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CRITICAL COMPOSITION AND CRITICAL SOLUTION TEMPERATURE OF A BINARY MIXTURE OF ACETONITRILE AND WATER DETERMINED BY VARIABLE-TEMPERATURE PMR SPECTROSCOPIC METHOD

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Each of two PMR signals for a mixture of acetonitrile and water has been found to split into two peaks in a limited composition range at low temperatures. The splittings are attributable to the two-phase separation of the mixture. The critical composition and the critical solution temperature have been estimated by use of this phenomenon.

During a study on selective solvation of some metal cations by PMR spectroscopy, we have found that each proton signal for water and acetonitrile in a mixture splits into two peaks at low temperatures and considered that the splittings result from the two-phase separation of the acetonitrile-water mixture. The present communication deals with the first example of application of variable-temperature PMR spectroscopic method to determine both the critical composition and the critical solution temperature of a partially miscible liquid system.

PMR spectra were obtained with a Varian A 60D spectrometer at 60 MHz using tetramethylsilane as an internal standard. Temperatures were controlled within ±1°C by adjusting a flow rate of nitrogen gas stream precooled with liquid nitrogen, and were calibrated on the basis of temperature dependence of chemical shifts for methanol. Signal peak areas were determined with a planimeter made by Uchida Yoko, and the reproducibility in measurement was within 10%. Acetonitrile was purified by distillation under a nitrogen atmosphere after successive treatment with sodium hydride, phosphorus pentoxide, and calcium hydride.

PMR measurements were carried out for sixteen samples of acetonitrile-water mixtures with mole fractions of acetonitrile covering the range from 1.0 to 0.34 at temperatures between 40 and -20°C. At all the compositions of the mixture investigated, the PMR signals due to water and acetonitrile shifted to lower fields as the temperature decreased from a room temperature to 0°C. This downfield shift of the water proton signal, being attributed to an increase in the water structure at low temperatures, was ten times as large as that of the acetonitrile proton signal.

At a mole fraction for acetonitrile (x) of 0.945, two peaks due to the water and acetonitrile protons were observed above the freezing point. At $x = 0.797$, the water signal was shifted to a higher field below ca. -20°C, and x = 0.691, it split into two signals. At x = o.609, the splitting was also observed. At x from 0.568 to 0.423, the splitting could be seen clearly. Each of the signals due to water and acetonitrile split into two signals simultaneously at a certain temperature; with a decrease in temperature, each of the upfield peaks was shifted to a higher field, whereas each of the downfield peaks was shifted to a lower field.

Figure 1 shows the temperature dependence of the proton signals for a mixture with x = 0.463. The shapes and areas of the proton signals changed with decreasing temperature. The ratio of the area for the upfield peak to the

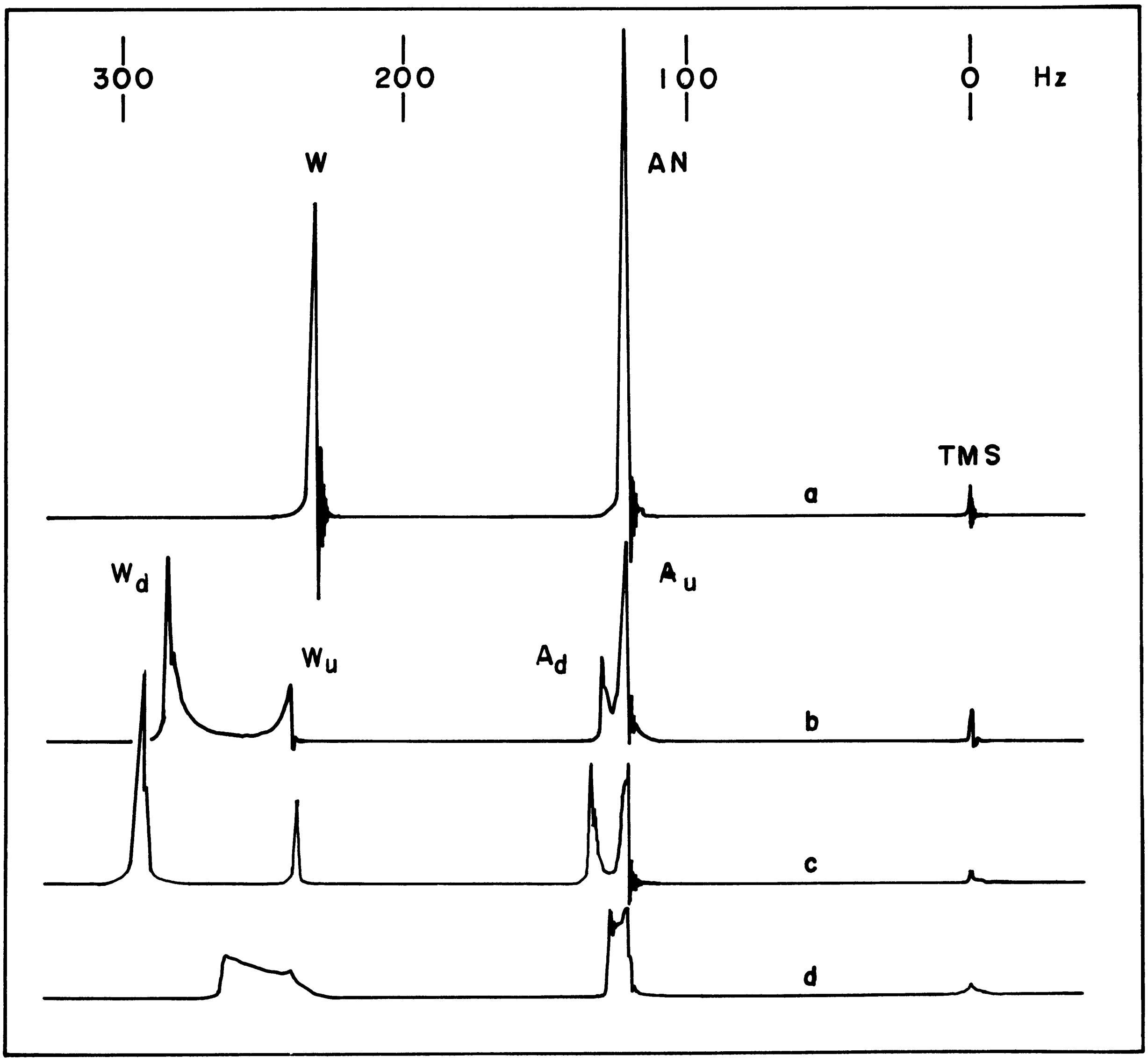

Fig. 1. Temperature dependence of 60-MHz PMR spectra for a mixture with a mole fraction of acetonitrile, 0.463.
(a) 32.5, (b) 0, (c) -2.5°C, and (d) allowed to stand at 24.5°C for 2 hr after having been cooled below -8°C.
Spectral amplitude for TMS is ten times as large as that for W and AN.

total area of the two peaks due to acetonitrile proton, $A_u/(A_d + A_u)$, changed with temperature in the same way as the ratio of the area for the upfield peak to the total area of the two peaks due to water proton, $W_u/(W_d + W_u)$. These temperature dependences of the four peak areas lead us to assume that a set of the upfield proton peaks and a set of the downfield proton peaks may be attributed to the mixtures different in composition of acetonitrile and water, such as the two phases of partially miscible acetonitrile-water system at low temperatures. Since the proton signal for water is shifted to a higher field with increasing acetonitrile content at a room temperature, it may be reasonable to assume that a set of the upfield proton peaks, A_u and W_u, corresponds to acetonitrile and water in a saturated solution of water in acetonitrile, and a set of the downfield proton peaks, A_d and W_d, corresponds to those in a saturated solution of acetonitrile in water. With this assumption, we can estimate the compositions of acetonitrile and water phases from the four peak areas.

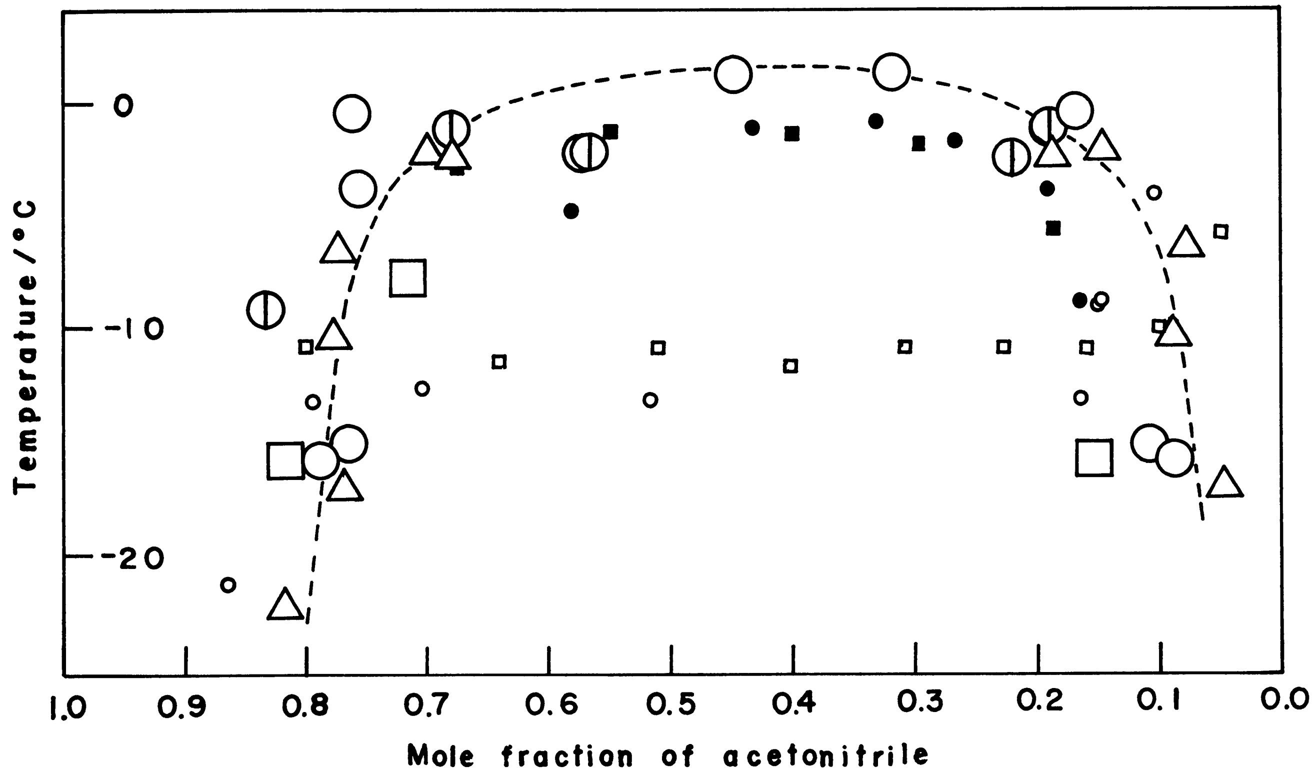

Fig. 2. The acetonitrile-water system.
A broken line represents the mutual-solubility curve, which connects the compositions of acetonitrile and water phases, determined by the PMR method, for acetonitrile-water mixtures with mole fractions of acetonitrile: 0.423(△), 0.459(○), 0.463(⦶), and 0.544 (□). The solubility data obtained by Benjamin and Ewert, ■, and ● ; the freezing points measured by Benjamin and Ewert, □ , and ○ , respectively.

For any mixtures with x from 0.568 to 0.423, we can easily estimate the mole fractions of acetonitrile for both phases from the four peak areas as a function of temperature. For mixtures with x from 0.3 to 0.4 and from 0.6 to 0.8, however, it is difficult to measure the peak areas precisely because of the overlapping of signal peaks, and therefore, we cannot estimate the compositions. Figure 2 shows that the compositions calculated for the two phases fall on nearly the same two-phase composition-temperature curve. The present curve covers a wider region in both composition and temperature than do the mutual-solubility curves obtained by Benjamin and Ewert.1) The critical composition and the critical solution temperature evaluated from the curve obtained by the PMR method are 0.43 and $+1._5$°C, respectively, which may be reasonable in comparison with the respective values of 0.31 and -1.4°C measured by Masuda et al. by use of an ultrasonic absorption technique.2) Neither separated phase nor turbidity was detected with naked eyes at temperatures where the phase separation was detected by the PMR method. Below temperatures where the phase separation was detected, the apparent mole fraction for acetonitrile estimated from the observed peak areas did not coincide with the original mole fraction x in a mixture. The reason is not yet clear.

Although there may be left some important points to be settled such as the improvements in accuracy and precision of temperature and peak area measurements, the above findings seem to prove the novel possibility that each component in two microscopically different states of partially miscible liquids may be distinguished by the PMR method if necessary conditions are satisfied. In the acetonitrile-water system, because the difference in temperature between the critical temperature and the freezing point is small, the two kinds of molecular clusters with the compositions of the two phases may coexist in a well-mixed condition as the result of a slowdown of molecular motions near the freezing temperature.

References

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