J. Chem. Eng. Data **2008,** *53,* 2275–2281 **2275**

Liquid−Liquid Equilibria of Ternary Systems Sulfide + Octane + Solvents at Different Temperatures

Wenlin Zhang, Kaihu Hou,* Guanjie Mi, and Na Chen

School of Chemical Engineering, Hebei University of Technology, Tianjin 300130, China

Liquid−liquid equilibria (LLE) data of five ternary systems of sulfide + octane + solvents were measured at 313.15 K, 323.15 K, and 333.15 K, respectively, under atmospheric pressure. Dimethyl sulfoxide, sulfolane, and tetraethylene glycol were used as solvents, respectively. The distribution of sulfide (thiophene, *n*-butyl mercaptan, *n*-dibutyl sulfide) between the extract phase and the raffinate phase was obtained. The experimental data were correlated through the well-known NRTL and UNIQUAC models for the activity coefficient, and the model parameters were estimated using the simplex minimization method and a composition-based objective function. The results were analyzed in terms of average absolute deviations between experimental and calculated mass percentage of thiophene, *n*-butyl mercaptan, and *n*-dibutyl sulfide. The results were considered satisfactory, with the NRTL model yielding a better representation of the equilibria data for the systems studied. The two models were suitable for calculating the LLE data of these systems.

Introduction

Sulfur is an undesirable component in gasoline as it creates corrosive combustion byproducts, releases sulfur oxides into the atmosphere, and increases deposits on fuel injection and combustion systems. Increasingly tight emission standards are or will be imposed worldwide aiming to reduce air pollution and the greenhouse effect. Such standards are forcing the oil refiners over the world to produce low-sulfur gasoline starting now or soon.

Hydrodesulfurization (HDS) is a key process in current petroleum refining operations. It uses catalysts for hydrogenation to reduce undesired sulfur components. Unfortunately, the gasoline HDS is a high cost process under high pressure (up to 500 psig) and high temperature [(523.15 to 673.15) K]. For gasoline deep desulfurization, the HDS technique also suffers from high octane number loss and low liquid product yield. Compared to the HDS technique, a technique combining extractive distillation (ED) and HDS shows many advantages, such as low cost, low octane number loss, and high liquid product yield.[1−3]

Component distribution between the two phases of the extraction system can be estimated using suitable thermodynamic models (NRTL, UNIQUAC, UNIFAC, et al.).[4] Liquid−liquid equilibria (LLE) data of sulfide (existing in gasoline) + hydrocarbons + solvent (selected) are necessary for estimating the model parameters used for the design and modeling of gasoline extractive distillation. Unfortunately, such data have rarely been reported in the literature.

The main aim of this work is to obtain the model parameters for these systems and to evaluate the performance of the models (NRTL,[5] UNIQUAC [6]) for gasoline extractive distillation. In this paper, *n*-butyl mercaptan, *n*-dibutyl sulfide, and thiophene were selected as the typical sulfides; dimethyl sulfoxide, sulfolane, and tetraethylene glycol were selected as the solvents by experiments (for details see ref 7); and octane was selected as the typical hydrocarbon. Experimental LLE data were obtained for five ternary systems at 313.15 K, 323.15 K, and 333.15 K, respectively, under atmospheric pressure. The experimental data were correlated using the NRTL and UNIQUAC models for the activity coefficient. New model parameters for both models were estimated using the simplex minimization method and a composition-based objective function. The results were evaluated in terms of average absolute deviations between experimental and calculated mass percentage of thiophene, *n*-butyl mercaptan, and *n*-dibutyl sulfide.

Table 1. LLE Data of the Thiophene (1) + Octane (2) + Dimethyl Sulfoxide (3) System (ω, %)

raffinate phase			extract phase		
x_1	x_2	x_3	x_1	x_2	x_3
		T/K = 313.15			
1.04	98.75	0.21	1.44	0.09	98.47
0.65	99.01	0.34	0.93	0.14	98.93
0.57	99.01	0.42	0.89	0.17	98.94
0.45	99.10	0.45	0.75	0.19	99.06
0.36	99.16	0.48	0.66	0.20	99.14
0.34	99.17	0.49	0.56	0.20	99.24
0.27	99.23	0.50	0.53	0.20	99.27
0.26	99.23	0.51	0.44	0.21	99.35
		T/K = 323.15			
0.84	98.95	0.21	1.36	0.09	98.55
0.65	99.01	0.34	1.01	0.14	98.85
0.52	99.07	0.41	0.82	0.17	99.01
0.42	99.12	0.46	0.66	0.19	99.15
0.35	99.17	0.48	0.54	0.20	99.26
0.35	99.16	0.49	0.41	0.20	99.39
0.30	99.20	0.50	0.45	0.21	99.34
0.19	99.30	0.51	0.42	0.21	99.37
		T/K = 333.15			
0.78	99.00	0.22	1.21	0.09	98.70
0.81	98.85	0.34	0.99	0.14	98.87
0.59	99.00	0.41	0.88	0.17	98.95
0.51	99.04	0.45	0.64	0.19	99.17
0.42	99.10	0.48	0.54	0.20	99.26
0.43	99.08	0.49	0.47	0.20	99.33
0.39	99.11	0.50	0.43	0.21	99.36
0.30	99.19	0.51	0.39	0.21	99.40

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* Corresponding author. Tel.: +86-22-2658-1584. E-mail address: khou@hebut.edu.cn.

10.1021/je800340v CCC: $40.75

Table 2. LLE Data of the Thiophene (1) + Octane (2) + Sulfolane (3) System (ω, %)

raffinate phase			extract phase		
x_1	x_2	x_3	x_1	x_2	x_3
T/K = 313.15					
0.85	98.84	0.32	0.80	0.10	99.10
0.71	98.82	0.47	0.70	0.14	99.16
0.60	98.85	0.54	0.54	0.17	99.30
0.51	98.91	0.58	0.53	0.18	99.29
0.47	98.93	0.60	0.47	0.18	99.35
0.43	98.97	0.60	0.42	0.19	99.39
0.40	99.00	0.61	0.38	0.19	99.43
0.34	99.05	0.61	0.36	0.19	99.45
T/K = 323.15					
0.79	98.89	0.32	0.84	0.10	99.07
0.79	98.74	0.47	0.71	0.15	99.14
0.64	98.82	0.54	0.54	0.17	99.29
0.58	98.84	0.58	0.49	0.18	99.33
0.54	98.86	0.60	0.43	0.18	99.39
0.43	98.97	0.60	0.42	0.19	99.39
0.34	99.05	0.61	0.38	0.19	99.43
0.28	99.11	0.61	0.35	0.19	99.46
T/K = 333.15					
0.83	98.85	0.32	0.75	0.10	99.28
0.70	98.83	0.47	0.62	0.15	99.31
0.52	98.94	0.54	0.54	0.17	99.41
0.48	98.94	0.58	0.43	0.18	99.40
0.42	98.98	0.60	0.42	0.18	99.41
0.43	98.97	0.60	0.41	0.19	99.51
0.35	99.04	0.61	0.30	0.19	99.50
0.35	99.04	0.61	0.31	0.19	99.81

Table 3. LLE Data of the Thiophene (1) + Octane (2) + Tetraethylene Glycol (3) System (ω, %)

raffinate phase			extract phase		
x_1	x_2	x_3	x_1	x_2	x_3
T/K = 313.15					
12.87	78.30	8.83	8.72	29.47	61.81
11.12	60.29	28.59	7.22	2.70	90.08
9.25	66.04	24.71	6.28	10.98	82.74
7.79	67.20	25.01	5.74	29.64	64.62
1.45	60.80	37.75	1.14	36.37	62.49
1.32	62.47	36.22	0.48	40.12	59.41
1.28	67.04	31.68	1.28	28.88	69.84
1.15	68.36	30.49	0.71	31.51	67.78
T/K = 323.15					
10.37	80.20	9.43	7.15	2.24	90.61
9.07	82.33	8.60	5.77	6.34	87.89
9.36	88.38	2.26	6.23	2.37	91.40
7.89	88.95	3.16	5.15	1.27	93.58
6.77	90.41	2.83	4.57	23.50	71.93
5.56	67.64	26.80	4.14	30.72	65.14
4.71	66.53	28.76	3.24	16.54	80.22
4.03	54.93	41.04	2.79	39.39	57.82
T/K = 333.15					
13.35	67.06	19.59	8.74	46.43	44.83
11.88	62.08	26.04	6.95	40.35	52.70
10.26	49.27	40.47	6.20	37.27	56.53
8.85	46.81	44.34	5.47	39.63	54.90
3.27	75.91	20.81	2.26	23.89	73.85
2.46	72.44	25.10	0.80	33.55	65.65
2.85	79.26	17.89	0.68	31.85	67.47
2.07	78.26	19.66	0.61	33.31	66.08

Table 4. LLE Data of the *n*-Butyl Mercaptan (1) + Octane (2) + Sulfolane (3) System (ω, %)

raffinate phase			extract phase		
x_1	x_2	x_3	x_1	x_2	x_3
T/K = 313.15					
8.00	87.49	4.51	1.96	8.08	89.96
7.09	90.30	2.61	1.69	7.83	90.48
6.22	70.26	23.53	1.47	7.91	90.63
4.18	84.46	11.36	1.29	15.02	83.69
2.82	87.97	9.21	0.73	17.78	81.50
2.83	91.86	5.31	0.43	30.31	69.26
1.51	77.25	21.24	0.61	21.84	77.55
2.62	76.45	20.93	0.71	24.87	74.42
T/K = 323.15					
7.46	64.60	27.90	3.49	4.50	92.01
6.10	51.59	42.31	0.56	29.33	70.11
5.23	47.24	47.53	0.32	37.14	62.53
3.80	43.41	52.79	0.33	34.60	65.07
2.64	86.16	11.21	0.39	32.23	67.38
2.62	78.68	18.69	0.53	27.77	71.70
2.86	74.86	22.28	0.46	29.05	70.48
3.63	66.28	30.09	0.44	31.57	67.99
T/K = 333.15					
6.26	76.30	17.44	0.99	21.76	77.25
5.35	79.92	14.73	0.62	27.13	72.25
3.92	69.44	26.63	0.61	22.54	76.84
3.51	67.86	28.63	0.66	19.87	79.48
2.71	80.46	16.84	1.26	3.15	95.59
2.62	70.43	26.96	0.91	11.49	87.60
2.78	61.71	35.51	0.82	20.22	78.97
3.19	53.78	43.03	1.01	4.47	94.52

Table 5. LLE Data of the *n*-Dibutyl Sulfide (1) + Octane (2) + Sulfolane (3) System (ω, %)

raffinate phase			extract phase		
x_1	x_2	x_3	x_1	x_2	x_3
T/K = 313.15					
8.70	90.98	0.32	0.35	0.10	99.55
9.10	90.43	0.47	0.42	0.15	99.44
7.91	91.54	0.54	0.36	0.17	99.47
8.03	91.39	0.58	0.28	0.18	99.54
7.65	91.75	0.60	0.34	0.18	99.48
7.51	91.88	0.60	0.31	0.19	99.50
7.18	92.21	0.61	0.30	0.19	99.51
6.44	92.95	0.61	0.26	0.19	99.55
T/K = 323.15					
6.70	92.68	0.32	0.30	0.10	99.60
7.95	91.58	0.47	0.44	0.15	99.41
7.55	91.93	0.54	0.31	0.17	99.52
7.21	92.21	0.58	0.32	0.18	99.50
7.21	92.19	0.60	0.35	0.18	99.47
7.19	92.21	0.60	0.31	0.19	99.50
6.92	92.47	0.61	0.32	0.19	99.49
6.94	92.45	0.61	0.30	0.19	99.52
T/K = 333.15					
6.78	92.91	0.32	0.63	0.10	99.27
6.83	92.70	0.47	0.34	0.15	99.51
6.25	93.21	0.54	0.33	0.17	99.50
6.70	92.72	0.58	0.34	0.18	99.48
6.57	92.84	0.60	0.36	0.18	99.46
5.70	93.70	0.60	0.31	0.19	99.50
6.02	93.37	0.61	0.32	0.19	99.49
5.87	93.52	0.61	0.25	0.19	99.56

The aim is to produce low-sulfur gasoline. The concentration of sulfur components in the FCC gasoline is about (500 to 1000) ppm; therefore, these systems in the paper are studied in a very limited range of compositions, and the full phase behavior will be investigated in the future.

Experimental Section

Chemicals. Octane (AR) was supplied by Tianjin Guangfu Fine Chemical Research Institute. *n*-Butyl mercaptan and *n*-dibutyl sulfide (AR) were supplied by Shijiazhuang Dongfeng Chemicals Ltd. Co. Thiophene (AR) was purchased from J&K Chemical Ltd. Octane and sulfides, thiophene, *n*-butyl mercaptan, and *n*-dibutyl sulfide were used without further purification. Experimental solvents, dimethyl sulfoxide, sulfolane, and tetraethylene glycol, also supplied by Tianjin Guangfu Fine Chemical Research Institute, were purified and dehydrated using 3A activated molecular sieves. The purities of the experimental

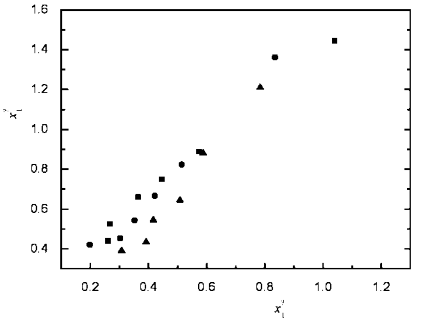

Figure 1. Distribution curves of the thiophene (1) + octane (2) + dimethyl sulfoxide (3) system.

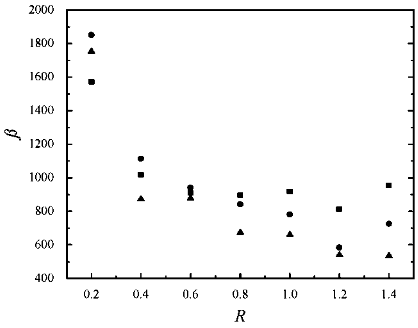

Figure 2. Selectivity coefficients of the thiophene (1) + octane (2) + dimethyl sulfoxide (3) system.

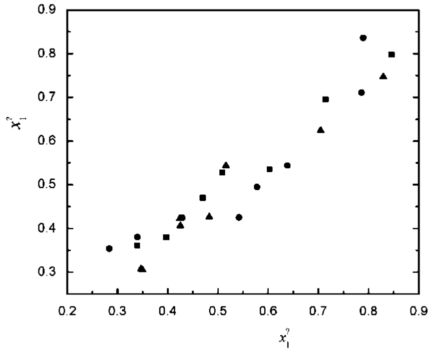

Figure 3. Distribution curves of the thiophene (1) + octane (2) + sulfolane (3) system.

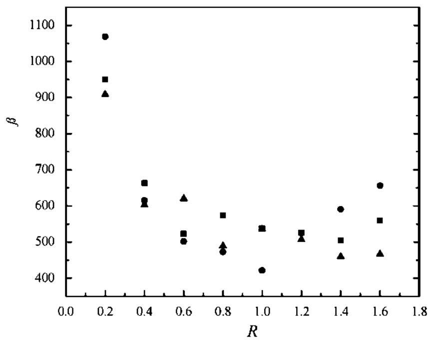

Figure 4. Selectivity coefficients of the thiophene (1) + octane (2) + sulfolane (3) system.

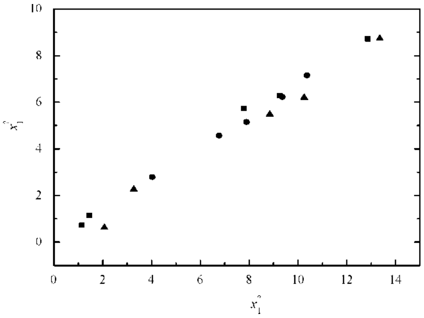

Figure 5. Distribution curves of the thiophene (1) + octane (2) + tetraethylene glycol (3) system.

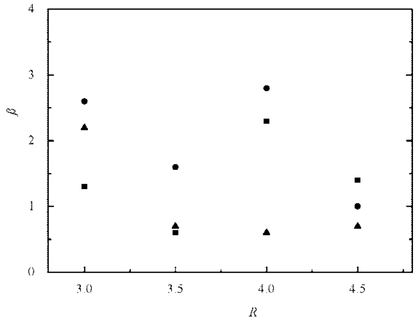

Figure 6. Selectivity coefficients of the thiophene (1) + octane (2) + tetraethylene glycol (3) system.

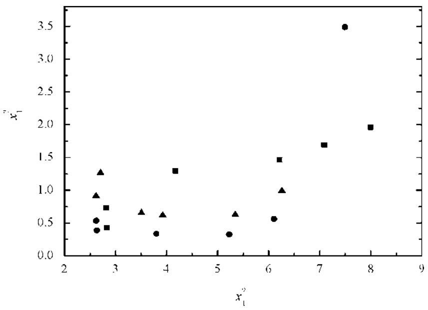

Figure 7. Distribution curves of the *n*-butyl mercaptan (1) + octane (2) + sulfolane (3) system.

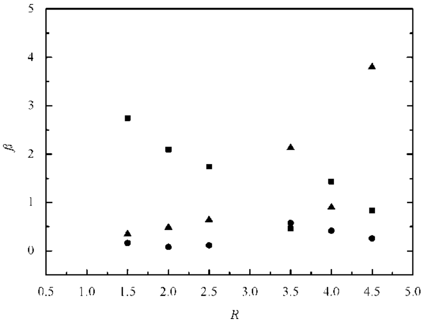

Figure 8. Selectivity coefficients of the *n*-butyl mercaptan (1) + octane (2) + sulfolane (3) system.

solvents were higher than 99.5 wt % as checked by gas chromatography (SP3420, Beijing Analysis Instrument Corp., FID). The GC analysis conditions are: these components were obtained on a 50 m long AT.OV-1 column (0.32 mm in diameter and 0.5 μm film thickness). The column temperature was 583.15 K; the injector temperature was 593.15 K; and the detector temperature was 653.15 K. Hydrogen was used as the carrier gas at 30 $\text{mL} \cdot \text{min}^{-1}$, and the volume of the injected liquid sample was 1 μL.

Equilibria Measurements. LLE measurements of the five ternary systems were carried out at three different temperatures (313.15 K, 323.15 K, and 333.15 K, respectively) under atmospheric pressure. Liquid mixtures with known compositions in mass percentage were prepared and introduced into a glass equilibria cell with a water jacket to maintain isothermal conditions.[8] The volume of the cell was about 60 mL and was almost completely filled. The mixture was vigorously agitated

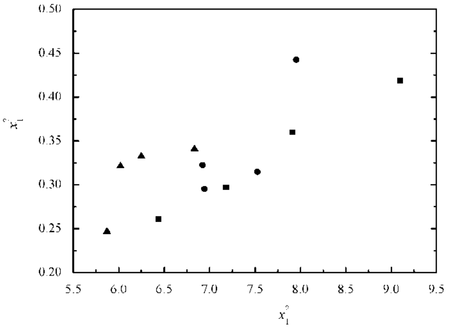

Figure 9. Distribution curves of the *n*-dibutyl sulfide (1) + octane (2) + sulfolane (3) system.

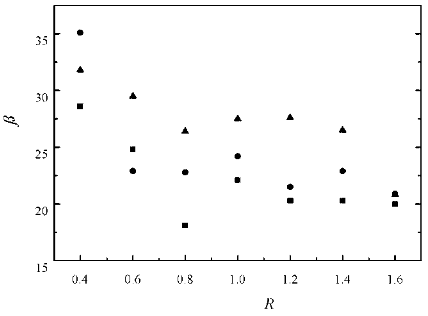

Figure 10. Selectivity coefficients of the *n*-dibutyl sulfide (1) + octane (2) + sulfolane (3) system.

by a magnetic stirrer. After several initial tries and taking samples at different time intervals, it was found that further increases in the agitation time (minimum time 2 h) and the settling time (minimum time 3 h) had no significant effect on the equilibria phase compositions. Therefore, the mixture was stirred for at least 2 h and then left to settle for 3 h for phase separation.

The cell's temperature was regulated by circulating water from a thermostatic bath (CS501, from Shanghai precision science instrument Co., Ltd.), which was equipped with a temperature controller. It is capable of maintaining the temperature fluctuation within ± 0.1 K, using a high precision digital thermometer. During the experiments, the actual fluctuation of the temperature was within ± 0.05 K.

At the end of the settling period, six to eight samples were carefully taken from the raffinate and the extract phases, respectively, and analyzed by gas chromatography (SP3420, Beijing Analysis Instrument Corp., FID). The compositions were calculated to be accurate within ± 0.01 in the mass percentage. Good separation of these components was obtained on a 50 m long AT.OV-1 column (0.32 mm in diameter and 0.5 μm film thickness) and used with a programmed temperature analysis. First, the column temperature was increased from (353.15 to 553.15) K at an increment rate of 25 $\text{K} \cdot \text{min}^{-1}$ and maintained at 553.15 K for 1 min. Then, it was further increased to 583.15 K at an increment rate of 10 $\text{K} \cdot \text{min}^{-1}$ and maintained at 583.15 K for 10 min. The injector temperature was 593.15 K, and the detector temperature was 653.15 K. Hydrogen was used as the carrier gas at 30 $\text{mL} \cdot \text{min}^{-1}$, and the volume of the injected liquid sample was 1 μL.

Table 6. Correlation Results of NRTL Model Parameters of the Thiophene (1) + Octane (2) + Dimethyl Sulfoxide (3) System

	model parameters						
T/K	Δg_{12}	Δg_{13}	Δg_{21}	Δg_{23}	Δg_{31}	Δg_{32}	*F*
313.15	−9434.7	−1395137.5	2160.9	−2160.9	−42822.3	8078.5	0.2777
323.15	−9881.0	−1146509.2	2287.2	−5932.7	−45660.5	8337.5	0.2698
333.15	−11720.7	−1181988.3	4184.4	−8006.4	−57415.6	8975.0	0.2138

Table 7. Correlation Results of UNIQUAC Model Parameters of the Thiophene (1) + Octane (2) + Dimethyl Sulfoxide (3) System

	model parameters						
T/K	Δu_{12}	Δu_{13}	Δu_{21}	Δu_{23}	Δu_{31}	Δu_{32}	*F*
313.15	23979.39	−10861.69	16603.04	23979.39	23979.39	977.80	1.4778
323.15	22882.88	−11396.61	24745.14	24745.14	24745.14	1008.63	1.4071
333.15	−10346.62	−10827.80	25510.88	25510.88	25510.88	637.87	4.4596

Table 8. Correlation Results of NRTL Model Parameters of the Thiophene (1) + Octane (2) + Sulfolane (3) System

	model parameters						
T/K	Δg_{12}	Δg_{13}	Δg_{21}	Δg_{23}	Δg_{31}	Δg_{32}	*F*
313.15	3122.4	−18365.8	−49495.7	6737.9	−851.1	2188.5	0.1472
323.15	3864.2	−19163.7	−48672.8	7004.1	−1254.1	2045.6	0.1433
333.15	3986.6	−19756.8	−50245.4	7171.6	−1607.6	2315.3	0.1475

Table 9. Correlation Results of UNIQUAC Model Parameters of the Thiophene (1) + Octane (2) + Sulfolane (3) System

	model parameters						
T/K	Δu_{12}	Δu_{13}	Δu_{21}	Δu_{23}	Δu_{31}	Δu_{32}	*F*
313.15	23979.39	23979.39	−5676.37	2811.78	−4410.43	1203.75	0.0389
323.15	24745.14	24745.14	−8452.56	2900.78	−6675.70	1300.41	0.0841
333.15	−2178.21	9874.07	25510.88	3380.39	25510.88	1708.77	0.3092

Table 10. Correlation Results of NRTL Model Parameters of the Thiophene (1) +Octane (2) + Tetraethylene Glycol (3) System

	model parameters						
T/K	Δg_{12}	Δg_{13}	Δg_{21}	Δg_{23}	Δg_{31}	Δg_{32}	*F*
313.15	3361.16	−17534.77	−2556.41	6141.73	8565.09	−5169.31	0.0530
323.15	9335.64	9746.43	1978.46	−4186.64	−29650.62	7375.18	0.2154
333.15	8464.26	6358.37	−18970.42	3159.52	1497.64	2331.63	5.9683×10^{-5}

Table 11. Correlation Results of UNIQUAC Model Parameters of the Thiophene (1) + Octane (2) + Tetraethylene Glycol (3) System

	model parameters						
T/K	Δu_{12}	Δu_{13}	Δu_{21}	Δu_{23}	Δu_{31}	Δu_{32}	F
313.15	23979.39	23979.39	−2046.14	−1299.84	−1045.38	3165.13	0.1290
323.15	21020.62	24745.14	11487.84	−702.61	8367.67	2808.27	0.9761
333.15	3910.46	755.04	6269.09	12.21	7733.24	1031.79	$1.6746 \cdot 10^{-4}$

Table 12. Correlation Results of NRTL Model Parameters of the *n*-Butyl Mercaptan (1) + Octane (2) + Sulfolane (3) System

	model parameters						
T/K	Δg_{12}	Δg_{13}	Δg_{21}	Δg_{23}	Δg_{31}	Δg_{32}	F
313.15	107546.32	941.44	28759.10	−4215.11	−839.12	−795.12	0.0149
323.15	−11702.86	−8023.20	875.59	−5456.36	−14992.96	48.63	0.0131
333.15	−1649.14	−4046.41	−2082.90	−1823.09	−3544.80	−3694.65	0.0087

Table 13. Correlation Results of UNIQUAC Model Parameters of the *n*-Butyl Mercaptan (1) + Octane (2) + Sulfolane (3) System

	model parameters						
T/K	Δu_{12}	Δu_{13}	Δu_{21}	Δu_{23}	Δu_{31}	Δu_{32}	F
313.15	23979.39	23979.39	954.03	2320.67	−2853.67	−177.12	0.2586
323.15	−1242.52	−1561.67	11838.32	822.80	7246.24	1258.45	0.0113
333.15	25510.88	4291.22	−5396.87	2954.90	−1252.92	−604.52	0.0091

Table 14. Correlation Results of NRTL Model Parameters of the *n*-Dibutyl Sulfide (1) + Octane (2) + Sulfolane (3) System

	model parameters						
T/K	Δg_{12}	Δg_{13}	Δg_{21}	Δg_{23}	Δg_{31}	Δg_{32}	F
313.15	−1007.4	−9560.6	−16549.7	8458.7	4237.8	−6048.6	0.1842
323.15	71.0	−32701.2	−57709.5	8592.5	5017.6	−5239.6	0.1668
333.15	−22837.3	−1006.0	−67098.3	8987.7	5717.8	−5882.9	0.1525

Table 15. Correlation Results of UNIQUAC Model Parameters of the *n*-Dibutyl Sulfide (1) + Octane (2) + Sulfolane (3) System

	model parameters						
T/K	Δu_{12}	Δu_{13}	Δu_{21}	Δu_{23}	Δu_{31}	Δu_{32}	F
313.15	−3169.93	2694.85	23979.39	16603.04	−686.48	1174.56	0.2305
323.15	−2599.50	313.09	633.31	4239.40	−1461.10	1387.69	0.2671
333.15	25510.88	25510.88	25510.88	3391.67	6430.85	1846.63	0.2716

Table 16. Average Absolute Deviation of Calculated and Experimental Data of the Thiophene (1) + Octane (2) + Dimethyl Sulfoxide (3) System Using the NRTL Model

	average deviation of composition					
T/K	Δx_1^{I}	Δx_2^{I}	Δx_3^{I}	Δx_1^{II}	Δx_2^{II}	Δx_3^{II}
313.15	0.0046	0.2451	$8.9513 \cdot 10^{-4}$	0.0072	0.0981	0.1905
323.15	0.0039	0.2873	$8.6819 \cdot 10^{-4}$	0.0053	0.1135	0.1791
333.15	0.0036	0.2041	$9.3005 \cdot 10^{-4}$	0.0064	$7.7136 \cdot 10^{-4}$	0.2116
Average	0.0040	0.2455	$8.9779 \cdot 10^{-4}$	0.0063	0.0708	0.1937

Table 17. Average Absolute Deviation of Calculated Results and Experimental Data of the Thiophene (1) + Octane (2) + Dimethyl Sulfoxide (3) System Using the UNIQUAC Model

	average deviation of composition					
T/K	Δx_1^{I}	Δx_2^{I}	Δx_3^{I}	Δx_1^{II}	Δx_2^{II}	Δx_3^{II}
313.15	0.0022	0.0048	0.0022	$2.5000 \cdot 10^{-4}$	0.0018	$2.6926 \cdot 10^{-4}$
323.15	0.0020	0.0046	0.0021	$2.5000 \cdot 10^{-4}$	0.0018	$2.6926 \cdot 10^{-4}$
333.15	0.0193	0.0274	0.0129	$9.2534 \cdot 10^{-4}$	0.0018	$1.9365 \cdot 10^{-4}$
Average	0.0078	0.0123	0.0057	$4.7511 \cdot 10^{-4}$	0.0018	$2.4406 \cdot 10^{-4}$

Table 18. Average Absolute Deviation of Calculated Results and Experimental Data of the Thiophene (1) + Octane (2) + Sulfolane (3) System Using the NRTL Model

	average deviation of composition					
T/K	Δx_1^{I}	Δx_2^{I}	Δx_3^{I}	Δx_1^{II}	Δx_2^{II}	Δx_3^{II}
313.15	0.0023	0.1887	0.0104	0.0058	$2.7613 \cdot 10^{-4}$	0.0970
323.15	0.0023	0.1867	0.0129	0.0063	$2.8284 \cdot 10^{-4}$	0.1509
333.15	0.0024	0.1872	0.0120	0.0073	$2.7613 \cdot 10^{-4}$	0.0990
Average	0.0023	0.1875	0.0118	0.0065	$2.7837 \cdot 10^{-4}$	0.1156

Experimental Results and Discussion

Experimental Data. The liquid−liquid equilibria (LLE) data of the five ternary systems of sulfide (1) + octane (2) + solvent (3) at 313.15 K, 323.15 K, and 333.15 K, respectively, under atmospheric pressure are presented in Tables 1 to 5. x_i ($i = 1, 2, 3$) is the concentration of the ith component expressed in mass percentage, ω (%).

These ternary systems are listed as follows:

(1) thiophene + octane + dimethyl sulfoxide system, (2) thiophene + octane + sulfolane system, (3) thiophene + octane + tetraethylene glycol system, (4) *n*-butyl mercaptan + octane + sulfolane system, (5) *n*-dibutyl sulfide + octane + sulfolane system.

Data Correlation. The effectiveness of a solvent can be expressed by the selectivity, β, and the distribution coefficients, K_i.[9] The selectivity coefficient β can be calculated by eq 1, and the distribution coefficients K_i can be calculated by eq 2.

$$\beta = \frac{K_1}{K_2} \tag{1}$$

$$K_i = \frac{x_i^{\Pi}}{x_i^{\mathrm{I}}} \tag{2}$$

where K_i is the distribution coefficient of the ith component and the superscripts I and II represent raffinate and extract, respectively.

On the basis of the experimental data, the distribution coefficients of sulfide and octane and the selectivity coefficients of solvents at different temperatures were calculated. The

Table 19. Average Absolute Deviation of Calculated Results and Experimental Data of the Thiophene (1) + Octane (2) + Sulfolane (3) System Using the UNIQUAC Model

	average deviation of composition					
T/K	Δx_1^{I}	Δx_2^{I}	Δx_3^{I}	Δx_1^{II}	Δx_2^{II}	Δx_3^{II}
313.15	1.0521	0.5487	0.0598	0.0029	0.0017	0.1079
323.15	1.1154	0.5915	0.0530	$8.4113 \cdot 10^{-4}$	0.0017	0.0742
333.15	0.0052	0.0028	0.0019	$5.3968 \cdot 10^{-4}$	0.0017	0.1458
Average	0.7242	0.3810	0.0382	0.0014	0.0017	0.1093

Table 20. Average Absolute Deviation of Calculated Results and Experimental Data of the Thiophene (1) + Octane (2) + Tetraethylene Glycol (3) System Using the NRTL Model

	average deviation of composition					
T/K	Δx_1^{I}	Δx_2^{I}	Δx_3^{I}	Δx_1^{II}	Δx_2^{II}	Δx_3^{II}
313.15	0.2244	0.2725	0.2781	0.0558	0.1675	0.1889
323.15	0.0200	0.1064	0.1147	0.0190	0.1282	0.1341
333.15	0.0205	0.1363	0.0720	0.0193	0.1150	0.1316
Average	0.0883	0.1717	0.1549	0.0314	0.1369	0.1515

Table 21. Average Absolute Deviation of Calculated Results and Experimental Data of the Thiophene (1) + Octane (2) + Tetraethylene Glycol (3) System Using the UNIQUAC Model

	average deviation of composition					
T/K	Δx_1^{I}	Δx_2^{I}	Δx_3^{I}	Δx_1^{II}	Δx_2^{II}	Δx_3^{II}
313.15	0.5076	0.0224	0.2609	0.0123	0.831	0.8195
323.15	0.8508	0.598	0.8954	0.013	0.6999	0.6905
333.15	0.3762	0.6086	0.3991	0.0089	0.828	0.8192
Average	0.5782	0.4097	0.5185	0.0114	0.7863	0.7764

Table 22. Average Absolute Deviation of Calculated Results and Experimental Data of the *n*-Butyl Mercaptan (1) + Octane (2) + Sulfolane (3) System Using the NRTL Model

	average deviation of composition					
T/K	Δx_1^{I}	Δx_2^{I}	Δx_3^{I}	Δx_1^{II}	Δx_2^{II}	Δx_3^{II}
313.15	0.0150	0.1049	0.0995	0.0093	0.0942	0.0974
323.15	0.0535	0.1830	0.1847	0.0213	0.2458	0.1256
333.15	0.0450	0.2867	0.2904	0.0061	0.1183	0.1187
Average	0.0378	0.1915	0.1915	0.0122	0.1528	0.1139

Table 23. Average Absolute Deviation of Calculated Results and Experimental Data of the *n*-Butyl Mercaptan (1) + Octane (2) + Sulfolane (3) System Using the UNIQUAC Model

	average deviation of composition					
T/K	Δx_1^{I}	Δx_2^{I}	Δx_3^{I}	Δx_1^{II}	Δx_2^{II}	Δx_3^{II}
313.15	0.0424	0.0439	0.2336	0.0123	0.7506	0.7395
323.15	10.7451	0.6796	9.9858	0.0130	0.6977	0.6896
333.15	0.8445	0.5858	0.2901	0.0089	0.7309	0.7223
Average	3.8773	0.4364	3.5032	0.0114	0.7264	0.7171

Table 24. Average Absolute Deviation of Calculated Results and Experimental Data of the *n*-Dibutyl Sulfide (1) + Octane (2) + Sulfolane (3) System Using the NRTL Model

	average deviation of composition					
T/K	Δx_1^{I}	Δx_2^{I}	Δx_3^{I}	Δx_1^{II}	Δx_2^{II}	Δx_3^{II}
313.15	0.0129	0.1554	$6.7268 \cdot 10^{-4}$	$5.6899 \cdot 10^{-4}$	$2.7613 \cdot 10^{-4}$	0.1166
323.15	0.0359	0.1587	0.0027	0.0126	$3.4460 \cdot 10^{-4}$	0.0799
333.15	0.0077	0.1759	0.0018	0.0024	$3.0208 \cdot 10^{-4}$	0.0467
Average	0.0188	0.1633	0.0017	0.0052	$3.0760 \cdot 10^{-4}$	0.0811

Table 25. Average Absolute Deviation of Calculated Results and Experimental Data of the *n*-Dibutyl Sulfide (1) + Octane (2) + Sulfolane (3) System Using the UNIQUAC Model

	average deviation of composition					
T/K	Δx_1^{I}	Δx_2^{I}	Δx_3^{I}	Δx_1^{II}	Δx_2^{II}	Δx_3^{II}
313.15	0.0938	0.2131	0.4558	0.0033	0.0017	0.2128
323.15	0.0143	0.0429	0.0691	0.0033	0.0017	0.1439
333.15	0.2644	0.3738	0.1545	0.2663	0.0046	0.3428
Average	0.1242	0.2099	0.2265	0.0910	0.0027	0.2332

calculated distribution coefficients and selectivity coefficient curves are shown in Figures 1 to 10. The horizontal axis of Figures 2, 4, 6, 8, and 10, R, is the ratio of solvent to oil.

In Figures 1 to 10: □, $T = 313.15$ K; ●, $T = 323.15$ K; ▲, $T = 333.15$ K.

Thermodynamic Modeling

There are several thermodynamic models for the activity coefficient. Some are completely empirical, such as those by Margules and van Laar cited by Prausnitz et al.[10] Others are based on the local composition concept, such as Wilson[11] and NRTL;[5] others, such as UNIQUAC,[6] have a more theoretical basis; and some use the group contribution concept, as ASOG[12] and UNIFAC.[13] All the equations mentioned are semiempirical, regardless of the basis of their development.

The NRTL and UNIQUAC models were used to correlate the experimental data of the ternary systems discussed here. During fitting, the UNIQUAC interaction parameters and the structural parameters were used for the pure components. The nonrandomness parameter α_{ji} of the NRTL model was set to 0.3.[10,14] The model parameters were determined by minimizing an objective function on mass percentage deviation using the simplex optimization method.[15] The rule of thermodynamic equilibria was used to deal with the multiroots problem in the correlating process. The objective function[16] (F) is given as

$$F = \min \sum_{i=1}^{N_{\mathrm{P}}} \sum_{j=1}^{N_{\mathrm{C}}} \left| \frac{\gamma_{ij}^{\mathrm{I}}}{\gamma_{ij}^{\mathrm{II}}} x_{ij}^{\mathrm{I}} - x_{ij}^{\mathrm{II}} \right|^2 \tag{3}$$

where N_{p} is the number of experimental points; N_{c} is the number of experimental components; and γ_i is the activity coefficient.

Thermodynamic Modeling Results and Discussion

Correlating Results of Model Parameters. The interaction parameters for the NTRL and UNIQUAC models are shown in Tables 6 to 15. g is the interaction parameter for NRTL in J·mol^{-1}, u is the parameter for UNIQUAC in J·mol^{-1}.

Correlation Results. An attempt was made to examine the correlating capability of the NRTL and UNIQUAC models with the model parameters obtained above. The average absolute deviations[15] between the calculated data and experimental data can be obtained using eqs 4 and 5, respectively

$$\Delta x_i^{\mathrm{I}} = \sqrt{\sum_{k=1}^{N_{\mathrm{P}}} (x_{ki}^{\mathrm{I}} - x_{ki}^{*\mathrm{I}})^2 / N_{\mathrm{P}}} \tag{4}$$

$$\Delta x_i^{\mathrm{II}} = \sqrt{\sum_{k=1}^{N_{\mathrm{P}}} (x_{ki}^{\mathrm{II}} - x_{ki}^{*\mathrm{II}})^2 / N_{\mathrm{P}}} \tag{5}$$

where x^* is the calculated composition of the liquid phase, %

The average absolute deviations obtained by using the NRTL and UNIQUAC models are given in Tables 16 to 25, respectively.

The results showed that the NRTL and UNIQUAC models were capable of reproducing the LLE data of these systems, and there is good agreement between experimental and predicted LLE data.

Conclusions

Liquid−liquid equilibria (LLE) data of the five ternary systems of sulfide + octane + solvent at 313.15 K, 323.15 K, and 333.15 K, respectively, under atmospheric pressure were measured using a glass equilibria cell with the standard curve method. The results showed that sulfolane was more efficient than tetraethylene glycol for FCC (Fluid Catalytic Cracking) gasoline extractive distillation deep desulfurization.

The NRTL and UNIQUAC models were used to correlate and calculate LLE data of these ternary systems. The results for both models were considered very satisfactory. New model parameters for both models were estimated using the simplex minimization method and a composition-based objective function. Using the NRTL model, the average absolute deviation of mass percentage for thiophene is about 0.0040; for *n*-butyl mercaptan, it is about 0.0378; and for *n*-dibutyl sulfide it is about 0.0188, for systems using sulfolane as solvent. The NRTL model performed better than the UNIQUAC model and was more suitable for the predication of the LLE data for the five ternary systems studied.

The liquid−liquid equilibria (LLE) of other systems, including (1) the *n*-butyl mercaptan + octane + dimethyl sulfoxide system, (2) the *n*-butyl mercaptan + octane + tetraethylene glycol system, (3) the *n*-dibutyl sulfide + octane + dimethyl sulfoxide system, and (4) the *n*-dibutyl sulfide + octane + tetraethylene glycol system for FCC gasoline extractive distillation deep desulfurization, will be studied for building up to a systematic study.

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Received for review December 7, 2007. Accepted August 13, 2008. Financial support for this work was provided by the Natural Science Foundation of Tianjin, China (No. 043613211).

JE800340V