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Liquid−Liquid Equilibria of the Ternary Systems Dodecane + Butylbenzene + Sulfolane, Dodecane + 1,4-Diisopropylbenzene + Sulfolane, and Dodecane + Octylbenzene + Sulfolane

Chen-Feng Kao* and Wen-Churng Lin

Department of Chemical Engineering, National Cheng Kung University, Tainan, 70101, Taiwan

Liquid−liquid equilibria of the ternary systems dodecane + butylbenzene + sulfolane, dodecane + 1,4-diisopropylbenzene + sulfolane, and dodecane + octylbenzene + sulfolane have been determined at the temperatures of 323.15 K, 348.15 K, and 373.15 K. The tie line data were correlated with the well-known NRTL and UNIQUAC models. The experimental data were filled in the UNIQUAC equation better than in the NRTL equation; the average root-mean-square deviations phase composition error was 0.3215 for UNIQUAC compared to 0.4520 for NRTL.

Introduction

Sulfolane is used widely in the chemical industry for the extraction of aromatic hydrocarbons; thus, many investigators (Cassell et al., 1989a, 1989b; Mondragón-Garduño et al., 1991; Lee and Kim, 1995; Letcher et al., 1996) have studied the liquid−liquid equilibria (LLE) of the ternary systems containing sulfolane and aromatic hydrocarbons.

Experimental studies of the ternary systems containing carbon number for hydrocarbons larger than nine and carbon number in aromatic hydrocarbons larger than nine (Masohan et al., 1990) are few. Therefore, most thermodynamic models cannot estimate LLE when trying to simulate extractive separations.

The main purpose of this study is to obtain LLE data of the dodecane + butylbenzene + sulfolane, dodecane + 1,4-diisopropylbenzene + sulfolane, and dodecane + octylbenzene + sulfolane. The LLE data for these ternary systems were measured at 323.15 K, 348.15 K, and 373.15 K and were correlated by the UNIQUAC model of Abrams and Prausnitz (1975) and the NRTL model of Renon and Prausnitz (1968).

Experimental Section

Chemicals. All of the chemicals used were high-purity grade reagents. Sulfolane and dodecane were obtained from Merck products with a stated purity of 99%. Butylbenzene and 1,4-diisopropylbenzene were obtained from the Acros Organics with 99% purity, and octylbenzene was obtained from Tokyo Chemical Industry Company with a purity of 99.7%.

Analytical grades of carbon disulfide and anisole were purchased from E. Merck with a purity of 99.5% and 99%, respectively. They were used without further purification.

Equilibrium Measurements. Measurements were made by using a 5.0×10^{-5} m^3 jacketed separation funnel controlled at temperatures of 323.15 K, 348.15 K, and 373.15 K. Specific amounts of dodecane, sulfolane, and the aromatics were introduced into the cell and agitated while maintained at a constant temperature by circulation of silicon oil through the external jacket from a thermostatic bath. The mixture was stirred for at least 1 h with a stirrer at a speed of 1300 rpm. The two-phase mixture was allowed to settle for at least 6 h. Samples of both phases were carefully withdrawn with syringes and diluted with carbon disulfide (Cassell et al., 1989a). A fixed amount of anisole was added as internal standard. And samples were analyzed by gas chromatograph, using a flame ionization detector, and a HP Ultra 1 column (cross-linked methylsilicone gum, 25 m × 3.2×10^{-4} m × 5.2×10^{-7} m film thickness). The injector and detector temperatures were maintained at 573.15 K. The column temperature was programmed for an initial temperature of 353.15 K, maintained for 1 min, and a final temperature of 393.15 K, maintained for 1 min. The heating rate was 5 K/min, and the flow rate of nitrogen carrier gas was 2.5×10^{-5} m^3/min. The temperature was controlled at ±0.03 K, and the compositions were measured at ±0.0001.

Table 1. Experimental LLE Data for Dodecane (1) + Butylbenzene (2) + Sulfolane (3)

	dodecane-rich phase			sulfolane-rich phase		
T/K	x_1	x_2	x_3	x_1	x_2	x_3
323.15	0.9940	0.0000	0.0060	0.0021	0.0000	0.9979
	0.7969	0.1928	0.0103	0.0022	0.0221	0.9757
	0.6329	0.3508	0.0163	0.0025	0.0440	0.9535
	0.4907	0.4836	0.0257	0.0027	0.0634	0.9339
	0.3966	0.5675	0.0359	0.0029	0.0846	0.9125
	0.3088	0.6399	0.0513	0.0037	0.1061	0.8902
	0.2394	0.6913	0.0692	0.0034	0.1255	0.8711
	0.1802	0.7269	0.0929	0.0036	0.1481	0.8483
348.15	0.9892	0.0000	0.0108	0.0037	0.0000	0.9963
	0.7784	0.2011	0.0205	0.0043	0.0255	0.9702
	0.6315	0.3527	0.0158	0.0046	0.0506	0.9448
	0.4995	0.4603	0.0402	0.0061	0.0881	0.9058
	0.3823	0.5576	0.0601	0.0058	0.1028	0.8914
	0.3051	0.6155	0.0794	0.0066	0.1362	0.8572
	0.2293	0.6647	0.1060	0.0073	0.1677	0.8250
	0.1648	0.6883	0.1469	0.0081	0.2074	0.7845
373.15	0.9788	0.0000	0.0212	0.0049	0.0000	0.9951
	0.7917	0.1778	0.0305	0.0109	0.0259	0.9632
	0.6153	0.3383	0.0464	0.0109	0.0619	0.9272
	0.5114	0.4277	0.0609	0.0091	0.0853	0.9056
	0.3871	0.5226	0.0903	0.0090	0.1100	0.8810
	0.2909	0.5854	0.1237	0.0070	0.1398	0.8532
	0.2250	0.6119	0.1631	0.0093	0.1813	0.8094
	0.1486	0.6099	0.2415	0.0079	0.2011	0.7910

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Table 2. Experimental LLE Data for Dodecane (1) + 1,4-Diisopropylbenzene (2) + Sulfolane (3)

	dodecane-rich phase			sulfolane-rich phase		
T/K	x_1	x_2	x_3	x_1	x_2	x_3
323.15	0.9940	0.0000	0.0060	0.0021	0.0000	0.9979
	0.8117	0.1802	0.0081	0.0020	0.0120	0.9860
	0.6477	0.3340	0.0183	0.0023	0.0252	0.9725
	0.5323	0.4478	0.0199	0.0022	0.0340	0.9638
	0.4275	0.5467	0.0257	0.0022	0.0467	0.9510
	0.3501	0.6162	0.0337	0.0017	0.0480	0.9502
	0.2732	0.6845	0.0423	0.0017	0.0561	0.9423
	0.2118	0.7383	0.0498	0.0000	0.0714	0.9286
	0.0000	0.8755	0.1245	0.0000	0.1018	0.8982
348.15	0.9892	0.0000	0.0108	0.0040	0.0000	0.9960
	0.8065	0.1766	0.0169	0.0046	0.0157	0.9797
	0.6416	0.3330	0.0254	0.0049	0.0303	0.9648
	0.5246	0.4418	0.0337	0.0042	0.0430	0.9528
	0.4269	0.5308	0.0422	0.0040	0.0507	0.9453
	0.3448	0.6039	0.0513	0.0039	0.0626	0.9336
	0.2682	0.6650	0.0668	0.0034	0.0708	0.9258
	0.2098	0.7069	0.0833	0.0033	0.0843	0.9125
	0.0000	0.7935	0.2065	0.0000	0.1216	0.8784
373.15	0.9790	0.0000	0.0210	0.0054	0.0000	0.9946
	0.8013	0.1701	0.0286	0.0063	0.0169	0.9769
	0.6489	0.3153	0.0358	0.0069	0.0326	0.9604
	0.5252	0.4215	0.0533	0.0060	0.0455	0.9485
	0.4181	0.5086	0.0733	0.0059	0.0619	0.9322
	0.3344	0.5816	0.0840	0.0056	0.0728	0.9217
	0.2537	0.6317	0.1146	0.0058	0.0909	0.9033
	0.2039	0.6641	0.1320	0.0051	0.0915	0.9034
	0.0000	0.5841	0.4159	0.0000	0.1483	0.8517

Table 3. Experimental LLE Data for Dodecane (1) + Octylbenzene (2) + Sulfolane (3)

	dodecane-rich phase			sulfolane-rich phase		
T/K	x_1	x_2	x_3	x_1	x_2	x_3
323.15	0.9940	0.0000	0.0060	0.0021	0.0000	0.9979
	0.8707	0.1214	0.0079	0.0021	0.0016	0.9963
	0.7666	0.2220	0.0114	0.0018	0.0061	0.9921
	0.6026	0.3792	0.0182	0.0016	0.0106	0.9878
	0.4537	0.5195	0.0268	0.0014	0.0149	0.9837
	0.3419	0.6215	0.0366	0.0000	0.0185	0.9815
	0.2450	0.7074	0.0477	0.0000	0.0222	0.9778
	0.1553	0.7852	0.0595	0.0000	0.0260	0.9740
	0.0000	0.9048	0.0952	0.0000	0.0313	0.9687
348.15	0.9892	0.0000	0.0108	0.0040	0.0000	0.9960
	0.8883	0.0998	0.0119	0.0036	0.0039	0.9925
	0.7608	0.2190	0.0202	0.0035	0.0084	0.9881
	0.5885	0.3803	0.0312	0.0030	0.0152	0.9819
	0.4461	0.5091	0.0448	0.0028	0.0213	0.9759
	0.3382	0.6031	0.0587	0.0024	0.0263	0.9714
	0.2495	0.6756	0.0749	0.0017	0.0293	0.9690
	0.1584	0.7414	0.1002	0.0012	0.0345	0.9643
	0.0000	0.8441	0.1559	0.0000	0.0415	0.9585
373.15	0.9790	0.0000	0.0210	0.0054	0.0000	0.9946
	0.8785	0.1001	0.0214	0.0053	0.0056	0.9891
	0.7514	0.2138	0.0348	0.0050	0.0108	0.9842
	0.5797	0.3694	0.0509	0.0052	0.0202	0.9745
	0.4342	0.4907	0.0751	0.0032	0.0261	0.9708
	0.3200	0.5826	0.0974	0.0021	0.0307	0.9672
	0.2313	0.6474	0.1213	0.0019	0.0370	0.9611
	0.1280	0.6932	0.1788	0.0010	0.0489	0.9501
	0.0000	0.7272	0.2728	0.0000	0.0544	0.9456

Results

The experimental tie-line data for the dodecane + butylbenzene + sulfolane, dodecane + 1,4-diisopropylbenzene + sulfolane, and dodecane + octylbenzene + sulfolane are shown in Tables 1, 2 and 3, respectively. Concentrations of components i (i = 1, 2, 3) in phase L (L = 1, raffinate phase; L = 2, extract phase) are given in mole fraction χ_{iL}.

Data Correlation. The experimental tie-line data were correlated with the NRTL model (Renon and Prausnitz, 1968) and UNIQUAC model (Abrams and Prausnitz, 1975).

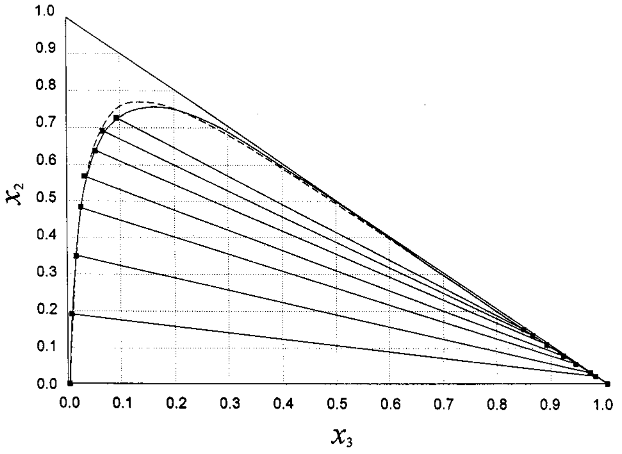

Figure 1. LLE data for the dodecane (1) + butylbenzene (2) + sulfolane (3) at 323.15 K: (−) UNIQUAC model; (- - -) NRTL model; (■) experimental tie line.

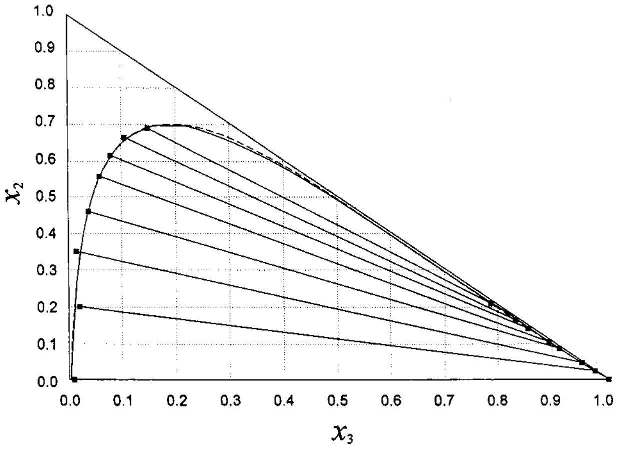

Figure 2. LLE data for the dodecane (1) + butylbenzene (2) + sulfolane (3) at 348.15 K: (−) UNIQUAC model; (- - -) NRTL model; (■) experimental tie line.

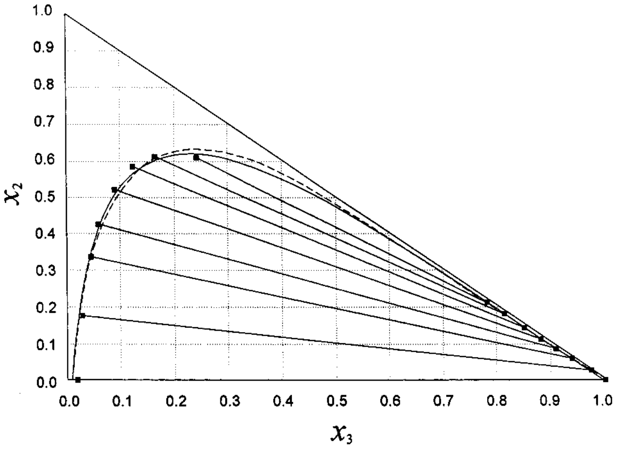

Figure 3. LLE data for the dodecane (1) + butylbenzene (2) + sulfolane (3) at 373.15 K: (−) UNIQUAC model; (- - -) NRTL model; (■) experimental tie line.

The corresponding sets of binary interaction parameters were determined by minimizing the differences between the experimental and calculated concentrations over all the tie lines for each ternary system using the Newton−Raphson method. The objective function (F) used is

$$F = \min \sum_{i} \sum_{L} \sum_{K} (\chi_{iLK} - \chi^{c}_{iLK})^2 \qquad (1)$$

Table 4. UNIQUAC and NRTL Parameters for Dodecane (1) + Butylbenzene (2) + Sulfolane (3) at (323.15, 348.15, and 373.15) K and the Calculated Root Mean Square Deviation rmsd

		UNIQUAC parameters/K			NRTL[a] parameters/K		
T/K	$i-j$	$(u_{ij} - u_{jj})/R$	$(u_{ji} - u_{ii})/R$	rmsd	$(g_{ij} - g_{jj})/R$	$(g_{ji} - g_{ii})/R$	rmsd
323.15	1−2	−285.27	364.23	0.6083	−811.04	391.82	0.9762
	1−3	516.36	34.93		1102.30	1383.10	
	2−3	248.32	−30.62		412.39	245.12	
348.15	1−2	201.68	−172.31	0.3647	102.87	−220.67	0.3768
	1−3	618.42	−17.43		1326.60	1320.50	
	2−3	217.43	−6.75		412.40	354.19	
373.15	1−2	201.73	−154.38	0.5177	501.14	−372.23	0.7050
	1−3	577.65	−12.01		1071.20	1416.80	
	2−3	150.55	48.31		365.19	437.75	

[a] Calculated with $\alpha_{ij} = 0.2$.

Table 5. UNIQUAC and NRTL Parameters for Dodecane (1) + 1,4-Diisopropylbenzene (2) + Sulfolane (3) at (323.15, 348.15, and 373.15) K and the Calculated Root Mean Square Deviation rmsd

		UNIQUAC parameters/K			NRTL[a] parameters/K		
T/K	$i-j$	$(u_{ij} - u_{jj})/R$	$(u_{ji} - u_{ii})/R$	rmsd	$(g_{ij} - g_{jj})/R$	$(g_{ji} - g_{ii})/R$	rmsd
323.15	1−2	−162.19	213.86	0.1871	−257.44	316.55	0.2049
	1−3	513.03	54.32		1366.00	1343.50	
	2−3	310.94	−30.10		463.74	553.44	
348.15	1−2	85.56	−69.52	0.2345	−255.76	396.00	0.2702
	1−3	598.14	1.36		1359.80	1273.60	
	2−3	275.18	−13.86		346.99	651.35	
373.15	1−2	28.67	2.58	0.4817	−298.30	391.23	0.8871
	1−3	345.27	243.53		1365.20	1499.10	
	2−3	171.48	49.32		128.84	838.77	

[a] Calculated with $\alpha_{ij} = 0.2$.

Table 6. UNIQUAC and NRTL Parameters for Dodecane (1) + Octylbenzene (2) + Sulfolane (3) at (323.15, 348.15, and 373.15) K and the Calculated Root Mean Square Deviation rmsd

		UNIQUAC parameters/K			NRTL[a]parameters/K		
T/K	$i-j$	$(u_{ij} - u_{jj})/R$	$(u_{ji} - u_{ii})/R$	rmsd	$(g_{ij} - g_{jj})/R$	$(g_{ji} - g_{ii})/R$	rmsd
323.15	1−2	−77.00	80.84	0.0894	−877.36	1323.00	0.1414
	1−3	524.76	33.29		1124.60	1379.20	
	2−3	303.67	−3.80		390.53	867.83	
348.15	1−2	−23.96	32.29	0.1183	−517.33	799.20	0.1304
	1−3	538.35	18.65		1122.50	1366.60	
	2−3	273.62	6.41		275.64	960.45	
373.15	1−2	−23.20	33.51	0.2915	−594.79	773.07	0.3755
	1−3	445.83	85.54		1019.70	1499.90	
	2−3	213.09	36.17		115.01	1075.90	

[a] Calculated with $\alpha_{ij} = 0.2$.

where χ and χ^c are the experimental and calculated mole fractions, respectively, and the subscripts i, L, and K denote number of components, phases and tie lines, respectively.

For the NRTL model, the third nonrandomness parameter, α_{ij}, was set to a value of 0.2 (Cassell et al., 1989c). The parameters calculated are shown in Tables 4−6, together with the root-mean-square deviation (rmsd), which is defined as

$$\mathrm{rmsd} = 100[\sum_i \sum_L \sum_K (\chi_{iLK} - \chi^c_{iLK})^2/(6N)]^{1/2} \qquad (2)$$

As can be seen from Tables 4−6, the calculation based on both the UNIQUAC and the NRTL models gave good representation of the tie-line data for these systems. However, the UNIQUAC model, fitted to the experimental data, is more accurate than the NRTL model, according to the analysis of rmsd.

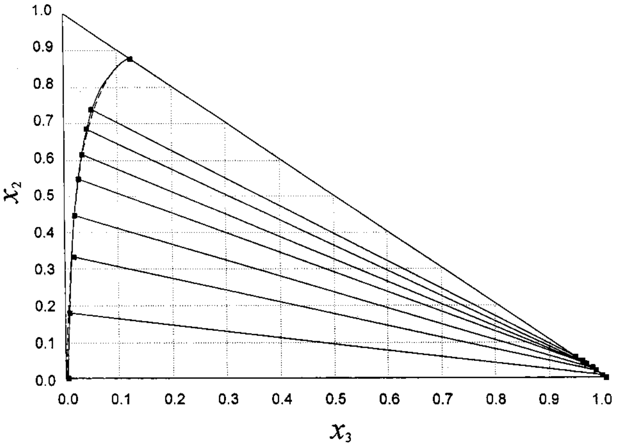

Figure 4. LLE data for the dodecane (1) + 1,4-diisopropylbenzene (2) + sulfolane (3) at 323.15 K: (−) UNIQUAC model; (- - -) NRTL model; (■) experimental tie line.

Discussion

Figures 1−9 show that the area of the two-phase region increases in the order of butylbenzene < 1,4-diisopropylbenzene < octylbenzene. As predicted, the size of the two-phase region decreased with increasing temperature.

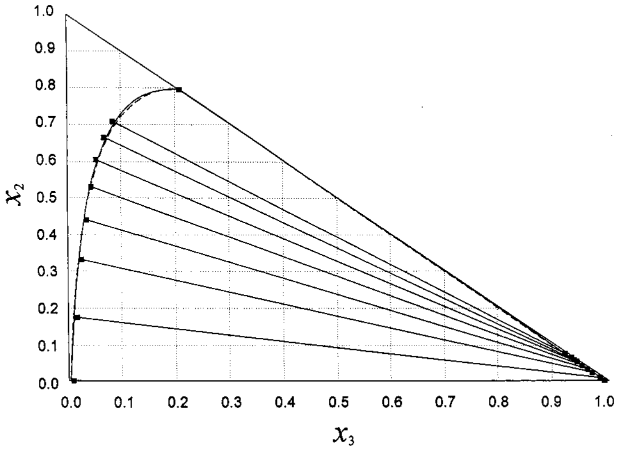

Figure 5. LLE data for the dodecane (1) + 1,4-diisopropylbenzene (2) + sulfolane (3) at 348.15 K: (—) UNIQUAC model; (- - -) NRTL model; (■) experimental tie line.

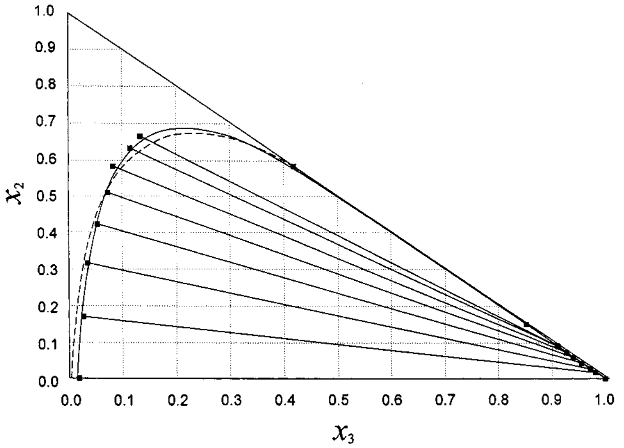

Figure 6. LLE data for the dodecane (1) + 1,4-diisopropylbenzene (2) + sulfolane (3) at 373.15 K: (—) UNIQUAC model; (- - -) NRTL model; (■) experimental tie line.

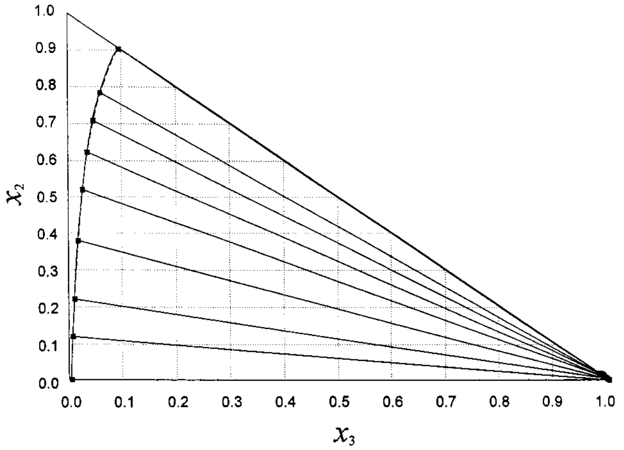

Figure 7. LLE data for the dodecane (1) + octylbenzene (2) + sulfolane (3) at 323.15 K: (—) UNIQUAC model; (- - -) NRTL model; (■) experimental tie line.

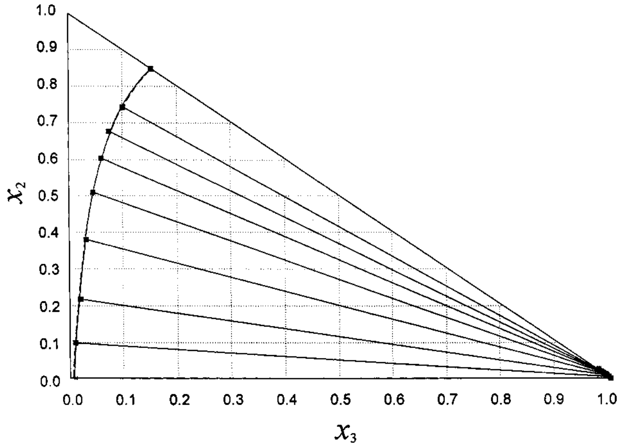

Figure 8. LLE data for the dodecane (1) + octylbenzene (2) + sulfolane (3) at 348.15 K: (—) UNIQUAC model; (- - -) NRTL model; (■) experimental tie line.

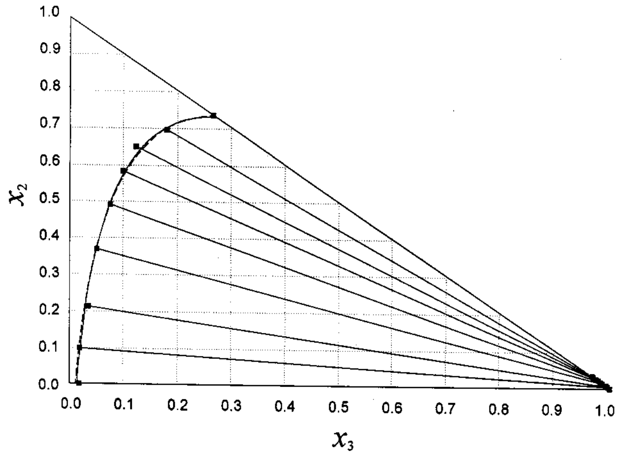

Figure 9. LLE data for the dodecane (1) + octylbenzene (2) + sulfolane (3) at 373.15 K: (—) UNIQUAC model; (- - -) NRTL model; (■) experimental tie line.

Table 7. Experimental Selectivity Values *S* for Each System

S for the system	323.15 K	348.15 K	373.15 K
butylbenzene	23.83	15.67	11.21
1,4-diisopropylbenzene	18.37	12.16	9.45
octylbenzene	9.29	6.67	6.10

The slopes of the tie lines presented in Figures 1−9 show that butylbenzene, 1,4-diisopropylbenzene, or octylbenzene is more soluble in dodecane than in sulfolane.

The effectiveness of extraction of aromatics by sulfolane is given by its selectivity (*S*), which is a measure of the ability of sulfolane to separate aromatics from dodecane:

$$S = (\chi_2/\chi_1)_{\text{sulfolane−rich phase}}/(\chi_2/\chi_1)_{\text{dodecane−rich phase}} \quad (3)$$

where the subscript 2 can represent butylbenzene, 1,4-diisopropylbenzene, or octylbenzene and subscript 1 means dodecane.

The values of selectivity for the middle of the area of measured tie lines are listed in Table 7 for butylbenzene, 1,4-diisopropylbenzene, and octylbenzene systems. It is obvious from Table 7 that for the same system, the higher the temperature, the lower the selectivity. At the same temperature for the different system the order of the selectivity of sulfolane to aromatic hydrocarbons is butylbenzene > 1,4-diisopropylbenzene > octylbenzene. Hence, sulfolane is more selective to lower carbon number than to higher carbon number in aromatic hydrocarbons. Since the selectivity in all cases is greater than 1, it means that the extraction is possible.

Conclusions

Liquid−liquid equilibrium data of the ternary systems dodecane (1) + butylbenzene (2) + sulfolane (3), dodecane (1) + 1,4-diisopropylbenzene (2) + sulfolane (3), and dodecane (1) + octylbenzene (2) + sulfolane (3) were determined at 323.15 K, 348.15 K, and 373.15 K.

The calculation based on both the UNIQUAC model and the NRTL model gives good representation of the tie-line data for the system of this study. However, the calculated values based on the UNIQUAC model are found to be better than those based on the NRTL model. The binodal curves calculated by the UNIQUAC model and the NRTL model for each system show that the size of the two-phase region decreases with increasing temperature. Sulfolane can be used to extract aromatic hydrocarbons from dodecane mixtures. Sulfolane shows a greater selectivity for the lower carbon number aromatic hydrocarbons. This is no doubt due to the different steric effects present in each of the aromatic hydrocarbons.

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