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Prediction of Mutual Solubility Curve for *t*-Butyl Alcohol-Water System Utilizing Salting Out Phenomenon

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Synopsis. The consolute temperatures (T_s) for ternary solutions of water-tetrahydrofuran-salt and water-*t*-butyl alcohol (TBA)-salt (salt: ammonium chloride or potassium chloride) were measured. From a plot of T_s against the salt concentration, the mutual solubility curve for the water–TBA system was predicted. The critical solution temperature and the critical composition were estimated to be about 200 °C and 0.15—0.2 (mole fraction of TBA), respectively.

Although *t*-butyl alcohol (TBA) is completely miscible with water, some experimental results suggest the existence of the lower critical solution temperature (LCST) above the boiling pont.[1—4] As is well-known, one of the criteria for an LCST is the relation $T|\Delta S^E|>|\Delta H^E|$, where ΔS^E and ΔH^E are the excess entropy and excess enthalpy, respectively. This relation holds for the TBA–water system.[1,5] Iwasaki and Fujiyama[2] have shown that the concentration fluctuations obtained from light scattering intensities increase rapidly with increasing temperature. This indicates that the system approaches the critical point as the temperature increases. However, the mutual solubility curve itself has not yet been predicted. In the present work, we have attempted to obtain a mutual solubility curve indirectly by utilizing the salting-out phenomenon for the water–TBA system. For a comparison, we have also studied a water–tetrahydrofuran (THF) system whose solubility curve can be measured directly under ordinary conditions.

Experimental

All the reagents used in this work were analytically pure reagent grade and were purified by the conventional method. Water was triply distilled in an all-Pyrex still.

The experimental procedures are summerized as follows.[6,7] Weighed ammounts of water, organic reagent (TBA or THF), and salt were sealed in ampoules. These ampoules were then put into a temperature-controlled water bath whose temperature was increased at a constant rate (about 0.2 °C per minute). The consolute temperature was determined by visual observation.

Results and Discussion

Figures 1—3 show semilogarithmic plots of the consolute temperature (T_s) against the mole fraction of salt (x_3) for ternary solutions of water–THF–ammonium chloride, water–THF–potassium chloride, and water–TBA–potassium chloride, respectively. In each series of measurements, the mole fraction of nonelctrolyte before adding salt,

$$x_2' = \frac{n_2}{n_1+n_2}, \tag{1}$$

was kept constant. Here, n_1 and n_2 are the number of moles of water and nonelectrolyte (THF or TBA), respectively. It can be seen from the figure that T_s^0 decreases with an increase in the salt concentration.

In the water–THF system, the consolute temperature for the salt-free system, T_s^0, can be observed directly under an atmosphere, as is illustrated in Fig. 1. Although the water–TBA system does not have the

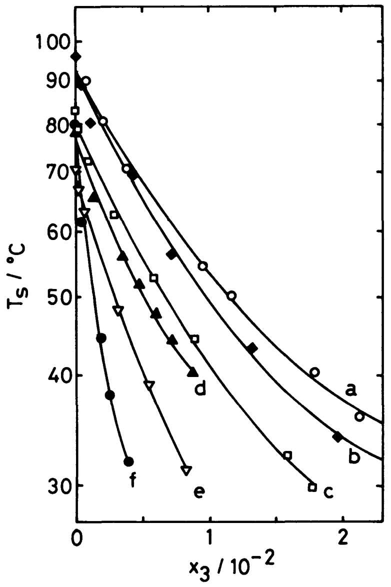

Fig. 1. A semilogarithmic plot of the consolute temperature against the mole fraction of salt for water–THF–ammonium chloride system. a: x_2'= 0.082, b: 0.095, c: 0.116, d: 0.136, e: 0.195, f: 0.364.

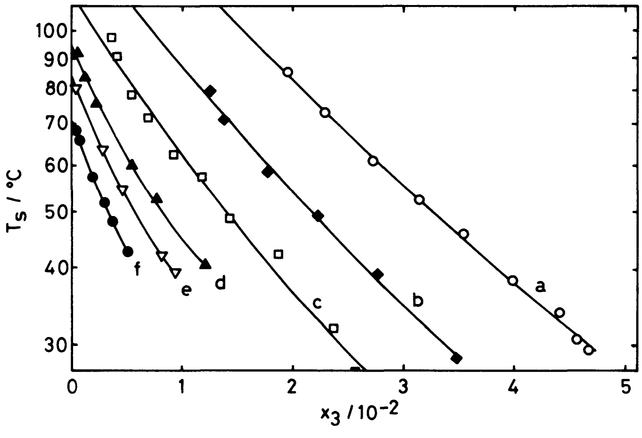

Fig. 2. A semilogarithmic plot of the consolute temperature against the mole fraction of salt for water–THF–potassium chloride system. a: x_2'= 0.035, b: 0.047, c: 0.065 d: 0.087, e: 0.097, f: 0.141.

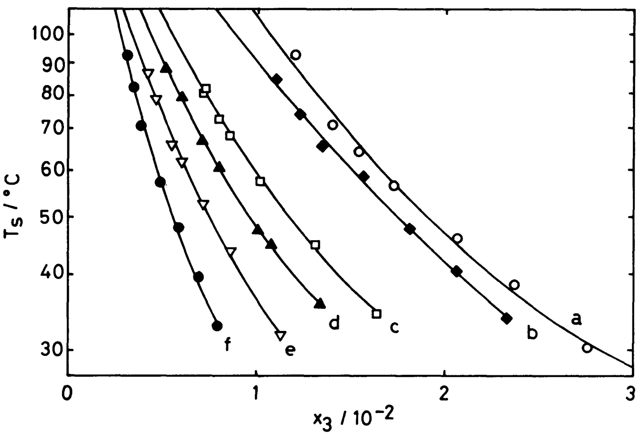

Fig. 3. A semilogarithmic plot of the consolute temperature against the mole fraction of salt for water–TBA–potassium chloride system. a: $x_2'=0.049$, b: 0.055, c: 0.097, d: 0.135, e: 0.190, f: 0.267.

LCST under ordinary conditions, the limiting value of T_s as $x_3\to 0$ may be regarded as the consolute temperature for the salt-free system. As can be seen from Fig. 3, however, it seems difficult to obtain the limiting value uniquely. We therefore have tried to determine an empirical formula for describing the relation between T_s and X_s. It has been found that all the present data can be fitted to the equation

$$\log T_s = a + bx_3 + cx_3^2, \qquad (2)$$

where a, b, and c are the fitting parameters. The solid lines in Figs. 1—3 represent the best-fit curves obtained by the least-squares method. The T_s^0 values for the water–THF and water–TBA systems have been calculated from the parameter a ($=\log T_s^0$). It should be noted that the validity of this procedure depends on the applicability of Eq. 2 in the low x_3 region.

In Figs. 4 and 5, the T_s^0 values, thus obtained, are plotted against the mole fraction of THF and TBA (x_2), respectively.[8] The closed circles in Fig. 4 represent T_s^0 values directly observed. It can be seen from the figure that the T_s^0 values obtained from the fitting procedure coinside with the observed values, at least in the range $0.08<x_2<0.4$. This indicates that Eq. 2 can be applied to the THF system at least in the range $x_3<0.02$ (see Figs. 1 and 2). We have assumed that the same holds true for the TBA system.[9]

Figure 5 suggests the existence of a minimum in the solubility curve. The LCST and the critical composition are thus estimated to be 200 °C and 0.15—0.2, respectively. Bender and Pecora[10] have obtained concentration dependence of the correlation length by means of dynamic light scattering. They have shown that the correlation length takes a maximum at $x_2=0.15$ in the temperature range 10—40 °C. The Kirkwood-Buff integral G_{ij} ($i, j=1$ or 2 for a binary solution composed of 1 and 2) for the water–TBA system have been reported by several authors.[3,11,12] According to these data, G_{12} also takes a minimum at $x_2=0.15$. These x_2 values are closed to the critical composition estimated in the present work.

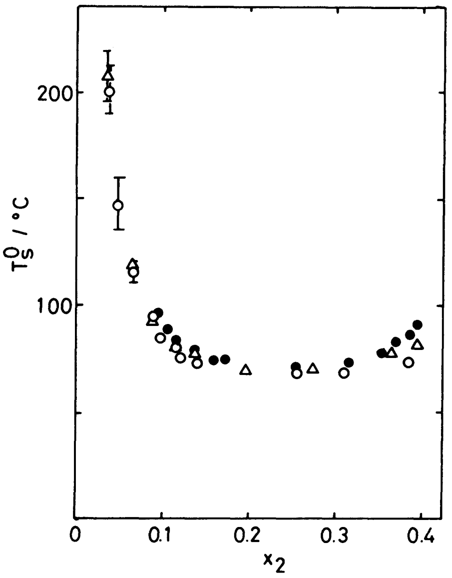

Fig. 4. Mutual solubility curve for water–THF system calculated from $\log T_s - x_3$ plots for water–THF–potassium chloride(○) and water–THF–ammonium chloride(△) systems. Closed circles represent observed values.

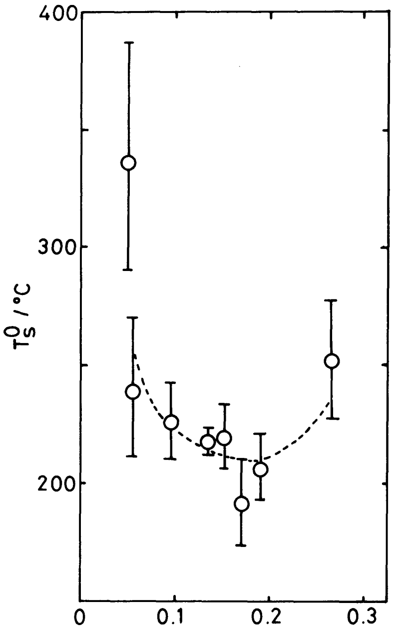

Fig. 5. Mutual solubility curve for water–TBA system calculated from $\log T_s - x_3$ plots for water–TBA–potassium chloride system.

This suggests that the critical phenomenon of demixing dominates the mixing states, even at temperatures some 150—200 °C below the critical consolute temperature.

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8) Measurements of T_s were made also at compositions other than those shown in Figs. 1—3.

9) The slight difference between calculated and observed T_s^0 values for the potassium chloride system arises from the lack of data in the low x_3 region. This may cause serious error in the estimation of T_s^0 for the water–TBA system because T_s cannot be observed up to much higher concentration of salt than the THF system. At present, however, it seems difficult to confirm the validity of Eq. 2 for the TBA system.

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