Measurement of Ultralow Interfacial Tension in the Vicinity of Critical Solution Temperature

Makoto ARATONO* and Kinsi MOTOMURA
Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812
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Synopsis. A new apparatus adopting the sessile drop technique has been designed to measure the ultralow interfacial tension between two liquids of a binary mixture. The equilibrium interfacial tension of the mixture of isobutyric acid and water has been determined near its upper critical solution temperature up to the value of 0.02 $\mu N\ m^{-1}$.

When two liquids are practically immiscible with each other, the properties and structure of the interface between the liquids have been clarified by measuring the dependence of interfacial tension on temperature and pressure and evaluating the thermodynamic quantities of interface formation.[1-3] When two liquids are practically miscible and have the critical solution temperature, however, thermodynamic investigations of the interface are scarce.[4-9] This may be attributable to the difficulty of the precise measurement of ultralow interfacial tension at temperatures near the critical solution temperature. In the present study, we made an apparatus for measuring the ultralow interfacial tension and determined the equilibrium interfacial tension values near the critical solution temperature.

Experimental

Materials. Isobutyric acid (Nakarai's guaranteed reagent) was distilled fractionally at atmospheric pressure and the middle fraction was used for the experiments. The sample was found to be 99.9% pure by gas-liquid chromatography with a 3 m long and 3 mm in diameter column packed with Unisole 400 (Gaskuro Kogyo Inc.). The doubly distilled water was further distilled after refluxing with alkaline permanganate.

Interfacial Tension Measurement. The measurements of the interfacial tension between the two phases in equilibrium near the upper critical solution temperature T_c of binary liquid mixture under atmospheric pressure were carried out by a new sessile drop method. Figure 1 shows the sessile drop cell which was mounted in the jacketed vessel made of acrylate resin. The temperature control of the cell is an important matter in the present study. To minimize a fluctuation in temperature, the whole system was placed in the air thermostat. In result, the temperature of the cell measured by the Beckmann thermometer was found to be constant within ±0.002 K. The sessile drop was formed in the following way. The binary mixture (80—100 ml) having a composition close to the critical one in the cell was vigorously stirred by a rotor (a) for about 30 min at the desired temperature and permitted to stand for from 1 to 7 h to separate completely into the water-rich (b) and acid-rich (c) phases. Then a part of the upper layer solution was sucked up into the syringe (d) by the plunger (e) and then the optical flat (f) attached to the bottom of syringe was dipped into the lower layer solution. At this stage, the sessile drop (g) was formed on the surface of the optical flat by pushing the plunger by rotating micrometer (h) and located by the level adjuster in the position which permits to take its photograph. By the use of the camera with the bellows of about five magnification and the light ray parallel to the optical axis, we could have a clear, enlarged, and undistorted profile.

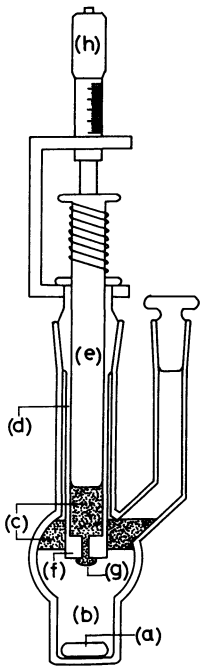

Fig. 1. Cross sectional view of a quartz sessile drop cell. (a): Rotor, (b): water-rich phase, (c): acid-rich phase, (d): syringe, (e): plunger, (f): optical flat, (g): sessile drop, (h): micrometer.

The interfacial tension γ was calculated by making use of the following equation[10,11]

$$\gamma = (1/2)g\Delta d a^2 \quad (1)$$

where g is the acceleration of gravity and Δd the density difference between two conjugate solutions. The values of Δd were available from the literature.[12] The capillary constant a^2 is correlated to the dimensions of the image on the negative film by the relation

$$a^2 = r^2 f(h/r), \quad (2)$$

where r is the radius of the drop in the equatorial plane, h the distance from the apex to the plane, and $f(h/r)$ the function of h/r. The values of h and r were determined by Nikon measurescope (model II) with the precision of ±1 μm. The experimental error of the interfacial tension did not exceed two percent of the obtained value.

Figure 2 shows the time dependence of interfacial tension. It can be seen that the equilibrium value can be obtained within a few minutes. Therefore, the drop was stood for about 15 min and photographed.

Results and Discussion

The γ *vs.* $T-T_c$ curves are shown in Fig. 3; the value of T_c determined by making use of the mutual solubility curve[13] has been used. It is seen from Fig. 3 that the value of γ decreases monotonously with rising

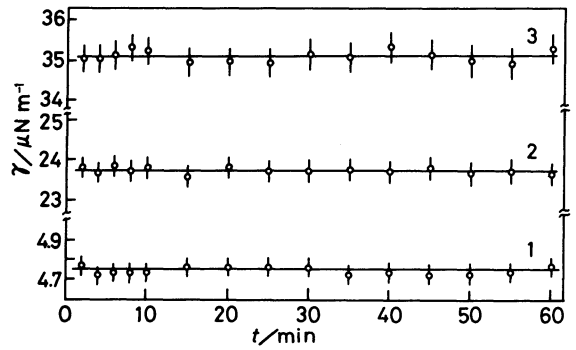

Fig. 2. Interfacial tension *vs.* time curves. 1: $T-T_c$=−0.708 K, 2: −2.365, 3: −3.175.

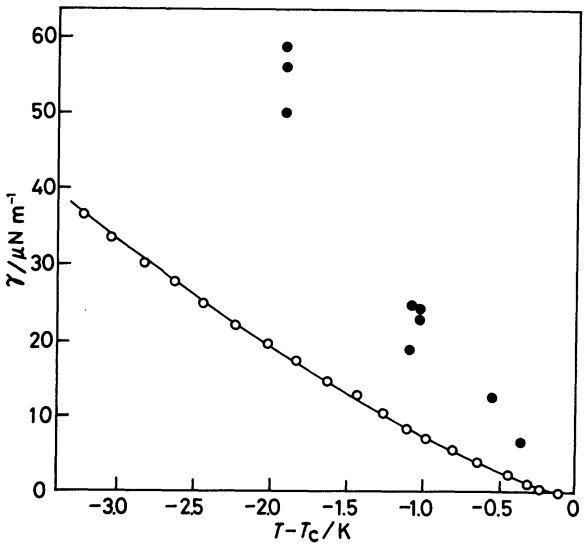

Fig. 3. Interfacial tension *vs.* temperature curve. (○): Present study, (●): data from reference 9.

temperature and approaches zero at the critical solution temperature. This is the behavior expected for the binary liquid mixture which has the upper critical solution temperature. Further it is worth noting that the value varies from 35 to 0.02 μN m^{-1} in the narrow temperature range in $T-T_c$ from −3.2 to −0.1 K. The closed symbols in Fig. 3, the γ values of Howland *et al.*,[9] are larger than ours and show considerable scatter. In addition, the lowest value of the former is found to be significantly high compared to the one of the latter. Taking into account that the capillary rise method employed by Howland *et al.* is unsuitable in principle for measuring the ultralow interfacial tension, the above results may indicate that the sessile drop method of the present study provides the ultralow interfacial tension values accurate enough to consider the behavior of the interface between the two phases of binary liquid mixture near the critical solution temperature.

It has been shown that the dependence of γ on temperature at constant pressure gives useful information regarding the entropy of interface formation.[1,4] It is supposed, therefore, that the formation of the interface from the two phases of binary liquid mixture in equilibrium near the upper critical solution temperature is attended by an increase in entropy and the entropy of interface formation is reduced to zero at the upper critical solution temperature. Further discussion will be made in the separate paper.[13]

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