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Liquid−Liquid Equilibria of Quaternary and Quinary Systems Including Sulfolane at 298.15 K

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Liquid−liquid equilibria (LLE) were measured at 298.15 K for three quaternary systems—hexane + heptane + toluene + sulfolane, heptane + octane + *m*-xylene + sulfolane, and heptane + benzene + toluene + sulfolane—and for two quinary systems—hexane + heptane + toluene + *m*-xylene + sulfolane and heptane + octane + benzene + *m*-xylene + sulfolane. The equilibrium data of these systems are compared with those predicted using the nonrandom two-liquid (NRTL) model with parameters fitted from ternary LLE data. The predicted data are in good agreement with experimental ones.

Introduction

Because sulfolane has been widely used as a solvent in the recovery of high-purity aromatics, such as benzene, toluene, and xylenes, from refinery process streams, 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, 1995, 1998; Kao and Lin, 1999a,b). Almost all of the literature data concern ternary systems. 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 liquid−liquid equilibria (LLE).

In a previous paper (Chen et al., 2000a), LLE data for ternary systems including cyclohexane, 1-heptane, benzene, toluene, and sulfolane had been shown. Further, values for the quaternary systems cyclohexane + 1-heptene + benzene + sulfolane and cyclohexane + 1-heptene + toluene + sulfolane were shown and compared with the values predicted using the NRTL equation with parameters regressed from the ternary systems.

In this paper, quaternary and quinary LLE data including sulfolane were measured and compared with values predicted using the NRTL equation with parameters regressed from ternary systems. The results show that quaternary and quinary LLE can be predicted using the NRTL equation with parameters from 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.

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 mass %.

Procedures. The measurement procedure is almost the same as that described in the previous paper (Chen et al., 2000a). For clarity, this procedure is not presented here again.

Table 1. LLE Data of Quaternary Systems Including Sulfolane at 298.15 K

hydrocarbon-rich phase			sulfolane-rich phase		
x_1	x_2	x_3	x_1	x_2	x_3
Hexane (1) + Heptane (2) + Toluene (3) + Sulfolane (4)					
0.699	0.139	0.151	0.012	0.004	0.068
0.236	0.515	0.241	0.005	0.013	0.106
0.407	0.240	0.336	0.013	0.008	0.155
0.201	0.250	0.514	0.014	0.017	0.271
0.177	0.151	0.603	0.024	0.024	0.381
Heptane (1) + Octane (2) + *m*-Xylene (3) + Sulfolane (4)					
0.442	0.380	0.168	0.007	0.003	0.058
0.305	0.363	0.313	0.007	0.004	0.087
0.331	0.197	0.433	0.012	0.005	0.136
0.136	0.251	0.579	0.006	0.008	0.191
0.158	0.052	0.688	0.018	0.005	0.316
Heptane (1) + Benzene (2) + Toluene (3) + Sulfolane (4)					
0.671	0.163	0.147	0.014	0.106	0.068
0.635	0.231	0.114	0.018	0.165	0.057
0.505	0.188	0.285	0.023	0.132	0.150
0.412	0.390	0.154	0.038	0.310	0.097
0.294	0.197	0.431	0.045	0.155	0.277

Table 2. LLE Data of Quinary Systems Including Sulfolane at 298.15 K

hydrocarbon-rich phase				sulfolane-rich phase			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
Hexane (1) + Heptane (2) + Toluene (3) + *m*-Xylene (4) + Sulfolane (5)							
0.227	0.492	0.132	0.138	0.004	0.009	0.051	0.034
0.407	0.166	0.198	0.210	0.012	0.006	0.091	0.067
0.204	0.314	0.283	0.176	0.008	0.012	0.125	0.058
0.280	0.150	0.171	0.364	0.015	0.008	0.076	0.131
0.162	0.139	0.472	0.136	0.019	0.018	0.236	0.065
Heptane (1) + Octane (2) + Benzene (3) + *m*-Xylene (4) + Sulfolane (5)							
0.276	0.475	0.162	0.084	0.004	0.004	0.094	0.019
0.451	0.240	0.174	0.126	0.008	0.003	0.099	0.032
0.232	0.355	0.247	0.150	0.007	0.009	0.163	0.041
0.272	0.191	0.202	0.302	0.011	0.006	0.130	0.094
0.156	0.148	0.498	0.119	0.030	0.023	0.406	0.067

Results and Discussion

Experimental Data. The experimental tie-line data for three quaternary systems—hexane + heptane + toluene

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Table 3. NRTL Parameters, $(g_{ij} - g_{jj})/R$ in Kelvin, Regressed from Ternary Systems at 298.15 K: 1, Hexane; 2, Heptane; 3, Octane; 4, Benzene; 5, Toluene; 6, *m*-Xylene; 7, Sulfolane

	$j = 1$	$j = 2$	$j = 3$	$j = 4$	$j = 5$	$j = 6$	$j = 7$
$i = 1$	0.0000	0.0000	0.0000	0.1523×10^1	0.3470×10^3	0.1155×10^3	0.2045×10^4
$i = 2$	0.0000	0.0000	0.0000	-0.1813×10^2	0.3598×10^3	0.1398×10^3	0.1960×10^4
$i = 3$	0.0000	0.0000	0.0000	-0.1635×10^3	0.1155×10^3	-0.3318×10^3	0.2235×10^4
$i = 4$	0.9089×10^2	0.9893×10^2	0.2837×10^3	0.0000	0.0000	0.0000	0.4032×10^3
$i = 5$	-0.2676×10^3	-0.2798×10^3	-0.8422×10^2	0.0000	0.0000	0.0000	0.5623×10^3
$i = 6$	-0.9856×10^2	-0.5849×10^2	0.3645×10^3	0.0000	0.0000	0.0000	0.4137×10^3
$i = 7$	0.8706×10^3	0.1018×10^4	0.1231×10^4	-0.1038×10^3	-0.5359×10^2	0.1451×10^3	0.0000

Table 4. Predicted Results for the Quaternary System Hexane (1) + Heptane (2) + Toluene (3) + Sulfolane (4) (RMSD = 0.0048)

hydrocarbon-rich phase								sulfolane-rich phase							
x_1^{exp}	x_1^{cal}	x_2^{exp}	x_2^{cal}	x_3^{exp}	x_3^{cal}	x_4^{exp}	x_4^{cal}	x_1^{exp}	x_1^{cal}	x_2^{exp}	x_2^{cal}	x_3^{exp}	x_3^{cal}	x_4^{exp}	x_4^{cal}
0.699	0.701	0.139	0.142	0.151	0.155	0.010	0.002	0.012	0.013	0.004	0.002	0.068	0.064	0.916	0.921
0.236	0.235	0.515	0.517	0.241	0.244	0.008	0.004	0.005	0.006	0.013	0.009	0.106	0.103	0.875	0.882
0.407	0.408	0.240	0.243	0.336	0.339	0.017	0.009	0.013	0.015	0.008	0.007	0.155	0.153	0.823	0.825
0.201	0.199	0.250	0.249	0.514	0.516	0.036	0.036	0.014	0.017	0.017	0.018	0.271	0.269	0.698	0.697
0.177	0.167	0.151	0.148	0.603	0.606	0.068	0.079	0.024	0.028	0.024	0.022	0.381	0.368	0.572	0.583

+ sulfolane, heptane + octane + *m*-xylene + sulfolane, and heptane + benzene + toluene + sulfolane—were measured, and the results are shown in Table 1.

The experimental tie-line data for two quinary systems—hexane + heptane + toluene + *m*-xylene + sulfolane and heptane + octane + benzene + *m*-xylene + sulfolane—are shown in Table 2.

Data Correlation and Prediction. The NRTL thermodynamic model was used to express LLE as in the previous paper (Chen et al., 2000a). 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 deviations of mole fractions for all components:

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

$x_{ijk}{}^{\mathrm{cal}}$ 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, n is the total number of components, and M is the total number of LLE sets.

For the regression of NRTL parameters needed to predict the LLE data of quaternary and quinary systems in this paper, literature LLE data for ternary systems are used (Chen et al., 2000a,b). The parameters obtained are listed in Table 3 . To ensure consistency, the parameters for the same pairs, such as hexane—sulfolane, heptane—sulfolane, octane—sulfolane, benzene—sulfolane, toluene—sulfolane, and *m*-xylene—sulfolane, in different ternary systems are kept the same.

With the NRTL parameters in Table 3 regressed using the LLE data of ternary systems, LLE of three quaternary and two quinary systems were predicted. No more parameters are added. The unknown parameters between any two aliphatic hydrocarbons or between any two aromatic hydrocarbons are suggested to be zero. One example is given in Table 4 for the quaternary system hexane + heptane + toluene + sulfolane. The RMSDs of the predicted results with experimental ones for tie-line data are listed in Table 5 for all quaternary and quinary systems. The results show that the NRTL equation with the parameters from ternary LLE systems can be used to predict LLE of quaternary and quinary systems. But for the calculation of other properties such as vapor—liquid equilibria, parameters between two aliphatic hydrocarbons or between two aromatic hydrocarbons should be used for better results.

Table 5. Prediction RMSDs for LLE of Three Quaternary and Quinary Systems

system	RMSD
Quaternary Systems	
hexane + heptane + toluene + sulfolane	0.0048
heptane + octane + *m*-xylene + sulfolane	0.0069
heptane + benzene + toluene + sulfolane	0.0059
Quinary Systems	
hexane + heptane + toluene + *m*-xylene + sulfolane	0.0086
heptane + octane + benzene + *m*-xylene + sulfolane	0.0098

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