1464 *J. Chem. Eng. Data* **2007,** *52,* 1464−1467

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

Minsu Ko,[†] Jihoon Im,[†] Joon Yong Sung,[‡] and Hwayong Kim*,[†]

School of Chemical Engineering & Institute of Chemical Processes, Seoul National University, Shinlim-dong, Gwanak-gu, Seoul 151-744, Korea, Center for Clean Technology, Yonsei University, Chinchon-Dong 134, Seodaemun-Gu, Seoul, Korea

Liquid−liquid equilibrium (LLE) data were measured for four binary systems containing sulfolane and alkanes (pentane, hexane, heptane, and octane) 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 alkane-rich and sulfolane-rich phases were analyzed by on-line gas chromatography. The binary liquid−liquid equilibrium data were correlated with the nonrandom two-liquid (NRTL) model using temperature-dependent parameters. The NRTL model correlated with good accuracy.

Introduction

Many pairs of liquids of industrial importance have limited mutual solubilities. Liquid−liquid equilibrium (LLE) data are essential for the design and operation of the separation processes. Recently, there have been ever-increasing demands for high-purity aromatic compounds as a feedstock for chemical synthesis. The aromatics are obtained from the reformates, which are the products of catalytic reforming of naphtha. Extractive distillation and extraction processes are used to separate aromatics from hydrocarbon mixtures, especially to recover aromatics from reformates. Many solvents such as sulfolane,[1−5] glycol,[6,7] and *N*-formylmorpholine[8,9] are used in these processes. The extractive distillation process using sulfolane as a solvent is suitable for the separation of aromatics from reformates.[9] This process minimizes aromatic content in gasoline and refines the extracted aromatics which are used as raw materials for petrochemical processes. These days, commercial simulators are used for optimization of chemical processes. The optimum variable in the extractive distillation unit is a solvent-to-feed ratio. The operating cost and the initial equipment cost for the overall plant can be reduced by optimizing the solvent-to-feed ratio. Binary LLE data containing sulfolane for wide temperature ranges have become necessary to simulate the extractive distillation process for the separation of aromatics from hydrocarbon mixtures. However, LLE data for these mixtures are poorly available in the literature and the databank of simulators. The liquid−liquid equilibria for the sulfolane and alkane (pentane, hexane, heptane, and octane) binary systems were measured in 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) model[10] 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 an HP 5890 gas chromatograph with a thermal conductivity detector. The chemicals were used without further purification.

Table 1. Suppliers and Purity of the Used Chemicals

chemical	supplier	spec. %[a]	purity %[b]
sulfolane	Fluka Chemical Co.	> 99.50	> 99.96
pentane	Kanto Chemical Co., Inc.	> 99.00	> 99.99
hexane	Junsei Chemical Co., Ltd.	> 99.50	> 99.99
heptane	Aldrich	> 99.00	> 99.93
octane	ACROS	> 99.00	> 99.94

[a] The purity reported by the supplier. [b] The purity determined as the area ratio by gas chromatography with a thermal conductivity detector.

Experimental Apparatus. Details of this apparatus are given in our previous studies.[11] 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 of 573.2 K). The cell and the quartz window were sealed with PTFE (Teflon) gaskets. The mixing was promoted by the 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 × 0.003 175 m column packed with Chromosorb WHP 100/120 coated with OV-101.

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 ± 0.02 K for 10 min. The samples were analyzed by gas chromatography. The temperatures of the injector and the detector were maintained at 523.15 K. After 1 min holding at 353.15 K, the column temperature was raised to the final temperature of 423.15 K at the rate of 25 $K\cdot min^{-1}$. Helium was used as the carrier gas at the rate of 23 $cm^3\cdot min^{-1}$. 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

---

* To whom correspondence should be addressed. Fax: +82-2-888-6695. E-mail: hwayongk@snu.ac.kr.

[†] Seoul National University.

[‡] Yonsei University.

10.1021/je7001607 CCC: $37.00

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

	pentane-rich phase, x_{11}		sulfolane-rich phase, x_{12}	
T/K	exptl	NRTL	exptl	NRTL
304.31	0.9989	0.9990	0.0584	0.0623
310.80	0.9984	0.9984	0.0661	0.0684
320.72	0.9972	0.9971	0.0796	0.0789
330.41	0.9950	0.9948	0.0952	0.0912
340.50	0.9909	0.9905	0.1148	0.1076
350.15	0.9838	0.9831	0.1377	0.1288
354.82	0.9785	0.9776	0.1507	0.1420
359.64	0.9708	0.9698	0.1661	0.1584
364.75	0.9592	0.9583	0.1849	0.1800
369.78	0.9422	0.9422	0.2071	0.2072
374.11	0.9204	0.9223	0.2303	0.2376
376.49	0.9043	0.9080	0.2455	0.2582
379.39	0.8788	0.8857	0.2672	0.2884
380.35	0.8687	0.8768	0.2756	0.3001

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

	hexane-rich phase, x_{11}		sulfolane-rich phase, x_{12}	
T/K	exptl	NRTL	exptl	NRTL
300.30	0.9999	0.9997	0.0092	0.0122
307.43	0.9995	0.9996	0.0150	0.0140
323.51	0.9987	0.9991	0.0203	0.0187
348.72	0.9966	0.9971	0.0276	0.0280
363.36	0.9918	0.9947	0.0332	0.0350
372.41	0.9893	0.9924	0.0432	0.0403
377.72	0.9849	0.9907	0.0469	0.0437
384.43	0.9842	0.9880	0.0520	0.0487
393.92	0.9788	0.9828	0.0584	0.0569
403.51	0.9756	0.9754	0.0698	0.0671
412.29	0.9706	0.9660	0.0794	0.0788
422.92	0.9681	0.9496	0.0980	0.0969
429.93	0.9608	0.9345	0.1161	0.1122

Table 4. Experimental and Calculated LLE Data for the Heptane (1) + Sulfolane (2) System

	heptane-rich phase, x_{11}		sulfolane-rich phase, x_{12}	
T/K	exptl	NRTL	exptl	NRTL
302.09	0.9995	0.9991	0.0059	0.0088
308.03	0.9981	0.9989	0.0109	0.0101
323.93	0.9974	0.9978	0.0186	0.0142
342.74	0.9955	0.9957	0.0230	0.0203
364.62	0.9934	0.9915	0.0312	0.0294
373.78	0.9893	0.9890	0.0367	0.0338
382.81	0.9854	0.9861	0.0424	0.0385
385.17	0.9854	0.9853	0.0392	0.0398
389.11	0.9854	0.9838	0.0423	0.0420
395.41	0.9800	0.9813	0.9716	0.0456
404.30	0.9781	0.9773	0.0475	0.0509
413.87	0.9716	0.9725	0.0546	0.0568
423.39	0.9661	0.9672	0.0567	0.0628
429.24	0.9603	0.9637	0.0637	0.0666

Table 5. Experimental and Calculated LLE Data for the Octane (1) + Sulfolane (2) System

	octane-rich phase, x_{11}		sulfolane-rich phase, x_{12}	
T/K	exptl	NRTL	exptl	NRTL
298.15	0.9990	0.9988	0.0092	0.0094
303.15	0.9986	0.9985	0.0100	0.0101
308.34	0.9968	0.9981	0.0110	0.0109
313.15	0.9981	0.9976	0.0120	0.0117
318.25	0.9964	0.9970	0.0134	0.0126
323.15	0.9958	0.9963	0.0140	0.0137
328.15	0.9959	0.9955	0.0143	0.0148
332.80	0.9957	0.9946	0.0150	0.0161
339.15	0.9937	0.9932	0.0178	0.0179
348.15	0.9925	0.9907	0.0203	0.0210
352.65	0.9866	0.9893	0.0233	0.0228
361.65	0.9838	0.9858	0.0287	0.0268
373.15	0.9811	0.9800	0.0322	0.0332

Table 6. Temperature Dependence of the Parameters of the NRTL Model for the Alkane (1) + Sulfolane (2) Binary Systems

	parameters	pentane	hexane	heptane	octane
NRTL	a_{12}	16.56	−20.24	−82.16	−115.33
	a_{21}	−21.29	−21.29	−80.43	43.17
	b_{12}/K	4095.84	5279.57	7058.4	8949.93
	b_{21}/K	2842.68	3086.87	5544.8	−1607.64
	α_{12}	0.3	0.3	0.2	0.12
	c_{12}/(ln K)$^{-1}$	−4.25	1.68	11.24	15.88
	c_{21}/(ln K)$^{-1}$	2.49	2.6	11.39	−6.28
	AAD %^{a}	4.92	7.142	10.67	3.35

^{a} AAD % = $(1/N)\sum_{i=1}^{N} |(x_{1,\text{calcd}} - x_{1,\text{exptl}})/x_{1,\text{exptl}}|\cdot 100$.

values were used. The liquid-phase compositions were determined with a maximum relative error of 0.1 %.

Results and Discussion

The measurements for the four systems, pentane (1) + sulfolane (2), hexane (1) + sulfolane (2), heptane (1) + sulfolane (2), and octane (1) + sulfolane (2), were performed within the range of about 300 K to the vicinity of the UCST. The experimental data are given in Tables 2 to 5.

The binary liquid−liquid equilibrium data were correlated using the NRTL model. The NRTL model could not correlate the binary LLE data in the vicinity of the critical temperature because of the nonanalytical behavior with the flat slopes of the two branches of the coexistence curve near the critical region. Therefore, these models were modified to use the 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.[12−16] In this work, temperature-dependent binary interaction parameters suggested by Aspen Technology Inc. were chosen.[16] The excess Gibbs energy for the binary systems of the NRTL model is expressed by the following equations

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

$$G_{12} = \exp(-\alpha_{12}\tau_{12}),\ \alpha_{12} = \alpha_{21} \tag{2}$$

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

where x is the mole fraction; α_{12} (= α_{21}) is the nonrandomness parameter; and τ_{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.

The parameters were found by minimizing the objective function

$$\mathrm{OF} = \sum_{k=1}^{N}\left\{\left(\frac{T_k^{\text{calcd}} - T_k^{\text{exptl}}}{\sigma_{T_k}}\right)^2 + \sum_{i=1}^{2}\sum_{j=1}^{2}\left(\frac{x_{ij}^{\text{calcd}} - x_{ij}^{\text{exptl}}}{\sigma_{x_{ijk}}}\right)^2\right\} \tag{4}$$

The binary parameters for this model were evaluated by a nonlinear regression method based on the maximum likelihood. The temperature-dependent binary parameters of this model are given in Table 6.

Figures 1 to 4 show graphical representations of the experimental data and the calculated data in the form of T, x', x''

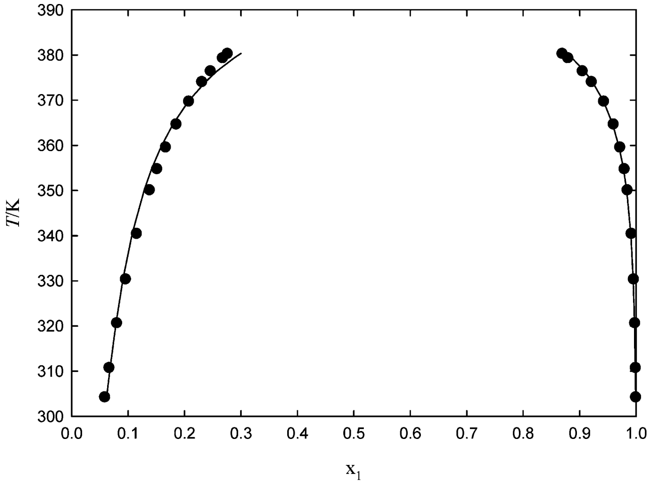

Figure 1. Experimental and calculated liquid−liquid equilibrium data for the pentane (1) + sulfolane (2) mixture: ●, experimental results; −, NRTL.

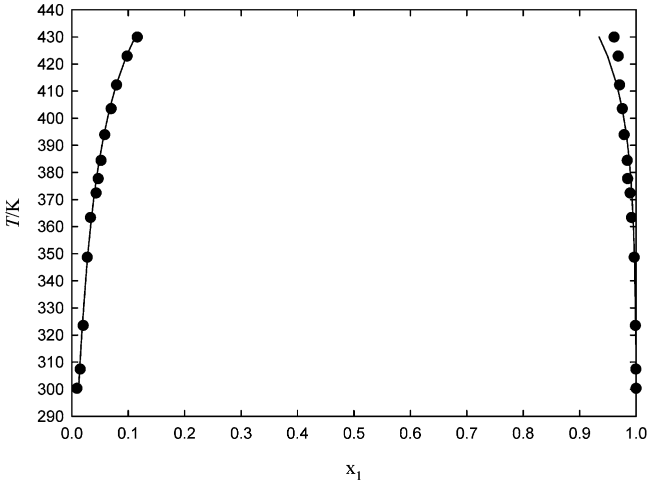

Figure 2. Experimental and calculated liquid−liquid equilibrium data for the hexane (1) + sulfolane (2) mixture: ●, experimental results; −, NRTL.

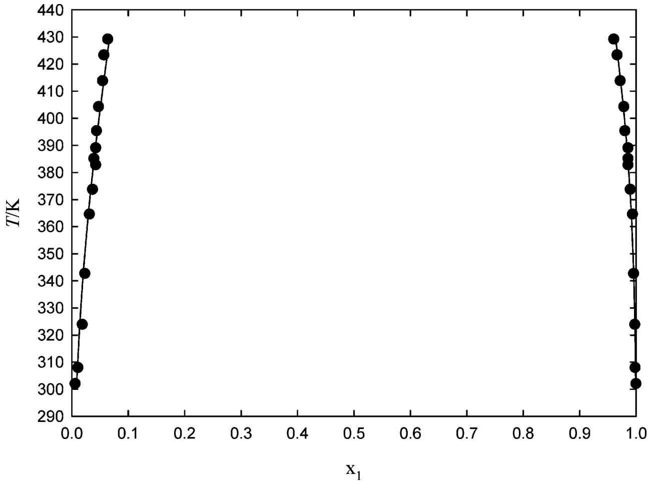

Figure 3. Experimental and calculated liquid−liquid equilibrium data for the heptane (1) + sulfolane (2) mixture: ●, experimental results; −, NRTL.

diagrams, whereby the calculated values have been obtained by means of the NRTL equation. The percent absolute average deviations (AAD %) of the composition in both phases over the considered temperature range for the NRTL model are listed in Table 6. The measured data were correlated well by the NRTL model.

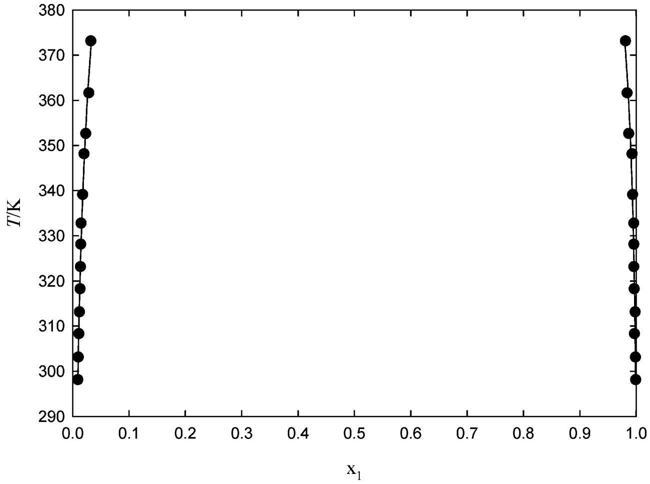

Figure 4. Experimental and calculated liquid−liquid equilibrium data for the octane (1) + sulfolane (2) mixture: ●, experimental results; −, NRTL.

Conclusions

Liquid−liquid equilibrium data for four binary alkanes + sulfolane systems were measured in the temperature range around 300 K to the near UCST. The measured data were correlated well with the temperature-dependent interaction parameters of the NRTL model. Thus a quantitative description of liquid−liquid equilibria of industrial interest containing sulfolane and alkanes is available to accurately simulate and optimize the extractive distillation units where these systems are involved.

Literature Cited

(1) Deal, C. H.; Evans, H. D.; Oliver, E. D.; Papadopoulus, M. N. Extraction of Aromatics with Sulfolane. *Fifth World Pet. Congr. Proc.* **1959**, *3*, 283−297.

(2) Voetter, H.; Kosters, W. C. G. The Sulfolane Extraction Process. *Sixth World Pet. Congr. Proc.* **1963**, *3*, 131−145.

(3) Broughton, D. B.; Asselin, G. F. Production of High Purity Aromatics by the Sulfolane Process. *Seventh World Pet. Congr. Proc.* **1967**, *4*, 65−73.

(4) 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*, 499−502.

(5) Sungjin, L.; Hwayong, K. Liquid−liquid Equiliubria 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.

(6) Symoniak, M. F.; Ganju, Y. N.; Vidueira, J. A. Plant Data for Tetra Process. *Hydrocarbon Process.* **1981**, *60*, 139−142.

(7) Al-Sahhaf, T. A.; Kapetanovic, E. Measurement and prediction of phase equilibria in the extraction of aromatics from naphtha reformate by tetraethylene glycol. *Fluid Phase Equilib.* **1996**, *118*, 271−285.

(8) Al Quattan, M. A.; Al-Sahhaf, T. A.; Fahim, M. A. Liquid−Liquid Equilibria in Some Binary and Ternary Mixtures with *N*-Formylmorpholine. *J. Chem. Eng. Data* **1995**, *40*, 88−90.

(9) Cincotti, A.; Murru, M.; Cao, G.; Marongiu, B.; Masia, F.; Sannia, M. Liquid−Liquid Equilibria of Hydrocarbons with *N*-Formylmorpholine. *J. Chem. Eng. Data* **1999**, *44*, 480−483.

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

(11) Ko, M.; Lee, S.; Cho, J.; Kim, H. Liquid−Lquid Equilibria for Binary Systems Containing *N*-Formylmorpholine. *J. Chem. Eng. Data* **2002**, *47*, 923−926.

(12) Escobedo-Alvarado, G. N.; Sandler, S. I. Study of EOS-Gex Mixing Rules for Liquid−Liquid Equilibria. *AIChE J.* **1998**, *44*, 1178−1187.

(13) Matsuda, H.; Kurihara, K.; Ochi, K.; Kojima, K. Prediction of liquid−liquid equilibria at high pressure for binary systems using EOS-G^E

models: methanol + hydrocarbon systems. *Fluid Phase Equilib.* **2002**, *5097*, 1−16.

(14) Zielke, F.; Lempe, D. A. Generalized calculation of phase equilibria by using cubic equations of state. *Fluid Phase Equilib.* **1997**, *141*, 63−85.

(15) Derawi, S. O.; Kontogeorgis, G. M.; Stenby, E. H.; Haugum, T.; Fredheim, A. O. Liquid−Liquid Equilibria for Glycols + Hydrocarbons: Data and Correlation. *J. Chem. Eng. Data* **2002**, *47*, 169−173.

(16) Simulation software: *ASPEN PLUS of ASPENTECH, Aspen Physical Property System 2004.1 Physical Property Methods and Models*; Aspen Technology Inc.: Cambridge, MA 02141−2201.

Received for review March 29, 2007. Accepted May 1, 2007. This work was supported by the Brain Korea 21 Program supported by the Ministry of Education and GS-Caltex Research and by the National Research Laboratory (NRL) Program supported by Korea Institute of S&T Evaluation and Planning.

JE7001607