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Ultrasonic Absorption Mechanism in an Aqueous Solution of Isopropyl Alcohol

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Synopsis. Ultrasonic absorption measurements in an aqueous solution of isopropyl alcohol were made in the frequency range from 5 to 220 MHz and in the concentration range from 3 to 10 M. The excess absorption which is characteristic of a single relaxation process was observed. The mechanism of the excess absorption was interpreted in terms of a reaction expressed by AB⇌A+B, where A and B are monomeric molecules of alcohol and water respectively. The rate constants for forward and backward reactions were determined from the concentration dependences of the relaxation frequencies. The results obtained were compared with those of aqueous solutions of other alcohols which had already been published.

The structural properties of aqueous solutions of various alcohols have been studied in relation to biological reaction mechanisms. The ultrasonic studies have been also applied to the investigations of the dynamical properties of aqueous solutions of alcohols.[1-3] The present authors have previously reported the results of the ultrasonic absorption measurements in aqueous solutions of propyl, *t*-butyl, and allyl alcohols, and they have interpreted the excess absorptions from the point of view of reaction kinetics.[4,5] In this paper, we will report the results of the ultrasonic absorption measurements in an aqueous solution of isopropyl alcohol; the results will be compared with those of other alcohols.

Experimental

The isopropyl alcohol was a reagent-grade commercial product and was distilled once. No impurity was observed by gas-chromatography. The water used in the experiments was doubly distilled. The sample solutions were made at the desired concentrations by weight. The concentration range of the experiments was from 3.00 to 10.01 M. The apparatus for the ultrasonic absorption and velocity measurements have been previously described in detail.[4,6] The frequency range of the ultrasonic absorption measurements was from 5 to 220 MHz, while the sound velocity was measured at 1.92 MHz by a sing-around technique. All the measurements were made at 25 °C.

Results and Discussion

Figure 1 shows the representative ultrasonic absorption spectra in an aqueous solution of isopropyl alcohol. All the spectra in the solution can be described by the following expression of a single relaxation in the frequency range measured.

$$\alpha/f^2 = A/[1+(f/f_r)^2] + B \qquad (1)$$

where α is the absorption coefficient; f, the frequency; f_r, the relaxation frequency, and A and B, constants. The relaxation parameters were determined by the usual procedure.[5] In Table 1, the obtained values of ultrasonic parameters are listed together with the sound velocities and densities.

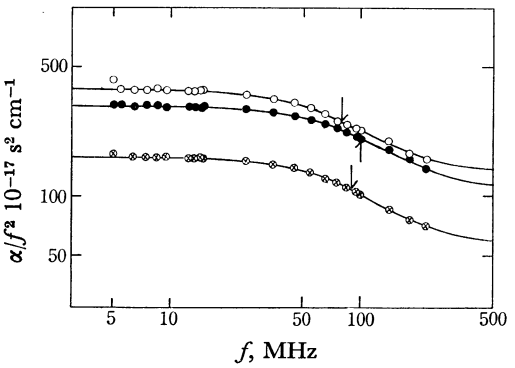

Fig. 1. Ultrasonic absorption spectra in an aqueous solution of isopropyl alcohol at 25 °C.
⊗; 4.00M, ○; 5.50M ●; 7.00M

Table 1. Relaxation parameters, sound velocities and densities in aqueous solution of isopropyl alcohol

C_a (M)	ρ (g ml^{-1})	c (m s^{-1})	f_r (MHz)	A (10^{-17} s^2 cm^{-1})	B
3.00	0.9718	1597	100	25.7	38.8
4.00	0.9620	1595	90	144	73.7
4.50	0.9570	1578	92	279	92.1
5.00	0.9500	1558	85	275	170
5.50	0.9428	1532	80	318	177
6.00	0.9324	1501	85	299	168
6.50	0.9310	1481	95	274	170
7.00	0.9146	1465	100	260	145
8.00	0.8995	1409	110	197	137
10.01	0.8551	1315	145	59.9	119

The sound absorption in aqueous solutions of propyl and *t*-butyl alcohols features a characteristic double relaxation; the mechanisms were interpreted in terms of the solute-solvent interaction and the molecular aggregation of alcohol by hydrophobic interaction. While, the excess absorption in an aqueous solution of allyl alcohol was expressed by a single relaxation process, and the mechanism was attributed to the solute-solvent interaction, as in a previous study.[5] Therefore, the cause of the ultrasonic absorption in an aqueous solution of isopropyl alcohol may be expected to be associated with the solute-solvent interaction, because the region of the relaxation frequency is roughly the same as that of allyl alcohol. The model for the relaxation process is as follows;

$$AB \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A + B \qquad (2)$$

where A and B are the molecules of alcohol and water respectively, and k_{ij}, the rate constant. The relations for the relaxation frequency and the maximum excess absorption per wavelength are;

$$2\pi f_r = 1/\tau = k_{21}(C_2+C_3) + k_{12} \quad (3)$$

$$\mu_{max} = Af_r c/2 = \pi\rho c^2/[VRT(1/C_1+1/C_2+1/C_3-1/C_T)] \times (\Delta V-\alpha_p^\infty \Delta H/\rho C_p^\infty)^2 \quad (4)$$

All the symbols in these equations are defined as in the previous paper.[5] Equation 3 can be rewritten as:

$$2\pi f_r = 1/\tau = k_{21}\sqrt{(C_a-\beta C_w+K_{12})^2+4\beta C_w K_{12}} \quad (5)$$

where K_{12} is the equilibrium constant and C_a and C_w are the analytical concentrations of alcohol and water respectively. The parameter, β, is the mole fraction of the water monomer. The introduction of β into the interpretation of the excess absorption means that only the monomer of the water molecule can participate in the reaction expressed by Eq. 2. The values of k_{21}, β and K_{12} were determined so as to obtain a best fit of the data to Eq. 5. Here, the fact that the relaxation frequencies went through a minimum at the concentration of C_a=5.50 M was also used to estimate the parameters. The kinetic parameters obtained are listed in Table 2, along with those of aqueous solutions

Table 2. The reaction parameters and the stability of water structure in aqueous solutions of alcohols

Solute	k_{12} (s^{-1})	k_{21} ($M^{-1}s^{-1}$)	k_{23}[a] ($M^{-2}s^{-1}$)	k_{32}[a] (s^{-1})	β
t-Butyl alcohol	1.2×10^8	7.2×10^7	5.5×10^5	4.9×10^7	0.12
Propyl alcohol	1.6×10^8	6.2×10^7	2.2×10^5	6.9×10^7	0.15
Isopropyl alcohol[b]	1.4×10^8	8.8×10^7	—	—	0.17
Allyl alcohol	1.5×10^8	6.3×10^7	—	—	0.19

a) The rate constants, k_{23} and k_{32}, are for the aggregation reaction by hydrophobic interaction. b) This work.

of other alcohols. The concentration dependence of the relaxation frequency calculated with these values and Eq. 5 is shown in Fig. 2 by a solid line; the circles indicate the experimental values. In order to confirm the excess absorption mechanism, it is appropriate to inspect the concentration dependence of the maximum excess absorption per wavelength, μ_{max}. From Eq. 4, μ_{max} may be expected to be approximately proportional to $\rho c^2(1/C_1+1/C_2+1/C_3-1/C_T)^{-1}$. In Fig. 3, the concentration dependence of the maximum excess absorption per wavelength is shown, together with that of the calculated values of $\rho c_2(1/C_1+1/C_2+1/C_3-1/C_T)^{-1}$. As may be seen in this figure, the tendency of the concentration dependence of the maximum excess absorption per wavelength is similar to that of the calculated curve (solid line). This confirms that the excess absorption mechanism in an aqueous solution of isopropyl alcohol may be attributed to the perturbation of the equilibrium expressed by Eq. 2.

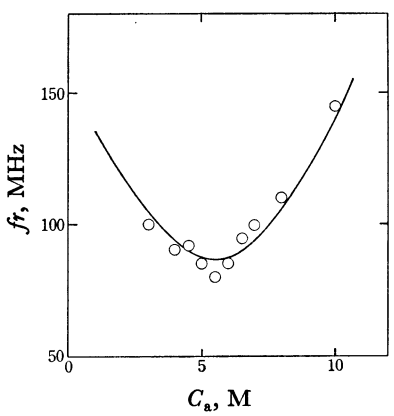

Fig. 2. Concentration dependence of the relaxation frequency in an aqueous solution of isopropyl alcohol.

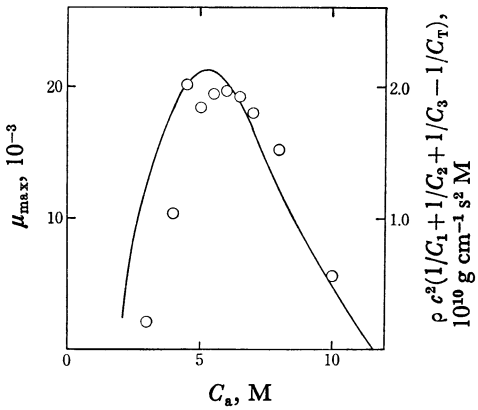

Fig. 3. The variations of μ_{max} and $\rho c^2(1/C_1+1/C_2+1/C_3-1/C_T)^{-1}$ with the concentration of isopropyl alcohol.

The dependencies of the forward and backward rate constants for the AB⇌A+B reaction on the solute molecules (see Table 2) are not remarkable. This may indicate that the complex formed by alcohol and water is due to a hydrogen bonding. However, the β parameter, which indicates the stability of the water structure, varies considerably depending on the solute molecules. When the strength of the hydrophobic interaction increases,[7] the β parameter decreases. In aqueous solutions of propyl and *t*-butyl alcohols, another excess absorption in the lower frequency range was observed; this mechanism was associated with the aggregation reaction of alcohol by hydrophobic interaction.[5] The strength of the hydrophobic interaction of isopropyl and allyl alcohols, however, is not so strong enough that these alcohols do not aggregate in aqueous solutions by hydrophobic interaction, and only a single relaxational absorption is observed in the frequency range measured

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