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Measurement and Correlation of Mutual Solubilities in 2-Butanol + Water

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A newly developed laser scattering technique was tested for the determination of mutual solubilities in the 2-butanol + water system at moderate pressures. The liquid−liquid solubility data were measured from the region of solid−liquid equilibria to the upper critical solution temperature. Freezing points in this system were determined by a cooling curve method. A concave curvature of the liquid−liquid line was observed in the vicinity of the freezing points. The solubility data were satisfactorily correlated with Hiranuma's modification of the Wilson equation. The newly measured data compare favorably with previous measurements.

Introduction

Liquid−liquid equilibrium data are essential for the design and development of separation processes. However, it is common that literature values of liquid−liquid solubilities show discrepancies. Since a thermodynamic analysis cannot be used to establish the accuracy of liquid−liquid measurements, it is often difficult to select reliable experimental data as a basis for further work.

In our recent studies we developed and tested a laser scattering method for an accurate determination of mutual solubilities in liquid mixtures at moderate pressures (Ochi and Kojima, 1990; Ochi et al., 1993). In the present work, we have extended the range of applicability of our method by modifying the temperature-controlling system. This modification allows measurement of liquid−liquid solubilities also at low temperatures.

Hefter et al. (1991) have recently proposed 2-butanol + water as a suitable test system for newly developed solubility apparatuses. The complete liquid−liquid curve for this system covers the temperature range of ca. 260−390 K which is very common in many organic and aqueous systems. At temperatures below 283 K, the liquid−liquid line exhibits unusual inflection points (Hefter, 1984). This concave curvature of the solubility line is a very strict test of the experimental procedure because it is strongly dependent on impurities in the input material (Hefter et al., 1991).

In this work, we made a detailed measurement of the solubility curve of 2-butanol + water from the region of solid−liquid equilibria up to the upper critical solution temperature. Additionally, we determined freezing points for this system by a cooling curve method. The liquid−liquid solubility data were correlated by Hiranuma's modification of the Wilson equation.

Experimental Section

Measurement of Cloud Points. A schematic diagram of the apparatus used in this work is shown in Figure 1. Details of the equipment and the measurement procedure have been described elsewhere (Ochi et al., 1993). In this work, the temperature-controlling system was modified and the equilibrium cell was covered with a double jacket for thermostating and evacuation. At temperatures above 283 K, water was used as the heating/cooling medium. Below 283 K, the system temperature was controlled by circulating ethanol.

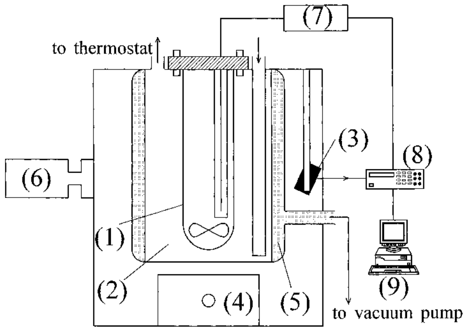

Figure 1. A schematic diagram of the apparatus for measuring the mutual solubility curve: (1) equilibrium cell (pressure glass), (2) temperature bath, (3) light sensor (selenium cell), (4) magnetic stirrer, (5) adiabatic jacket, (6) He−Ne laser, (7) thermometer, (8) digital multimeter, (9) personal computer.

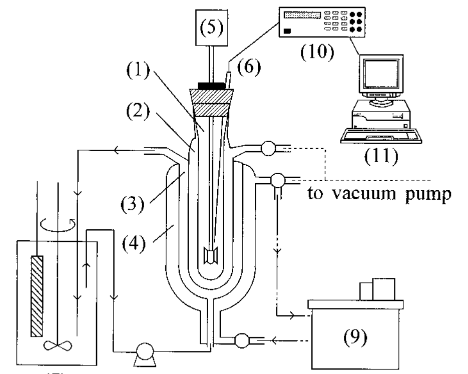

Figure 2. A schematic diagram of the apparatus for freezing point measurements: (1) equilibrium cell, (2) vacuum jacket, (3) cooling medium jacket, (4) vacuum or heating medium jacket, (5) stirrer, (6) thermometer, (7) cooling medium bath, (8) pump, (9) heating medium bath, (10) digital multimeter, (11) personal computer.

Measurement of Freezing Points. The apparatus for the measurement of freezing points is schematically shown in Figure 2. The equipment consists of an equilibrium cell with a capacity of ca. 150 cm^3 covered with a triple jacket (vacuum and cooling and heating media). The combination of cooling and heating jackets significantly reduces the time requirements for the experiment.

About 100 cm^3 of a mixture of known composition was charged into the equilibrium cell. Temperature measurements were made with a Pt resistance thermometer

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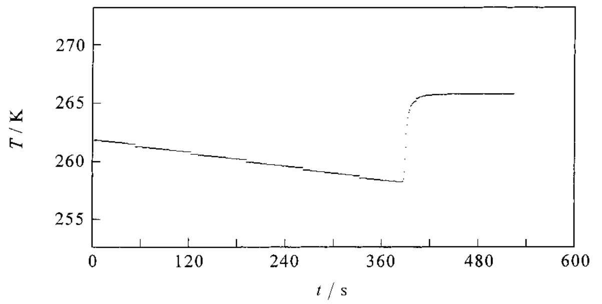

Figure 3. Typical experimental cooling curve monitored by a computer for 2-butanol (1) + water (2) (x_1 = 0.2593 mole fraction 2-butanol).

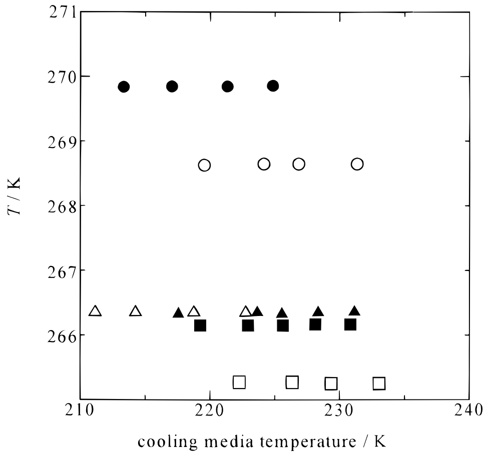

Figure 4. Illustrative diagram of the experimental freezing points for 2-butanol (1) + water (2): ●, x_1 (mole fraction of 2-butanol) = 0.0282; ○, x_1 = 0.0391; △, x_1 = 0.1415; ▲, x_1 = 0.2593; ■, x_1 = 0.3139; □, x_1 = 0.3911.

connected to a personal computer via a YHP 3478A digital multimeter.

The freezing points were considered to be the highest temperatures reached after subcooling. The measurements were then repeated at several different temperatures of the cooling medium. Some experimental results are illustrated in Figures 3 and 4. These figures show an example of the computer output of the cooling curve (Figure 3) and a diagram of freezing points against the temperature of the cooling medium (Figure 4).

Materials. Deionized and freshly distilled water was prepared in the laboratory. A special grade 2-butanol was supplied by Wako Pure Chemical Industries Ltd., Japan. The purity of this material was established by gas chromatography to be better than 99.94 mol %. The analysis showed no significant impurities except water. The water content in 2-butanol was incorporated into the calculation of the composition charged into the equilibrium cell.

Results and Discussion

Hefter (1984) provided a critical review of the solubility data for 2-butanol + water available in the literature. These experimental data indicate that the solubility curve for this system has an unusual Ω shape with inflection points located near the freezing line. Hefter et al. (1991) have studied this behavior in detail and attribute it to the presence of molecular aggregates or hydrate formation in the solution. They also discuss a great sensitivity of this phenomenon to small amounts of impurities. As a result of their work, the experimental data of Stephenson and Stuart (1986) are considered incorrect since they exhibit a closed miscibility loop. Similarly, the samples of Bozdag and Lamb (1983) likely contained hydrophobic impurities. The most reliable data to date by Moriyoshi et al. (1975) and Hefter et al. (1991) are shown in Figure 5.

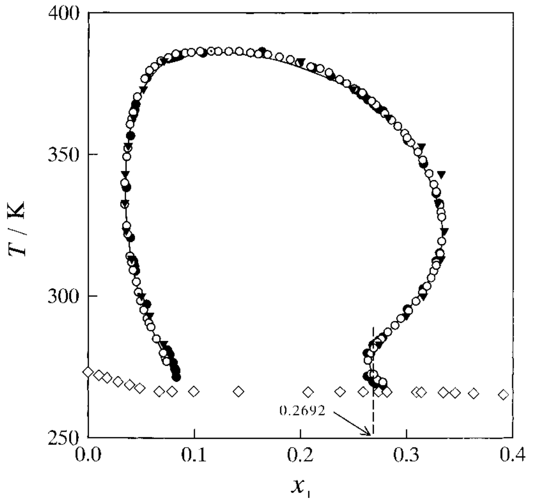

Figure 5. Liquid mutual solubilities and freezing points for 2-butanol (1) + water (2); ○, this work; ●, Hefter et al. (1991); ▼, Moriyoshi et al. (1975); ⊙, experimental upper critical solution point; ◇, experimental freezing points, —, correlated by Hiranuma's modification of the Wilson equation.

Table 1. Experimental Cloud Point Results for 2-Butanol (1) + Water (2)

T/K	x_1[a]	T/K	x_1[a]	T/K	x_1[a]
276.94	0.0738	386.23	0.0965	337.04	0.3279
278.13	0.0725	386.58	0.1050	333.00	0.3307
279.96	0.0705	386.65[b]	0.1151[b]	332.27	0.3312
284.94	0.0642	386.58	0.1219	329.88	0.3321
289.08	0.0590	386.60	0.1318	328.06	0.3330
290.58	0.0571	386.53	0.1417	319.46	0.3330
292.18	0.0553	386.09	0.1524	315.24	0.3312
295.15	0.0522	385.64	0.1599	315.35	0.3307
298.43	0.0491	385.46	0.1686	315.01	0.3314
301.48	0.0471	384.62	0.1796	311.92	0.3279
305.14	0.0452	383.75	0.1900	310.90	0.3279
309.18	0.0421	382.59	0.1985	308.94	0.3277
311.88	0.0406	381.24	0.2094	306.54	0.3253
314.10	0.0393	380.57	0.2181	303.67	0.3229
321.88	0.0371	379.15	0.2267	301.37	0.3191
324.99	0.0361	376.67	0.2365	298.33	0.3150
332.50	0.0342	375.20	0.2434	294.99	0.3088
340.01	0.0342	373.45	0.2503	292.22	0.3019
349.30	0.0361	371.99	0.2580	289.82	0.2947
352.25	0.0371	369.09	0.2668	287.42	0.2891
360.81	0.0393	367.60	0.2708	284.98	0.2823
362.51	0.0406	364.66	0.2791	283.81	0.2762
364.96	0.0421	362.25	0.2857	281.76	0.2692
370.41	0.0459	360.16	0.2914	280.00	0.2667
376.89	0.0530	357.60	0.2981	277.45	0.2636
379.76	0.0573	356.10	0.3003	272.65	0.2667
381.25	0.0621	354.34	0.3036	272.51	0.2692
383.23	0.0680	351.02	0.3104	270.52	0.2726
384.39	0.0751	348.24	0.3150	269.75	0.2726
385.63	0.0820	343.40	0.3211		
386.04	0.0908	339.63	0.3253		

[a] Mole fraction of 2-butanol. [b] The upper critical solution point.

In this study the cloud points were measured in small composition increments in order to verify the unusual behavior of this system. The experimental cloud points are listed in Table 1 and compared with the literature values in Figure 5. It can be seen that our liquid–liquid solubility data are in excellent agreement with the data of Moriyoshi et al. (1975) and Hefter et al. (1991) over the whole temperature range.

A concave curvature of the liquid–liquid solubility was also observed at low temperatures. This unusual behavior

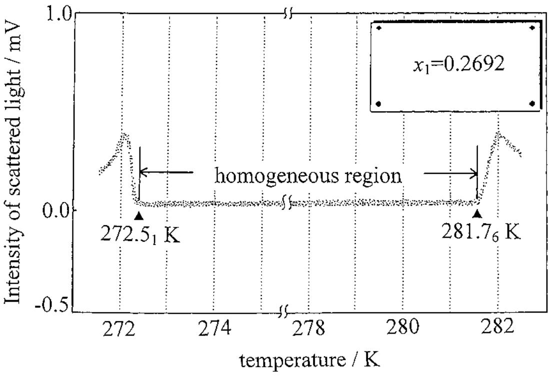

Figure 6. An illustration of the intensity of scattered light vs the temperature of solution for 2-butanol (1) + water (2) monitored by a computer.

Table 2. Experimental Freezing Point Results for 2-Butanol (1) + Water (2)

T/K	x_1[a]	T/K	x_1[a]
273.15	0.0000	266.35	0.2817
272.05	0.0102	266.25	0.3093
271.15	0.0178	266.15	0.3139
269.85	0.0282	266.05	0.3345
268.65	0.0391	265.95	0.3457
267.55	0.0486	265.75	0.3630
266.45	0.0668	265.25	0.3911
266.45	0.0788	264.85	0.4201
266.45	0.0992	264.25	0.4445
266.35	0.1415	263.07	0.4813
266.35	0.2073	261.55	0.5210
266.35	0.2375	260.14	0.5441
266.35	0.2593	258.41	0.5801
266.35	0.2738	256.06	0.6124

[a] Mole fraction of 2-butanol.

with double cloud points is illustrated in Figures 5 and 6 for the composition of 26.92 mol % 2-butanol. A plot of the intensity of scattered light against temperature is shown in Figure 6. Increasing the temperature from about 270 K, the system becomes homogeneous at 272.51 K when the lower solubility limit is reached. A second cloud point is observed at 281.76 K when the system becomes immiscible again.

The lower limit of the liquid−liquid solubility curve was determined by measuring the freezing points. The experimental freezing points are listed in Table 2 and also shown in Figure 5. Hefter et al. (1991) report a marked freezing point depression at ca. 26−30 mol % 2-butanol where the alcohol-rich branch of the solubility curve meets the freezing line. However, no such tendency was observed in the present work.

Data Reduction

The experimental cloud point data were correlated with the following modified Wilson equation (Hiranuma, 1983):

$$g^{\mathrm{E}}/RT = -\chi_1 \ln\left(\frac{x_1 + \alpha_{12}\Lambda_{12}x_2}{x_1 + \alpha_{12}x_2}\right) - x_2 \ln\left(\frac{x_2 + \alpha_{21}\Lambda_{21}x_1}{x_2 + \alpha_{21}x_1}\right) \quad (1)$$

$$\Lambda_{12} = \frac{V_2^{\mathrm{l}}}{V_1^{\mathrm{l}}}\exp\left(-\frac{a_{12}}{T}\right), \qquad \Lambda_{21} = \frac{V_1^{\mathrm{l}}}{V_2^{\mathrm{l}}}\exp\left(-\frac{a_{21}}{T}\right) \quad (2)$$

where V_1^{l} and V_2^{l} are the liquid molar volumes of pure components and α_{12} and α_{21} are temperature independent parameters. In this work, we adopted the constant values $\alpha_{12} = 1.1$ and $\alpha_{21} = 1.5$ recommended by Hiranuma (1983).

Table 3. Parameters of Eq 3

C_0/K = 1.04296×10^3	D_0/K = 8.17265×10^2
$C_1 = -5.11797$	$D_1 = 0.502984$
C_2/K^{-1} = 0.261654	D_2/K^{-1} = -9.28315×10^{-2}
C_3/K^{-2} = -6.90269×10^{-3}	D_3/K^{-2} = 1.79095×10^{-3}
C_4/K^{-3} = 6.74939×10^{-5}	D_4/K^{-3} = -1.71437×10^{-5}
C_5/K^{-4} = -2.30746×10^{-7}	D_5/K^{-4} = 6.03797×10^{-8}

The temperature dependence of the binary interaction parameters a_{12} and a_{21} was expressed by the following functions:

$$a_{12} = \sum_{i=0}^{n} C_i(T_{\mathrm{c}} - T)^i, \qquad a_{21} = \sum_{i=0}^{n} D_i(T_{\mathrm{c}} - T)^i \quad (3)$$

where T_{c} is the upper critical solution temperature. The coefficients of eq 3 were estimated by the Marquardt method (Marquardt, 1963). The following constrains for the upper solution critical point and liquid−liquid equilibria were employed in the estimation

$$\frac{1}{x_1x_2} + \frac{\partial^2(g^{\mathrm{E}}/RT)}{\partial x_1^{\,2}} = 0 \quad (4)$$

$$\frac{(x_1 - x_2)}{x_1^{\,2}x_2^{\,2}} - \frac{\partial^3(g^{\mathrm{E}}/RT)}{\partial x_1^{\,3}} = 0 \quad (5)$$

$$\frac{2(1 - 3x_1x_2)}{x_1^{\,3}x_2^{\,3}} - \frac{\partial^4(g^{\mathrm{E}}/RT)}{\partial x_1^{\,4}} > 0 \quad (6)$$

$$\partial^2 h^{\mathrm{M}}/\partial x_1^{\,2} < 0 \text{ (UCS point)} \quad (7)$$

$$\gamma_1'x_1' = \gamma_1''x_1'' \quad \text{and} \quad \gamma_2'x_2' = \gamma_2''x_2'' \quad (8)$$

The liquid−liquid equilibrium compositions necessary for the reduction of data were obtained by smoothing the experimental cloud points. The estimated coefficients of eq 2 are given in Table 3. As can be seen in Figure 5, Hiranuma's model compares favorably with the data, giving rise to an average deviation of only 0.0013 mole fraction.

Conclusion

A newly developed laser scattering technique was tested for the determination of mutual solubilities in the 2-butanol + water system. A comparison with literature values shows that the experimental technique provides reliable results from low temperatures up to the upper critical solution point.

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