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Liquid−Liquid Equilibria of Ternary and Quaternary Systems Including Cyclohexane, 1-Heptene, Benzene, Toluene, and Sulfolane at 298.15 K

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Liquid−liquid equilibria (LLE) were measured at 298.15 K for six ternary systems—heptane + toluene + sulfolane, heptane + *m*-xylene + sulfolane, cyclohexane + benzene + sulfolane, cyclohexane + toluene + sulfolane, 1-heptene + benzene + sulfolane, and 1-heptene + toluene + sulfolane—and for two quaternary systems—cyclohexane + 1-heptene + benzene + sulfolane and cyclohexane + 1-heptene + toluene + sulfolane. LLE data of two systems including heptane are compared with the results of Cassell et al. (*J. Chem. Eng. Data* **1989**, *34*, 434−438). The equilibrium data of four ternary systems including cyclohexane and 1-heptene were used to regress interaction parameters in a nonrandom two-liquid (NRTL) model. These parameters were used to predict equilibrium data of the quaternary systems. The predicted data are in good agreement with experimental ones.

Introduction

Sulfolane (tetramethylene sulfone) has been widely used as a solvent in the recovery of high-purity aromatics, such as benzene, toluene, and xylenes, from refinery process streams. Because of the important industrial application of sulfolane, many investigators have studied the liquid−liquid-phase equilibria for ternary systems containing sulfolane and aromatic hydrocarbons (De Fré and Verhoeye, 1976; Hassan et al., 1988; Cassell et al., 1989a,b; Masohan et al., 1990; Mondragón-Garduño et al., 1991; Letcher et al., 1996; Lee and Kim, 1998a,b; Kao and Lin, 1999a,b). Almost all of the literature data concern ternary systems. Only one article by Naithani et al. (1992) deals with quaternary liquid−liquid equilibrium (LLE) data, which includes two extraction solvents (benzene + heptane + sulfolane + triethylene glycol and 1-methylnaphthalene + dodecane + sulfolane + triethylene glycol). In most of the above literature, the well-known nonrandom two-liquid (NRTL; Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) models were used for the correlation and prediction of LLE.

Experimental data for LLE of systems including 1-heptene and cyclohexane are scarce. The purpose of the present study was to measure LLE data for systems heptane + toluene + sulfolane, heptane + *m*-xylene + sulfolane, cyclohexane + benzene + sulfolane, cyclohexane + toluene + sulfolane, 1-heptene + benzene + sulfolane, and 1-heptene + toluene + sulfolane and to correlate these data with the NRTL equation. Further, the quaternary systems cyclohexane + 1-heptene + benzene + sulfolane and cyclohexane + 1-heptene + toluene + sulfolane were measured, and results were compared with the values predicted using the NRTL equation with parameters regressed from the ternary systems.

Experimental Section

Materials. Sulfolane, imported by China Medicine Co., was purified by distillation. The fraction distilling between 383 K and 393 K at 0.67 kPa was collected for use. The purified sulfolane was transparent without smell and color.

Table 1. LLE Data of Heptane + Toluene + Sulfolane and Heptane + *m*-Xylene + Sulfolane at 298.15 K

heptane-rich phase		sulfolane-rich phase	
x_1	x_2	x_1	x_2
Heptane (1) + Toluene (2) + Sulfolane (3)			
0.908	0.083	0.013	0.034
0.827	0.160	0.013	0.065
0.739	0.246	0.016	0.106
0.663	0.320	0.019	0.140
0.595	0.390	0.020	0.175
0.525	0.450	0.023	0.216
0.459	0.505	0.026	0.259
0.399	0.555	0.030	0.300
0.317	0.610	0.039	0.365
0.239	0.629	0.053	0.438
Heptane (1) + *m*-Xylene (2) + Sulfolane (3)			
0.904	0.094	0.013	0.026
0.836	0.156	0.013	0.039
0.747	0.244	0.014	0.066
0.680	0.311	0.015	0.088
0.596	0.390	0.016	0.116
0.529	0.457	0.018	0.137
0.459	0.512	0.019	0.160
0.396	0.564	0.017	0.247
0.324	0.618	0.027	0.236
0.238	0.664	0.026	0.305

Other chemicals were produced by Beijing Chemical Co. and were purified also by distillation. All of the chemicals used were analyzed by gas chromatography to be at least 99.5% in mass.

Procedures. The measurement was carried out in the two-phase region. The sample mixture in a sealed tube was shaken more than 3 h at 298.15 ± 0.1 K to reach complete mixing and then separated by centrifugation. Approximately a 1 μL sample of liquid taken from each phase was injected into the 102G chromatograph (Shanghai Analysis Apparatus Co.). A C-RIB integrator (Shimadzu) was used to obtain the chromatographic areas for all components.

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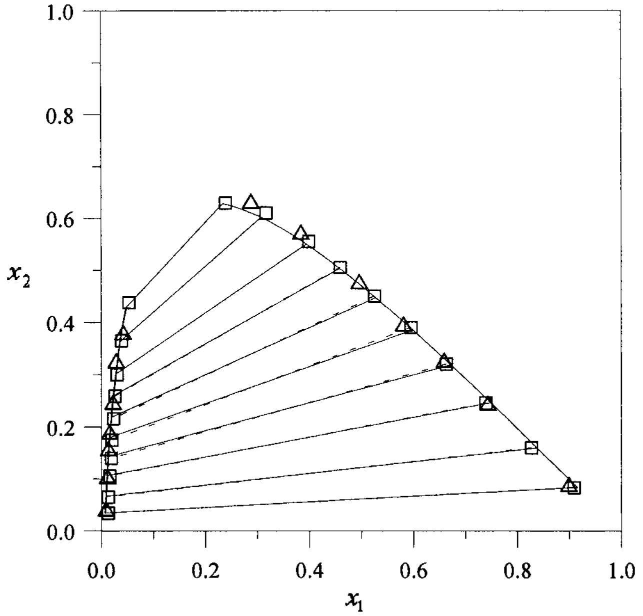

Figure 1. LLE of heptane + toluene + sulfolane with RMSD = 0.0060: - -□, experimental data of this work; —, results predicted by NRTL with parameters in Table 4; △, experimental data by Cassell et al. (1989b).

Table 2. LLE Data of Cyclohexane + Benzene + Sulfolane and Cyclohexane + Toluene + Sulfolane at 298.15 K

cyclohexane-rich phase		sulfolane-rich phase	
x_1	x_2	x_1	x_2
Cyclohexane (1) + Benzene (2) + Sulfolane (3)			
0.963	0.036	0.027	0.015
0.856	0.133	0.037	0.069
0.829	0.158	0.038	0.086
0.764	0.217	0.039	0.118
0.701	0.268	0.050	0.156
0.649	0.310	0.055	0.186
0.586	0.356	0.065	0.225
0.530	0.394	0.078	0.263
0.458	0.433	0.099	0.314
0.387	0.457	0.130	0.361
Cyclohexane (1) + Toluene (2) + Sulfolane (3)			
0.917	0.073	0.037	0.024
0.883	0.100	0.038	0.034
0.840	0.140	0.030	0.052
0.759	0.213	0.037	0.075
0.700	0.265	0.041	0.097
0.632	0.330	0.036	0.123
0.570	0.378	0.038	0.151
0.513	0.430	0.043	0.177
0.456	0.470	0.050	0.211
0.316	0.537	0.073	0.301

The gas chromatography response factors for each of the components were obtained by using a standard mixture sample of pure components. The composition of this standard sample was obtained through weighing with an electronic balance and should be in the one-phase region to ensure that there is no phase split at the time of sample injection to the gas chromatography. One component in the mixture was set as the standard, and its response factor was given as 1.0. Then response factors of other components were calculated using the renormalization method; i.e., the summation of mole factions of all components should be 1. The repeat error of measured response factors was smaller than 0.25%, so a concentration of LLE should have an error of less than 0.5%. For the mole fraction x (0.0~1.0), its absolute error should be less than 0.005.

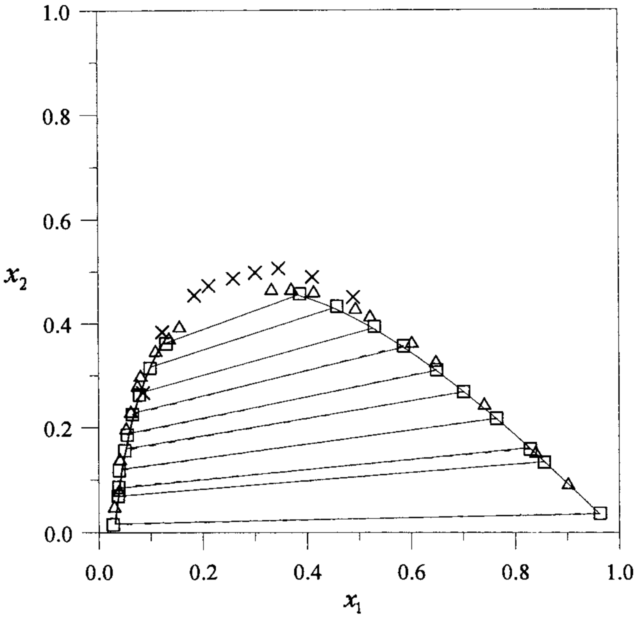

Figure 2. LLE of cyclohexane (1) + benzene (2) + sulfolane (3) at 298.15 K with RMSD = 0.0038: - -□, experimental data of this work; —, results predicted by NRTL with parameters in Table 5; △, literature data of De Fré and Verhoeye (1976); ×, data at 303.15 K of Karvo and Nissema (1979).

Table 3. LLE Data of 1-Heptene + Benzene + Sulfolane and 1-Heptene + Toluene + Sulfolane at 298.15 K

1-heptene-rich phase		sulfolane-rich phase	
x_1	x_2	x_1	x_2
1-Heptene (1) + Benzene (2) + Sulfolane (3)			
0.934	0.064	0.029	0.028
0.887	0.110	0.045	0.052
0.819	0.171	0.035	0.101
0.759	0.232	0.038	0.121
0.711	0.273	0.044	0.141
0.652	0.322	0.045	0.181
0.591	0.363	0.053	0.218
0.526	0.407	0.069	0.271
0.433	0.445	0.097	0.315
0.321	0.461	0.157	0.388
1-Heptene (1) + Toluene (2) + Sulfolane (3)			
0.917	0.073	0.028	0.023
0.793	0.196	0.029	0.063
0.715	0.258	0.033	0.090
0.584	0.367	0.038	0.144
0.517	0.427	0.039	0.176
0.458	0.472	0.045	0.215
0.361	0.519	0.055	0.273
0.321	0.535	0.068	0.303
0.256	0.527	0.080	0.323
0.244	0.514	0.101	0.372

When LLE data were measured, the conditions of the gas chromatograph, such as the carrier gas flow rate, injection room temperature, column head pressure, column room temperature, detection room temperature, etc., should be the same as those when the response factors were measured. Because of this requirement, the response factors were measured before a LLE measurement of every system in order to ensure measurement accuracy.

Results and Discussion

Experimental Data. The experimental tie-line data for systems heptane + toluene + sulfolane and heptane + *m*-xylene + sulfolane measured were measured, and the results are shown in Table 1. These two systems will be compared with the results of Cassell et al. (1989b).

Table 4. NRTL Parameters for Heptane + Toluene + Sulfolane and Heptane + Xylene + Sulfolane Given by Cassell et al. (1989b)

$(g_{ij} - g_{jj})/R$, K	$j = 1$	$j = 2$	$j = 3$
Heptane (1) + Toluene (2) + Sulfolane (3)			
$i = 1$	0.0000	0.1033×10^3	0.1934×10^4
$i = 2$	-0.3194×10^2	0.0000	0.3801×10^3
$i = 3$	0.1033×10^4	0.6746×10^2	0.0000
Heptane (1) + *m*-Xylene (2) + Sulfolane (3)			
$i = 1$	0.0000	0.3434×10^3	0.1622×10^4
$i = 2$	-0.3081×10^3	0.0000	0.6383×10^3
$i = 3$	0.9661×10^3	0.1039×10^2	0.0000

Table 5. NRTL Parameters Correlated for Each Ternary System at 298.15 K

$(g_{ij} - g_{jj})/R$, K	$j = 1$	$j = 2$	$j = 3$
Cyclohexane (1) + Benzene (2) + Sulfolane (3)			
$i = 1$	0.0000	-0.1663×10^3	0.1449×10^4
$i = 2$	0.2221×10^3	0.0000	0.2461×10^2
$i = 3$	0.5627×10^3	0.2694×10^3	0.0000
Cyclohexane (1) + Toluene (2) + Sulfolane (3)			
$i = 1$	0.0000	-0.2634×10^3	0.1449×10^4
$i = 2$	0.2775×10^3	0.0000	0.1600×10^3
$i = 3$	0.5627×10^3	0.2540×10^3	0.0000
1-Heptene (1) + Benzene (2) + Sulfolane (3)			
$i = 1$	0.0000	0.9592×10^2	0.2183×10^4
$i = 2$	-0.9961×10^2	0.0000	0.2461×10^2
$i = 3$	0.6874×10^3	0.2694×10^3	0.0000
1-Heptene (1) + Toluene (2) + Sulfolane (3)			
$i = 1$	0.0000	0.5100×10^2	0.2183×10^4
$i = 2$	-0.9492×10^2	0.0000	0.1600×10^3
$i = 3$	0.6874×10^3	0.2540×10^3	0.0000

The experimental tie-line data for the cyclohexane + benzene + sulfolane, cyclohexane + toluene + sulfolane, 1-heptene + benzene + sulfolane, and 1-heptene + toluene + sulfolane systems are shown in Tables 2 and 3.

Data Correlation and Prediction. The thermodynamic model NRTL was used to express ternary LLE. First the calculation of equilibrium data from NRTL with parameters was carried out with the minimization of Gibbs energy as the objective function, and the equality of activity for each component in two phases was carefully confirmed. Then the parameters in NRTL were regressed with the minimization of all root-mean absolute deviation of mole fractions for three components:

$$\mathrm{RMSD} = [\sum_{i=1}^{3}\sum_{j=1}^{2}\sum_{k}^{M}|(x_{ijk}{}^{\mathrm{cal}} - x_{ijk}{}^{\mathrm{exp}})^2|/6M]^{1/2}$$

$x_{ijk}{}^{\mathrm{cal}}$ is the calculated mole fraction, $x_{ijk}{}^{\mathrm{exp}}$ is the experimental one, *i* is the number of components, *j* is the number of phases, *k* is the number of tie-line points, and *M* is the total number of LLE sets.

Table 6. LLE of Quaternary Systems at 298.15 K

hydrocarbon-rich phase								sulfolane-rich phase							
$x_1{}^{\mathrm{exp}}$	$x_1{}^{\mathrm{cal}}$	$x_2{}^{\mathrm{exp}}$	$x_2{}^{\mathrm{cal}}$	$x_3{}^{\mathrm{exp}}$	$x_3{}^{\mathrm{cal}}$	$x_4{}^{\mathrm{exp}}$	$x_4{}^{\mathrm{cal}}$	$x_1{}^{\mathrm{exp}}$	$x_1{}^{\mathrm{cal}}$	$x_2{}^{\mathrm{exp}}$	$x_2{}^{\mathrm{cal}}$	$x_3{}^{\mathrm{exp}}$	$x_3{}^{\mathrm{cal}}$	$x_4{}^{\mathrm{exp}}$	$x_4{}^{\mathrm{cal}}$
Cyclohexane (1) + 1-Heptene (2) + Benzene (3) + Sulfolane (4) (RMSD = 0.0038)															
0.452	0.453	0.411	0.412	0.131	0.129	0.006	0.006	0.017	0.019	0.012	0.014	0.060	0.062	0.911	0.905
0.379	0.381	0.356	0.356	0.248	0.244	0.017	0.019	0.024	0.024	0.018	0.020	0.127	0.132	0.831	0.824
0.330	0.334	0.316	0.316	0.317	0.313	0.037	0.037	0.030	0.029	0.023	0.026	0.179	0.184	0.768	0.761
0.293	0.297	0.217	0.214	0.406	0.403	0.084	0.085	0.052	0.047	0.031	0.033	0.269	0.272	0.648	0.647
0.226	0.231	0.207	0.206	0.442	0.439	0.125	0.125	0.059	0.054	0.047	0.048	0.318	0.320	0.576	0.578
Cyclohexane (1) + 1-Heptene (2) + Toluene (3) + Sulfolane (4) (RMSD = 0.0087)															
0.434	0.437	0.410	0.411	0.149	0.147	0.007	0.005	0.013	0.016	0.007	0.012	0.039	0.043	0.941	0.929
0.352	0.351	0.351	0.348	0.280	0.282	0.017	0.018	0.017	0.017	0.013	0.015	0.099	0.096	0.871	0.871
0.228	0.229	0.235	0.233	0.462	0.463	0.075	0.075	0.029	0.023	0.025	0.022	0.216	0.209	0.730	0.746
0.183	0.182	0.170	0.166	0.529	0.520	0.118	0.132	0.036	0.030	0.029	0.027	0.284	0.282	0.651	0.661
0.179	0.180	0.173	0.168	0.513	0.520	0.135	0.132	0.038	0.030	0.029	0.027	0.300	0.282	0.633	0.661

For systems heptane + toluene + sulfolane and heptane + *m*-xylene + sulfolane, the NRTL parameters $(g_{ij} - g_{jj})/R$ with the unit, K, given by Cassell et al. (1989b) are listed in Table 4 and directly used to calculate the LLE. The calculated mole fractions are in good agreement with the experimental ones of this work (RMSDs are 0.0060 and 0.0059, respectively), although Cassell et al. (1989b) did not specify the kind of xylene. The results for heptane + toluene + sulfolane are shown in Figure 1.

For systems cyclohexane + benzene + sulfolane, cyclohexane + toluene + sulfolane, 1-heptene + benzene + sulfolane, and 1-heptene + toluene + sulfolane, the specific NRTL parameters were obtained using the Newton−Raphson iterative method to minimize the objective function. The third nonrandomness parameter, α_{ij}, was set to the value of 0.2. To ensure consistency, the parameters for the same pairs, such as cyclohexane−sulfolane, 1-heptene−sulfolane, benzene−sulfolane, and toluene−sulfolane, in different systems are kept the same.

The NRTL energy parameters of the four ternary systems correlated are listed in Table 5. Good agreement between the experimental points and the calculated ones obtained by the NRTL equation was achieved (RMSDs are 0.0038, 0.0062, 0.0067, and 0.0060 for these four systems, respectively).

The LLE results of the system cyclohexane + benzene + sulfolane are shown in Figure 2. Experimental data at 298.15 K of De Fré and Verhoeye (1976) and data at 303.15 K of Karvo and Nissema (1979) are also shown in Figure 2. The experimental data of this work are in agreement with those of De Fré and Verhoeye (1976).

Besides these four ternary systems, two quaternary systems were measured: cyclohexane + 1-heptene + benzene + sulfolane and cyclohexane + 1-heptene + toluene + sulfolane. With the NRTL parameters regressed using the LLE data of cyclohexane + benzene + sulfolane, cyclohexane + toluene + sulfolane, 1-heptene + benzene + sulfolane, and 1-heptene + toluene + sulfolane, these two quaternary systems were predicted. No more parameters are added. The experimental and predicted results for tie-line data are listed in Table 6. The parameters between cyclohexane and 1-heptene are suggested to be zero. The results show that the NRTL parameters from ternary LLE systems can be used to predict LLE of quaternary systems.

Literature Cited

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.

Cassell, G. W.; Dural, N.; Hines, A. L. Liquid−liquid equilibrium of sulfolane + benzene + pentane and sulfolane + toluene + pentane. *Ind. Eng. Chem. Res.* **1989a**, *28*, 1369−1374.

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* **1989b**, *34*, 434−438.

De Fré, R. M.; Verhoeye, L. A. Phase equilibria in systems composed of an aliphatic and an aromatic hydrocarbon and sulpholane. *J. Appl. Chem. Biotechnol.* **1976**, *26*, 469−487.

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.

Kao, C.-F.; Lin, W.-C. Liquid−liquid equilibria of alkane (C10−C14) + butylbenzene + sulfolane. *J. Chem. Eng. Data* **1999a**, *44*, 803−808.

Kao, C.-F.; Lin, W.-C. Liquid−liquid equilibria of the ternary systems dodecane + butylbenzene + sulfolane, dodecane + 1,4-diisopropylbenzene + sulfolane, and dodecane + octylbenzene + sulfolane. *J. Chem. Eng. Data* **1999b**, *44*, 338−342.

Karvo, M.; Nissema, A. Thermodynamic Properties of Binary and Ternary Mixtures Containing Sulfolane. Part II. Liquid−Liquid Equilibria in the Systems Sulfolane + Cyclohexane + Benzene/Toluene. *Finn. Chem. Lett.* **1979**, *1*, 3−6.

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.

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.

Letcher, T. M.; Redhi, G. G.; Radloff, S. E.; Domanska, U. Liquid−liquid equilibria of the ternary mixtures with sulfolane at 303.15 K. *J. Chem. Eng. Data* **1996**, *41*, 634−638.

Masohan, A.; Nanoti, S. M.; Sharma, K. G.; Puri, S. N.; Gupta, P.; Rawat, B. S. Liquid−liquid equilibrium studies on hydrocarbon (C_{10}−C_{20})−sulfolane systems. *Fluid Phase Equilib.* **1990**, *61*, 89−98.

Mondragón-Garduño, M.; Romero-Martinez, 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.

Naithani, J.; Khanna, M. K.; Nanoti, S. M.; Rawat, B. S. Quaternary liquid−liquid equilibrium studies on hydrocarbon−solvent systems. *J. Chem. Eng. Data* **1992**, *37*, 104−106.

Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.

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