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Liquid−Liquid Equilibria of Octane + (Benzene or Toluene or *m*-Xylene) + Sulfolane at 323.15, 348.15, and 373.15 K

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Equilibrium tie line data have been determined at 323.15 K, 348.15 K, and 373.15 K for the ternary liquid−liquid equilibria (LLE) of octane + (benzene or toluene or *m*-xylene) + sulfolane systems. The relative mutual solubility of benzene is higher than that of toluene or *m*-xylene in octane + sulfolane mixtures. The tie line data were correlated with the NRTL and UNIQUAC models. The calculated values based on the NRTL model were found to be better than those based on the UNIQUAC model; the average root-mean-square deviation between the phase composition obtained from experiment and that from calculation was 0.49 for NRTL compared to 0.53 for UNIQUAC. The values of selectivity and the distribution coefficient were derived from the equilibrium data at different temperatures.

Introduction

The design and evaluation of industrial units for separation processes require reliable phase equilibria data of the different mixtures involved in a given process. Especially, ternary liquid−liquid equilibria (LLE) data are essential for a proper understanding of the solvent extraction process. Sulfolane is used widely in the chemical industry for the extraction of aromatic hydrocarbons,[1−4] and many investigators[5−13] have studied liquid−liquid equilibria for the ternary systems containing sulfolane + alkanes (C5−C8) + (benzene, toluene, or xylene) near room temperature, but quantitative phase equilibrium data for the systems containing sulfolane + octane + *m*-xylene at higher temperatures are scarce.

Therefore, the purpose of this study was to obtain LLE data for the ternary mixtures octane + benzene + sulfolane, octane + toluene + sulfolane, and octane + *m*-xylene + sulfolane at 323.15 K, 348.15 K, and 373.15 K. The LLE data for these ternary systems were then correlated by the UNIQUAC model of Abrams and Prausnitz[14] and the NRTL model of Renon and Prausnitz.[15] The effects of temperature on the selectivity and the distribution coefficient were also discussed.

Experimental Section

Chemicals. All materials, sulfolane, octane, benzene, toluene, *m*-xylene, anisole, and carbon disulfide, were supplied by E. Merck with a stated purity of 99.0%. The purity of each of the components was checked by gas chromatography, and the results were confirmed to exceed 99.0%. All compounds were stored in a desiccator with a drying agent before use. They were used without further purification.

Apparatus and Procedure. The experimental points that define the binodal curves were determined by using a 50 cm^3 jacketed stainless steel cell controlled at a given temperature. Temperatures were controlled to ±0.03 K. Mixtures, comprised of 11 g to 26 g of sulfolane, 6 g to 15 g of octane, and up to 21 g of benzene, toluene, or *m*-xylene, were introduced into the cell using pipets and agitated while the temperature was maintained constant with circulation of silicon oil through the external jacket from a thermostatic bath. The sample was stirred for 1 h with a four-blade propeller stirrer at a speed of 1100 rpm and then left to settle for at least 4 h. After equilibrium was attained, the phases were allowed to separate and small samples of approximately 1 g were taken from each phase. A fixed amount of anisole was added as internal standard, and each sample was diluted with 50 g of carbon disulfide[5] in preparation for analysis. The accuracy of weighing was ±0.0001 g. The sample analysis was performed using a Hewlett-Packard Model 5890 gas chromatograph equipped with a flame ionization detector and a HP Ultra 1 column (cross-linked methyl silicone gum, 25 m × 3.2×10^{-4} m × 5.2×10^{-7} m film thickness). The injector and detector temperatures were maintained at 563.15 K. The column temperature was programmed for an initial temperature of 348.15 K, maintained for 1 min, and a final temperature of 383.15 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. Mass fraction measurements were reproducible to within ±0.005. The greatest error in the material balance in these experiments was found to be less than 2%.

Results and Discussion

The experimental tie line data are given in Table 1 for the ternary systems formed by octane (1) + sulfolane (3) with benzene, toluene, or *m*-xylene (2), respectively. The concentrations of components i (i = 1, 2, 3) in phase L (L = 1, raffinate phase; L = 3, extract phase) are given in mole fraction, x_{iL}. The effect of temperature on the equilibrium for the system octane (1) + benzene (2) + sulfolane (3) is shown in Figure 1. As seen, the size of the two-phase region decreases with an increase in temperature. Similar behavior was also noticed in the other two ternaries. These systems studied present a wide two-phase region which is important, together with the slope of the tie lines, when establishing the selectivity of sulfolane.

Data Correlation. The NRTL and UNIQUAC models were used to correlate and predict the LLE data in the present work. The corresponding sets of binary interaction parameters were determined by minimizing the differences between the experimental and calculated concentrations

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Table 1. Experimental LLE Data, Selectivities, *S*, and Distribution Coefficients, *κ*, for the System

	octane-rich phase			sulfolane-rich phase				
T/K	x_{11}	x_{21}	x_{31}	x_{13}	x_{23}	x_{33}	S	κ
Octane (1) + Benzene (2) + Sulfolane (3)								
323.15	0.997	0.000	0.003	0.006	0.000	0.994		
	0.905	0.091	0.004	0.013	0.045	0.942	34	0.49
	0.815	0.178	0.007	0.017	0.106	0.877	29	0.60
	0.732	0.259	0.009	0.017	0.162	0.821	27	0.63
	0.657	0.336	0.007	0.016	0.216	0.768	26	0.64
	0.550	0.434	0.016	0.016	0.289	0.695	23	0.67
	0.335	0.625	0.040	0.028	0.477	0.495	9	0.76
	0.279	0.668	0.053	0.034	0.535	0.431	7	0.80
348.15	0.993	0.000	0.007	0.011	0.000	0.989		
	0.897	0.093	0.010	0.013	0.044	0.943	33	0.47
	0.813	0.175	0.012	0.014	0.100	0.886	33	0.57
	0.712	0.272	0.016	0.019	0.176	0.805	24	0.65
	0.604	0.376	0.020	0.027	0.248	0.725	15	0.66
	0.475	0.491	0.034	0.033	0.349	0.618	10	0.71
	0.408	0.548	0.044	0.041	0.409	0.550	7	0.75
	0.328	0.617	0.055	0.046	0.490	0.464	6	0.79
373.15	0.992	0.000	0.008	0.013	0.000	0.987		
	0.893	0.093	0.014	0.013	0.044	0.943	32	0.48
	0.812	0.173	0.015	0.015	0.097	0.888	30	0.56
	0.720	0.259	0.021	0.015	0.140	0.845	26	0.54
	0.646	0.334	0.020	0.028	0.214	0.758	15	0.64
	0.476	0.477	0.047	0.032	0.281	0.687	9	0.59
	0.399	0.532	0.069	0.050	0.398	0.552	6	0.75
	0.300	0.598	0.102	0.057	0.482	0.461	4	0.81
Octane (1) + Toluene (2) + Sulfolane (3)								
323.15	0.997	0.000	0.003	0.006	0.000	0.994		
	0.791	0.206	0.003	0.007	0.062	0.931	34	0.30
	0.698	0.295	0.007	0.008	0.089	0.903	26	0.30
	0.612	0.380	0.008	0.008	0.129	0.863	26	0.34
	0.531	0.454	0.015	0.015	0.207	0.778	16	0.46
	0.443	0.536	0.021	0.020	0.258	0.722	11	0.48
	0.374	0.593	0.033	0.030	0.361	0.609	8	0.61
	0.329	0.631	0.040	0.037	0.415	0.548	6	0.66
348.15	0.993	0.000	0.007	0.011	0.000	0.989		
	0.888	0.104	0.008	0.014	0.039	0.947	24	0.38
	0.791	0.198	0.011	0.017	0.084	0.899	20	0.42
	0.683	0.302	0.015	0.017	0.126	0.857	17	0.42
	0.618	0.364	0.018	0.017	0.165	0.818	16	0.45
	0.521	0.448	0.031	0.018	0.208	0.774	13	0.46
	0.453	0.513	0.034	0.029	0.277	0.694	8	0.54
	0.275	0.650	0.075	0.036	0.440	0.524	5	0.68
373.15	0.992	0.000	0.008	0.013	0.000	0.987		
	0.898	0.093	0.009	0.019	0.029	0.952	15	0.31
	0.804	0.180	0.016	0.021	0.064	0.915	14	0.36
	0.730	0.254	0.016	0.021	0.096	0.883	13	0.38
	0.659	0.321	0.020	0.027	0.139	0.834	11	0.43
	0.587	0.387	0.026	0.027	0.182	0.791	10	0.47
	0.514	0.450	0.036	0.028	0.222	0.750	9	0.49
	0.438	0.518	0.044	0.028	0.254	0.718	7	0.49
Octane (1) + *m*-Xylene (2) + Sulfolane (3)								
323.15	0.997	0.000	0.003	0.006	0.000	0.994		
	0.882	0.114	0.004	0.007	0.022	0.971	24	0.19
	0.775	0.218	0.007	0.008	0.050	0.942	22	0.23
	0.685	0.308	0.007	0.009	0.077	0.914	19	0.25
	0.576	0.410	0.014	0.009	0.115	0.876	18	0.28
	0.507	0.475	0.018	0.012	0.143	0.845	13	0.30
	0.429	0.543	0.028	0.012	0.164	0.824	11	0.30
	0.351	0.610	0.039	0.014	0.208	0.778	8	0.34
348.15	0.993	0.000	0.007	0.011	0.000	0.989		
	0.891	0.100	0.009	0.012	0.031	0.957	23	0.31
	0.784	0.204	0.012	0.012	0.063	0.925	20	0.31
	0.698	0.282	0.020	0.014	0.100	0.886	18	0.35
	0.618	0.359	0.023	0.014	0.125	0.861	15	0.35
	0.536	0.437	0.027	0.015	0.163	0.822	13	0.37
	0.456	0.508	0.036	0.015	0.192	0.793	11	0.38
	0.379	0.573	0.048	0.018	0.255	0.727	9	0.45
	0.201	0.705	0.094	0.020	0.393	0.587	6	0.55
373.15	0.992	0.000	0.008	0.013	0.000	0.987		
	0.872	0.108	0.020	0.013	0.032	0.955	20	0.30
	0.772	0.209	0.019	0.014	0.064	0.922	17	0.31
	0.681	0.293	0.026	0.015	0.085	0.900	13	0.30
	0.601	0.364	0.035	0.015	0.109	0.876	12	0.30
	0.506	0.451	0.043	0.016	0.148	0.836	10	0.33
	0.431	0.519	0.050	0.016	0.185	0.799	10	0.36
	0.348	0.585	0.067	0.018	0.239	0.743	8	0.41

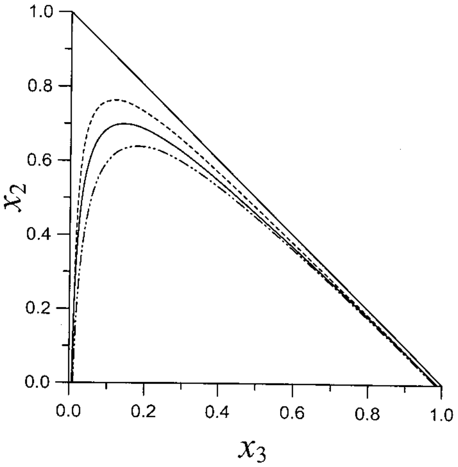

Figure 1. Effect of temperature on the liquid−liquid equilibrium for the octane (1) + benzene (2) + sulfolane (3) curves calculated by NRTL: - - -, 323.15 K; —, 348.15 K; —··—, 373.15 K.

over all the tie lines for each ternary system using the Simplex Search method. The objective function (F) used is

$$F = \min \sum_i \sum_L \sum_k (x_{iLk} - x^{c}_{iLk})^2 \qquad (1)$$

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

The UNIQUAC pure component parameters for the surface area (q) and volume (r) of sulfolane were 3.206 and 4.036,[16] respectively. For the NRTL model, the third nonrandomness parameter, α_{ij}, was set at the value 0.2.[7] The parameters calculated are shown in Table 2, together with the root-mean-square deviation (rmsd) values, defined as

$$\text{rmsd} = 100[\sum_i \sum_L \sum_k (x_{iLk} - x^{c}_{iLk})^2/6N]^{1/2} \qquad (2)$$

where N = number of tie lines.

The rmsd is a measure of the agreement between the experimental data and the calculated values. As can be seen from Table 2, the calculation based on both the UNIQUAC and the NRTL models gave a good representation of the tie line data for these systems. However, the NRTL model, fitted to the experimental data, is more accurate than the UNIQUAC model, according to the analysis of the rmsd (the average root-mean-square deviation between the phase composition obtained from experiment and that from calculation was 0.49 for NRTL as compared to 0.53 for UNIQUAC). This result is similar to those of the systems sulfolane + octane + (benzene or toluene or *p*-xylene) at 343.35, 372.35, and 402.35 K reported by Lee and Kim.[17]

The calculated values using both the UNIQUAC and NRTL models for the octane (1) + (toluene or *m*-xylene) (2) + sulfolane (3) system at 348.15 K are compared with the experimental data in Figures 2 and 3. It was observed that the slopes of the tie lines show that aromatics are more soluble in octane than in sulfolane. It is observed that the relative mutual solubility of toluene is higher than those of *m*-xylene in octane + sulfolane mixtures at the same temperature. This solubility effect is reflected in the size of the two-phase region, increasing slightly in the order *m*-xylene > toluene at the same temperature. All the

Table 2. UNIQUAC and NRTL Parameters for the Systems Octane (1) + (Benzene (2) or Toluene (2) or *m*-Xylene (2)) + Sulfolane (3) at (323.15, 348.15, and 373.15) K, as Well as the Calculated Root-Mean-Square Deviation, rmsd

		UNIQUAC parameters/K		NRTL parameters/K ($\alpha_{ij} = 0.2$)	
T/K	$i-j$	$(u_{ij} - u_{jj})/R$	$(u_{ji} - u_{ii})/R$	$(g_{ij} - g_{jj})/R$	$(g_{ji} - g_{ii})/R$
Octane (1) + Benzene (2) + Sulfolane (3)					
323.15	1−2	−165.04	93.84	−824.58	730.22
	1−3	551.84	68.23	1033.80	900.30
	2−3	135.07	−115.60	1057.40	−673.66
	rmsd	0.5116		0.6077	
348.15	1−2	3.77	−6.14	−487.61	273.47
	1−3	544.84	20.23	1210.50	974.96
	2−3	156.99	−40.21	998.92	−568.18
	rmsd	0.4089		0.3137	
373.15	1−2	−119.31	−9.47	−759.63	606.38
	1−3	541.37	49.47	1199.60	950.03
	2−3	59.01	−57.70	615.91	−425.55
	rmsd	0.8421		0.9048	
Octane (1) + Toluene (2) + Sulfolane (3)					
323.15	1−2	61.21	−210.08	−760.39	20.02
	1−3	492.98	54.18	1434.90	878.94
	2−3	452.75	−228.19	738.72	−528.00
	rmsd	0.7035		0.6667	
348.15	1−2	−186.01	322.23	−431.54	383.09
	1−3	616.61	27.64	1346.10	921.39
	2−3	196.82	1.74	721.49	−196.53
	rmsd	0.4969		0.4615	
373.15	1−2	−446.38	656.22	−132.05	42.38
	1−3	521.54	40.87	1338.40	933.59
	2−3	315.17	−194.11	799.03	−167.45
	rmsd	0.5299		0.3933	
Octane (1) + *m*-Xylene (2) + Sulfolane (3)					
323.15	1−2	−366.72	507.95	182.22	−196.74
	1−3	584.10	35.75	1420.00	1078.40
	2−3	300.16	−120.44	769.35	7.18
	rmsd	0.5962		0.2416	
348.15	1−2	−164.90	190.07	−362.27	438.53
	1−3	575.19	33.80	1180.90	992.54
	2−3	243.36	−53.82	691.44	−15.96
	rmsd	0.3905		0.3377	
373.15	1−2	−48.60	22.94	−464.22	539.01
	1−3	452.62	71.13	1039.20	967.75
	2−3	269.43	−50.16	714.99	24.06
	rmsd	0.3237		0.4408	

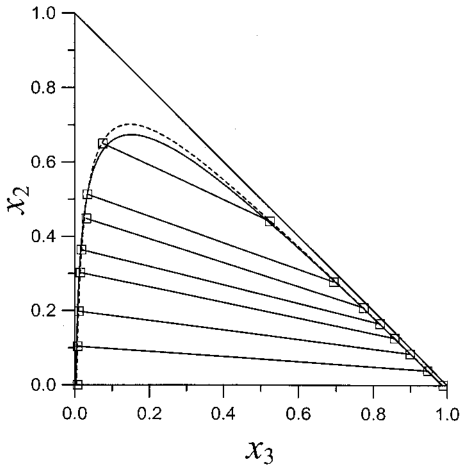

Figure 2. LLE data for octane (1) + toluene (2) + sulfolane (3) at 348.15 K: □, experimental tie line data; - - -, NRTL model; —, UNIQUAC model.

ternary systems octane (1) + (benzene or toluene or *m*-xylene) (2) + sulfolane (3) at any given temperature of this study are type 1 systems.[18]

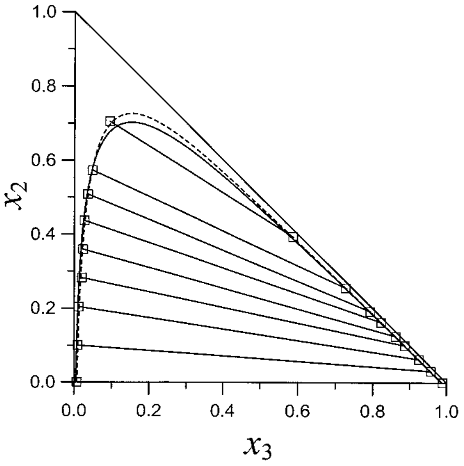

Figure 3. LLE data for octane (1) + *m*-xylene (2) + sulfolane (3) at 348.15 K: □, experimental tie line data; - - -, NRTL model; —, UNIQUAC model.

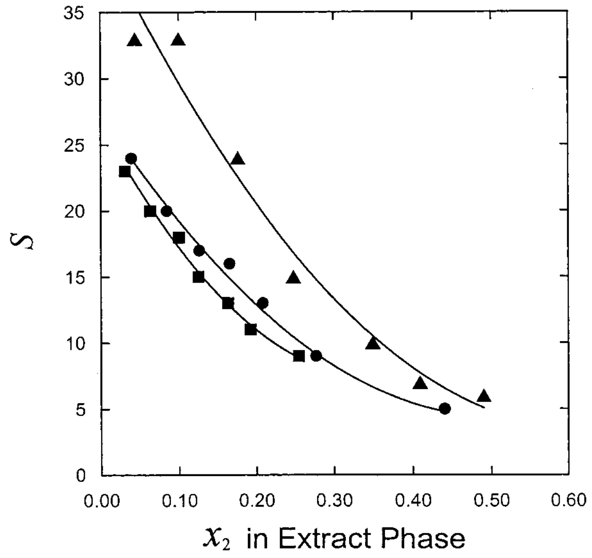

Figure 4. Experimental selectivity for the system at 348.15 K: ▲, benzene; ●, toluene; ■, *m*-xylene.

Selectivity and Distribution Coefficient. The effectiveness of extraction of aromatic compounds by sulfolane is given by its selectivity (S), which is a measure of the ability of sulfolane to separate aromatics from octane:

$$S = (x_2/x_1)_s/(x_2/x_1)_o \qquad (3)$$

where the subscript 2 represents benzene, toluene, or *m*-xylene, 1 represents octane, s is the sulfolane-rich phase, and o is the octane-rich phase.

This quantity is not constant over the whole two-phase region. The experimental values of S are listed in Table 1, and those for systems at 348.15 K are showed in Figure 4. From the data, we find the tendency 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 is benzene > toluene > *m*-xylene. Hence, sulfolane is more selective to lower carbon number than to higher carbon number in aromatic hydrocarbons. And as seen, S decreases when going through the tie lines from low concentration to high concentration of aromatic. This means the higher the concentration of aromatic in the feed, the lower the

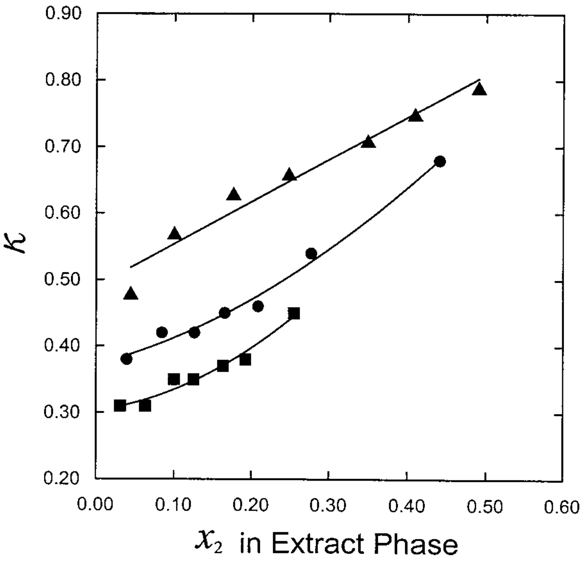

Figure 5. Experimental distribution coefficient for the system at 348.15 K: ▲, benzene; ●, toluene; ■, *m*-xylene.

selectivity of sulfolane to aromatic. Since the selectivity in all cases is greater than one, it means that extraction is possible.

The capacity or dissolving ability of a solvent is a measure of the ratio of solvent to feed required for the desired recovery of aromatics. The distribution coefficient for aromatic, which is the measure of the solvent power or capacity of sulfolane, is given as

$$\kappa = (x_2)_s/(x_2)_o \tag{4}$$

The experimental values of κ of this study are also presented in Table 1. We can find that, for the same system, there are not obvious differences between the κ values in the temperature range 323.15−373.15 K. At the same temperature for the different systems, as can be seen from Figure 5, the κ values for the system increase in the order benzene > toluene > *m*-xylene. This result is similar to the trend of *S* values.

Sulfolane has an excellent extractive ability for the aromatic ring, but that ability is worse than that for the aliphatic groups. In this study, sulfolane shows a greater selectivity and capacity for the aromatic hydrocarbons in the order benzene > toluene > *m*-xylene. This is no doubt due to the different methyl (aliphatic) groups' steric interference effects present in each of the aromatic hydrocarbons.

Conclusions

Liquid−liquid equilibrium data of the ternary systems octane (1) + benzene (2) + sulfolane (3), octane (1) + toluene (2) + sulfolane (3), and octane (1) + *m*-xylene (2) + sulfolane (3) were determined at 323.15 K, 348.15 K, and 373.15 K, respectively.

The calculation based on the NRTL and UNIQUAC models showed that the best results are given by the NRTL model. The binodal curves calculated by the NRTL model or UNIQUAC model for the systems studied here show that the size of the two-phase region decreases with increasing temperature. For the same system, the higher the temperature, the lower the selectivity. From the selectivity values, the separation of benzene, toluene, or *m*-xylene from octane by extraction with sulfolane is feasible. Not only the selectivity data but also the distribution coefficient data showed that sulfolane is more extractive for the lower carbon number aromatic hydrocarbons at a given temperature. This is no doubt due to the different steric effects present in each of the aromatic hydrocarbons.

Nomenclature

F = objective function to minimize (eq 1)
g_{ij} = NRTL parameter, J·mol^{-1}
N = number of experimental tie lines (eq 2)
q = UNIQUAC surface area parameter
R = universal gas constant, J·mol^{-1}·K^{-1}
r = UNIQUAC volume parameter
rmsd = root-mean-square deviation (eq 2)
S = selectivity (eq 3)
T = temperature, K
u_{ij} = UNIQUAC parameter, J·mol^{-1}
x = mole fraction

Greek Letters

α_{ij} = nonrandomness parameter in the NRTL model
κ = distribution coefficient (eq 4)

Subscripts

i = component i
j = component j
k = tie line k
L = phase L
s = sulfolane-rich phase
o = octane-rich phase

Superscripts

c = calculated values

Literature Cited

(1) Broughton, D. B.; Asselin, G. F. Production of High Purity Aromatics by the Sulfolane Process. *Seventh World Pet. Congr. Proc.* **1967**, *4*, 65−73.
(2) Evans, H. D. Extraction Process. U.S. Patent 3,222,416, 1965.
(3) Guccione, E. Largest Aromatics Plant is on Stream. *Chem. Eng.* **1965**, *72*, 112−114.
(4) Wheeler, T. *Handbook of Petroleum Refining Processes*; McGraw-Hill: New York, 1986.
(5) Cassell, G. W.; Dural, N.; Hines, A. L. Liquid−Liquid Equilibria of Sulfolane−Benzene−Pentane and Sulfolane−Toluene−Pentane. *Ind. Eng. Chem. Res.* **1989**, *28*, 1369−1374.
(6) Cassell, G. W.; Hassan, M. M.; Hines, A. L. Correlation of the Phase Equilibrium Data for the Heptane−Toluene−Sulfolane and Heptane−Xylene−Sulfolane Systems. *J. Chem. Eng. Data* **1989**, *34*, 434−438.
(7) Cassell, G. W.; Hassan, M. M.; Hines, A. L. Phase Equilibria of the Cyclohexane-Toluene-Sulfolane and Hexane-Toluene-Sulfolane Ternary Systems. *Chem. Eng. Commun.* **1989**, *85*, 233−243.
(8) Hassan, M. S.; Fahim, M. A.; Mumford, C. J. Correlation of Phase Equilibria of Naphtha Reformate with Sulfolane. *J. Chem. Eng. Data* **1988**, *33*, 162−165.
(9) Lee, S.; Kim, H. Liquid−Liquid Equilibria for the Ternary Systems Sulfolane + Octane + Benzene, Sulfolane + Octane + Toluene and Sulfolane + Octane + *p*-Xylene. *J. Chem. Eng. Data* **1995**, *40*, 499−503.
(10) Letcher, T. M.; Redhi, G. G.; Radloff, S. E.; Domańska, U. Liquid−Liquid Equilibria of the Ternary Mixtures with Sulfolane at 303.15K. *J. Chem. Eng. Data* **1996**, *41*, 634−638.
(11) Mondragón-Garduño, M.; Romero-Martínez, A.; Trejo, A. Liquid−Liquid Equilibria for Ternary systems. I. C_6-isomers + Sulfolane + Toluene at 298.15K. *Fluid Phase Equilib.* **1991**, *64*, 291−303.
(12) Rawat, B. S.; Gulati, I. B. Liquid−Liquid Equilibrium Studies for Separation of Aromatics. *J. Appl. Chem. Biotechnol.* **1976**, *26*, 425−435.
(13) Tripathi, R. P.; Ram, A. R.; Rao, P. B. Liquid−Liquid Equilibria in Ternary System Toluene−*n*-Heptane−Sulfolane. *J. Chem. Eng. Data* **1975**, *20*, 261−264.

(14) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116−128.
(15) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.
(16) Domańska, U.; Sporzyński, A.; Moollan, W. C.; Letcher, T. M. Vapor-Liquid Equilibria of Binary Mixtures Containing Sulfolane. *J. Chem. Eng. Data* **1996**, *41*, 624−628.
(17) Lee, S.; Kim, H. Liquid−Liquid Equilibria for the Ternary Systems Sulfolane + Octane + Benzene, Sulfolane + Octane + Toluene and Sulfolane + Octane + *p*-Xylene at Elevated Temperatures. *J. Chem. Eng. Data* **1998**, *43*, 358−361.
(18) Sorensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, A. Liquid−Liquid Equilibrium Data: Their Retrieval, Correlation and Prediction. Part I: Retrieval. *Fluid Phase Equilib.* **1979**, *2*, 297−309.

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