Liquid−Liquid Equilibria for the Ternary Systems Sulfolane + Octane + Benzene, Sulfolane + Octane + Toluene, and Sulfolane + Octane + *p*-Xylene at Elevated Temperatures

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Liquid−liquid equilibrium data for the systems sulfolane + octane + benzene, sulfolane + octane + toluene, and sulfolane + octane + *p*-xylene were determined at 343.35 K, 372.35 K, and 402.35 K. Tie line data were satisfactorily correlated by the Othmer and Tobias method. The experimental data were compared with the values calculated by the UNIQUAC and NRTL models. Good qualitative agreement was obtained with these models. However, the calculated values based on the NRTL model were found to be better than those based on the UNIQUAC model.

Introduction

In the sulfolane extraction process, aromatics such as benzene, toluene, and *p*-xylene are extracted from reformed naphthas and pyrolysis gasolines with sulfolane at temperatures ranging generally from 343 to 413 K. The liquid−liquid equilibrium (LLE) data at the operating conditions are essential to design this process. Such data on hydrocarbon + solfolane systems are also useful for better understanding of the molecular behavior in nonideal solutions.

Quantitative phase-equilibrium data for the systems containing sulfolane have been presented at near room temperatures (Achcroft et al., 1982; Rawat and Gulati, 1976; Lee and Kim, 1995). But, to our knowledge, phase-equilibrium data at higher temperatures on sulfolane + octane + aromatic compounds (benzene, toluene, and *p*-xylene) have not been published in the literature. Therefore, the purpose of this study was to measure the data for these systems to aid in the correlation and prediction of liquid−liquid equilibria. LLE data for these ternary systems were measured at 343.35 K, 372.35 K, and 402.35 K and correlated by the UNIQUAC and NRTL models.

Experimental Section

Chemicals. Sulfolane was purchased from Fluka Chemie AG with a minimum purity of 99.5%, and octane from Janssen Chemica with a minimum purity 99.0%. Toluene and benzene were supplied by Associate of E. Merck, Germany, with 99.97% and 99.94% purities, respectively. The minimum purity of *p*-xylene from Janssen Chemica was 99.0%. All these chemicals were used directly without any purification.

Procedure. Liquid−liquid equilibrium for the ternary systems were measured by an apparatus similar to that of Rawat and Prasad (1980). The volume of equilibrium cell was 270 cm^3. The cell was made of stainless steel and was placed inside an air bath controlled to the desired temperature (±0.1 K). The pure components were added by mass, and the mixture was stirred for at least 1 h with a magnetic stirrer. Then the mixture was allowed to settle for at least 2 h. Samples of both liquid phases were carefully withdrawn and analyzed by gas chromatography with a thermal conductivity detector. A 6 ft × $^1/_8$ in. column packed with Chromosorb WHP 100/120 coated with OV-101 was used. The injector and detector temperatures were maintained at 573 K. The column temperature was programmed for an initial temperature of 333 K and a final temperature of 443 K. The heating rate was 20 K·min^{-1}, and the flow rate of nitrogen carrier gas was 25 cm^3·min^{-1}.

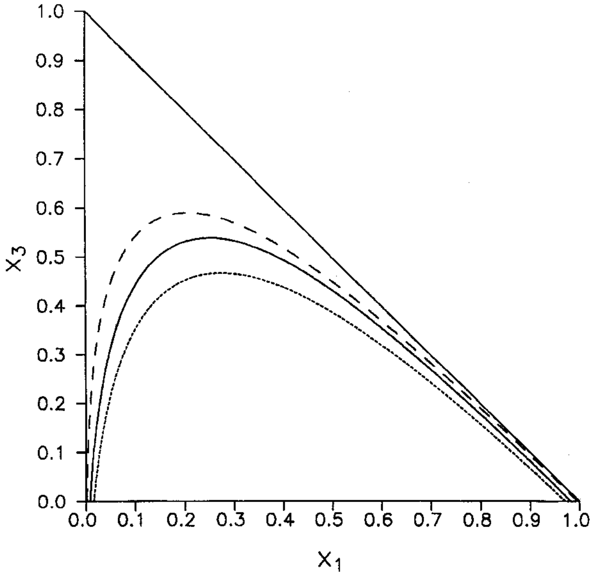

Figure 1. Effect of temperature of the LLE for the system sulfolane (1) + octane (2) + *p*-xylene (3). Curves calculated by UNIQUAC: (—) 343.35 K (···) 372.35 K, (- - -) 402.35 K.

Results and Discussion

Experimental Results. The results obtained in this work for these systems, sulfolane (1) + octane (2) + benzene (3), sulfolane (1) + octane (2) + toluene (3), and

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Table 1. Experimental LLE Data for the System Sulfolane (1) + Octane (2) + Benzene (3)

	bottom phase (1)		top phase (2)	
T/K	x_{11}	x_{21}	x_{12}	x_{22}
343.35	0.7705	0.0292	0.0377	0.6613
	0.7113	0.0311	0.0465	0.5090
	0.6990	0.0326	0.0675	0.4781
	0.6712	0.0374	0.0720	0.4390
	0.5104	0.0714	0.1825	0.2721
372.35	0.8927	0.0219	0.0369	0.7572
	0.8573	0.0262	0.0446	0.6780
	0.8237	0.0301	0.0496	0.6462
	0.7937	0.0279	0.0648	0.5534
	0.7689	0.0362	0.0786	0.5232
	0.7031	0.0466	0.0972	0.4572
	0.5782	0.0768	0.1840	0.3144
402.35	0.9198	0.0332	0.0692	0.8847
	0.8293	0.0425	0.0856	0.6598
	0.7316	0.0620	0.1091	0.5238
	0.6252	0.0936	0.2062	0.3706

Table 2. Experimental LLE Data for the System Sulfolane (1) + Octane (2) + Toluene (3)

	bottom phase (1)		top phase (2)	
T/K	x_{11}	x_{21}	x_{12}	x_{22}
343.35	0.8804	0.0204	0.0197	0.7584
	0.7753	0.0326	0.0437	0.5455
	0.6040	0.0849	0.0845	0.4099
	0.5028	0.0843	0.1039	0.3287
372.35	0.8486	0.0290	0.0381	0.6341
	0.7565	0.0387	0.0827	0.5289
	0.6891	0.0541	0.1230	0.3911
	0.5296	0.0977	0.2157	0.2719
402.35	0.9083	0.0330	0.0531	0.7625
	0.8071	0.0528	0.1223	0.5432
	0.6330	0.1034	0.2486	0.3077
	0.4975	0.1358	0.4793	0.1424

Table 3. Experimental LLE Data for the System Sulfolane (1) + Octane (2) + *p*-Xylene (3)

	bottom phase (1)		top phase (2)	
T/K	x_{11}	x_{21}	x_{12}	x_{22}
343.35	0.8737	0.0182	0.0551	0.4873
	0.8467	0.0207	0.0632	0.4359
	0.8415	0.0194	0.0743	0.4075
	0.8137	0.0230	0.0851	0.3681
	0.7806	0.0256	0.1294	0.2953
	0.7671	0.0263	0.1660	0.2449
372.35	0.9684	0.0072	0.0357	0.7615
	0.9279	0.0130	0.0433	0.6179
	0.7358	0.0330	0.2267	0.2129
	0.6940	0.0387	0.2535	0.1771
402.35	0.9420	0.0250	0.0641	0.7711
	0.9260	0.0261	0.0665	0.7229
	0.8699	0.0361	0.0806	0.5898
	0.8330	0.0392	0.1278	0.4902
	0.8154	0.0396	0.1861	0.3713
	0.7105	0.0550	0.2480	0.2775

sulfolane (1) + octane (2) + *p*-xylene (3), are presented in Tables 1–3, respectively. Concentrations of components j ($j = 1, 2, 3$) in phase L ($L = 1$, bottom phase; $L = 2$, top phase) are given in mole fraction, x_{jL}. The effect of temperature on LLE for the system sulfolane + octane + *p*-xylene is shown in Figure 1. As expected, the size of the two-phase region decreases with an increase in temperature.

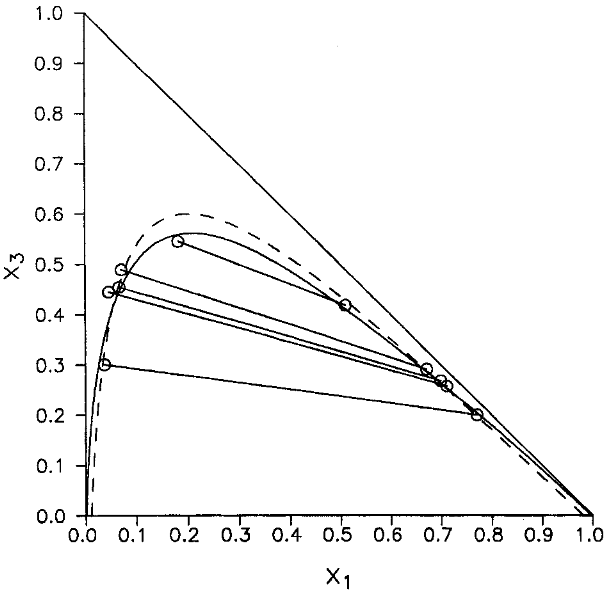

Figure 2. LLE data for the system sulfolane (1) + octane (2) + benzene (3) at 343.35 K. Curves calculated: (- - -) UNIQUAC model, (—) NRTL model. Experimental tie line: (○—○).

Table 4. Othmer–Tobias Correlation of Equilibrium Data for the Systems (a) Sulfolane (1) + Octane (2) + Benzene (3), (b) Sulfolane (1) + Octane (2) + Toluene (3), and (c) Sulfolane (1) + Octane (2) + *p*-Xylene (3)

system	T(K)	a	b	r	F	S
a	343.35	1.3954	0.5980	0.9834	87.74	0.0565
	372.35	1.0943	0.5507	0.9951	509.09	0.0306
	402.35	1.2927	0.6128	0.9962	260.38	0.0481
b	343.35	0.9171	0.3498	0.9892	158.29	0.0522
	372.35	1.0173	0.5292	0.9912	111.78	0.0486
	402.35	1.3009	0.8011	0.9946	182.62	0.0726
c	343.35	1.4133	1.2258	0.9826	111.88	0.0365
	372.35	1.0730	1.0738	0.9968	310.06	0.0570
	402.35	1.2064	0.9420	0.9858	137.89	0.0689

The Othmer–Tobias correlation (Othmer and Tobias, 1942) was used to ascertain the reliability of the experimental results for each system. The correlation calls for the tie line data to have the following functional relationship

$$\log\left(\frac{1-w_{22}}{w_{22}}\right) = a\cdot\log\left(\frac{1-w_{11}}{w_{11}}\right) + b \qquad (1)$$

where w_{11} and w_{22} are the mass fractions.

The results of regression analysis are presented in Table 4. The values of the coefficient of correlation (r) are close to unity. F-values (F) are sufficiently large, and the estimated standard deviations (S) are very small (Box et al., 1978). The quality of the fit confirms the reliability of the experimental LLE data.

Data Correlation. Thermodynamic models, such as the UNIQUAC (Anderson and Prausnitz, 1978) and the NRTL (Renon and Prausnitz, 1968) activity coefficient models, were used to correlate the experimental data for these systems.

The objective function, F, was used to minimize the difference between the experimental and calculated mole fractions:

$$F = \sum_{i=1}^{n} \min \sum_{j=1}^{3} \sum_{L=1}^{2} (x_{jL}^{\text{exp}}(i) - x_{jL}^{\text{cal}}(i))^2 \qquad (2)$$

$x_{jL}^{\text{exp}}(i)$ is the experimental mole fraction, $x_{jL}^{\text{cal}}(i)$ is the calculated mole fraction, and n is the number of the experimental tie lines.

Table 5. UNIQUAC Parameters (U_{ij}) and Root-Mean-Square Deviation (RMSD) Values for the Systems (a) Sulfolane (1) + Octane (2) + Benzene (3), (b) Sulfolane (1) + Octane (2) + Toluene (3), and (c) Sulfolane (1) + Octane (2) + *p*-Xylene (3)

system	T/K	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	RMSD
a	343.35	4184.0	7804.7	3422.1	8085.3	4586.2	6241.0	1.1831
	372.35	4184.0	8204.1	3362.1	8252.5	4378.5	6109.6	0.9303
	402.35	4184.0	7765.1	2535.8	7821.7	4288.3	5930.7	1.2994
b	343.35	4184.0	8261.3	4374.3	8772.0	4493.7	6272.2	1.5969
	372.35	4184.0	8350.3	4006.6	8530.8	4366.6	5982.0	1.0421
	402.35	4184.0	8815.8	3318.3	8577.0	4348.1	6264.2	1.2950
c	343.35	4184.0	8360.2	3462.1	9266.1	4414.7	6063.2	1.0213
	372.35	4184.0	8482.9	3191.2	8729.5	4441.3	6136.1	0.5885
	402.35	4184.0	8539.9	3490.4	8628.4	4504.0	6259.2	0.9251

Table 6. NRTL Parameters (g_{ij}) and Root-Mean-Square Deviation (RMSD) Values for the Systems (a) Sulfolane (1) + Octane (2) + Benzene (3), (b) Sulfolane (1) + Octane (2) + Toluene (3), and (c) Sulfolane (1) + Octane (2) + *p*-Xylene (3)

system	T/K	g_{11}	g_{22}	g_{33}	g_{12}	g_{13}	g_{23}	α_{12}	α_{13}	α_{23}	RMSD
a	343.35	4184.0	6147.0	12264.0	20047.8	8923.3	8665.6	0.3	0.2	0.2	0.9670
	372.35	4184.0	6718.5	8098.8	18099.4	8393.5	7424.8	0.3	0.2	0.2	0.5924
	402.35	4184.0	3847.7	6386.3	12575.1	7921.4	6195.2	0.3	0.2	0.2	1.0577
b	343.35	4184.0	7917.1	11959.8	17479.9	9574.1	8461.2	0.3	0.2	0.2	0.9439
	372.35	4184.0	6719.6	8606.3	18371.2	8385.9	6945.7	0.3	0.2	0.2	0.8397
	402.35	4184.0	7514.3	5970.1	16534.8	7536.8	6194.8	0.3	0.2	0.2	0.9706
c	343.35	4184.0	7778.9	6707.3	18768.4	8553.8	6924.2	0.3	0.2	0.2	0.7368
	372.35	4184.0	8638.4	5463.1	23303.8	8253.9	6669.0	0.3	0.2	0.2	0.5754
	402.35	4184.0	4667.8	4460.5	13875.9	7129.2	3940.1	0.3	0.2	0.2	0.8255

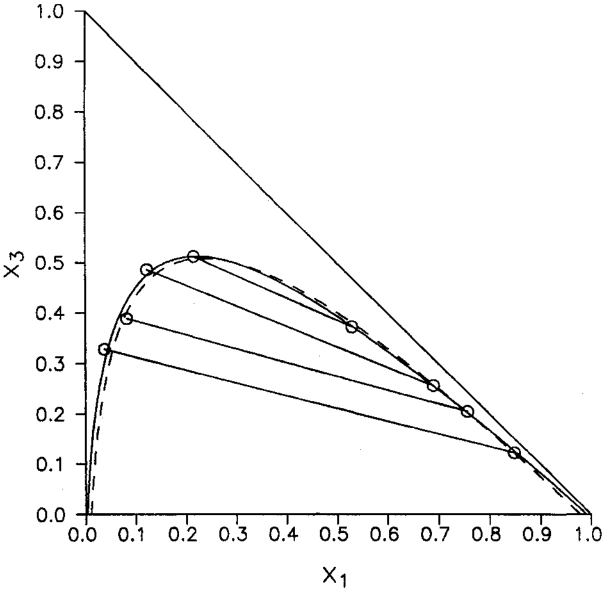

Figure 3. LLE data for the system sulfolane (1) + octane (2) + toluene (3) at 343.35 K. Curves calculated: (- - -) UNIQUAC model, (—) NRTL model. Experimental tie line: (○—○).

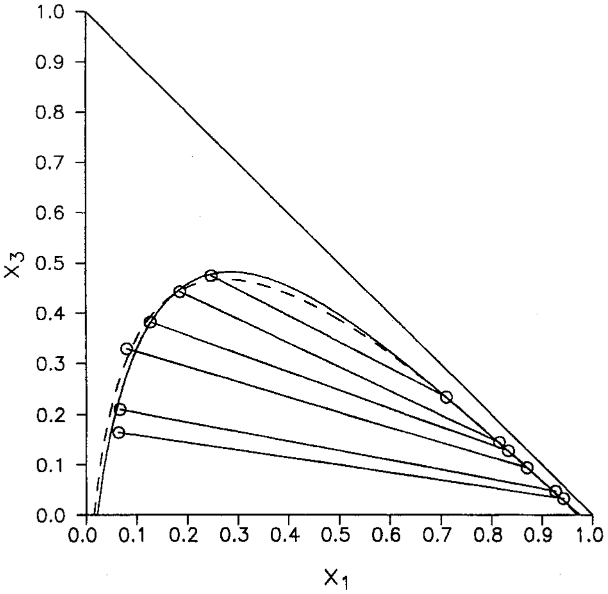

Figure 4. LLE data for the system sulfolane (1) + octane (2) + *p*-xylene (3) at 402.15 K. Curves calculated: (- - -) UNIQUAC model, (—) NRTL model. Experimental tie line: (○—○).

The values of the parameters that minimized this objective function were sought, using both the UNIQUAC model and the NRTL model. Applying the method of Varhegyi and Eon (1977), the value of U_{11} was set, and the values of the five parameters for the UNIQUAC model

$$U_{22}, U_{33}, U_{12}, U_{13}, U_{23}\ (\mathrm{J{\cdot}mol^{-1}}) \tag{3}$$

were calculated. The values of g_{11}, α_{12}, α_{13}, and α_{23} were set, and the values of the five parameters for the NRTL model

$$g_{22}, g_{33}, g_{12}, g_{13}, g_{23}\ (\mathrm{J{\cdot}mol^{-1}}) \tag{4}$$

for the ternary liquid−liquid system were calculated by using Hooke and Jeeves' direct search method (Hooke and Jeeve, 1961). The parameters calculated in this way are shown in Tables 5 and 6.

Also included in the tables is the root-mean-square deviation (RMSD) defined as

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

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

The calculations based on both the UNIQUAC model and the NRTL model gave a good representation of the tie line data for the systems sulfolane + octane + benzene, sulfolane + octane + toluene, and sulfolane + octane + *p*-xylene. However, the NRTL model, fitted to the experimental data, is more accurate than the UNIQUAC model, as can be seen from the RMSD. The calculated values using both the UNIQUAC model and the NRTL model for the systems are presented in Figures 1−4.

Conclusions

LLE data for the ternary systems, sulfolane (1) + octane (2) + benzene (3), sulfolane (1) + octane (2) + toluene (3), and sulfolane (1) + octane (2) + *p*-xylene (3) were determined at 343.35 K, 372.35 K, and 402.35K.

The Othmer−Tobias correlation was used to ascertain the reliability of the experimental data. The good fit confirms the reliability of the data.

The calculation based on both the UNIQUAC model and the NRTL model gave a good representation of the tie line data for the systems, sulfolane + octane + benzene, sulfolane + octane + toluene, and sulfolane + octane + *p*-xylene. However, the calculated values based on the NRTL model are found to be better than the ones based on the UNIQUAC model.

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