636 *J. Chem. Eng. Data* **2006,** *51,* 636−638

Liquid−Liquid Equilibria for the Binary Systems of Sulfolane with Cycloalkanes

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Liquid−liquid equilibrium (LLE) data were measured for two binary systems containing sulfolane and cycloalkanes (cyclohexane and cyclooctane) over the temperature range around 300 K to the near upper critical solution temperature (UCST) using circulation-type equipment with an equilibrium view cell. The compositions of both cycloalkane-rich and sulfolane-rich phases were analyzed by on-line gas chromatography. The binary liquid−liquid equilibrium data were correlated with the NRTL and UNIQUAC models using temperature-dependent parameters. The NRTL and UNIQUAC models correlate the experimental data well.

Introduction

The sulfolane extraction process separates aromatics from reformates.[1−4] The design and operation of the extraction column require the quantitative information of the phase equilibria. The commercial process simulators such as Aspen Plus, Hysys, and Pro II have been used to optimize the operating conditions. However, the thermodynamic properties data of sulfolane are not workable in the commercial simulators, and the liquid−liquid equilibrium (LLE) data are also scarce for the binary systems containing sulfolane. To our knowledge, the LLE on cycloalkane and sulfolane systems have not been published. The LLE for the sulfolane and cycloalkane (cyclohexane and cyclooctane) binary systems were measured at the temperature range from about 300 K to the vicinity of the upper critical solution temperature (UCST). Experimental data were correlated with the nonrandom two-liquid (NRTL)[5] and universal quasi-chemical (UNIQUAC)[6] models with the temperature-dependent parameters.

Experimental Section

Chemicals. The suppliers and purities of the chemicals are listed in Table 1 together with the purities determined using a HP 5890 gas chromatograph with a thermal conductivity detector. The chemicals were purified with molecular sieves 13X.

Experimental Apparatus. Details of this apparatus are given in our previous studies.[7] The volume of the equilibrium cell was 240 cm^3. The cell was made of stainless steel (SUS. 316) and placed inside the air bath, controlled by a PID temperature controller to the desired temperature within ± 0.1 K (maximum temperature 573.2 K). The cell and the quartz window were sealed with PTFE (Teflon) gaskets. The mixing was promoted by a magnetic stirrer. The temperature was measured using a platinum resistance thermometer (1502A by Hart Scientific, Inc). Its uncertainty was estimated to be within ± 0.006 K. The thermometer was calibrated at the ice point and by comparison to standard platinum thermometers (SPRTs) calibrated on the basis of the international temperature scale of 1990 (ITS-90). The sampling system was connected to a gas chromatograph (Hewlett-Packard 5890 series II) with a thermal conductivity detector (TCD) and a 1.828 m × 0.003175 m column packed with Chromosorb WHP 100/120 coated with OV-101.

Table 1. Suppliers and Purity of the Used Chemicals

chemical	supplier	spec. %[a]
sulfolane	Fluka Chemical Co.	>99.50
cyclohexane	Kanto Chemical Co., Inc.	>99.50
cyclooctane	Tokyo Kasei Kogyo Co., Ltd.	>99.96

[a] Purity reported by the supplier.

Experimental Procedure. The mixture was fed into the equilibrium cell that was initially evacuated. The mixture was stirred for at least 1 h with the magnetic stirrer and then left to settle for at least 2 h. Each phase was circulated with recirculation pumps for 1 h. The sampling was made when the cell temperature change was within ± 0.002 K for 10 min. The samples were analyzed by gas chromatography. The temperatures of the injector and the detector were maintained at 593.15 K. After 1 min holding at 393.15 K, the column temperature was raised to the final temperature of 433.15 K at the rate of 25 K·min^{-1}. Helium was used as the carrier gas at the rate of 23 cm^3·min^{-1}. Single-phase samples of known composition were used to calibrate the gas chromatograph in the composition range of interest. The samples of each phase at the same temperature were analyzed at least three times, and the average values were used. The liquid-phase compositions were determined with a maximum relative error of 0.1 %.

Results and Discussion

The measurement for the two systems cyclohexane (1) + sulfolane (2) and cyclooctane (1) + sulfolane (2) were performed within the range from about 300 K to near the UCST. The experimental data are given in Tables 2 and 3.

The binary liquid−liquid equilibrium data were correlated using the NRTL and UNIQUAC models. ASPEN PLUS 2004.1 was used for the calculation. NRTL and UNIQUAC models in the vicinity of critical temperature could not correlate the binary LLE data because of the nonanalytic behavior with the flat slopes of the two branches of the coexistence curve Therefore,

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10.1021/je0504313 CCC: $33.50

Table 2. Experimental and Calculated LLE Data for the Cyclohexane (1) + Sulfolane(2) System

	cyclohexane-rich phase, x_{11}			sulfolane-rich phase, x_{12}		
T/K	exp	NRTL	UNIQUAC	exp	NRTL	UNIQUAC
303.10	0.9915	0.9910	0.9910	0.0221	0.0215	0.0211
318.16	0.9876	0.9880	0.9880	0.0238	0.0272	0.0273
333.24	0.9835	0.9845	0.9845	0.0406	0.0354	0.0358
349.40	0.9804	0.9807	0.9807	0.0435	0.0464	0.0470
363.42	0.9771	0.9770	0.9770	0.0664	0.0596	0.0602
372.87	0.9767	0.9745	0.9746	0.0721	0.0701	0.0706
384.00	0.9712	0.9714	0.9715	0.0799	0.0852	0.0854
393.57	0.9661	0.9684	0.9686	0.1010	0.1011	0.1009
403.25	0.9657	0.9654	0.9657	0.1135	0.1194	0.1187
413.49	0.9620	0.9619	0.9622	0.1382	0.1427	0.1415
423.25	0.9601	0.9583	0.9585	0.1733	0.1688	0.1672
431.76	0.9568	0.9549	0.9549	0.2007	0.1948	0.1933
442.84	0.9493	0.9498	0.9495	0.2331	0.2339	0.2332
452.67	0.9420	0.9447	0.9438	0.2724	0.2738	0.2755

Table 3. Experimental and Calculated LLE Data for the Cyclooctane (1) + Sulfolane (2) System

	cyclooctane-rich phase, x_{11}			sulfolane-rich phase, x_{12}		
T/K	exp	NRTL	UNIQUAC	exp	NRTL	UNIQUAC
306.84	0.9998	0.9993	0.9995	0.0151	0.0140	0.0152
313.35	0.9949	0.9982	0.9982	0.0174	0.0206	0.0198
333.40	0.9926	0.9957	0.9954	0.0319	0.0293	0.0264
353.40	0.9897	0.9908	0.9896	0.0393	0.0412	0.0368
372.39	0.9796	0.9811	0.9782	0.0540	0.0584	0.0539
392.01	0.9670	0.9636	0.9585	0.0769	0.0826	0.0804
404.21	0.9500	0.9457	0.9397	0.1061	0.1036	0.1045
413.53	0.9309	0.9277	0.9221	0.1205	0.1228	0.1271
431.39	0.8940	0.8785	0.8782	0.1777	0.1705	0.1835
439.21	0.8565	0.8470	0.8528	0.2129	0.1990	0.2163
447.27	0.8290	0.8083	0.8236	0.2496	0.2332	0.2544
456.55	0.7709	0.7483	0.7821	0.2968	0.2855	0.3082
462.61	0.6682	0.6887	0.7461	0.3557	0.3377	0.3542

these models were used with binary interaction parameters with temperature dependency. Different expressions for describing the temperature dependency of the binary interaction parameter of these models are found in the literature and commercial software.[8−12] The excess Gibbs energy for the binary systems of NRTL and UNIQUAC models with the following temperature-dependent binary parameters is given as follows:

NRTL model:

$$\frac{G^{\mathrm{E}}}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \tag{1}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad \alpha_{ij} = \alpha_{ji} \tag{2}$$

$$\tau_{ij} = a_{ij} + b_{ij}/T + c_{ij} \ln T \tag{3}$$

where x is the mole fraction, $\alpha_{ij} (= \alpha_{ji})$ is the nonrandomness parameter, and $\tau_{ij} (\neq \tau_{ji})$ is the interaction parameter. For a binary mixture, the NRTL model contains seven parameters. The nonrandomness parameter is optimized along with the other binary parameters.

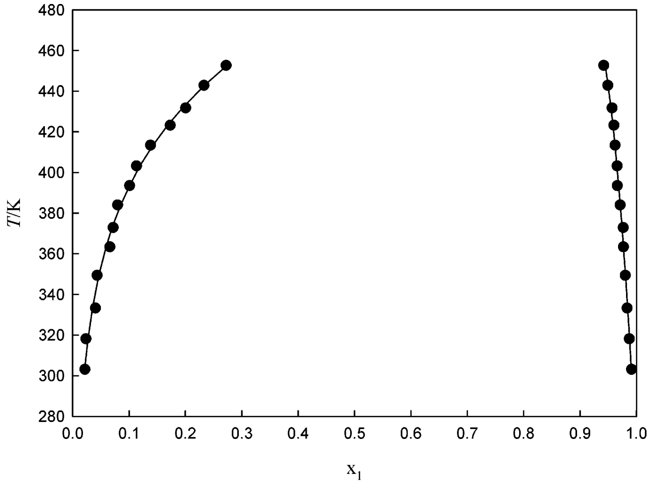

Figure 1. Experimental and calculated liquid−liquid equilibrium data for the cyclohexane (1) + sulfolane (2) mixture: points, experimental results; black solid line, NRTL with $\alpha = 0.2$.

UNIQUAC model:

$$G^{\mathrm{E}} = G^{\mathrm{E}}_{\mathrm{C}} + g^{\mathrm{E}}_{\mathrm{R}} \tag{4}$$

$$\frac{G^{\mathrm{E}}_{\mathrm{C}}}{RT} = x_1 \ln\frac{\Phi_1}{x_1} + x_2 \ln\frac{\Phi_2}{x_2} + \frac{z}{2}\left(q_1 x_1 \ln\frac{\theta_1}{\Phi_1} + q_2 x_2 \ln\frac{\theta_2}{\Phi_2} \right) \tag{5}$$

$$\frac{G^{\mathrm{E}}_{\mathrm{R}}}{RT} = -q_1 x_1 \ln[\theta_1 + \theta_2 \tau_{21}] - q_2 x_2 \ln[\theta_2 + \theta_1 \tau_{12}] \tag{6}$$

$$\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad \theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \tag{7}$$

$$\tau_{ij} = \exp(a_{ij} + b_{ij}/T + c_{ij} \ln T) \tag{8}$$

where Φ is the segment fraction; θ is the area fraction; r and q are pure component relative volume and surface area parameters, respectively; and $\tau_{ij} (\neq \tau_{ji})$ is the interaction parameter. The parameters in both models were found by minimizing the objective function:

$$\mathrm{OF} = \sum_{k=1}^{N} \left\{ \left(\frac{T_k^{\mathrm{calc}} - T_k^{\mathrm{exp}}}{\sigma_{T_k}} \right)^2 + \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} \left(\frac{x_{ij}^{\mathrm{calc}} - x_{ij}^{\mathrm{exp}}}{\sigma_{x_{ijk}}} \right)^2 \right\} \tag{9}$$

where N is the number of the experimental data in each group k, σ_k is the standard deviation of group k. The superscripts calc and exp present calculated property and experimental property, respectively. The binary parameters for these models were evaluated by a nonlinear regression method based on the

Table 4. Temperature Dependence of the Parameters of the NRTL Equation for the Cycloalkanes (1) + Sulfolane (2) Binary Systems

	binary interaction parameters						
system	a_{12}	a_{21}	b_{12}/K	b_{21}/K	α_{12}	c_{12}	c_{21}
cyclohexane + sulfolane	−122.5	92.03	6919	−3184	0.2	18.03	−13.86
cyclooctane + sulfolane	−80.00	−80.00	7700	5439	0.2	10.54	11.29

Table 5. Temperature Dependence of the Parameters of the UNIQUAC Equation for the Cycloalkanes (1) + Sulfolane (2) Binary Systems

	binary interaction parameters					
system	a_{12}	a_{21}	b_{12}/K	b_{21}/K	c_{12}	c_{21}
cyclohexane + sulfolane	−47.35	−33.12	−2526	1218	−7.01	4.99
cyclooctane + sulfolane	80.00	−14.87	−5400	645	−11.27	2.21

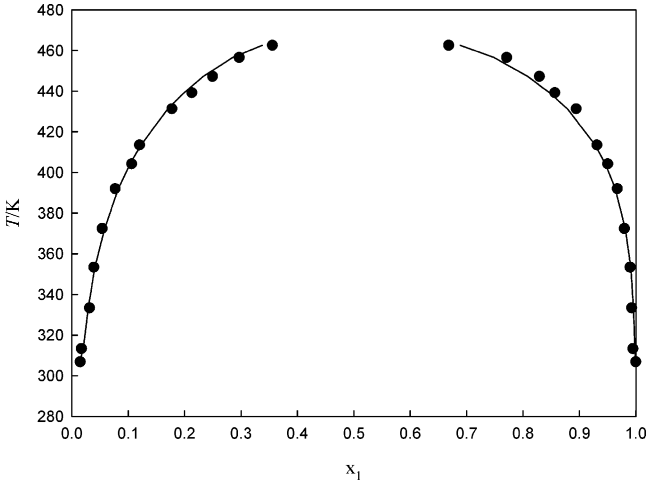

Figure 2. Experimental and calculated liquid−liquid equilibrium data for the cyclooctane (1) + sulfolane (2) mixture: points, experimental results; black solid line, NRTL with $\alpha = 0.2$.

Table 6. Percent Absolute Average Deviations (AAD %)[a] of the NRTL and UNIQUAC Equations for the Cycloalkanes (1) + Sulfolane (2) Binary Systems

	cycloalkane-rich phase		sulfolan-rich phase	
system	NRTL	UNIQUAC	NRTL	UNIQUAC
cyclohexane + sulfolane	0.11	0.09	5.10	5.21
cyclooctane + sulfolane	1.03	1.51	6.47	4.65

[a] AAD % = $(1/N)\sum_{i=1}^{N} |(x_{1,\mathrm{cal}} - x_{1,\mathrm{exp}})/x_{1,\mathrm{exp}}| \times 100$.

maximum-likelihood. The temperature-dependent binary parameters of these models are given in Tables 4 and 5.

Figures 1 and 2 show graphical representations of the experimental data and the calculated data in the form of T, x', and x'' diagrams, whereby the calculated values have been obtained by means of the NRTL equation. The NRTL and UNIQUAC models predict similar coexistence curves over a wide temperature range.

The percent absolute average deviations (AAD %) of the composition in both phases over the considered temperature range for the NRTL and UNIQUAC equations are listed in Table 6. Both the NRTL and the UNIQUAC models give good correlations of the experimental solubility data for both the liquid phases.

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Received for review October 19, 2005. Accepted December 1, 2005. This work was supported by the Brain Korea 21 Program supported by the Ministry of Education and LG-Caltex Research and by the National Research Laboratory (NRL) Program supported by Korea Institute of S&T Evaluation and Planning.

JE0504313