Determination and Correlation of LLE and SLE Data for the Methanol + Cyclohexane, Aniline + Heptane, and Phenol + Hexane System

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In this paper, a laser light scattering method was used for the determination of mutual solubilities in the systems of methanol + cyclohexane, aniline + heptane, and phenol + hexane at moderate pressures. Liquid−liquid equilibria (LLE) were measured from the region of solid−liquid equilibria (SLE) to the upper critical solution temperature. Freezing points in these systems were determined by a cooling curve method. The experimentally determined cloud points were satisfactory correlated by three local-composition models (NRTL, Tsuboka−Katayama's modification of the Wilson, and the modified complete local composition suggested by Nagata and Tamura). We also attempted to predict the SLE by means of these models with the parameters obtained from the LLE data.

Introduction

Liquid−liquid equilibrium (LLE) data are essential for the design and development of separation processes. Such data are also valuable in theoretical studies, such as the applicability of activity coefficient models. However, the experimental values of the solubilities reported in the literature frequently show discrepancies, and it is thus difficult to select reliable experimental data as the basis of further work.

In recent studies, we developed and tested a laser scattering method for the accurate determination of mutual solubilities in liquid mixtures at moderate pressures.[1−6] As a extension of that work, we made measurements of the solubility curves of methanol + cyclohexane, aniline + heptane, and phenol + hexane systems from the region of solid−liquid equilibria (SLE) to the upper critical solution temperature (UCST). Especially, aniline + heptane and phenol + hexane systems have a high viscosity. Additionally, we determined freezing points for these systems by a cooling curve method. The liquid−liquid solubility data were correlated by the three local-composition (LC) models: NRTL,[7] Tsuboka−Katayama's modification of the Wilson equation (T−K−Wilson),[8] and the modified complete local-composition (CLC) model suggested by Nagata and Tamura.[9] The prediction of SLE was also tested using these three LC models with parameters obtained from the experimental LLE data for the three systems.

Experimental Section

Apparatus and Procedure. The cloud points of the binary mixtures were measured using a laser scattering technique. Details of the apparatus and its operation have been described elsewhere.[1−4] In this study, a light sensor (NP type silicon capsule module, model 3-400S, Solar Tech, Japan) was used to effectively detect the weakly scattered beams. A thermo-regulator temperature control system (model UT/350, Yokokawa Electric Co. Ltd.) was adopted for the purpose of shortening of measurement time and improving the measurement accuracy. The equilibrium cell was covered with a film heater for heating.

The freezing points were determined using the cooling curve method. Details of the equipment and the measurement procedure have been described previously.[3,4] The combination of cooling and heating jackets significantly reduces the time requirements for the experiment. In this study, ethanol was used as the cooling medium.

The liquid mole fraction was determined by a weight method, and the reproducibility of temperature of the cloud and freezing point was within ±0.1K over all mole fraction range.

Materials. Special grade methanol, cyclohexane, aniline, heptane, phenol, and hexane were supplied by Wako Pure Chem. Ind. Ltd., Japan. All chemicals were dried with the help of molecular sieves. The mass fraction of these chemicals was established by gas chromatography to be greater than 99.96% for methanol, 99.95% for cyclohexane, 99.91% for aniline, 99.92% for heptane, 99.9% for phenol, and 99.95% for hexane.

Results and Discussion

Methanol(1) + Cyclohexane(2). The experimental solubility data are listed in Table 1 and shown in Figure 1. The determined UCST in this study is marked with the sign of a circle within a circle in this figure. This UCST was interpolated on the basis of the experimental cloud points near the UCST. For this system, many values are reported,[10−16] as shown in Figure 1. Especially, Becker et al.[11] and Ewing et al.[13] have measured liquid mutual solubilities in the vicinity of the UCST in detail. Our experimental data showed almost the same tendency as these reported values. The determined UCST has the

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Table 1. Experimental Cloud Point Results for the Methanol(1) + Cyclohexane(2) System

T/K	x_1^a	T/K	x_1^a	T/K	x_1^a
284.14	0.0615	316.59	0.3092	316.87	0.6750
291.05	0.0819	317.08	0.3132	315.92	0.6905
292.35	0.0890	317.15	0.3222	315.35	0.6986
291.98	0.0904	317.46	0.3324	314.76	0.7111
297.15	0.1108	317.65	0.3412	313.64	0.7234
298.38	0.1207	318.02	0.3586	312.67	0.7355
300.66	0.1284	318.65	0.3858	311.37	0.7486
301.95	0.1380	318.67	0.3906	311.60	0.7523
303.69	0.1486	319.03	0.4116	309.88	0.7605
304.66	0.1569	319.04	0.4233	308.41	0.7712
306.25	0.1725	319.07	0.4383	306.90	0.7797
307.86	0.1820	319.01	0.4579	305.65	0.7887
308.01	0.1838	319.07	0.4864	305.23	0.7916
309.70	0.1948	319.13^b	0.4974^b	303.48	0.7987
310.31	0.2024	319.02	0.5061	302.48	0.8045
310.81	0.2080	318.99	0.5337	301.81	0.8091
312.38	0.2243	318.84	0.5567	299.81	0.8182
312.98	0.2356	318.80	0.5737	296.98	0.8293
312.77	0.2357	318.82	0.5807	294.70	0.8379
314.51	0.2545	318.61	0.5880	291.21	0.8494
315.44	0.2759	318.53	0.6055	289.86	0.8528
315.60	0.2837	318.18	0.6219	286.95	0.8608
315.79	0.2838	318.10	0.6360	282.81	0.8715
315.84	0.2860	317.65	0.6529	280.45	0.8774
316.71	0.2975	317.23	0.6618		

[a] Mole fraction of methanol. [b] The upper critical solution point.

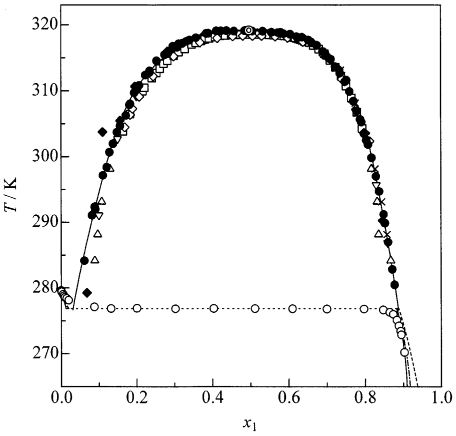

Figure 1. Liquid mutual solubilities and freezing points for the methanol(1)+ cyclohexane(2) system. ●, this work (cloud point); ○, this work (freezing point); circle within a circle, UCST; △, Alessi et al. (1989); □, Becker et al. (1978); ◇, Eckfeldt and Lucasse (1943); ▲, Ewing et al. (1988); ◆, Jones and Amstell (1930); ▽, Kato et al. (1992); ×, Kiser et al. (1961); —, NRTL equation; - - -, T−K−Wilson equation; —•—, modified CLC equation.

Table 2. Experimental Cloud Point Results for the Aniline(1) + Heptane(2) System

T/K	x_1^a	T/K	x_1^a	T/K	x_1^a
276.41	0.0340	339.64	0.3618	341.62	0.6972
285.11	0.0506	340.68	0.3973	341.24	0.7319
291.46	0.0613	341.40	0.4207	339.75	0.7566
296.74	0.0749	341.79	0.4401	339.02	0.7743
305.51	0.1004	342.18	0.4718	337.41	0.7931
313.21	0.1291	342.26	0.5022	333.16	0.8288
317.43	0.1467	342.66	0.5261	329.72	0.8468
322.85	0.1758	342.71	0.5387	325.11	0.8676
327.20	0.1981	342.84	0.5527	323.49	0.8778
330.39	0.2321	342.86	0.5655	314.81	0.9058
331.53	0.2439	343.11^b	0.5782^b	304.72	0.9297
333.87	0.2674	342.63	0.6132	299.44	0.9395
335.90	0.2965	342.35	0.6300	294.10	0.9483
337.68	0.3193	342.22	0.6602	279.61	0.9647

[a] Mole fraction of aniline. [b] The upper critical solution point.

Table 3. Experimental Cloud Point Results for the Phenol(1) + Hexane(2) System

T/K	x_1^a	T/K	x_1^a	T/K	x_1^a
306.03	0.1323	325.10	0.4208	319.92	0.6745
311.22	0.1583	325.40	0.4522	316.91	0.7082
315.44	0.1962	325.62^b	0.4657^b	311.56	0.7463
318.10	0.2219	325.49	0.4921	309.85	0.7594
321.69	0.2877	325.29	0.5133	309.41	0.7656
322.56	0.3105	324.93	0.5393	308.33	0.7714
323.41	0.3362	323.51	0.5982		
324.34	0.3728	321.74	0.6365		

[a] Mole fraction of phenol. [b] The upper critical solution point.

Table 4. Experimental Freezing Point Results for the Methanol(1) + Cyclohexane(2) System

T/K	x_1^a	T/K	x_1^a	T/K	x_1^a	T/K	x_1^a
279.59	0.0000	278.12	0.0194	276.84	0.5118	275.98	0.8737
279.39	0.0009	277.10	0.0877	276.82	0.6097	275.09	0.8836
279.00	0.0051	276.86	0.1321	276.78	0.6999	274.21	0.8886
278.77	0.0075	276.89	0.2012	276.79	0.7973	273.41	0.8931
278.55	0.0100	276.83	0.3027	276.64	0.8478	272.86	0.8947
278.38	0.0145	276.86	0.4033	276.28	0.8647	270.19	0.9028

[a] Mole fraction of methanol.

difference of about 0.2 K compared with the data of Kato et al.[15] and about 0.6 K compared with the data of Becker et al. and Ewing et al. We consider that these differences are due to using the laser scattering system in this study, whereas the cloud point is determined by the visual determination for the data of Ewing et al. and Kato et al. On the other hand, Becker et al. have determined the cloud point by the method with electrooptical indication. We consider the difference of UCST between our and their data to the difference of sensitivity of the light sensor.

The lower limit of the liquid−liquid solubility curve was determined by measuring the freezing points. The experimental freezing points are listed in Table 4 and also shown in Figure 1.

Aniline(1) + Heptane(2). Our experimental cloud point values for the aniline(1) + heptane(2) system are reported in Table 2 and compared with reported values,[17−25] many of which are available, in Figure 2. It can be seen that the data of Arich et al.[17] and Sen et al.[24] provide a schematic shape of the liquid−liquid solubility curve. However, the behavior of the system in the vicinity of the UCST still requires experimental verification. Therefore, in this study, the cloud points were measured in small composition increments.

The lower limit of the liquid−liquid solubility curve was determined by measuring the freezing points. The experimental freezing points are listed in Table 5 and also shown in Figure 2. In this study, the measurement in the heptane rich region was difficult.

Phenol(1) + Hexane(2). Table 3 reports the experimental cloud point values for the phenol(1) + hexane(2) system. Figure 3 also shows a comparison of the reported data[26,27] and our results. Serious differences can be recognized between our experimental data and the value of Campetti and Grosso.[26] In this system, our optical measurement showed that the scattered light appearing in the vicinity of the cloud point was weak. In our experimental apparatus, the light sensor was placed away from the path of the light beam so that the weak scattered light appearing at the beginning of the formation of turbidity can be detected effectively, even in the vicinity of the UCST.

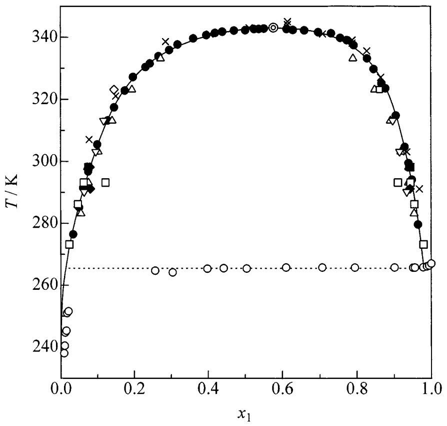

Figure 2. Liquid mutual solubilities and freezing points for the aniline(1)+ heptane(2) system. ●, this work (cloud point); ○, this work (freezing point); circle within a circle, UCST; △, Arich et al. (1956); □, Durandet and Gladel (1954); ◇, Griswold et al. (1950); ▲, Hunter and Brown (1947); ■, Nagata (1991); ◆, Palatnik et al. (1959); ▽, Palatnik et al. (1960); ×, Sen et al. (1991); +, Varteressian and Fenske (1937); —, NRTL equation; - - -, T−K−Wilson equation; —•—, modified CLC equation. (The line —•— is overlapped with the line — because the predicted result by the modified CLC equation is same as the result by the NRTL equation.)

Table 5. Experimental Freezing Point Results for the Aniline(1) + Heptane(2) System

T/K	x_1[a]	T/K	x_1[a]	T/K	x_1[a]	T/K	x_1[a]
238.06	0.0086	251.52	0.0208	265.70	0.6106	265.80	0.9784
240.47	0.0106	264.69	0.2571	265.70	0.7069	266.10	0.9883
244.67	0.0120	264.11	0.3045	265.67	0.7947	266.32	0.9940
245.30	0.0153	265.30	0.3984	265.70	0.9011	267.01	1.0000
250.92	0.0168	265.48	0.4425	265.66	0.9512		
250.94	0.0170	265.36	0.5049	265.70	0.9563		

[a] Mole fraction of aniline.

Therefore, our measurements for this system should be more precise than the mutual solubility data determined visually by Campetti and Grosso[26] and Vondracek.[27]

The freezing point data obtained in this study for this system are presented in Table 6 and shown in Figure 3.

Data Reduction

The experimental cloud point data were correlated with the NRTL, T−K−Wilson equation, and modified CLC equation suggested by Nagata and Tamura.

NRTL Equation

$$\ln \gamma_i = x_j^{\,2}\left[\tau_{ji}\left(\frac{G_{ji}}{x_i + G_{ji}x_j}\right)^2 + \frac{\tau_{ij}G_{ij}}{(G_{ij}x_i + x_j)^2}\right] \tag{1}$$

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

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \tag{3}$$

In eqs 1−3, x_i is the mole fraction of component i, γ_i is the activity coefficient of component i, α_{ij} is the nonrandomness parameter of the NRTL equation, $g_{ij} - g_{jj}$ is the binary interaction parameter, T is the absolute temperature, and R is the gas constant. In this study, we adopted the constant value $\alpha_{12} = 0.2$ for the three systems so that better correlation results can be provided for all three binary systems.

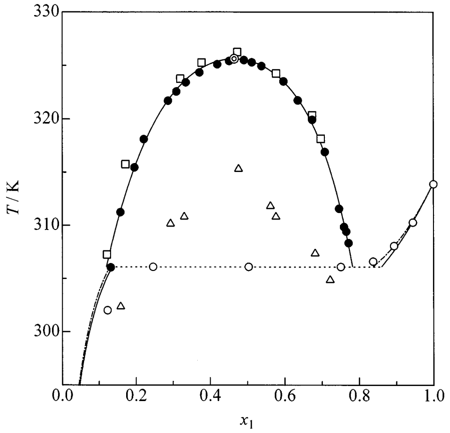

Figure 3. Liquid mutual solubilities for the phenol(1)+ hexane(2) system. ●, this work (cloud point); ○, this work (freezing point); circle within a circle, UCST; △, Campetti and Grosso (1913); □, Vondracek (1937); —, NRTL equation; - - -, T−K−Wilson equation; —•—, modified CLC equation.

Table 6. Experimental Freezing Point Results for the Phenol(1) + Hexane(2) System

T/K	x_1[a]	T/K	x_1[a]	T/K	x_1[a]	T/K	x_1[a]
302.00	0.1234	306.08	0.5039	306.59	0.8379	310.27	0.9443
306.08	0.2463	306.08	0.7505	308.06	0.8941	313.88	1.0000

[a] Mole fraction of phenol.

Table 7. Parameters L_i, M_i, and N_i of eq 8 for Used for Calculating Liquid Molar Volumes

component	L_i/m^3 mol^{-1}	M_i/m^3 mol^{-1} K^{-1}	N_i/m^3 mol^{-1} K^{-2}
methanol	3.68717×10^{-5}	-2.19582×10^{-8}	1.17085×10^{-10}
cyclohexane	8.97323×10^{-5}	-5.29018×10^{-9}	2.31873×10^{-10}
aniline	7.41450×10^{-5}	3.88072×10^{-8}	6.54293×10^{-11}
heptane	-1.15533×10^{-4}	1.49912×10^{-6}	-2.07500×10^{-9}
phenol	8.05245×10^{-5}	-1.75440×10^{-8}	1.41377×10^{-10}
hexane	1.23931×10^{-4}	-1.33265×10^{-7}	5.32960×10^{-10}

T−K−Wilson Equation

$$\ln \gamma_i = \ln\frac{x_i + (v_j^{\mathrm{L}}/v_i^{\mathrm{L}})x_2}{x_i + \Lambda_{ij}x_j} + (\beta - \beta_v)x_j \tag{4}$$

$$\beta = \frac{\Lambda_{ij}}{x_i + \Lambda_{ij}x_j} - \frac{\Lambda_{ji}}{\Lambda_{ji}x_i + x_j} \tag{5}$$

$$\beta_v = \frac{v_j^{\mathrm{L}}/v_i^{\mathrm{L}}}{x_i + (v_j^{\mathrm{L}}/v_i^{\mathrm{L}})x_j} - \frac{v_i^{\mathrm{L}}/v_j^{\mathrm{L}}}{(v_i^{\mathrm{L}}/v_j^{\mathrm{L}})x_i + x_j} \tag{6}$$

$$\Lambda_{ij} = \frac{v_j^{\mathrm{L}}}{v_i^{\mathrm{L}}}\exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \tag{7}$$

where v_i^{L} is the liquid molar volume of the pure component i and $\lambda_{ij} - \lambda_{ii}$ is the binary interaction parameter of the T−K−Wilson equation. The value of v_i^{L} was calculated as a function of temperature using the following equation:

$$v_i^{\mathrm{L}} = L_i + M_iT + N_iT^{\,2} \tag{8}$$

The parameters, L_i, M_i, and N_i, were determined from the v_i^{L} data in the compilation of Timmermans,[28] and are shown in Table 7.

Table 8. Determined Parameters and Deviations between Calculated and Experimental Cloud Points for the Three Binary Systems Using the Three Local Composition Models

	NRTL		T−K−Wilson		modified CLC	
	$ij = 12$	$ij = 21$	$ij = 12$	$ij = 21$	$ij = 12$	$ij = 21$
			Methanol(1) + Cyclohexane(2) System			
A_{ij}/J mol^{-1}	4.241508×10^3	4.272055×10^3	7.203204×10^3	-1.637790×10^2	8.902840×10^2	1.289276×10^3
B_{ij}/J mol^{-1} K^{-1}	5.328729×10^1	9.462572×10^2	1.019401×10^2	5.100948×10^1	-1.092600	3.036248×10^1
C_{ij}/J mol^{-1} K^{-2}	-1.902814	-2.978277	-3.304126	-1.339628	-6.051253×10^{-2}	-9.303832×10^{-1}
D_{ij}/J mol^{-1} K^{-3}	2.967266×10^{-2}	5.553928×10^{-2}	6.396838×10^{-2}	1.828437×10^{-2}	4.555168×10^{-4}	1.795614×10^{-2}
$\lvert\Delta x_1\rvert_{av}$[a]	0.0091		0.0090		0.0089	
			Aniline(1) + Heptane(2) System			
A_{ij}/J mol^{-1}	5.054318×10^3	4.008345×10^3	6.425173×10^3	4.872804×10^3	1.066709×10^3	6.727000×10^2
B_{ij}/J mol^{-1} K^{-1}	5.604031×10^1	8.554012×10^1	1.075693×10^2	6.512373×10^1	-5.305921×10^{-1}	2.630472×10^1
C_{ij}/J mol^{-1} K^{-2}	-9.058710×10^{-1}	-1.601137	-2.055111	-8.524217×10^{-1}	6.080291×10^{-2}	-5.409326×10^{-1}
D_{ij}/J mol^{-1} K^{-3}	9.018766×10^{-3}	1.632584×10^{-2}	2.056428×10^{-2}	8.842891×10^{-3}	-4.670884×10^{-4}	5.416222×10^{-3}
$\lvert\Delta x_1\rvert_{av}$[a]	0.0091		0.0091		0.0086	
			Phenol(1) + Hexane(2) System			
A_{ij}/J mol^{-1}	4.127266×10^3	4.543114×10^3	7.727082×10^3	4.127789×10^3	5.484080×10^2	1.264982×10^3
B_{ij}/J mol^{-1} K^{-1}	3.459755×10^1	5.596266×10^1	8.068251×10^1	5.700641×10^1	4.559843×10^1	1.669354×10^1
C_{ij}/J mol^{-1} K^{-2}	-1.141206	-5.963873×10^{-1}	-6.671812×10^{-1}	-1.644176	-2.256473×10^{-1}	7.631992×10^{-2}
D_{ij}/J mol^{-1} K^{-3}	2.469513×10^{-2}	2.423809×10^{-2}	2.729612×10^{-2}	2.960776×10^{-2}	3.836374×10^{-3}	2.684091×10^{-3}
$\lvert\Delta x_1\rvert_{av}$[a]	0.0064		0.0064		0.0068	

[a] $\lvert\Delta x_1\rvert_{av} = [\sum_{k=1}^{NDP} \lvert x_{1,exptl} - x_{1,calcd}\rvert_k]/NDP$, where NDP is the number of data points.

Modified CLC Equation

$$\ln \gamma_i = x_j^2\left[\tau_{ji}\left(\frac{G_{ji}}{x_i + G_{ji}x_j}\right)^2 + \frac{\tau_{ij}G_{ij}}{(G_{ij}x_i + x_j)^2}\right] - \ln(x_i + \Lambda_{ij}x_j) + x_j\left[\frac{\Lambda_{ij}}{x_i + \Lambda_{ij}x_j} - \frac{\Lambda_{ji}}{x_j + \Lambda_{ji}x_i}\right] \quad (9)$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad (10)$$

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L}\exp(-\alpha_{ij}\tau_{ij}) \quad (11)$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \quad (12)$$

The liquid molar volume v_i^L was as used in eq 8 in the T−K−Wilson equation. In this work, the constant value $\alpha_{12} = 1.0$ was used for the three systems according to the recommendation by Nagata and Tamura.[9]

The temperature dependences of the binary interaction parameters in eqs 3, 7, and 11 were expressed by the following equations, respectively:

NRTL and Modified CLC Equation

$$g_{12} - g_{22} = A_{12} + B_{12}(T_c - T) + C_{12}(T_c - T)^2 + D_{12}(T_c - T)^3 \quad (13a)$$

$$g_{21} - g_{11} = A_{21} + B_{21}(T_c - T) + C_{21}(T_c - T)^2 + D_{21}(T_c - T)^3 \quad (13b)$$

T−K−Wilson equation

$$\lambda_{12} - \lambda_{11} = A_{12} + B_{12}(T_c - T) + C_{12}(T_c - T)^2 + D_{12}(T_c - T)^3 \quad (14a)$$

$$\lambda_{21} - \lambda_{22} = A_{21} + B_{21}(T_c - T) + C_{21}(T_c - T)^2 + D_{21}(T_c - T)^3 \quad (14b)$$

where T_c is the upper critical solution temperature. The coefficients of eqs 13a−14b were estimated by a previously reported method.[1] The LLE compositions necessary for the reduction of the data were obtained by smoothing of the experimental cloud points.

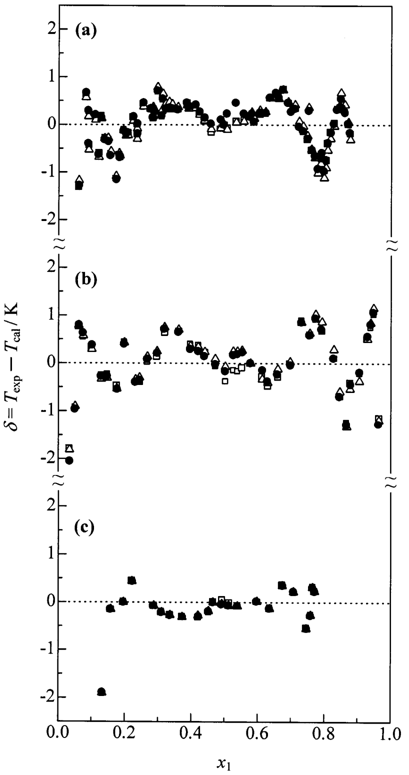

Figure 4. Plots of the difference between experimental and calculated temperature $T_{exp} - T_{cal}$ vs x_1 by three LC models for **(a)** methanol(1) + cyclohexane(2), **(b)** aniline(1) + heptane(2), and **(c)** phenol(1) + hexane(2) systems. ●, NRTL equation; △, T−K−Wilson equation; □, modified CLC equation.

The estimated coefficients of eqs 13a−14b and the average deviations between the correlated and experimental mutual solubility data are given in Table 8. The difference of the average deviation $\lvert\Delta x_1\rvert_{av}$ by three equations is within 0.0005 mole fraction, and then three equations yielded similar results for the three systems. The results correlated by the NRTL equation are illustrated in Figures 1−3. Figure 4 also shows plots of $\delta = T_{exp} - T_{cal}$

Table 9. Molar Enthalpy of Melting for Pure Components Taken from the Dortmund Data Bank (DDB)

component	$\Delta H_{m,i}$ [J mol^{-1}]	component	$\Delta H_{m,i}$ [J mol^{-1}]
methanol	3180	heptane	14030
cyclohexane	2630	phenol	11290
aniline	10560	hexane	13070

Table 10. Predicted Results of the SLE Using Three LC Models Based on the Adjusted Parameters from the LLE Data

	$|\Delta x_1|_{av}$^{a}		
system	NRTL	T−K−Wilson	modified CLC
methanol(1) + cyclohexane(2)	0.0059	0.0102	0.0061
aniline(1) + heptane(2)	0.0093		0.0093
phenol(1) + hexane(2)	0.0160		0.0125

^{a} $|\Delta x_1|_{av} = [\sum_{k=1}^{NDP}|x_{1,exptl} - x_{1,calcd}|_k]/NDP$, where NDP is the number of data points.

vs x_1 by three LC models for each system. The values of δ for three LC models are small for all liquid mole fractions. These results indicate that it is possible to correlate the LLE for three systems with almost good accuracy.

Prediction of the SLE

We have calculated the SLE of the binary systems using the three investigated LC models with the parameters estimated from the LLE data. In this study, we have adopted the approximated expression of the condition of the SLE of eutectic systems,[29] which is not considered the difference of the molar heat capacities of pure component $\Delta C_{P,i}$, because the temperature range of the SLE for three binary systems is not far from the melting point of pure components:

$$\ln \gamma_i = \left(\frac{T - T_{m,i}}{RT}\right)\left(\frac{\Delta H_{m,i}}{T_{m,i}}\right) - \ln x_i \qquad (15)$$

where $T_{m,i}$ is the melting point of the pure component and $\Delta H_{m,i}$ is the molar enthalpy of melting. In this study, the value of $\Delta H_{m,i}$ was taken from the Dortmund Data Bank (DDB).[30] $\Delta H_{m,i}$ of pure components are listed in Table 9.

In this study, the parameters of the LC models listed in Table 8 were used directly for the prediction of the SLE. The results of the SLE relevant to one liquid phase predicted by the three equations based on the experimental LLE data are listed in Table 10 and shown in Figures 1−3. The T−K−Wilson equation was not able to express the solid−liquid separation except for the methanol + cyclohexane system. On the other hand, the NRTL and modified CLC equations were capable of reproducing the SLE qualitatively for the three systems. These two equation gave similar results for the methanol + cyclohexane and aniline + heptane systems, although the predicted results of the modified CLC equation were better than that of the NRTL equation for phenol + hexane system.

Conclusion

The laser light scattering technique was used for the determination of mutual solubilities in the methanol + cyclohexane, aniline + heptane, and phenol + hexane systems. LLE data were determined for temperatures up to the critical solution temperature; T_c = 319.13K and $x_{1,UCST}$ = 0.4974 for methanol + cyclohexane, T_c = 343.11K and $x_{1,UCST}$ = 0.5782 for aniline + heptane, and T_c = 325.62K and $x_{1,UCST}$ = 0.4657 for phenol + hexane. We also measured the freezing points in these systems by a cooling curve method. Experimental LLE data were satisfactorily correlated with the NRTL, T−K−Wilson, and modified CLC equations. Finally, the SLE of these binary systems was predicted using three equations based on the adjusted parameters from the LLE data. The results predicted by the NRTL and modified CLC equations indicated a qualitative solid−liquid separation for the three systems, whereas the T−K−Wilson equation was not able to express the SLE, except for the methanol + cyclohexane system.

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