtures with sulfolane at 303.15 K. *J. Chem. Eng. Data* **1996**, *41*, 634−638.

(3) Chen, J. M. J.; Fei, W.; Li, Z. Liquid−liquid equilibria of quaternary systems including cyclohexane, 1-heptane, benzene, toluene, and sulfolane at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 689−692.

(4) Lee, S.; Kim, H. Liquid−liquid equilibria for ternary systems sulfolane + octane + benzene, sulfolane + octane + toluene and sulfolane + octane + *p*-xylene at elevated temperatures. *J. Chem. Eng. Data* **1998**, *43*, 358−361.

(5) Renon, H.; Prausnitz, J. M. Local composition in thermodynamics excess function for liquid mixtures. *AICHE J.* **1968**, *14*, 135−144.

(6) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Techniques of Chemistry, Vol. II; Wiley: New York, 1986.

(7) Awwad, A. M.; Al-Dujaili, A. H.; Essa, H. M. Liquid−liquid equilibria for 2-ethoxyethanol + water + *n*-alkane + benzene at 293.15 K. *J. Chem. Eng. Data* **2004**, *49*, 741−743.

(8) Briggs, S. W.; Comings, E. W. Tie-line correlation and plait point determination. *Ind. Eng. Chem.* **1943**, *35*, 411−415.

(9) Hook, R.; Jeeves, T. A. Direct search solution of numerical and statistical problems. *J. Assoc. Comput. Mach.* **1961**, *8*, 212−229.

Received for review March 11, 2005. Accepted November 29, 2005.

JE050096I