Ultralow Interfacial Tension in the Vicinity of the Upper Critical Solution Temperature of the Mixture of Water and Isobutyric Acid

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The ultralow interfacial tension of the binary liquid mixture of water and isobutyric acid has been measured as a function of temperature under atmospheric pressure in the vicinity of the upper critical solution temperature. It has been observed that the interfacial tension decreases monotonously as the temperature increases and is reduced to zero at the critical solution temperature. The results have been analyzed on the basis of the thermodynamics of interfaces. It has been found that the formation of interface is accompanied by increases in entropy and energy, which vanish at the critical solution temperature. This behavior has been considered in terms of the partial molar thermodynamic quantities of components. The brief discussion of the critical exponent has been also given for the present system.

The interfacial tension between two phases of a binary liquid mixture has been found to be reduced to zero as temperature approaches the critical solution temperature. In connection with the critical phenomena, therefore, it seems to be great interest to clarify the interfacial behavior in the vicinity of the critical solution temperature. However, the thermodynamic investigations of the interface are scarcely undertaken at temperatures near the critical solution temperature,[1-6] which is probably due to the difficulty of the precise measurement of ultralow interfacial tension. In our previous paper,[7] a new apparatus adopting a sessile drop technique was designed and the ultralow interfacial tension was measured accurately up to the value of 0.02 μN m^{-1}. Further it has been proved that the thermodynamic analysis of the interfacial tension measured as a function of thermodynamic variables is useful to shed light on the properties and structures of interfaces.[8-10] In the present paper, as a part of our thermodynamic studies of interfaces, the interfacial tension of the water–isobutyric acid mixture, of which the upper critical solution temperature is close to room temperature, was measured at temperatures near the upper critical solution temperature and analyzed on the basis of the thermodynamics of interfaces. The comment is also made on the critical exponent of this system.

Experimental

The purification of materials and the purity of isobutyric acid have been described previously.[7] The mutual solubility curve was drawn by using the phase separation temperature and phase mixing temperature determined visually according to the following procedure. The mixture of about 20 cm^3 was weighed and the sample tube was placed in a water bath having a volume of about 65 dm^3. The bath was thermostated by employing a mercury-toluene regulator; the temperature measured by a Beckmann thermometer was found to be constant within ±0.002 K. First, the temperature of the bath was set to a temperature about 0.1 K below or above the phase separation temperature expected. After the mixture was stirred by a magnetic rotor for about 10 min, the temperature was raised by about 0.01 K when the mixture was turbid and the temperature lowered when the mixture transparent. By repeating this procedure, the phase separation temperature and the phase mixing temperature were determined. Both temperatures were found to agree with each other within 0.01 K.

The sessile drop method was adopted to measure the interfacial tension between the two phases at temperatures near the upper critical solution temperature under atmospheric pressure. The apparatus and procedure of the measurement were described in detail in the previous paper.[7]

Results and Discussion

The phase separation and the phase mixing temperature were determined at about 70 different concentrations of the water–isobutyric acid mixture in the relatively narrow temperature range under atmospheric pressure. The mutual solubility curve is shown in Fig. 1 in the form of temperature T *vs.*

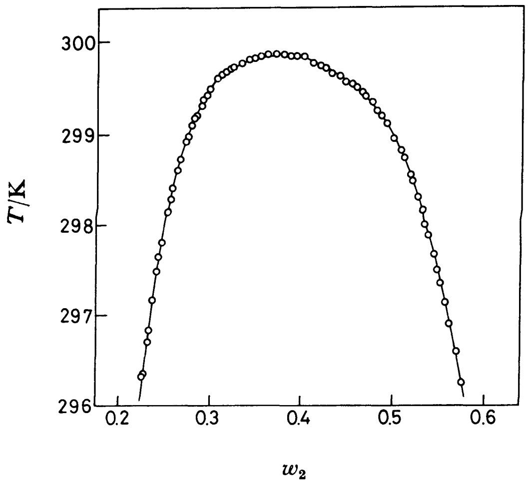

Fig. 1. Phase separation temperature *vs.* mass fraction curve under atmospheric pressure.

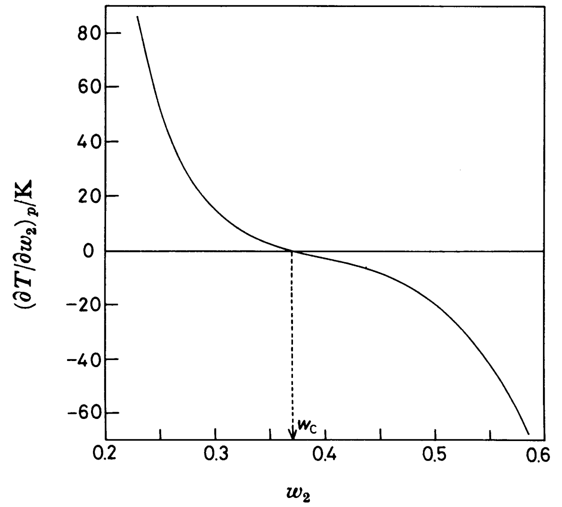

Fig. 2. $(\partial T/\partial w_2)_p$ *vs.* mass fraction curve under atmospheric pressure.

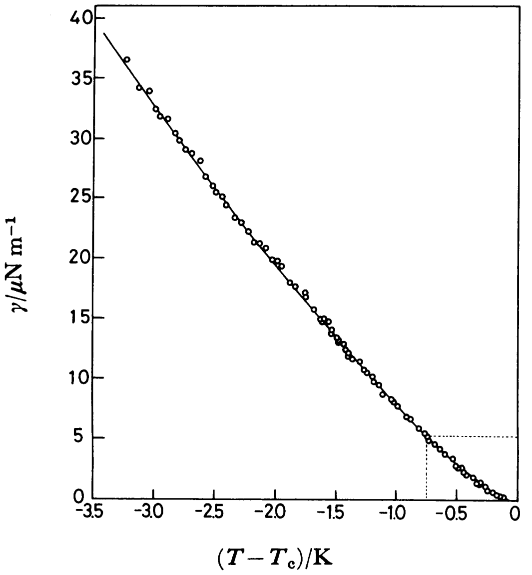

Fig. 3(a). Interfacial tension *vs.* temperature curve under atmospheric pressure.

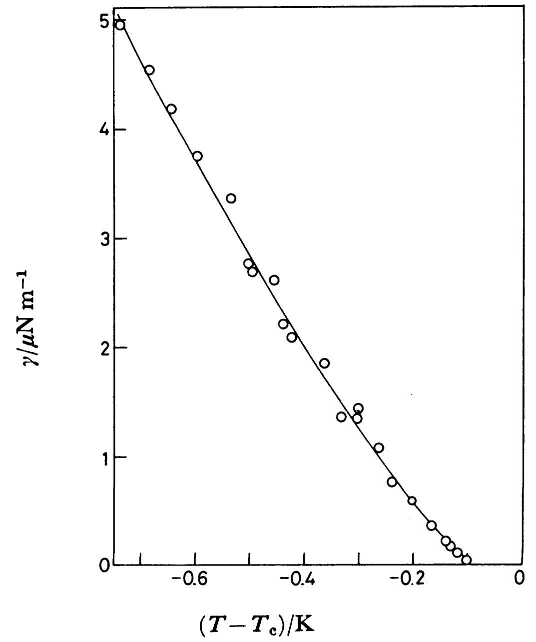

Fig. 3(b). Interfacial tension *vs.* temperature curve under atmospheric pressure.

mass fraction of isobutyric acid w_2 curve. The mass fraction at which the value of $\partial T/\partial w_2$ is zero was regarded as the critical composition w_c and the temperature corresponding to w_c as the upper critical solution temperature T_c. The $\partial T/\partial w_2$ *vs.* w_2 curve is shown in Fig. 2; the values of T_c and w_c were determined to be 299.88 K and 0.370, respectively.[11,12] At temperatures just below T_c, deep brown critical opalescence was observed. However, the determination of the phase separation and the phase mixing temperature was little affected by the opalescence.

The equilibrium interfacial tension γ was measured on critical mixtures at about 80 different temperatures in the vicinity of the critical solution temperature under atmospheric pressure. The γ *vs.* $T-T_c$ curve is drawn in Fig. 3(a) and the magnification of the curve very close to T_c is given in Fig. 3(b). It can be seen that the interfacial tension decreases monotonously from 35 to 0.02 μN m^{-1} with rising temperature in the narrow range of temperature. Further the γ value seems to approach zero at the critical solution temperature. This is the behavior expected for binary liquid mixtures having the upper critical solution temperature.[1-6] It is important to recognize that the slope of the curve is closely related to the entropy of interface formation.

By making use of Fig. 1, the interfacial tension shown in Fig. 3 can be plotted against the composition of the coexisting phases. The result is shown in Fig. 4 in the form of γ *vs.* w_2-w_c plot; the left and right parts of the curve correspond to the water-rich and acid-rich phases, respectively. It is seen that the interfacial tension decreases with decreasing the difference in composition between the conjugate phases and approaches zero at the critical composition. This is in harmony with the observation that an increase in mutual solubilities is responsible for a decrease in interfacial tension.[13,14] It is also seen that the curve is slightly unsymmetrical about the line parallel to the ordinate at the critical composition, which reflects the unsymmetry of the mutual solubility curve given in Fig. 1.

It has been well known that the temperature dependence of the interfacial tension in the vicinity of the critical solution temperature is described by the power law given by

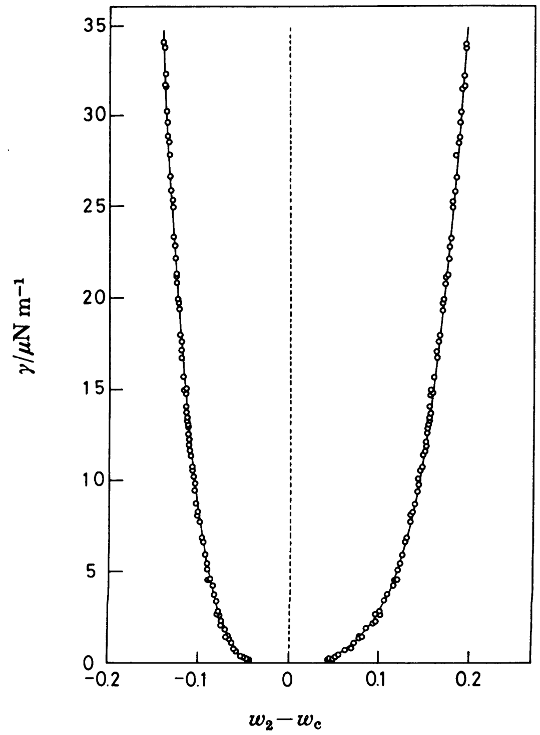

Fig. 4. Interfacial tension *vs.* mass fraction curve under atmospheric pressure.

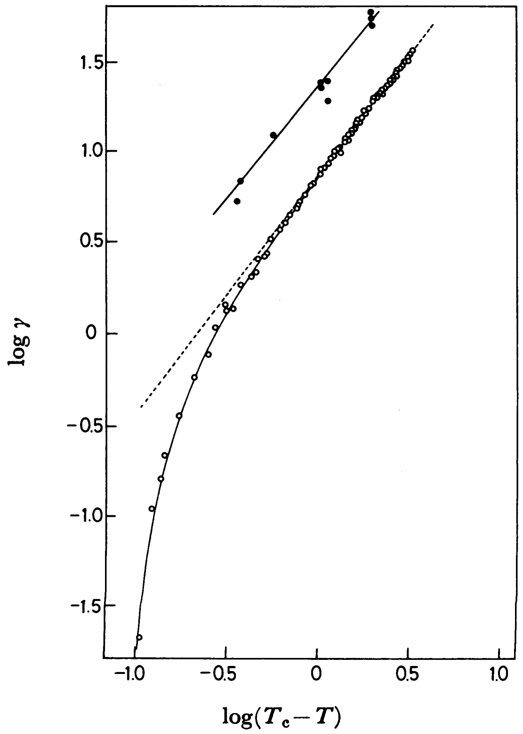

Fig. 5. log γ *vs.* log (T_c-T) curves under atmospheric pressure: (○) present study, (●) data from reference (6).

$$\gamma = k|T_c-T|^{\mu}, \qquad (1)$$

where k is a proportionality constant and μ the critical exponent. Further, the temperature range where experimental results obey Eq. 1 has been discussed.[4] To examine the applicability of Eq. 1 to the present system, the value of log γ is plotted against $\log(T_c-T)$ in Fig. 5. It is seen that the curve follows the power law only in a limited temperature range and deviates from it at temperatures very close to T_c. The slope of the straight line was found to give $\mu=1.33$ in the range $0.003<(T_c-T)/T_c<0.01$. Also included in this figure for comparison are the results of Howland *et al.*;[6] they obtained $\mu=1.23\pm0.09$ by the unweighted least-squares analysis. It should be noted, however, the γ values of Howland *et al.* are higher than those of the present study and show considerable scatter. Furthermore, the lowest γ value measured is seen to be significantly high compared to that of the present study. Therefore, there seems to be some doubt as to whether Eq. 1 expresses the temperature dependence of the interfacial tension in the vicinity of T_c over a wide range of temperature.

To clarify the properties and structure of liquid/liquid interface, it is of great importance to examine the thermodynamic quantities of interface formation evaluated from experimental results by applying the thermodynamics of interfaces.[8–10] Immediately we notice that the temperature dependence of interfacial tension at constant pressure shown in Fig. 3 is closely related to the entropy of interface formation. The degree of freedom is two since the system under consideration is composed of two components and has two bulk phases separated by a plane interface. From the experimental point of view, therefore, it is convenient to choose temperature T and pressure p of the system as the independent variables. From Eqs. [8], [37], and [39] of Ref. (8), the interfacial tension is expressed in the differential form as

$$\mathrm{d}\gamma = -\Delta s\mathrm{d}T + \Delta v\mathrm{d}p, \qquad (2)$$

where Δs and Δv are the entropy and volume of interface formation, respectively. Thus we can estimate the value of Δs by applying Eq. 3 to the results given in Fig. 3:

$$\Delta s = -(\partial\gamma/\partial T)_p. \qquad (3)$$

Figure 6 shows the change of the Δs value with temperature. It can be said that the interface formation of the binary mixture having upper critical solution temperature is accompanied by the increase in entropy. However, the value of Δs seems to decrease rapidly as the temperature approaches T_c and to be reduced to zero at T_c. Taking into account that the Δs values obtained for the systems of virtually immiscible oil and water are fairly larger than the above one and closely related to the mutual solubility between them,[10] it is also understandable from Figs. 1 and 6 that the rapid decrease of the difference between the compositions of the two phases is responsible for the rapid decrease of the entropy of interface formation in the close vicinity of the critical solution temperature.

Now let us consider the contributions of components to the entropy of interface formation in some detail. According to the quasithermodynamics, the entropy of interface formation of two-component system can be expressed by use of the partial molar entropy changes of the components in the form[8)]

$$\Delta s = \Gamma_1^I \Delta s_1 + \Gamma_2^I \Delta s_2, \tag{4}$$

where Γ_i^I is the number of moles of component i participating in the interface per unit area and Δs_i the partial molar entropy change of component i caused by the interface formation. In case that the two component are practically immiscible with each other, the two terms on the right side of Eq. 4 can be written as

$$\Gamma_i^I \Delta s_i = \Gamma_i^I (\bar{s}_i^I - s_i), \quad i=1,\ 2, \tag{5}$$

where $\bar{s}_i^I$ is the mean partial molar entropy in the interfacial region and s_i the partial molar entropy in the pure bulk phase. In the case of the present system where the two components are partly miscible with each other, on the other hand, $\Gamma_i^I \Delta s_i$ consists of two terms, *i.e.*, the one resulted from the transfer of component i from the component 1-rich phase α to the interfacial region and the other from the component 2-rich phase β; correspondingly, Γ_i^I is divided into the two parts $\Gamma_i^{I,\alpha}$ and $\Gamma_i^{I,\beta}$ which are attributable to the phases α and β, respectively. Therefore, it can be written as

$$\Gamma_i^I \Delta s_i = \Gamma_i^{I,\alpha}(\bar{s}_i^I - s_i^\alpha) + \Gamma_i^{I,\beta}(\bar{s}_i^I - s_i^\beta), \quad i=1,\ 2. \tag{6}$$

In the result, we have

$$\Delta s = [\Gamma_1^{I,\alpha}(\bar{s}_1^I - s_1^\alpha) + \Gamma_1^{I,\beta}(\bar{s}_1^I - s_1^\beta)] + [\Gamma_2^{I,\alpha}(\bar{s}_2^I - s_2^\alpha) + \Gamma_2^{I,\beta}(\bar{s}_2^I - s_2^\beta)]. \tag{7}$$

Comparing Eq. 7 with the positive value of Δs shown in Fig. 6, we may conclude, that the entropy of transfer of components from the two phases to the interfacial region, as a whole is positive. Accordingly, the contact of two different molecules which form a mixture with the upper critical solution temperature is said to be accompanied by an increase in entropy. Further, since the physical properties of the conjugate phases become identical as the temperature approaches the critical solution temperature, the partial molar entropies in the bulk phases and the interfacial region turn out to have the same values at T_c.

Now we can calculate the energy of interface formation Δu by applying the following equation to the above results;

$$\Delta u = \gamma + T\Delta s - p\Delta v. \tag{8}$$

The Δu *vs.* $T-T_c$ curve is shown in Fig. 7, where the value of $p\Delta v$ has been assumed to be negligibly small under atmospheric pressure when compared with the values of γ and $T\Delta s$ terms.[15-17)] It is seen that the value of Δu is positive and reduced to zero at the critical solution temperature in a similar manner to that of Δs. The analog of Eq. 7 holds for Δu:

$$\Delta u = [\Gamma_1^{I,\alpha}(\bar{u}_1^I - u_1^\alpha) + \Gamma_1^{I,\beta}(\bar{u}_1^I - u_1^\beta)] + [\Gamma_2^{I,\alpha}(\bar{u}_2^I - u_2^\alpha) + \Gamma_2^{I,\beta}(\bar{u}_2^I - u_2^\beta)], \tag{9}$$

where $\bar{u}_i^I$ and u_i are the mean partial molar energy of component i in the interfacial region and the corresponding partial molar energy in the bulk phase, respectively. Therefore, we can say that the overall value of energy of transfer is positive and the differences among $\bar{u}_i^I$, u_i^α, and u_i^β disappear at the critical solution temperature. These facts lead us to the conclusion that the interface formation from the

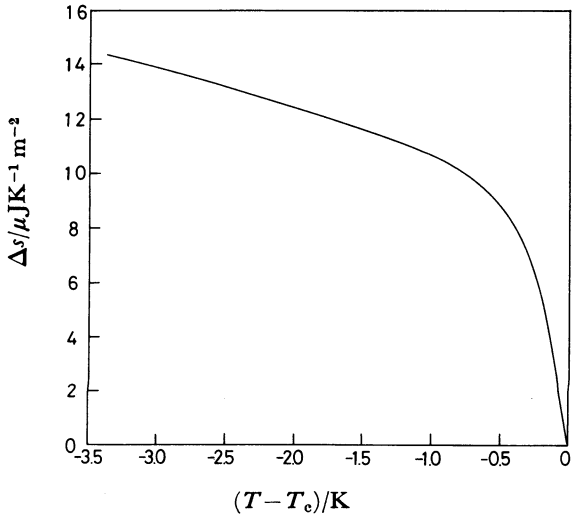

Fig. 6. Entropy of interface formation *vs.* temperature curve under atmospheric pressure.

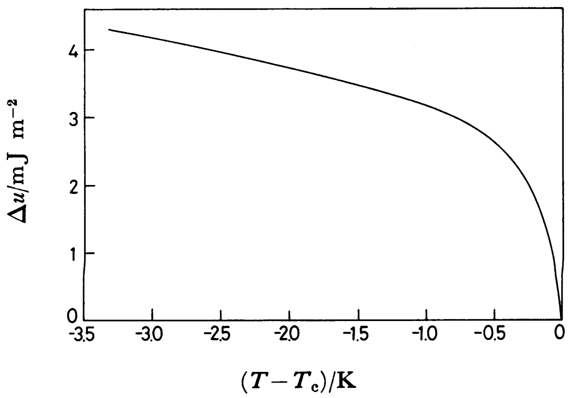

Fig. 7. Energy of interface formation *vs.* temperature curve under atmospheric pressure.

two conjugate phases of a binary system in the vicinity of the upper critical solution temperature is an unfavorable process from the viewpoint of energy, but favorable process from the viewpoint of entropy. Further information regarding the interfacial behavior of molecules will be provided by investigating a binary liquid mixture having the lower critical solution temperature.

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