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Ultrasonic Absorption Mechanism in an Aqueous Solution of *n*-Propyl Alcohol

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Ultrasonic absorption in aqueous solutions of *n*-propyl alcohol was measured in the frequency range of 4.5—220 MHz and in the concentration range of 2.0—13.4 M at 25 °C. Two different relaxation processes were observed; they were attributed to the perturbation of the equilibria expressed by $AB \underset{B}{\rightleftarrows} A \rightleftarrows 1/3A_3$ where A and B are a single water molecule and an alcohol molecule respectively. The forward and backward rate constants for the two processes were determined from the concentration dependences of the relaxation frequencies. Furthermore, the influence of *n*-propyl alcohol on the water structure was discussed; the addition of *n*-propyl alcohol to liquid water was concluded to promote the water structure.

Because of the predominance of water as the medium in living systems, the hydrogen-bonding properties of water have been of particular interest to chemists and biologists. The effects of electrolyted on the structure of water have attractes considerable attention in recent years, but relatively little work has been published dealing with the solution properties and hydrodynamic behavior of neutral solutes. During the course of an investigation of the properties of aqueous solutions of several amines[1–5] by means of ultrasonic absorption, it became desirable to understand the properties of alcohols in aqueous solutions. The physico-chemical properties of aqueous solutions of alcohols have been studied by many authors[6–9], and the ultrasonic techniques[10–13] have also been applied to the investigation of these solutions. However, though Blandamer and his co-workers[14] have reported on the ultrasonic absorption spectra in an aqueous solution of *n*-propyl alcohol, no quantitative analysis of the excess absorption mechanisms has been done.

The present investigation has aimed at the establishment of the excess absorption mechanisms of ultrasonic waves in an aqueous solution of *n*-propyl alcohol on the basis of the water structure. This type of information is particularly desirable for an understanding of more complex biochemical reactions.

Experimental

The chemicals used were of a guaranteed reagent grade; the purity of the *n*-propyl alcohol, which had been distilled once, was verified to be more than 99.9% by gas chromatography. Water which had been deionized and then distilled was used as the solvent. The sample solutions were made at the required concentrations by weight. The concentration range of all the measurements was 2.00—13.4 M, which corresponded to 0.0402—1.00 mole fractions of *n*-propyl alcohol. The measurements of the ultrasonic absorption were carried out at the odd harmonic frequencies of 0.5, 5, and 20 MHz X-cut transducers by means of the pulse technique.[15] The frequency range of the absorption measurement was 4.5—220 MHz. The sing-around technique operated at a fixed frequency of 1.92 MHz was used to measure the sound velocity. The densities were measured by means of a standard pycnometer, the volume of which was 3.717 cm^3. All the measurements were made at 25 °C. A thermostat was built capable to perform within ±0.03 °C.

Results

The quantity α/f^2, where α is the sound absorption coefficient, and f, the frequency, was found to be frequency dependent for an aqueous solution of *n*-propyl alcohol. The plots of α/f^2 *vs.* the concentration of *n*-propyl alcohol are shown in Fig. 1 at various frequencies. The fact that α/f^2 depends on the frequency leads us to the idea that relaxational phenomena exist in the frequency range measured. In general, the sound absorption caused by the several relaxation processes can be described by the following equation:

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

where f_{ri} is the relaxation frequency for the i-th process and where A_i and B are constants. Figure 2 shows some representative ultrasonic absorption spectra of aqueous solutions of *n*-propyl alcohol. The spectra in the concentrations lower than 2.75 M show the behavior characteristic of a single relaxation process, which is expressed by $i=1$ in Eq. (1). On the other hand, the experimental results in the concentrations higher than 2.95 M can be expressed by two relaxation processes. The double relaxation spectra were analyzed by a nonlinear least-squares routine, employing a Toshiba 3400 computer. In Table 1, the ultrasonic

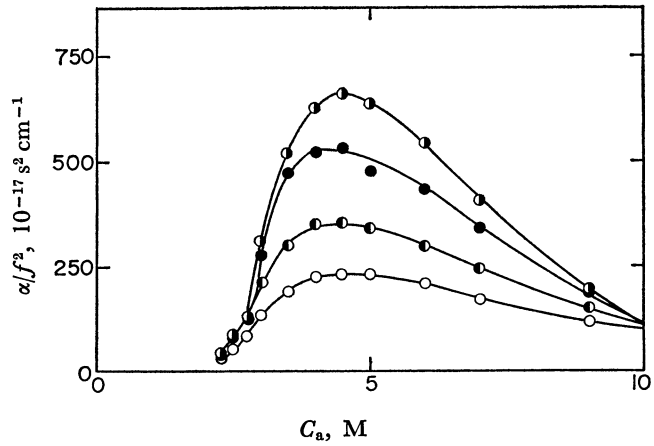

Fig. 1. The plots of α/f^2 *vs.* concentration for the aqueous solution of *n*-propyl alcohol at 25 °C.
◑: f=6.5 MHz, ●: f=15 MHz, ◐: f=45 MHz, ○: f=100 MHz.

Table 1. Relaxation parameters, sound velocity in the aqueous solution of *n*-propyl alcohol

C_a	n_f[a)]	ρ	c	f_{r_1}	f_{r_2}	A_1	A_2	B
(M)		(g mℓ$^{-1}$)	(m s^{-1})	(MHz)		(10^{-17} s^2 cm^{-1})		
2.00	0.0402	0.9797	1583.7	—	—	—	—	34.5
2.25	0.0461	0.9771	1588.1	85	—	17.3	—	55.3
2.50	0.0518	0.9752	1590.6	80	—	61.0	—	41.4
2.75	0.0579	0.9723	1589.2	78	—	145	—	54.1
2.95	0.0630	0.9699	1585.0	82	18	196	80	69.0
3.03	0.0649	0.9690	1581.8	86.5	21	220	113	37.8
3.50	0.0772	0.9647	1566.6	80	12	425	273	44.7
4.00	0.0914	0.9570	1546.8	71	11	432	387	140
4.50	0.107	0.9500	1527.3	90	14	378	463	131
5.00	0.123	0.9429	1508.3	85.5	13	355	457	143
6.02	0.161	0.9280	1471.0	81	12	287	379	151
7.00	0.204	0.9130	1436.5	84	16	193	246	144
9.00	0.322	0.8816	1371.9	110	26	71.0	83.8	116
13.4	1.00	0.8005	1207.5	—	—	—	—	69.1

a) n_f is the mole fraction of *n*-propyl alcohol.

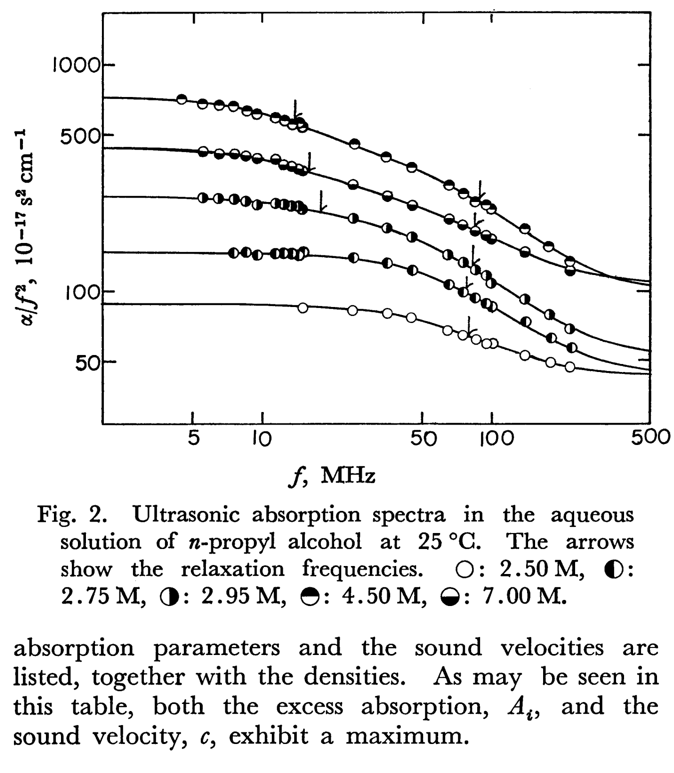

Fig. 2. Ultrasonic absorption spectra in the aqueous solution of *n*-propyl alcohol at 25 °C. The arrows show the relaxation frequencies. ○: 2.50 M, ◐: 2.75 M, ◑: 2.95 M, ◓: 4.50 M, ◒: 7.00 M.

absorption parameters and the sound velocities are listed, together with the densities. As may be seen in this table, both the excess absorption, A_i, and the sound velocity, c, exhibit a maximum.

Interpretation of Results

Both water and alcohol molecules have a tendency to form hydrogen bonding, and the latter also has a hydrophobic group. Therefore, the following reaction mechanisms for the relaxation processes will be considered:

$$\mathrm{AB}_m \underset{k_{21}\ \searrow m\mathrm{B}}{\overset{k_{12}}{\longleftrightarrow}} \mathrm{A} \underset{k_{32}}{\overset{k_{23}}{\longleftrightarrow}} \frac{1}{n}\mathrm{A}_n \tag{2}$$

where A is the molecule of alcohol; B, that of water, and k_{ij}, the rate constant. In this equation, the first equilibrium indicates the interaction between alcohol and water molecules, and the second, the self-association reaction of alcohol. The general approach of the treatment used here is similar to that of Eigen and de Maeyer[16)] or that of Hammes and Knoche.[17)] If one denotes the molar concentrations of the components, AB$_m$, B, A, and A$_n$ by C_1, C_2, C_3, and C_4 respectively, the returning rate of the system to equilibrium is governed by the rate law:

$$\frac{\mathrm{d}C_1}{\mathrm{d}t} = -k_{12}C_1 + k_{21}C_2^mC_3 \tag{3}$$

$$\frac{\mathrm{d}C_4}{\mathrm{d}t} = k_{22}C_3^n - k_{32}C_4 \tag{4}$$

These equations can be linearized in the neighborhood of the equilibrium by the usual procedure:

$$\frac{\mathrm{d}\Delta C_1}{\mathrm{d}t} = a_{11}\Delta C_1 + a_{21}\Delta C_4 \tag{3'}$$

$$\frac{\mathrm{d}\Delta C_4}{\mathrm{d}t} = a_{21}\Delta C_1 + a_{22}\Delta C_4 \tag{4'}$$

with $a_{11}=-[k_{12}+k_{21}\ (m^2\bar{C}_2{}^{m-1}\bar{C}_3+\bar{C}_2{}^m)]$, $a_{12}=-k_{21}$-$n\bar{C}_2{}^m$, $a_{21}=-k_{23}n\bar{C}_3{}^{n-1}$ and $a_{22}=-(k_{23}n^2\bar{C}_3{}^{n-1}+k_{32})$, where a bar over a symbol indicates the equilibrium value. In the derivation of Eqs. (3′) and (4′), the relations of $\Delta C_3=-n\Delta C_4-\Delta C_1$ and $\Delta C_1=-1/m\Delta C_2$ were used. The (3′) and (4′) rate equations can be written as:

$$\frac{\mathrm{d}\boldsymbol{X}}{\mathrm{d}t} = \boldsymbol{AX} \tag{5}$$

where $\boldsymbol{A}$ is the column matrix made up of the a_{ij}'s. Using the normal coordinate transformation, Eq. (5) can be transformed to:

$$\frac{\mathrm{d}\boldsymbol{Y}}{\mathrm{d}t} = \boldsymbol{BY} \tag{6}$$

where $\boldsymbol{Y}$ is the column matrix of eigenvectors, and $\boldsymbol{B}$, a diagonal matrix of the negative reciprocal relaxation times. The transformation matrix is as follows[17)]:

$$\boldsymbol{M} = \begin{bmatrix} 1 & -[(1/\tau_1+a_{11})/a_{11}] \\ a_{21}/a_{11} & -[(1/\tau_2+a_{11})/a_{11}] \end{bmatrix} \tag{7}$$

where the relations of $\boldsymbol{Y}=\boldsymbol{MX}$ and $\boldsymbol{B}=\boldsymbol{MAM}^{-1}$ are satisfied. If the first step in Eq. (2) is assumed to equilibriate rapidly compared to the second, one gets:

$$1/\tau_1 = 2\pi f_{r1} = -a_{11} = k_{21}(m^2\bar{C}_2^{m-1}\bar{C}_3+\bar{C}_2^m) + k_{12} \tag{8}$$

$$1/\tau_2 = 2\pi f_{r2} = \frac{a_{12}a_{21}}{a_{11}} - a_{22}$$

$$= k_{32}+k_{23}n^2\bar{C}_3^{n-1} - \frac{n^2k_{21}k_{23}\bar{C}_2^m\bar{C}_3^{n-1}}{k_{12}+k_{21}(m^2\bar{C}_2^{m-1}\bar{C}_3+\bar{C}_2^m)} \tag{9}$$

$$y_1 = \Delta C_1 + \frac{a_{12}}{a_{11}}\Delta C_4 \tag{10}$$

$$y_2 = -\Delta C_4 \tag{11}$$

For the two relaxation processes, the chemical absorption per wavelength is:

$$\mu_{\text{ch}} = 4\mu_{m_1}\pi f\tau_1/[1+(f/f_{r_1})^2] + 4\mu_{m_2}\pi f\tau_2/[1+(f/f_{r_2})^2] \tag{12}$$

The expression for the maximum excess absorption per wave length, μ_{mi}, for the i-th process is derived as follows:

$$\mu_{mi} = \frac{1}{2}A_i f_{ri} c = (\rho\pi c^2\Gamma_i/RT)\left(\Delta V_i - \frac{\alpha_p^\infty}{\rho\, C_p^\infty}\Delta H_i\right)^2 \tag{13}$$

where ρ is the density; R, the gas constant; T, the absolute temperature; $\alpha_p{}^\infty$, the high-frequency limit of the thermal expansion coefficient; $C_p{}^\infty$, the high-frequency limit of the constant pressure specific heat, and ΔV_i and ΔH_i, the parameters related to the volume and enthalpy changes associated with the reactions. The Γ_i terms is the function of the reactant concentrations and is derived by means of:

$$\Gamma_i = -\frac{RT}{V}\left(\frac{\partial y_i}{\partial A'_i}\right)_{TPy_j} \qquad i \neq j \tag{14}$$

where A_i' is the affinity. In the conditions of a constant temperature and a constant pressure, the maximum excess absorption per wavelength is proportional to $\rho c^2\Gamma_i$ and the other terms are nearly constant. For the reactions expressed by Eq. (2), one can calculate the Γ_i terms using Eq. (14):

$$\Gamma_1 = \frac{1}{V}\left(\frac{1}{\bar{C}_1}+\frac{1}{\bar{C}_3}+\frac{m^2}{\bar{C}_2}-\frac{m^2}{\bar{C}_T}\right)^{-1} \tag{15}$$

$$\Gamma_2 = \frac{1}{V}\left[\frac{n}{\bar{C}_3}\left(n-\frac{a_{12}}{a_{11}}\right)+\frac{n-1}{\bar{C}_T}\left(n-1+\frac{a_{12}}{a_{11}}\right)+\frac{1}{\bar{C}_4}\right]^{-1} \tag{16}$$

where $\bar{C}_T=\bar{C}_1+\bar{C}_2+\bar{C}_3+\bar{C}_4$.

If one denotes the analytical concentration of alcohol by C_a and that of water by C_w, the next equations are set up:

$$C_\text{a} = \bar{C}_1 + \bar{C}_3 + n\bar{C}_4 \tag{17}$$

$$C_\text{w} = C_\text{w}^\text{a} + m\bar{C}_1 + \bar{C}_2 \tag{18}$$

where C_w^a is the concentration of the cluster, that is, the concentration of the hydrogen-bonded water molecules. It is well known that the physico-chemical properties of liquid water can be interpreted by a two-state model.[18,19] Therefore, we assume that, in an aqueous solution of alcohol, there exists an equilibrium between hydrogen-bonded and non-hydrogen-bonded water in addition to those equilibria expressed by Eq. (2) and that only non-hydrogen-bonded water molecules participate in the interaction with alcohol molecules. Then, if one denotes the concentration of non-hydrogen-bonded water by C_w^s, the next equations are held:

$$C_\text{w}^\text{s}/C_\text{w}^\text{a} = \exp(-\Delta F_\text{w}/RT),\ C_\text{w} = C_\text{w}^\text{s} + C_\text{w}^\text{a} \tag{19}$$

where ΔF_w is the free energy difference between hydrogen-bonded and non-hydrogen-bonded water molecules.

At this stage, we shall first consider the reaction mechanism associated with the excess absorption observed in the higher frequency range and the case of $m=1$, namely, the case in which a single alcohol molecule interacts with a single water one. We also assume that the concentration of the aggregate of alcohol, $\bar{C}_4$, is very small as compared with those of the other components. Then, one obtains the next equation from Eqs. (8), (17), (18) and (19):

$$1/\tau_1 = 2\pi f_{r_1} = k_{21}\sqrt{(C_\text{a}-\beta C_\text{w}+K_{12})^2+4\beta C_\text{w}K_{12}} \tag{20}$$

where β is the mole fraction of non-hydrogen-bonded water and where K_{12} is defined as $K_{12}=k_{12}/k_{21}=\bar{C}_2\bar{C}_3/\bar{C}_1$. As may be seen in Table 1, the value of the relaxation frequency, f_{r_1}, goes through minimum near $C_\text{a}=4.5$ M. Therefore, the next condition must be satisfied at $C_\text{a}=4.5$ M.

$$\frac{\partial(1/\tau_1)}{\partial C_\text{a}} + \frac{\partial(1/\tau_1)}{\partial\beta C_\text{w}}\cdot\frac{\mathrm{d}\beta C_\text{w}}{\mathrm{d}C_\text{a}} = 0 \tag{21}$$

Thus, the parameters, β and K_{12}, are not independent of each other. A trial-and-error procedure was used to obtain the values of these parameters which provided the best fit to the experimental data using Eq. (20). The best values are $K_{12}=2.6$ M, $\beta=0.15$, and $k_{21}=6.2\times10^7$ M^{-1} s^{-1}. Then, one gets also $k_{12}=1.6\times10^8$ s^{-1} from the definition of K_{12}. The relaxation frequencies calculated by Eq. (20) using the obtained parameters are shown in Fig. 3, along with the experimental values. One can evaluate the concentration dependence of the maximum chemical absorption per wavelength using Eq. (15). Figure 4 shows the calculated values of $\rho c^2\Gamma_1 V$ along with the experimental values of $\mu_{\text{m}1}$. As may be seen in this figure, both maxima

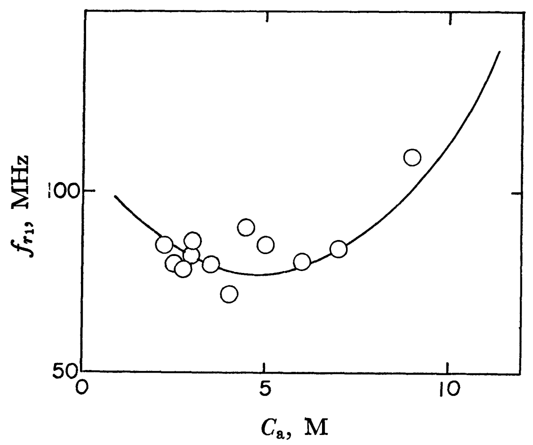

Fig. 3. Concentration dependence of the relaxation frequencies, f_{r_1}.

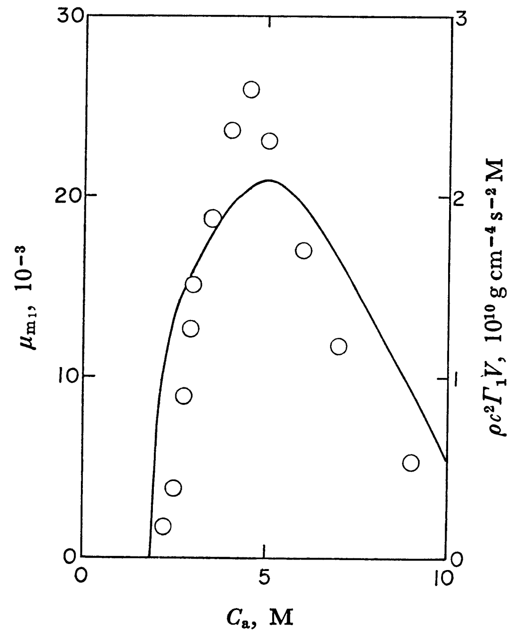

Fig. 4. The variation of μ_{m_1} and $\rho c^2 \Gamma_1 V$ with the concentration of *n*-propyl alcohol. The solid line represents the calculated values of $\rho c^2 \Gamma_1 V$. The circles are the experimental points of μ_{m_1}.

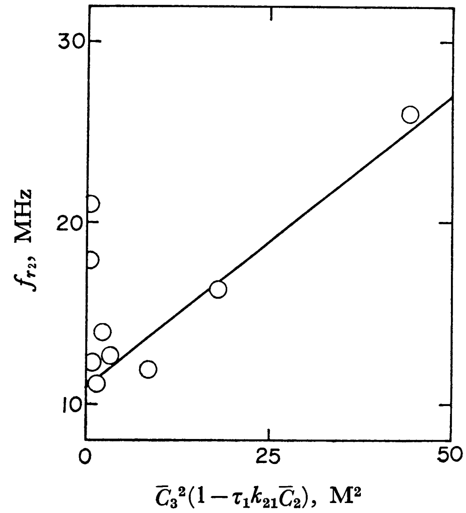

Fig. 5. The plots of f_{r_2} *vs.* $\bar{C}_3{}^2(1-\tau_1 k_{21}\bar{C}_2)$ for the aqueous solution of *n*-propyl alcohol at 25 °C.

appear at almost the same position. This confirms that the excess absorption mechanism in the higher frequency range is due to the perturbation of the first equilibrium expressed in Eq. (2).

Second, let us consider the mechanism of the excess absorption in the lower frequency range. Equation (9) can be transformed as follows.

$$1/\tau_2 = 2\pi f_{r_2} = n^2 k_{23}\bar{C}_3^{n-1}(1-\tau_1 k_{21}\bar{C}_2) + k_{32} \qquad (22)$$

Figure 5 shows the plots of f_{r_2} *vs.* $\bar{C}_3{}^2(1-\tau_1 k_{21}\bar{C}_2)$. The parameter, *n*, which is the aggregation number of *n*-propyl alcohol, was determined so as to give a straight line of the plots of f_{r_2} *vs* $\bar{C}_3{}^{n-1}$ $(1-\tau_1 k_{21}\bar{C}_2)$ and resulted in $n=3$. The rate constants were determined to be $k_{23}=2.2\times10^5$ M^{-2} s^{-1} and $k_{32}=6.9\times10^7$ s^{-1} from the slope and intercept of the straight line respectively. We also calculated the concentration dependence of the maximum chemical absorption per wavelength associated with this aggregation reaction, but the value of $\rho c^2 \Gamma_2 V$ increases monotonically with the alcohol concentration.

Discussion

The most interesting and important feature in the ultrasonic absorption study of an aqueous solution of *n*-propyl alcohol is that the excess absorption is observed only in the solutions, not in pure water and pure alcohol, in the frequency range investigated. This means that the causes of the excess absorption mechanisms are closely associated with the peculiar properties of water and *n*-propyl alcohol molecules. The model which is proposed here is a general one which covers all of the equilibria considered in an aqueous solution of neutral solutes, because any molecule which consists of hydrophilic and hydrophobic groups has a tendency to interact with water molecules and to aggregate. The equilibrium between hydrogen-bonded (cluster) and non-hydrogen-bonded water molecules is also taken into accout for the elucidation of the observed excess absorption mechanisms, although the relaxation time for the perturbation of this equilibrium is too short to be observed[18] (It is of the order of 10^{-12} s). At this stage, it is very useful to consider the water structure in an aqueous solution of *n*-propyl alcohol. The parameter, β, is related to the free energy difference between the two states for hydrogen-bonded and non-hydrogen-bonded water molecules, ΔF_w, by the relation; $\beta/(1-\beta)=\exp(-\Delta F_w/RT)$ and one gets $\Delta F_w=1.0$ kcal. In pure liquid water, however, the free energy difference is of an order of less than 1 kcal.[19] The increase in the free energy difference is due to the decrease in the non-hydrogen-bonded water molecule in an aqueous solution of *n*-propyl alcohol. This means that the *n*-propyl alcohol molecule acts as water structure promoter. This conclusion is consistent with the results of other investigations.[8,20] In order to examine the influence

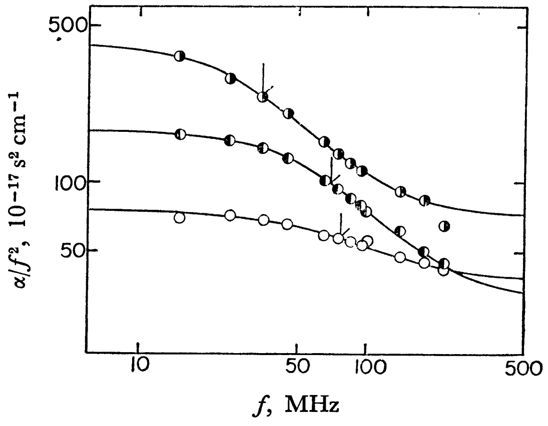

Fig. 6. Ultrasonic absorption spectra of the aqueous solution of 2.60 M *n*-propyl alcohol. The influence of NaCl to the absorption spectra. ○: no added, ◐: 0.507 M NaCl added, ◑: 1.00 M NaCl added.

of the water structure on the water and *n*-propyl alcohol interaction, we also measured the ultrasonic absorption in an aqueous solution of *n*-propyl alcohol to which NaCl was added. The measurements were performed in a solution of 2.60 M of *n*-propyl alcohol, where only a single relaxation process is observed in the higher frequency range. Figure 6 shows the absorption spectra in these solutions; the relaxation frequency decreases with increase of concentration of NaCl. Addition of NaCl to liquid water acts as water structure promoter.[21] According to Eq. (20), the decrease in the non-hydrogen-bonded water molecule must result in the decrease in the relaxation frequencies. As may be seen in Fig. 6, the experimental results are consistent with the above interpretation; this criterion is also taken as sufficient evidence for the correct assignment of the excess absorption mechanism in the higher frequency range observed.

More extensive ultrasonic absorption measurements in aqueous solutions of other alcohols may be desirable to confirm the ultrasonic absorption mechanisms of these solutions. The studies of these solutions are now in progress; the results will be reported in due course.

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