JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Liquid−Liquid Equilibria of the Ternary Systems Undecane + 1,4-Diethylbenzene + Tetrahydrothiophene 1,1-Dioxide and Tridecane + 1,4-Diethylbenzene + Tetrahydrothiophene 1,1-Dioxide at T = (323.15, 348.15, and 373.15) K

Wen-Churng Lin*

Department of Environmental Engineering, Kun Shan University, Tainan 71003, Taiwan

ABSTRACT: Equilibrium tie-line data have been determined at 323.15 K, 348.15 K, and 373.15 K for the liquid−liquid equilibria (LLE) of the ternary systems undecane + 1,4-diethylbenzene + tetrahydrothiophene 1,1-dioxide and tridecane + 1,4-diethylbenzene + tetrahydrothiophene 1,1-dioxide. The relative mutual solubility of 1,4-diethylbenzene is higher in undecane + tetrahydrothiophene 1,1-dioxide than in tridecane + tetrahydrothiophene 1,1-dioxide mixture. The tie-line data were correlated with the universal quasichemical (UNIQUAC) and nonrandom two-liquid (NRTL) models. The calculated values based on the UNIQUAC model were found to be better than those based on the NRTL model; the average root-mean-square deviation between the phase composition obtained from the experiment and that from the calculation was 0.3788 for UNIQUAC compared to 0.4459 for NRTL. The values of selectivity and distribution coefficients were derived from the equilibrium data.

INTRODUCTION

Ternary phase equilibrium data are essential for a proper understanding of the solvent extraction process. Tetrahydrothiophene 1,1-dioxide is widely used in the chemical industry for the extraction of aromatic hydrocarbons,[1−4] and many investigators[5−15] have studied liquid−liquid equilibria (LLE) for the ternary systems containing tetrahydrothiophene 1,1-dioxide + alkanes (pentane, hexane, cyclohexane, heptane, or octane) + aromatics (benzene, methylbenzene, 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene), but quantitative phase equilibrium data for the systems containing tetrahydrothiophene 1,1-dioxide and alkanes with carbon number larger than nine[16,17] are scarce. Therefore, most thermodynamic models cannot estimate LLE when trying to simulate extractive separations.

The purpose of this study is to obtain LLE data for the ternary mixtures undecane + 1,4-diethylbenzene + tetrahydrothiophene 1,1-dioxide and tridecane + 1,4-diethylbenzene + tetrahydrothiophene 1,1-dioxide at 323.15 K, 348.15 K, and 373.15 K. The LLE data for these ternary systems were then correlated by the universal quasichemical (UNIQUAC) model of Abrams and Prausnitz[18] and the nonrandom two-liquid (NRTL) model of Renon and Prausnitz.[19] The effects of temperature on the selectivity and the distribution coefficient were also discussed.

The data obtained in the present study can be used for design and simulation purposes when a solvent extraction process is applied to extract aromatics from medium petroleum fractions (e.g., kerosene).

EXPERIMENTAL SECTION

Chemicals. Tetrahydrothiophene 1,1-dioxide, undecane, tridecane, methoxybenzene, and carbon disulfide were supplied by E. Merck with a stated purity of 0.99 mass fraction. 1,4-Diethylbenzene was obtained from the Acros Organics, and further purification was achieved by distillation. The purities of all materials were checked by gas chromatograph and found to be better than 0.99 mass fraction. All compounds were stored in a desiccator with a drying agent before use.

Apparatus and Procedure. The experimental tie-line data in the two-phase region was determined by using a 50 cm^3 jacketed glass cell controlled at a temperature of (323.15, 348.15, or 373.15) K ± 0.03 K. Specific amounts of alkane (undecane or tridecane), tetrahydrothiophene 1,1-dioxide, and 1,4-diethylbenzene 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 sample was stirred for 1 h with a stirrer at a speed of 1100 rpm and then allowed to settle for at least 5 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 methoxybenzene was added as the internal standard and diluted with 50 g of carbon disulfide[6] to prepare them for analysis. The accuracy of weighing was ± 0.0001 g. The sample analysis was performed by using a Hewlett-Packard model 6890 gas chromatograph equipped with a flame ionization detector and a HP Ultra 1 column (cross-linked methyl silicone gum, 25 m × $3.2 \cdot 10^{-4}$ m × $5.2 \cdot 10^{-7}$ 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^{-1}, and the flow rate of nitrogen carrier gas was $2.5 \cdot 10^{-5}$ m^3·min^{-1}.

Special Issue: Kenneth N. Marsh Festschrift

Received: May 12, 2011
Accepted: June 19, 2011
Published: July 01, 2011

Table 1. Experimental LLE Data, Selectivities, S, and Distribution Coefficients, κ, for the System Undecane (1) + 1,4-Diethylbenzene (2) + Tetrahydrothiophene 1,1-Dioxide (3)

	alkane-rich phase			tetrahydrothiophene 1,1-dioxide-rich phase				
T/K	x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}	S	κ
323.15	0.9948	0.0000	0.0052	0.0029	0.0000	0.9971		
	0.8607	0.1331	0.0062	0.0030	0.0151	0.9819	32.5	0.113
	0.7495	0.2394	0.0111	0.0032	0.0295	0.9673	28.9	0.123
	0.6476	0.3355	0.0169	0.0035	0.0431	0.9534	23.8	0.128
	0.5452	0.4311	0.0237	0.0036	0.0576	0.9388	20.2	0.134
	0.4326	0.5319	0.0355	0.0038	0.0765	0.9197	16.4	0.144
	0.3100	0.6336	0.0564	0.0038	0.1068	0.8894	13.8	0.169
	0.2144	0.6998	0.0858	0.0040	0.1663	0.8297	12.7	0.238
348.15	0.9902	0.0000	0.0098	0.0052	0.0000	0.9948		
	0.8503	0.1354	0.0143	0.0055	0.0194	0.9751	22.2	0.143
	0.7457	0.2359	0.0184	0.0058	0.0339	0.9603	18.5	0.144
	0.6374	0.3367	0.0259	0.0061	0.0515	0.9424	16.0	0.153
	0.5400	0.4246	0.0354	0.0064	0.0727	0.9209	14.4	0.171
	0.4177	0.5248	0.0575	0.0069	0.1057	0.8874	12.2	0.201
	0.2993	0.6068	0.0939	0.0075	0.1457	0.8468	9.6	0.240
	0.1928	0.6599	0.1473	0.0083	0.1905	0.8012	6.7	0.289
373.15	0.9820	0.0000	0.0180	0.0073	0.0000	0.9927		
	0.8579	0.1239	0.0182	0.0074	0.0212	0.9714	19.8	0.171
	0.7395	0.2282	0.0323	0.0082	0.0401	0.9517	15.8	0.176
	0.6305	0.3238	0.0457	0.0093	0.0612	0.9295	12.8	0.189
	0.5312	0.4021	0.0667	0.0102	0.0805	0.9093	10.4	0.200
	0.3998	0.4910	0.1092	0.0109	0.1164	0.8727	8.7	0.237
	0.2554	0.5620	0.1826	0.0104	0.1549	0.8347	6.8	0.276
	0.1506	0.5702	0.2792	0.0104	0.1943	0.7953	4.9	0.341

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

The experimental tie-line data are given in Tables 1 and 2 for the ternary systems formed by tetrahydrothiophene 1,1-dioxide (3) + 1,4-diethylbenzene (2) with undecane or tridecane (1), respectively. Concentrations of components i ($i = 1, 2, 3$) in phase L ($L = 1$, alkane-rich phase; $L = 2$, tetrahydrothiophene 1,1-dioxide-rich phase) are given in mole fraction, x_{iL}. The effect of temperature on the equilibrium for the system undecane or tridecane (1) + 1,4-diethylbenzene (2) + tetrahydrothiophene 1,1-dioxide (3) is shown in Figures 1 or 2, respectively. As expected, the size of the two-phase region decreases with an increase in temperature. The two systems studied present a wide two-phase region that is important, together with the slope of the tie lines, when establishing the selectivity of tetrahydrothiophene 1,1-dioxide.

Data Correlation. The UNIQUAC and NRTL 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 the calculated concentrations over all of 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.

For the NRTL model, the third nonrandomness parameter, α_{ij}, was set at a value of 0.2.[8] The parameters calculated are shown in Tables 3 and 4, together with the root-mean-square deviation (rmsd) values, defined as:

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

where N = number of tie lines.

As can be seen from Tables 3 to 4, 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 UNIQUAC model, fitted to the experimental data, is more accurate than the NRTL model, according to the analysis of rmsd (the average rmsd phase composition error was 0.3788 for UNIQUAC as compared to 0.4459 for NRTL).

DISCUSSION

The slopes of the tie lines presented in Figures 1 and 2 show that 1,4-diethylbenzene is more soluble in alkanes than in tetrahydrothiophene 1,1-dioxide. It is observed that the relative mutual solubility of 1,4-diethylbenzene is higher in undecane + tetrahydrothiophene 1,1-dioxide than in tridecane + tetrahydrothiophene 1,1-dioxide mixture at the same

Table 2. Experimental LLE Data, Selectivities, S, and Distribution Coefficients, κ, for the System Tridecane (1) + 1,4-Diethylbenzene (2) + Tetrahydrothiophene 1,1-Dioxide (3)

	alkane-rich phase			tetrahydrothiophene 1,1-dioxide-rich phase				
T/K	x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}	S	κ
323.15	0.9939	0.0000	0.0061	0.0015	0.0000	0.9985		
	0.8671	0.1262	0.0067	0.0016	0.0122	0.9862	52.4	0.097
	0.7549	0.2356	0.0095	0.0017	0.0237	0.9746	44.7	0.101
	0.6216	0.3641	0.0143	0.0019	0.0430	0.9551	38.6	0.118
	0.5108	0.4673	0.0219	0.0020	0.0579	0.9401	31.6	0.124
	0.4057	0.5614	0.0329	0.0023	0.0825	0.9152	25.9	0.147
	0.2904	0.6572	0.0524	0.0026	0.1126	0.8848	19.1	0.171
	0.1622	0.7286	0.1092	0.0028	0.1686	0.8286	13.4	0.231
348.15	0.9888	0.0000	0.0112	0.0026	0.0000	0.9974		
	0.8633	0.1276	0.0091	0.0028	0.0158	0.9814	38.2	0.124
	0.7322	0.2538	0.0140	0.0030	0.0338	0.9632	32.5	0.133
	0.6041	0.3721	0.0238	0.0035	0.0570	0.9395	26.4	0.153
	0.4962	0.4676	0.0362	0.0038	0.0728	0.9234	20.3	0.156
	0.3750	0.5662	0.0588	0.0045	0.1045	0.8910	15.4	0.185
	0.2574	0.6469	0.0957	0.0056	0.1436	0.8508	10.2	0.222
	0.1632	0.6866	0.1502	0.0067	0.1908	0.8025	6.8	0.278
373.15	0.9790	0.0000	0.0210	0.0045	0.0000	0.9955		
	0.8236	0.1545	0.0219	0.0055	0.0247	0.9698	23.9	0.160
	0.7246	0.2495	0.0259	0.0065	0.0402	0.9533	18.0	0.161
	0.6212	0.3378	0.0410	0.0067	0.0598	0.9335	16.4	0.177
	0.5083	0.4308	0.0609	0.0072	0.0821	0.9107	13.5	0.191
	0.3588	0.5343	0.1069	0.0081	0.1246	0.8673	10.3	0.233
	0.2427	0.5923	0.1650	0.0083	0.1670	0.8247	8.2	0.282
	0.1475	0.5998	0.2527	0.0114	0.2299	0.7587	5.0	0.383

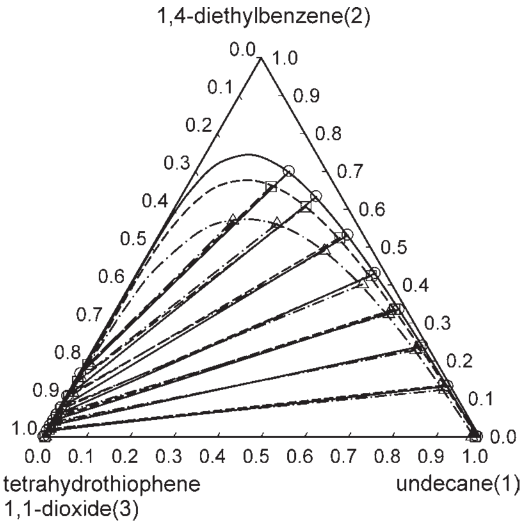

Figure 1. Effect of temperature on the liquid–liquid equilibrium for the undecane (1) + 1,4-diethylbenzene (2) + tetrahydrothiophene 1,1-dioxide (3) system. Curves calculated by UNIQUAC: —, 323.15 K; – –, 348.15 K; – · –, 373.15 K. Experimental tie line: ○–○, 323.15 K; □– –□, 348.15 K; △– · –△, 373.15 K.

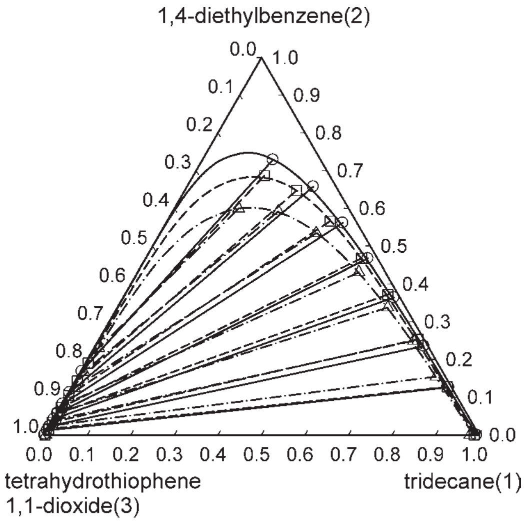

Figure 2. Effect of temperature on the liquid–liquid equilibrium for the tridecane (1) + 1,4-diethylbenzene (2) + tetrahydrothiophene 1,1-dioxide (3) system. Curves calculated by UNIQUAC: —, 323.15 K; – –, 348.15 K; – · –, 373.15 K. Experimental tie line: ○–○, 323.15 K; □– –□, 348.15 K; △– · –△, 373.15 K.

temperature. This solubility effect is reflected in the size of the two-phase region, increasing slightly in the order tridecane > undecane at the same temperature.

The effectiveness of extraction of an aromatic compound by tetrahydrothiophene 1,1-dioxide is given by its selectivity (S), which is a measure of the ability of tetrahydrothiophene 1,

Table 3. UNIQUAC and NRTL Parameters for the System Undecane (1) + 1,4-Diethylbenzene (2) + Tetrahydrothiophene 1,1-Dioxide (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		
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	−172.42	176.60	0.3788	−691.47	497.06	0.5817
	1−3	536.94	26.68		1140.90	1339.40	
	2−3	220.76	−14.16		379.56	313.68	
348.15	1−2	−273.99	453.97	0.2162	−603.26	913.98	0.2711
	1−3	541.02	15.67		1183.10	1208.70	
	2−3	259.89	−27.33		248.72	513.28	
373.15	1−2	17.14	13.11	0.3844	81.78	74.80	0.3282
	1−3	472.85	68.13		1165.10	1387.90	
	2−3	70.50	115.02		87.79	697.10	

Table 4. UNIQUAC and NRTL Parameters for the System Tridecane (1) + 1,4-Diethylbenzene (2) + Tetrahydrothiophene 1,1-Dioxide (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		
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	−233.17	310.39	0.3094	−536.06	164.29	0.8040
	1−3	508.66	50.21		1242.10	1340.90	
	2−3	219.06	−10.20		305.59	381.22	
348.15	1−2	−384.41	588.42	0.7548	72.42	−124.27	0.2859
	1−3	524.51	9.23		1472.30	1397.00	
	2−3	301.64	−83.34		345.20	437.54	
373.15	1−2	−247.98	339.12	0.3191	156.87	−168.87	0.4042
	1−3	523.70	21.89		1187.90	1329.20	
	2−3	171.90	16.15		236.40	516.88	

1-dioxide to separate aromatics from alkanes:

$$S = (x_2/x_1)_{\text{tetrahydrothiophene 1,1-dioxide-rich phase}}/(x_2/x_1)_{\text{alkane-rich phase}} \tag{3}$$

where subscript 2 represents 1,4-diethylbenzene and subscript 1 represents undecane or tridecane.

This quantity is not constant over the whole two-phase region. The experimental values of S are listed in Tables 1 and 2. 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 systems, the order of the selectivity of tetrahydrothiophene 1,1-dioxide to 1,4-diethylbenzene is tridecane > undecane. Since the selectivity in all cases is greater than one, it means that extraction is possible.

The distribution coefficient of 1,4-diethylbenzene over the two liquid phases in equilibrium is defined as

$$\kappa = (x_2)_{\text{tetrahydrothiophene 1,1-dioxide-rich phase}}/(x_2)_{\text{alkane-rich phase}} \tag{4}$$

This coefficient is related to the number of theoretical stages that are necessary for a given extraction. The lower number of theoretical stages is necessary for larger κ values. The experimental values of κ of this study are also presented in Tables 1 and 2. We can find the tendency that, for the same system, the higher the temperature, the larger the κ value. Also in our two different systems, there are not obvious differences between the κ values at the same temperature.

■ CONCLUSIONS

Liquid−liquid equilibrium data of the ternary systems undecane (1) + 1,4-diethylbenzene (2) + tetrahydrothiophene 1,1-dioxide (3) and tridecane (1) + 1,4-diethylbenzene (2) + tetrahydrothiophene 1,1-dioxide (3) were determined at (323.15, 348.15, and 373.15) K, respectively.

The calculation based on the UNIQUAC and NRTL models showed that the best results are given by the UNIQUAC model. The binodal curves calculated by the UNIQUAC model or NRTL model for the systems studied here reveal that the size of the two-phase region decreases with increasing temperature. From the selectivity data, it is concluded that the separation of 1,4-diethylbenzene from undecane or tridecane is feasible with tetrahydrothiophene 1,1-dioxide as a solvent.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: linwc@mail.ksu.edu.tw.

Funding Sources

The authors thank the National Science Council, NSC 99-2622-E-168-011-CC3, for financial support of this work.

■ REFERENCES

(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) Ashour, I.; Abu-Eishah, S. I. Liquid-Liquid Equilibria of Ternary and Six-Component Systems Including Cyclohexane, Benzene, Toluene, Ethylbenzene, Cumene, and Sulfolane at 303.15 K. *J. Chem. Eng. Data* **2006**, *51*, 1717–1722.

(6) 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.

(7) 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.

(8) 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.

(9) Chen, J.; Li, Z.; Duan, L. Liquid-Liquid Equilibria of Ternary and Quaternary Systems Including Cyclohexane, 1-Heptene, Benzene, Toluene, and Sulfolane at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 689–692.

(10) 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.

(11) 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.

(12) 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.

(13) Letcher, T. M.; Redhi, G. G.; Radloff, S. E. Liquid-Liquid Equilibria of the Ternary Mixtures with Sulfolane at 303.15K. *J. Chem. Eng. Data* **1996**, *41*, 634–638.

(14) Lin, W. C.; Tsai, T. H.; Lin, T. Y.; Yang, C. H. Influence of the Temperature on the Liquid-Liquid Equilibria of Heptane + Toluene + Sulfolane and Heptane + *m*-Xylene + Sulfolane. *J. Chem. Eng. Data* **2008**, *53*, 760–764.

(15) Mondragón-Garduño, M.; Romero-Martínez, A.; Trejo, A. Liquid—Liquid Equilibria for Ternary systems. I. C_6-isomers + Sulfolane + Toluene at 298.15 K. *Fluid Phase Equilib.* **1991**, *64*, 291–303.

(16) Lin, W. C.; Yang, C. H.; Pan, T. C.; Tsao, C. W. Liquid-Liquid Equilibria of Alkane (C10-C14) + Hexylbenzene + Sulfolane. *J. Chem. Eng. Data* **2007**, *52*, 1060–1064.

(17) Masohan, A.; Nanoti, S. M.; Sharma, K. G.; Puri, S. N.; Gupta, P.; Rawat, B. S. Liquid-Liquid Equilibria Studies on Hydrocarbon ($C_{10}-C_{20}$)-Sulfolane Systems. *Fluid Phase Equilib.* **1990**, *61*, 89–98.

(18) 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.

(19) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.