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Ternary Liquid−Liquid Equilibria for Systems of (Sulfolane + Toluene or Chloronaphthalene + Octane)

F. S. Mohammad Doulabi and M. Mohsen-Nia*

Thermodynamic Research Laboratory, Kashan University, Kashan, Iran

Tie-line data for ternary systems of (sulfolane + toluene + octane) at temperatures of 303.2 K and 313.2 K and (sulfolane + chloronaphthalene + octane) at temperatures of 298.2 K and 303.2 K are reported. The composition of liquid phases at equilibrium was determined by gas−liquid chromatography, and the results were correlated with the UNIQUAC and NRTL activity coefficient models to obtain the binary interaction parameters. Both the UNIQUAC and the NRTL models satisfactorily correlated the equilibrium compositions. The partition coefficients and the selectivity factor of sulfolane for extraction of toluene and chloronaphthalene from octane-containing systems are calculated. Then the efficiency of the extraction of toluene from the (toluene + octane) mixture is compared with that for the extraction of chloronaphthalene from the (chloronaphthalene + octane) mixture by using the calculated selectivity factors and the partition coefficients of the used solvent. The phase diagrams for the ternary systems are presented, and the correlated tie-line results have been compared with the experimental data.

Introduction

Experimental and theoretical studies of the phase equilibrium for ternary systems containing aromatic hydrocarbon compounds (e.g., toluene and chloronaphthalene) are essential in a number of practical extraction processes.[1−4] At the same time, they represent one of the most stringent tests for activity coefficient models (e.g., NRTL[5] and UNIQUAC[6]).

In chemical industries, especially in the liquid extraction processes, suitable solvents such as sulfolane, ethylene carbonate, and dimethyl sulfoxide (DMSO) play an important role from practical and economical viewpoints.[7,8] By considering the role of the solvents in the extraction of aromatic hydrocarbons from alkane mixtures in industrial processes, it is worthwhile to study the liquid−liquid equilibrium (LLE) of ternary systems of (solvent + aromatic hydrocarbons + alkanes). Therefore, the search for determining the optimum conditions of the liquid−liquid extraction processes is an ongoing study.

The design of industrial units for separation processes require reliable phase equilibrium data of the different systems involved in a given process. Ternary LLE data are essential for a proper understanding of the solvent extraction process.[1] Therefore, it is usual to measure the phase equilibrium properties of the ternary or quaternary liquid systems. Sulfolane has been widely used as a solvent in the recovery of high-purity aromatics, such as toluene and *m*-xylene from refinery process streams.[9,10] Experimental measurements of the extraction of aromatic hydrocarbons with sulfolane as the solvent were accomplished by Deal et al.[11] Solubility data for (benzene and toluene) + heptane + solvent were reported by Shaha et al.[12] and Rawat.[13] LLE data for a toluene + heptane + tetraethylene glycol + water system was published by Wang et al.[14] Aromatics extraction with solvent combinations was done by Muller and Hochfeld.[15]

In this work, we report the LLE results for the systems of (sulfolane + toluene + octane) at 303.2 K and 313.2 K and (sulfolane + chloronaphthalene + octane) at 298.2 K and 303.2 K. The LLE data were correlated using the UNIQUAC and the NRTL activity coefficient models to obtain the binary interaction parameters of these components. According to these comparisons, both the UNIQUAC and the NRTL models satisfactorily correlate the equilibrium compositions of the studied ternary systems.

Experimental Section

Chemicals. All materials had purity of 99 %. Sulfolane, toluene, chloronaphthalene, and octane were supplied by Merck Co. Inc., Germany. The purity of each compound was checked by gas chromatography, and the results indicated that the mass fraction purity was higher than 0.99 %. They were used without further purification.

Procedure. The experimental LLE data were determined by using a glass cell with a water jacket in order to maintain a constant temperature. The cell temperature was regulated by a thermostatic bath with an uncertainty ± 0.1 °C. The solutions were made by mass using a Sartorius analytical balance (model A200S with an uncertainty ± 0.0001 g). The mixtures were prepared inside the cell and vigorously agitated with a magnetic stirrer for 2.5 h. To achieve intimate contact between the phases and the equilibrium, the mixture was allowed to rest for at least 10 h. Then the mixture was split into two liquid phases, which become clear and transparent at equilibrium, with a well-defined interface. The samples of both phases were collected and analyzed. The sample analysis was performed by using a Perkin-Elmer model 8500 gas chromatography equipped with a flame ionization detector (FID). The operating condition for the GLC instrument is given in Table 1. The gas chromatography response factors for each of the components were obtained by using a standard mixture made from the pure components. The composition of this standard mixture was determined by mass and was in the one-phase region. One of the components in the mixture was set as the standard, and its response factor was

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* Corresponding author. E-mail: m.mohsennia@kashanu.ac.ir.

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Table 1. Operating Condition for Gas Chromatography Instrument

column size	2 m × 2.2 mm
column packing	6 % Silar 10 Csorb WHP 100−200 mesh
detector temperature	543.15 K
injector temperature	543.15 K
oven temperature	323.15 K (isotime = 1 min) $\xrightarrow{25\ \mathrm{K/min}}$ 470.15 K
carrier gas	nitrogen
flow rate	30 mL/min

Table 2. Experimental LLE Data for Ternary System {Sulfolane (1) + Aromatic Hydrocarbon (2) + Octane (3)}

feed		octane-rich phase		sulfolane-rich phase			
w_1	w_2	w_1	w_2	w_1	w_2	S	K
{Sulfolane (1) + Toluene (2) + Octane (3)} at 303.15 K							
0.330	0.530	0.283	0.565	0.413	0.497	1.48	0.88
0.540	0.360	0.045	0.593	0.673	0.298	6.37	0.50
0.295	0.400	0.025	0.504	0.760	0.220	11.00	0.44
0.400	0.305	0.011	0.422	0.810	0.174	15.69	0.41
{Sulfolane (1) + Toluene (2) + Octane (3)} at 313.15 K							
0.290	0.560	0.275	0.567	0.435	0.475	1.48	0.84
0.307	0.480	0.075	0.576	0.667	0.304	5.41	0.53
0.295	0.400	0.033	0.494	0.733	0.241	9.35	0.49
0.102	0.390	0.020	0.425	0.804	0.177	12.91	0.42
{Sulfolane (1) + 1-Chloronaphthalene (2) + Octane (3)} at 298.15 K							
0.300	0.510	0.054	0.516	0.419	0.504	5.45	0.98
0.235	0.465	0.044	0.462	0.452	0.483	8.00	1.04
0.195	0.425	0.024	0.431	0.523	0.427	10.85	0.99
0.148	0.405	0.023	0.392	0.575	0.385	14.67	0.98
{Sulfolane (1) + 1-Chloronaphthalene (2) + Octane (3)} at 303.15 K							
0.195	0.515	0.065	0.516	0.412	0.502	4.76	0.97
0.140	0.460	0.059	0.463	0.442	0.478	6.68	1.03
0.270	0.430	0.028	0.407	0.501	0.440	10.36	1.08
0.150	0.442	0.020	0.386	0.552	0.398	12.31	1.03

given as 1.0. Then the response factors of other components were calculated using the re-normalization method. The summation of the mass fraction of all components was 1.0. The measured LLE concentrations had an uncertainty less than 0.5 % for each mass fraction.

Results and Discussion

The measured mass fraction compositions (w) of the equilibrium phases for systems of {sulfolane (1) + toluene (2) or chloronaphthalene (2) + octane (3)} at two different temperatures are reported in Table 2. The solvent extraction performance is evaluated by the selectivity (S), as a measure of the ability of sulfolane (1) to separate toluene or chloronaphthalene (2) from octane (3):[16]

$$S = \frac{(w_2/w_3)^{\mathrm{S}}}{(w_2/w_3)^{\mathrm{O}}} \tag{1}$$

where the superscripts S and O indicate the sulfolane-rich phase and the octane-rich phase, respectively. This quantity is an important factor in examining the efficiency of solvent extraction processes. The measured selectivity of sulfolane for the extraction of toluene and chloronaphthalene as reported in Table 2 is greater than 1, and this means that extraction is possible.

The capacity or dissolving ability of a sulfolane as a measure of the ratio of sulfolane to the feed required for the desired recovery of toluene or chloronaphthalene is defined in the following form:

$$K = \frac{w_2^{\mathrm{S}}}{w_2^{\mathrm{O}}} \tag{2}$$

The experimental values of K in this study are also presented in Table 2.

Table 3. UNIQUAC Structural Parameters

component	r	q
n-octane	5.85	4.97
1-chloronaphthalene	8.77	7.27
sulfolane	4.04	3.20
toluene	3.92	2.97

Table 4. Binary Interaction Parameters of the UNIQUAC Model for the Studied Systems

$i-j$	A_{ij}	A_{ji}
Sulfolane (1) + Toluene (2) + Octane (3)		
1−2	4000.24	−570.20
1−3	500.05	50.04
2−3	−440.18	296.48
Sulfolane (1) 1-Chloronaphthalene (2) + Octane (3)		
1−2	180.25	−10.37
1−3	1380.04	235.42
2−3	−160.25	295.11

Table 5. Binary Interaction Parameters of the NRTL Model for the Studied Systems

$i-j$	A_{ij}	A_{ji}
Sulfolane (1) + Toluene (2) + Octane (3)		
1−2	2000.12	85.34
1−3	750.34	4000.12
2−3	−200.28	600.05
Sulfolane (1) 1-Chloronaphthalene (2) + Octane (3)		
1−2	3.24	50.41
1−3	2903	2048.22
2−3	70.39	60.23

The experimental LLE data were correlated using the UNIQUAC and NRTL activity coefficient models. For the UNIQUAC correlation, the pure component structural parameters (r and q) were calculated by the method outlined[5] and are listed in Table 3. The binary interaction parameters of the UNIQUAC and NRTL models for the studied systems are presented in Tables 4 and 5, respectively. All nonrandomness factors (α_{ij}) in the NRTR model were fixed and not adjusted during the correlation. Best results were obtained when α_{ij} was set at values of 0.46 (sulfolane + toluene), 0.2 (sulfolane + octane), 0.301 (toluene + octane), 0.202 (sulfolane + chloronaphthalene), 0.2 (sulfolane + octane), and 0.2 (chloronaphthalene + octane).

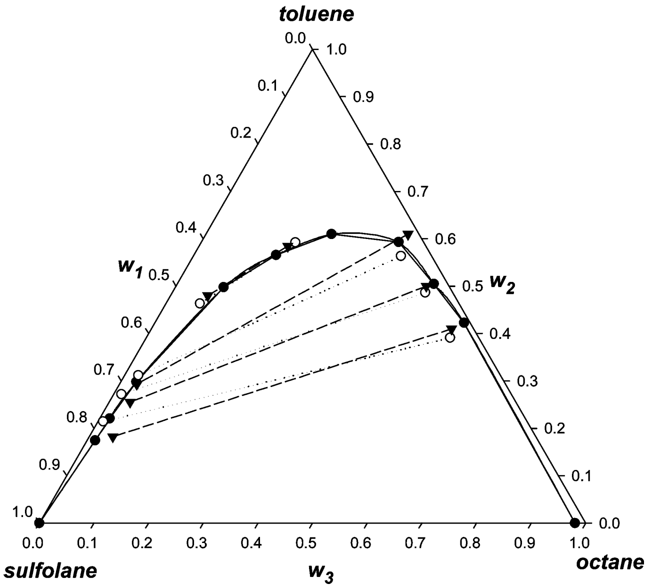

Figure 1. LLE data for {sulfolane (1) + toluene (2) + octane (3)} system at 303.15 K: ●, experimental tie line data; ○, NRTL model; ▲, UNIQUAC model.

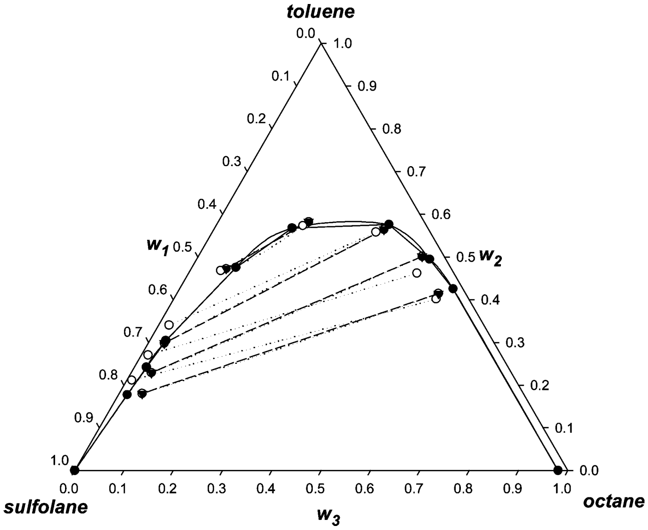

Figure 2. LLE data for {sulfolane (1) + toluene (2) + octane (3)} system at 313.15 K: ●, experimental tie line data; ○, NRTL model; ▲, UNIQUAC model.

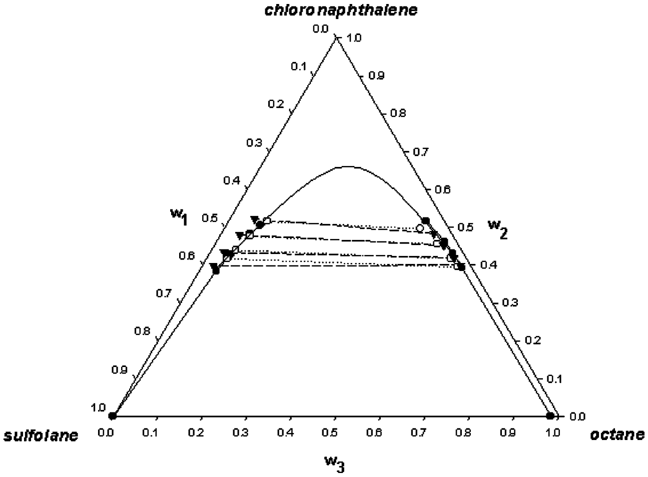

Figure 3. LLE data for {sulfolane (1) + 1-chloronaphthalene (2) + octane (3)} system at 298.15 K: ●, experimental tie line data; ○, NRTL model; ▲, UNIQUAC model.

The phase diagrams for the studied ternary systems are presented in Figures 1 to 4. From phase diagram Figures 1 and 2, the slopes of the tie-lines show that toluene is more soluble in octane than in sulfolane, but Figures 3 and 4 indicate that the solubility of chloronaphthalene in octane and sulfolane is almost equal.

The experimental data were correlated by using the UNIQUAC and NRTL models by minimizing the following objective function:[4]

$$\mathrm{OF} = \sum_i \sum_j \sum_k (w_{ijk}^{\mathrm{exp}} - w_{ijk}^{\mathrm{cal}})^2 \tag{3}$$

where w^{exp} and w^{cal} are the experimental and calculated mass fractions and the subscripts i, j, and k designate respectively the component, the phase, and the tie-line. The root-mean-square deviation (RMSD) is a measure of the agreement between the experimental data and the calculated values. The RMSD value is defined as follows:[17]

$$\mathrm{RMSD} = \left(\sum_i \sum_j \sum_k (w_{ijk}^{\mathrm{exp}} - w_{ijk}^{\mathrm{cal}})^2/6M\right)^{1/2} \tag{4}$$

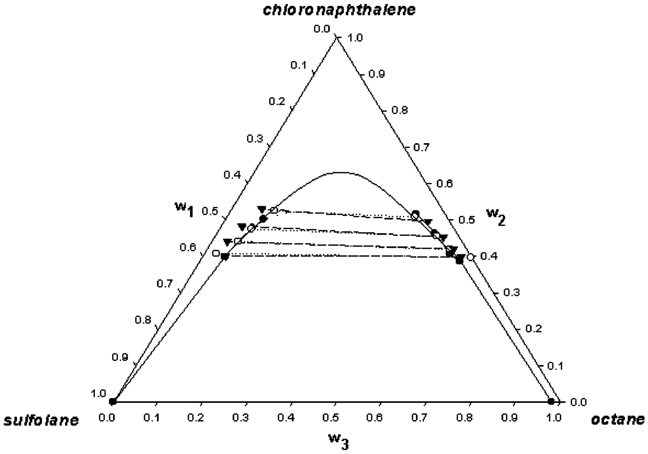

Figure 4. LLE data for {sulfolane (1) + 1-chloronaphthalene (2) + octane (3)} system at 303.15 K: ●, experimental tie line data; ○, NRTL model; ▲, UNIQUAC model.

Table 6. Root-Mean-Square Deviation Percent (RMSD) Values for the Studied Ternary Systems

systems	T/K	NRTL	UNIQUAC
sulfolane + toluene + octane	303.15	0.065	0.084
sulfolane + toluene + octane	313.15	0.069	0.079
sulfolane + 1-chloronaphthalene + octane	298.15	0.028	0.032
sulfolane + 1-chloronaphthalene + octane	303.15	0.016	0.021

Table 7. Parameters of Equation 5 for the Ternary Systems

systems	T/K	a	b	R^2
sulfolane + toluene + octane	303.15	3.273	0.9235	0.992
sulfolane + toluene + octane	313.15	3.343	0.9848	0.994
sulfolane + 1-chloronaphthalene + octane	298.15	0.9447	1.0052	0.987
sulfolane + 1-chloronaphthalene + octane	303.15	0.8784	1.6157	0.981

where, M is the total number of tie lines, w^{exp} is the experimental mass fraction, and w^{cal} indicates the calculated mass fraction. The RMSD values are listed in Table 6. The calculations based on both the UNIQUAC and NRTL models indicate a good fit with those of the representation of the tie-line data for these systems.

The effect of temperature on the selectivity of sulfolane for extraction of toluene from (toluene + octane) mixtures is shown in Figure 5. The obtained selectivity results at 303.2 K and 313.2 K in this work are compared with those at 298.2 K[18] and 343.2 K.[19] It is shown that decreasing temperature increases the

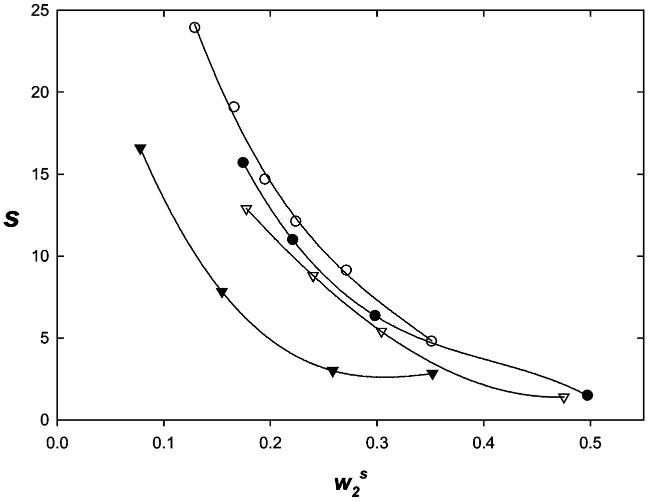

Figure 5. Experimental selectivity data for {sulfolane (1) + toluene (2) + octane (3)} system at ○, 298.15 K; ●, 303.15 K; ▽, 313.15 K; ▼, 343.15 K.

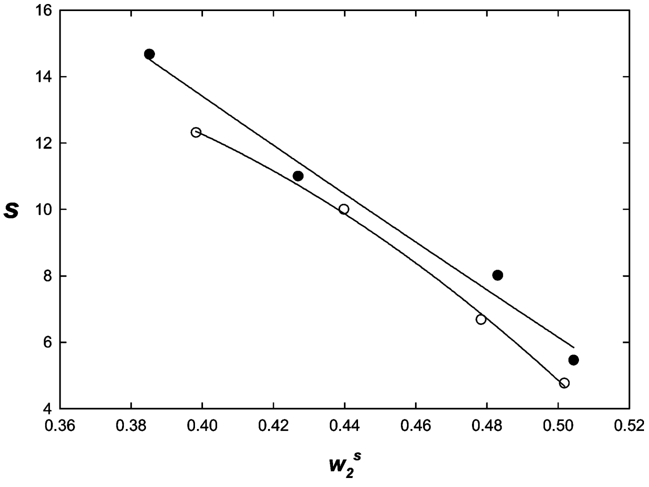

Figure 6. Experimental selectivity data for {sulfolane (1) + 1-chloronaphthalene (2) + octane (3)} system at ●, 298.15 K; ○, 303.15 K.

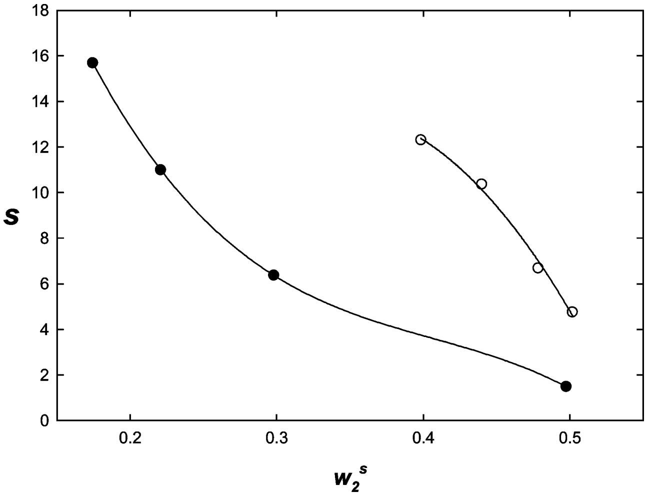

Figure 7. Experimental selectivity data for ○ chloronaphthalene and ● toluene in {sulfolane (1) + chloronaphthalene (2) or toluene (2) + octane (3)} system at 303.15 K.

selectivity of the sulfolane. Figure 6 shows the comparison of the experimental selectivity data for the {sulfolane (1) + chloronaphthalene (2) + octane (3)} system at 298.2 K and 303.2 K. The experimental selectivity data of sulfolane for extraction of chloronaphthalene and toluene from the {sulfolane (1) + chloronaphthalene (2) or toluene (2) + octane (3)} systems at 303.2 K are shown in Figure 7.

The experimental data for the studied ternary systems were correlated by the following equation proposed by Hand:[20]

$$\frac{w_2^{\mathrm{O}}}{w_3^{\mathrm{O}}} = a\left[\frac{w_2^{\mathrm{S}}}{w_1^{\mathrm{S}}}\right]^b \qquad (5)$$

represents a linear dependency of the ratio $w_2^{\mathrm{O}}/w_3^{\mathrm{O}}$ on the ratio $w_2^{\mathrm{S}}/w_1^{\mathrm{S}}$ in logarithmic coordinates and, for studied systems parameters *a* and *b*, are listed in Table 7.

Conclusions

LLE data of the ternary systems (sulfolane + toluene + octane) at temperatures of 303.2 K and 313.2 K and (sulfolane + chloronaphthalene + octane) at temperatures of 298.2 K and 303.2 K are reported. The UNIQUAC and NRTL activity coefficient models were satisfactorily correlated the LLE experimental data of the studied systems. The parameters of these models are presented.

From the selectivity values, the separation of toluene or chloronaphthalene from octane by extraction with sulfolane is feasible. The obtained selectivity results for the systems (sulfolane + toluene or chloronaphthalene + octane) at the different temperatures show that at lower temperatures the selectivity is higher but the effect of temperature variation on the distribution coefficient is negligible. Therefore, by considering the technical and economical viewpoints in a practical extraction, the lower temperature operations may be preferred.

The comparison between experimental selectivity data of sulfolane for the extraction of chloronaphthalene from the (chloronaphthalene + octane) mixture with that for extraction of toluene from the (toluene + octane) mixture at 303.2 K indicate that the extraction of chloronaphthalene is more efficient than toluene.

Literature Cited

(1) Mohsen-Nia, M.; Modarress, H.; Doulabi, F.; Bagheri, H. Liquid−liquid equilibria for ternary mixtures of (solvent + aromatic hydrocarbon + alkane). *J. Chem. Thermodyn.* **2005**, *37*, 1111−1118.
(2) Pan, Ch.; Radosz, M. Modeling of solid−liquid equilibria in naphthalene, normal-alkane and polyethylene solutions. *Fluid Phase Equilib.* **1999**, *155*, 57−73.
(3) Hong, S. P.; Green, K. A.; Luks, K. D. Phase equilibria of the mixtures methane + *n*-hexane + *n*-hexatriacontane, methane + toluene + naphthalene, and methane + *n*-hexane + naphthalene. *Fluid Phase Equilib.* **1993**, *87*, 255−272.
(4) Mohsen-Nia, M.; Modarress, H.; Mohammad Doulabi, F. S. Quaternary liquid−liquid equilibria for systems of {(water + methanol or ethanol) + *m*-xylene + *n*-dodecane}. *Fluid Phase Equilib.* **2006**, *239*, 1−7.
(5) 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.
(6) Renone, H.; Prausnitz, J. M. Local composition in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.
(7) Khanna, A.; Singh, M. K.; Bajpai, S.; Sanpui, D. Estimation of LLE for PIONA families of sulfolane and its validation. *Fluid Phase Equilib.* **2004**, *215*, 207−220.
(8) Lin, W. C.; Kao, N. H. Liquid−liquid equilibria of octane + (benzene or toluene or *m*-xylene) + sulfolane at 323.15, 348.15, and 373.15 K. *J. Chem. Eng. Data* **2002**, *47*, 1007−1011.
(9) Achcroft, S. J.; Clayton, A. D.; Shearn, R. B. Liquid−liquid equilibria for three ternary and six quaternary systems containing sulfolane, *n*-heptane, toluene, 2-propanol, and water at 303.15 K. *J. Chem. Eng. Data* **1982**, *27*, 148−151.
(10) Chen, J.; Mi, J. G.; Fei, W. Y.; Li, Z. Liquid−liquid equilibria of quaternary and quinary systems including sulfolane at 298.15 K. *J. Chem. Eng. Data* **2001**, *46*, 169−171.
(11) Deal, C. H.; Evans, H. D.; Oliver, E. D.; Papadopoulus, M. N. Extraction of aromatics with sulfolane. *Fifth World Pet. Congr. Proc.* **1959**, *3*, 283−297.
(12) Shaha, M.; Rawat, B. S.; Khanna, M. K.; Nautiyal, B. R. Liquid−liquid equilibrium studies on toluene + heptane + solvent. *J. Chem. Eng. Data* **1998**, *43*, 422−426.
(13) Rawat, B. S. Liquid−liquid equilibria for benzene−*n*-heptane systems with triethylene glycol, and sulfolane containing water at elevated temperatures. *J. Chem. Eng. Data* **1980**, *25*, 227−230.
(14) Wang, W.; Gou, Z.; Zha, S. Liquid−liquid equilibria for aromatics extraction systems with tetraethylene glycol. *J. Chem. Eng. Data* **1998**, *43*, 81−83.
(15) Muller, E.; Hochfeld, G. Aromatics extraction with solvent combinations. *Seventh World Pet. Conger. Proc.* **1967**, 4, 20−43.
(16) Letcher, T. M.; Redhi, G. G.; Radloff, S. E.; Domanksa, U. Liquid−liquid equilibria of the ternary mixtures with sulfolane at 303.15 K. *J. Chem. Eng. Data* **1996**, *41*, 634−638.
(17) Rappel, R.; de Gois, L. M. N.; Mattedi, S. Liquid−liquid equilibria data for systems containing aromatic + nonaromatic + sulfolane at 308.15 K and 323.15 K. *Fluid Phase Equilib.* **2002**, *202*, 263−276.
(18) 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**, *4*, 358−361.

(19) Chen, J.; Duan, L.-P.; Mi, J.-G.; Fei, W.-Y.; Li, Z.-C. Liquid−liquid equilibria of multi-component systems including *n*-hexane, *n*-octane, benzene, toluene, xylene and sulfolane at 298.15 K and atmospheric pressure. *Fluid Phase Equilibria* **2000**, *173*, 109−119.

(20) Hand, D. B. the distribution of a consolute liquid between two immiscible liquids. *J. Phys. Chem.* **1930**, *34*, 1961−2000.

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