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The Effects of Sodium Chloride on the Ultrasonic Properties of an Aqueous Solution of Isopropyl Alcohol

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Synopsis. The ultrasonic absorptions in an aqueous solution of isopropyl alcohol with sodium chloride (NaCl) were measured in the frequency range from 2.5 to 220 MHz at 25 °C. The ultrasonic properties were remarkably affected by the addition of NaCl, and a new absorption was found around 7 MHz in addition to that observed in the solution without NaCl. The results were discussed in terms of the forming effects of NaCl on the water structure.

As has been reported in previous papers,[1,2] ultrasonic absorptions in aqueous solutions of alcohols have been characterized by two kinds of relaxations. One is associated with the interaction between alcohol and water molecules, and the other, with aggregation reaction of alcohols having a relatively high hydrophobicity. However, the latter absorption was not observed in the aqueous solution of isopropyl alcohol over all the concentration range studied.[3]

In order to investigate further the properties of the aqueous solutions of alcohols and the structure of water, the ultrasonic absorption measurements were performed in the aqueous solution of isopropyl alcohol with sodium chloride (NaCl) added.

Experimental

The isopropyl alcohol and water used in this study were the same as those described in a previous paper.[3] The NaCl was the purest grade obtainable and was used without further purification. The ultrasonic absorption was measured in the manner described in previous work.[1] All the measurements were made at 25 °C.

Results and Discussion

The ultrasonic absorptions were measured under various concentrations of NaCl at a constant concentration of isopropyl alcohol (5.20 mol dm^{-3}), because the ultrasonic parameters for the aqueous solution could be determined with a relatively high accuracy at this concentration. Figure 1 shows the representative ultrasonic absorption spectra in the mixed solution. In general, the spectra associated with several relaxation processes can be expressed by the following equation:

$$\alpha/f^2 = \sum_i A_i/[1+(f/f_{ri})^2] + B, \tag{1}$$

where α is the absorption coefficient; f, the frequency; A_i, the amplitude of the excess absorption for the i-th process; f_{ri}, the relaxation frequency, and B, the constant. The absorption data in the concentration range of NaCl below 0.50 mol dm^{-3} were represented by a single relaxation formula and were analyzed graphically from the plot of α/f^2 *vs.* $[1+(f/f_r)^2]^{-1}$ so as to obtain a straight line. However, with an increase in the NaCl concentration, a new absorption appeared in the low frequency range (around 7 MHz); the absorption data were analyzed by means of a nonlinear least-squares routine. Figure 2 shows the variation in the relaxation frequencies with the NaCl concentration. The amplitudes of the excess absorptions are also shown in Fig. 3.

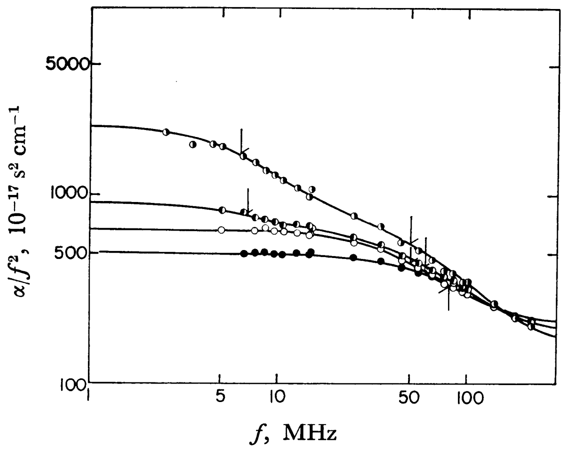

Fig. 1. Ultrasonic absorption spectra in 5.20 mol dm^{-3} solution of isopropyl alcohol with various NaCl concentrations at 25 °C. The arrow indicates the relaxation frequency. ●: without NaCl, ○: 0.40 mol dm^{-3} (NaCl), ◐: 0.60 mol dm^{-3} (NaCl), ◑: 1.20 mol dm^{-3} (NaCl).

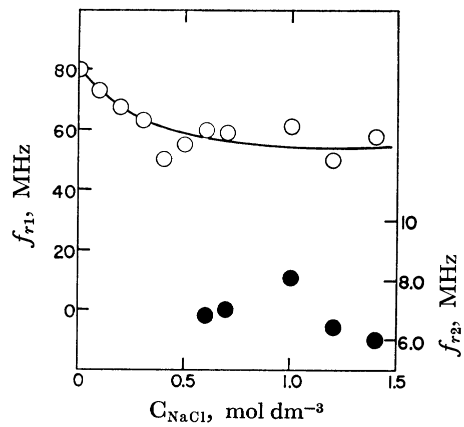

Fig. 2. Dependences of the relaxation frequencies in 5.20 mol dm^{-3} solution of isopropyl alcohol on the concentration of NaCl at 25 °C. ○: f_{r1}, ●: f_{r2}.

As has been reported in a previous study,[3] only a single relaxational absorption was observed over all the concentration range of isopropyl alcohol and the ab-

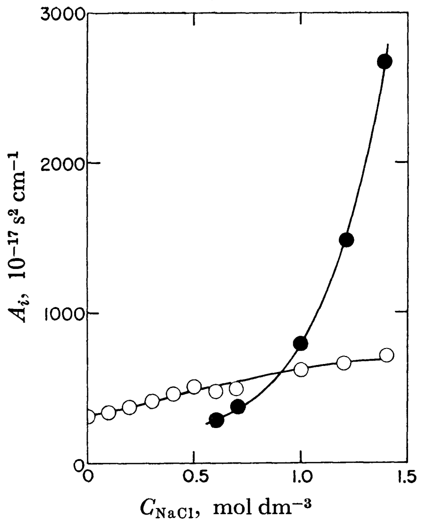

Fig. 3. Dependences of the amplitudes of the excess absorption in 5.20 mol dm^{-3} solution of isopropyl alcohol on the concentration of NaCl at 25 °C. ○: A_1. ●: A_2.

sorption mechanism was interpreted quantitatively in terms of a solute-solvent interaction as follows:

$$A + B \underset{k_b}{\overset{k_f}{\longleftrightarrow}} AB, \quad (2)$$

where A and B are the monomers of alcohol and water, and where k_f and k_b are the forward and backward rate constants respectively. The relaxation frequency for this process was related by the following equation:

$$2\pi f_r = k_f([A]+[B]) + k_b. \quad (3)$$

In this analysis, water molecules are assumed to be in two states; that is, there exists an equilibrium between hydrogen bonded and non-hydrogen bonded water, and only non-hydrogen bonded water molecules participate in the reaction with alcohol molecules. If the addition of NaCl disturbs the equilibrium in water, the ultrasonic parameters associated with the reaction of Eq. 2 will be affected. Considering that NaCl acts as the former of the water structure,[4] the relaxation frequency, f_{r1}, should be decreased through Eq. 3 by the decrease in the monomer concentration of water with an increase in the NaCl concentration. The experimental results are in agreement with this expectation, as is shown in Fig. 2.

Another important and interesting feature of the ultrasonic absorption in the mixed solution is the appearance of a new absorption in the low frequency range at concentrations of NaCl more than 0.50 mol dm^{-3}, as may be seen in Fig. 1. The frequency range in which the new absorption was found is near that in which the relaxational absorption associated with the hydrophobic effects were observed in aqueous solutions of *n*-propyl and *t*-butyl alcohols.[1,2] This shows that even the molecules with relatively low hydrophobicities can interact with each other by means of the hydrophobic effect when the enviroments of the molecules are changed by added substances.

Finally, urea is well known to be a breaker of the water structure, and its effect on the ultrasonic properties of the aqueous solution might be expected. However, no effective changes in the relaxation parameters were observed when urea was added to the aqueous solution of isopropyl alcohol.

References

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