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

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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 298.15, 308.15, and 318.15 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 quantitative 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

Although a large volume of liquid−liquid equilibrium (LLE) data exists in the literature, it has not received much attention in terms of theoretical interpretation until the mid 1970s. Much interest has been generated in this area since Sørensen (*1*, *2*) made a systematic study of the published LLE data and correlated these data using the UNIQUAC and NRTL models.

Sulfolane is widely used as a solvent for the extraction of aromatic hydrocarbons. Ternary phase equilibrium data are essential for the proper understanding of the solvent extraction process. Quantitative phase equilibrium data for the systems containing sulfolane are scarce. To our knowledge, phase equilibrium data 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 generate the data for these systems to aid the correlation and prediction of liquid−liquid equilibria. LLE data for these ternary systems were measured at 298.15, 308.15, and 318.15 K, and correlated by using 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 of 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 of these chemicals were used directly without any purification.

Procedure. Liquid−liquid equilibria for the ternary systems were measured by an apparatus similar to that described elsewhere (*3*, *4*). The tie-line measurements were made in a 150 cm^3 cylindrical glass vessel. The vessel was immersed in a thermostat controlled at the desired temperature (±0.1 K). The pure components were added, and the mixture was stirred for at least 1 h with a magnetic stirrer. The two-phase mixture was allowed to settle for at least 2 h. Samples of both phases were carefully withdrawn with syringes and analyzed by gas-liquid chromatography with the aid of a flame ionization detector. A good separation of the samples was obtained on a 6 ft × $^1/_8$ in. column, packed with Chromosorb WHP 100/120 coated with OV-101. 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}. Mass fraction measurements were reproducible to within ±0.003.

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_{31}	x_{12}	x_{22}	x_{32}
298.15	0.9237	0.0064	0.0699	0.0045	0.9119	0.0836
	0.8093	0.0095	0.1812	0.0104	0.7941	0.1955
	0.7541	0.0114	0.2345	0.0104	0.7435	0.2461
	0.7267	0.0113	0.2620	0.0117	0.7041	0.2842
	0.6167	0.0174	0.3659	0.0155	0.6093	0.3752
	0.5689	0.0201	0.4110	0.0147	0.5702	0.4151
	0.4869	0.0337	0.4794	0.0203	0.5120	0.4677
308.15	0.9738	0.0054	0.0208	0.0074	0.9458	0.0468
	0.8440	0.0090	0.1470	0.0134	0.8334	0.1532
	0.7400	0.0098	0.2502	0.0122	0.6580	0.3298
	0.6968	0.0122	0.2910	0.0136	0.5859	0.4005
	0.6236	0.0177	0.3587	0.0225	0.4950	0.4825
	0.6033	0.0187	0.3780	0.0235	0.4887	0.4878
	0.5323	0.0243	0.4434	0.0301	0.4341	0.5358
318.15	0.9728	0.0054	0.0218	0.0014	0.9716	0.0270
	0.9148	0.0065	0.0787	0.0169	0.8674	0.1157
	0.8642	0.0073	0.1285	0.0176	0.7974	0.1850
	0.7159	0.0132	0.2709	0.0179	0.6099	0.3722
	0.6934	0.0152	0.2914	0.0229	0.5497	0.4274
	0.6617	0.0184	0.3199	0.0231	0.5139	0.4630
	0.6155	0.0231	0.3614	0.0257	0.4955	0.4788

Results and Discussion

Experimental Results. The results obtained in this work for the systems, sulfolane (1) + octane (2) + benzene (3), sulfolane (1) + octane (2) + toluene (3), and sulfolane (1) + octane (2) + *p*-xylene (3), are presented on Tables 1,2, and 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 the equilibrium for the systems is shown in Figures 1−3. As expected, the size of the two-phase region decreases with an increase in temperature.

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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_{31}	x_{12}	x_{22}	x_{32}
298.15	0.9823	0.0055	0.0122	0.0017	0.9619	0.0364
	0.9599	0.0070	0.0331	0.0100	0.8947	0.0953
	0.9403	0.0070	0.0527	0.0154	0.8352	0.1494
	0.8782	0.0090	0.1128	0.0176	0.7000	0.2824
	0.8597	0.0092	0.1311	0.0173	0.6609	0.3218
	0.8168	0.0106	0.1726	0.0245	0.5580	0.4175
	0.8008	0.0109	0.1883	0.0259	0.5233	0.4508
308.15	0.9833	0.0056	0.0111	0.0053	0.9562	0.0385
	0.9650	0.0063	0.0287	0.0090	0.8998	0.0912
	0.9438	0.0071	0.0491	0.0134	0.8408	0.1458
	0.8985	0.0082	0.0933	0.0184	0.7450	0.2366
	0.8858	0.0094	0.1048	0.0183	0.7040	0.2777
	0.8728	0.0086	0.1186	0.0190	0.6677	0.3133
	0.8434	0.0108	0.1458	0.0217	0.6312	0.3471
	0.8152	0.0118	0.1730	0.0280	0.5637	0.4083
	0.7764	0.0140	0.2096	0.0346	0.5254	0.4400
318.15	0.9799	0.0082	0.0119	0.0066	0.9572	0.0362
	0.9545	0.0095	0.0360	0.0147	0.8869	0.0984
	0.9383	0.0097	0.0520	0.0194	0.8295	0.1511
	0.8858	0.0124	0.1018	0.0186	0.7279	0.2535
	0.8486	0.0131	0.1383	0.0304	0.6387	0.3309
	0.8299	0.0140	0.1561	0.0327	0.5968	0.3705
	0.8139	0.0141	0.1720	0.0354	0.5578	0.4068
	0.7667	0.0169	0.2164	0.0383	0.5022	0.4595

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_{31}	x_{12}	x_{22}	x_{32}
298.15	0.9448	0.0079	0.0473	0.0118	0.7811	0.2071
	0.8857	0.0083	0.1060	0.0134	0.6251	0.3615
	0.8490	0.0072	0.1438	0.0247	0.5551	0.4202
	0.8357	0.0112	0.1531	0.0345	0.5237	0.4418
	0.8183	0.0113	0.1704	0.0332	0.4852	0.4816
	0.8027	0.0117	0.1856	0.0348	0.4642	0.5010
	0.7877	0.0136	0.1987	0.0475	0.4289	0.5236
308.15	0.9802	0.0068	0.0130	0.0046	0.9419	0.0535
	0.9513	0.0094	0.0393	0.0050	0.8519	0.1431
	0.9291	0.0102	0.0607	0.0127	0.7800	0.2073
	0.9081	0.0112	0.0807	0.0157	0.7205	0.2638
	0.8889	0.0141	0.0970	0.0162	0.6672	0.3166
	0.8683	0.0157	0.1160	0.0253	0.6248	0.3499
	0.8515	0.0159	0.1326	0.0302	0.5837	0.3861
	0.8316	0.0162	0.1522	0.0304	0.5515	0.4181
	0.7962	0.0167	0.1871	0.0437	0.4803	0.4760
	0.7827	0.0179	0.1994	0.0426	0.4535	0.5039
	0.7449	0.0189	0.2362	0.0730	0.3780	0.5490
318.15	0.9755	0.0085	0.0160	0.0021	0.9382	0.0597
	0.9426	0.0109	0.0465	0.0133	0.8347	0.1520
	0.9095	0.0160	0.0745	0.0233	0.7570	0.2197
	0.8791	0.0186	0.1023	0.0237	0.6996	0.2767
	0.8536	0.0190	0.1274	0.0252	0.6461	0.3257
	0.8249	0.0226	0.1525	0.0383	0.6043	0.3574
	0.8023	0.0214	0.1763	0.0401	0.5635	0.3964
	0.7780	0.0216	0.2004	0.0411	0.5366	0.4223
	0.7588	0.0228	0.2184	0.0439	0.4999	0.4562
	0.7415	0.0252	0.2333	0.0607	0.4527	0.4866

The Othmer–Tobias correlation (*5*) was used to ascertain the reliability of the experimental results for each system. The correlation calls for the tie-line data to have the functional relationship

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

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 (*6*). The goodness of the fit confirms the reliability of the results.

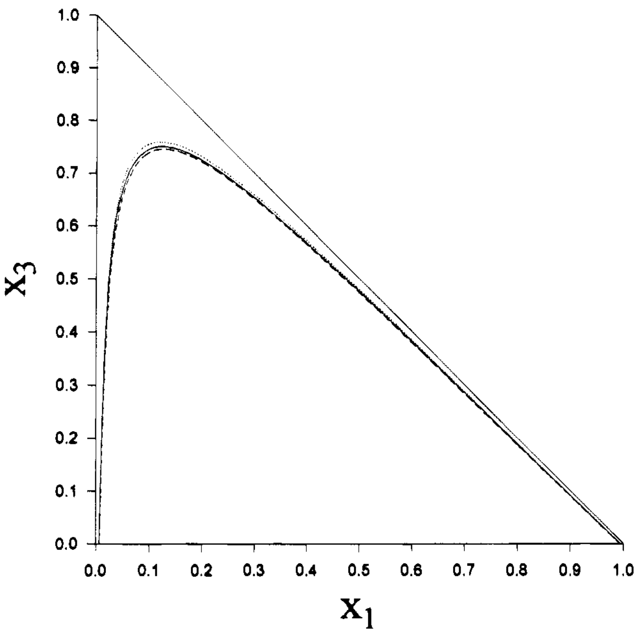

Figure 1. Effect of temperature on the LLE for the system sulfolane (1) + octane (2) + benzene (3): curves calculated by NRTL; (···) 298.15 K, (—) 308.15 K, (- - -) 318.15 K.

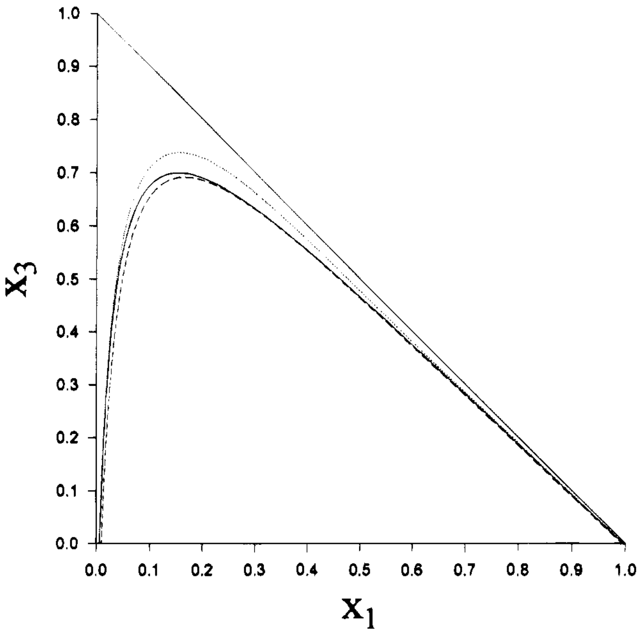

Figure 2. Effect of temperature on the LLE for the system sulfolane (1) + octane (2) + toluene (3): curves calculated by NRTL; (···) 298.15 K, (—) 308.15 K, (- - -) 318.15 K.

Data Correlation. Thermodynamic models, such as the UNIQUAC (*7*) and NRTL (*8*) activity coefficient models, are used to correlate the experimental data for these systems.

The objective function (Func) was used to minimize the difference between the experimental and calculated concentrations.

$$\text{Func} = \sum_{i=1}^{n} \min \sum_{j=1}^{3} \sum_{L=1}^{2} [x_{jL}\,(\text{exptl},i) - x_{jL}(\text{calcd},i)]^2 \qquad (2)$$

x_{jL}(exptl, i) is the experimental mole fraction, x_{jL}(calcd, i)

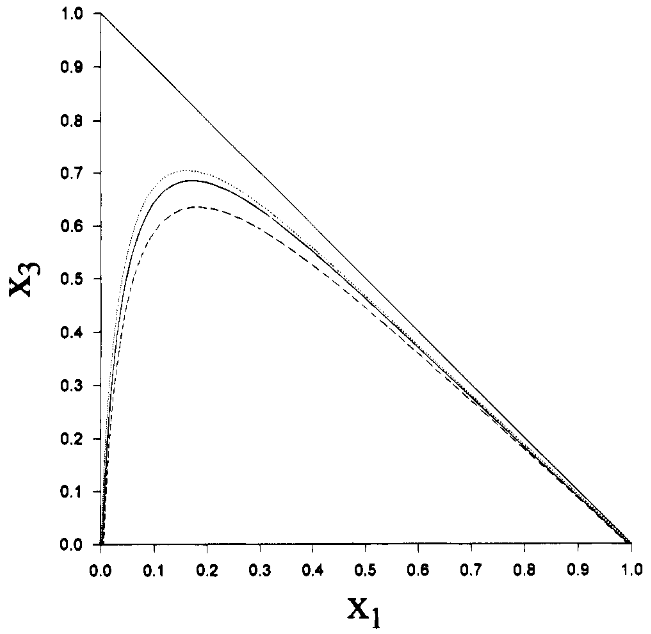

Figure 3. Effect of temperature on the LLE for the system sulfolane (1) + octane (2) + *p*-xylene (3): curves calculated by NRTL; (···) 298.15 K, (—) 308.15 K, (- - -) 318.15 K.

Table 4. Othmer–Tobias correlation 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	298.15	0.9113	−0.0102	0.9985	1702.14	0.0199
	308.15	0.9409	0.1741	0.9868	186.40	0.0853
	318.15	1.1564	0.3521	0.9949	486.16	0.0622
b	298.15	1.1856	0.7119	0.9983	1425.10	0.0319
	308.15	1.0735	0.5983	0.9986	2552.03	0.0236
	318.15	1.1680	0.6721	0.9978	1320.16	0.0333
c	298.15	1.0091	0.7037	0.9984	158.54	0.0141
	308.15	1.1509	0.7579	0.9996	10047.11	0.0131
	318.15	1.0632	0.5707	0.9978	1877.63	0.0265

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 both the UNIQUAC model and the NRTL model. Using the method of Varhegyi and Eon (*9*), the value of U_{11} was set, and the values of the five parameters for the UNIQUAC model

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

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

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

for the ternary liquid–liquid system were calculated by using Hook and Jeeves's direct search method (*10*). 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

$$\text{RMSD} = 100\left[\sum_{i=1}^{n}\sum_{j=1}^{3}\sum_{L=1}^{2}\frac{(x_{jL}(\text{extpl},i) - x_{jL}(\text{calcd},i))^2}{6n}\right]^{1/2} \tag{5}$$

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

As can be seen from the tables, the calculation based on both the UNIQUAC and NRTL models gave 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 analysis of RMSD, except for the sulfolane +octane + benzene system at 298.15 K.

The calculated values using both the UNIQUAC and NRTL models for the systems at 318.15 K are compared

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	298.15	4183.995	6758.199	8516.757	7761.592	4938.211	6166.527	0.4376
	308.15	4183.995	6837.063	4780.060	7925.650	4882.271	6059.095	0.8496
	318.15	4183.995	6820.967	4776.206	7831.782	4882.258	5990.774	0.5797
b	298.15	4183.995	6891.614	4699. 384	7748.575	5082.282	6022.054	0.2428
	308.15	4183.995	7014.611	4893.986	7788.784	5057.492	6002.448	0.2488
	318.15	4183.995	7030.188	4817.051	7736.634	5055.814	6004.908	0.2778
c	298.15	4183.995	6888.066	4896.756	8092.470	5076.542	5955.717	0.3743
	308.15	4183.995	6828.757	4884.869	7896.120	5085.529	5964.039	0.4290
	318.15	4183.995	6869.192	5052.074	7791.390	5066.643	5989.887	0.5399

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	298.15	4183.995	4022.410	15685.209	13901.785	11245.237	11151.222	0.3	0.2	0.2	0.5917
	308.15	4183.995	4239.525	14295.273	14674.422	11393.342	10595.588	0.3	0.2	0.2	0.8460
	318.15	4183.995	4415.149	14235.772	14569.551	11568.965	10595.031	0.3	0.2	0.2	0.5394
b	298.15	4183.995	3310.089	9707.539	14689.757	9624.478	7523.037	0.3	0.2	0.2	0.2227
	308.15	4183.995	3458.751	11545.802	14493.423	9815.691	7354.631	0.3	0.2	0.2	0.2414
	318.15	4183.995	3431.334	10452.085	13793.637	9712.434	7403.371	0.3	0.2	0.2	0.2458
c	298.15	4183.995	4996.803	9820.448	17432.228	9420.793	7160.854	0.3	0.2	0.2	0.2847
	308.15	4183.995	5161.929	9506.506	15688.686	9311.436	7303.386	0.3	0.2	0.2	0.2694
	318.15	4183.995	5044.773	10156.561	15003.435	9174.682	7308.503	0.3	0.2	0.2	0.3390

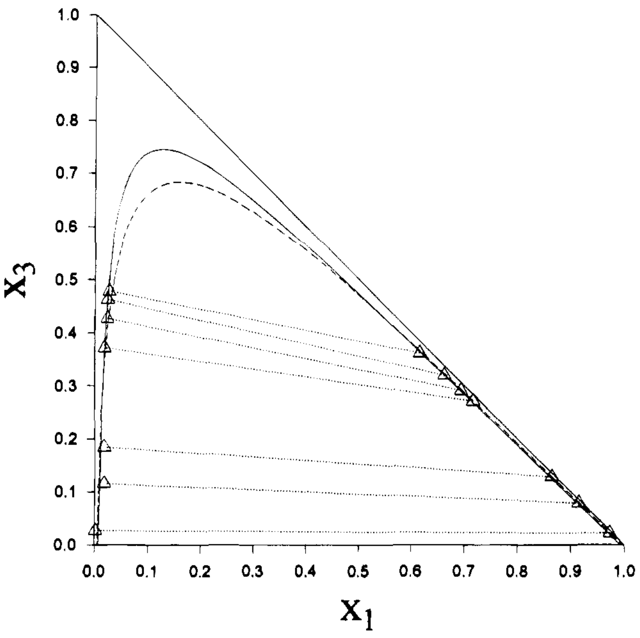

Figure 4. LLE data for the system sulfolane (1) + octane (2) + benzene(3) at 318.15 K: curves calculated by (- - -) UNIQUAC model, (—) NRTL model; experimental tie line (△· · ·△).

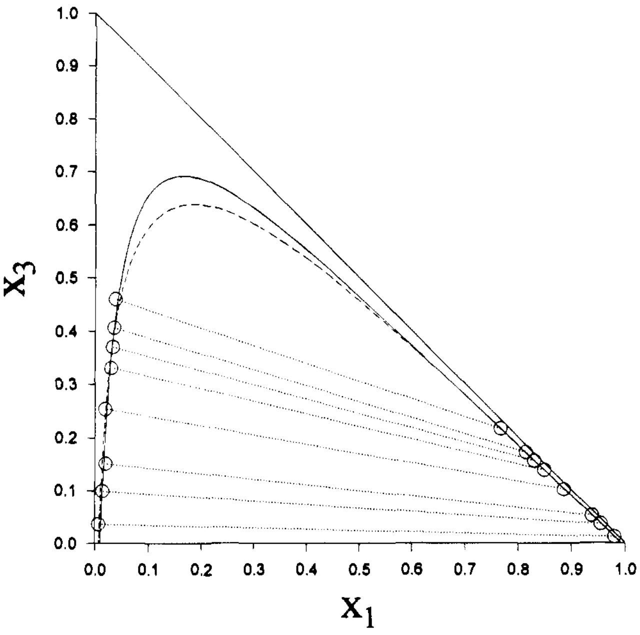

Figure 5. LLE data for the system sulfolane (1) + octane (2) + toluene (3) at 318.15 K: curves calculated by (- - -) UNIQUAC model, (—) NRTL model; experimental tie line (○· ·○).

with the experimental data in Figures 4–6. As shown in the figures, the size of the two-phase region calculated by the NRTL model tends to be larger than that by theUNIQUAC model. The effect is clearly noticeable near the plait point; the data at other temperatures have the same tendencies. The plait-point concentrations estimated from the UNIQUAC and NRTL models are presented in Table 7.

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 298.15, 308.15, and 318.15 K.

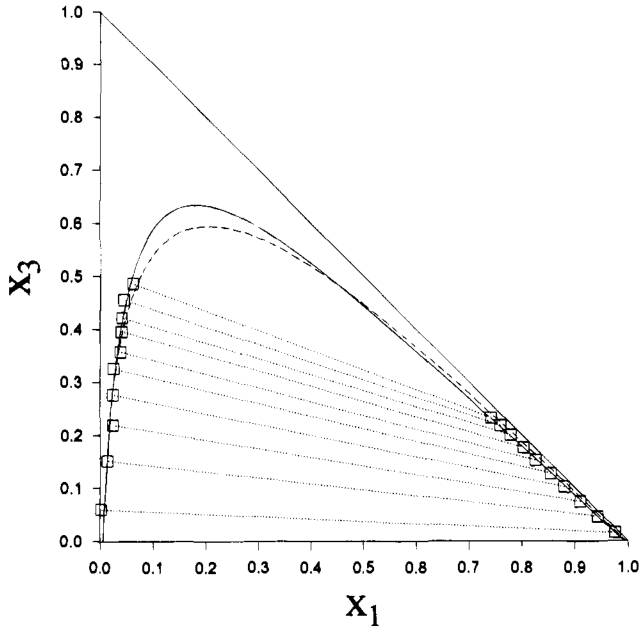

Figure 6. LLE data for the system sulfolane (1) + octane (2) + p-xylene (3) at 318.15 K: curves calculated by (- - -) UNIQUAC model, (—) NRTL model; experimental tie line (□· ·□).

Table 7. Plait-Point Mole Fraction x_i 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), Estimated from the UNIQUAC and NRTL Models

		UNIQUAC model			NRTL Model		
system	T/K	x_1	x_2	x_3	x_1	x_2	x_3
a	298.15	0.1489	0.1525	0.6986	0.1221	0.1189	0.7590
	308.15	0.1897	0.1175	0.6928	0.1643	0.0945	0.7412
	318.15	0.2049	0.1194	0.6757	0.1818	0.0884	0.7298
b	298.15	0.3302	0.0616	0.6082	0.3187	0.0351	0.6462
	308.15	0.2940	0.0926	0.6134	0.2474	0.0862	0.6664
	318.15	0.3098	0.0948	0.5954	0.2864	0.0736	0.6400
c	298.15	0.3526	0.0647	0.5827	0.3076	0.0592	0.6332
	308.15	0.3633	0.0730	0.5637	0.3200	0.0654	0.6146
	318.15	0.3291	0.1118	0.5591	0.2930	0.1102	0.5968

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

The calculation based on both the UNIQUAC and NRTL models gave 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.

The binodal curves calculated by the NRTL model for each system were drawn to investigate the temperature dependence. The size of the two-phase region decreased with an increase in temperature.

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