Ultrasonic Absorption Mechanisms in Aqueous Solutions of Alcohols

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Ultrasonic absorption measurements in aqueous solutions of *tert*-butyl and allyl alcohols were carried out in the frequency range of 4.5—220 MHz at 25 °C. Two relaxation processes were observed in aqueous solution of *tert*-butyl alcohol and a single one in that of allyl alcohol. The former relaxation mechanisms were revealed to be due to the perturbation of the equilibria expressed by $AB \underset{B}{\rightleftharpoons} A \rightleftharpoons 1/3A_3$ where A and B were alcohol and water molecule respectively. The latter mechanism was due to that expressed by $AB \rightleftharpoons A+B$. The rate constants for all these processes were determined from the concentration dependence of the relaxation frequencies. The water structure in aqueous solutions was discussed in terms of a hydrophobic interaction, and it was concluded that the hydrophobic interaction decreased in this sequence, *tert*-butyl, *n*-propyl and allyl alcohols.

The effects of alcohols upon the properties of water continue to be investigated,[1] since the explanation of biological reaction mechanisms is intimately connected with liquid water structure. To understand the structural characteristics of liquids on a molecular scale, the application of wave technique with ultrasonic vibrations seems to be most appropriate. Though Blandamer and Waddington[2] have reported the ultrasonic absorption spectra in aqueous solutions of some alcohols, no quantitative analyses of the excess absorptions have been done. In a previous paper[3], the present authors have measured the ultrasonic absorption in aqueous solution of *n*-propyl alcohol and clarified the excess absorption mechanisms in relation to water structure. It becomes desirable to understand the properties of aqueous solutions of other alcohols and to compare the results in the case of *n*-propyl alcohol with those of other ones.

For this purpose, *tert*-butyl and allyl alcohols have been chosen and the ultrasonic absorption mechanisms in these aqueous solutions will be elucidated in this paper.

Experimental

The *tert*-butyl and allyl alcohols were reagent-grade commercial products and were distilled once. The purities of these alcohols were verified by gas chromatography to be higher than 99.5%. Solutions were prepared with doubly distilled water and were made up to the desired concentrations by weight. The measurements of the ultrasonic absorption were made in the frequency range of 4.5—220 MHz, using an ultrasonic pulse technique previously described[3,4]. The sound velocities were measured at 1.92 MHz using a sing-around technique. The densities were measured by means of a standard pycnometer. All the measurements were made at 25 °C.

Results and Discussion

Figures 1 and 2 show the representative ultrasonic absorption spectra in aqueous solutions of *tert*-butyl and allyl alcohols respectively. In general, the sound absorption caused by the several relaxation processes can be described by the following equation:

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

where α is the absorption coefficient; f the frequency; f_{ri} the relaxation frequency for the i-th process, and A_i and B, constants. The absorption spectra in aqueous solution of *tert*-butyl alcohol show the characteristic behavior due to a single relaxation process in the concentration range of less than 2.61 M and that due to double relaxation processes in the concentration range of more than 2.99 M. On the other hand, the measurements of α/f^2 for aqueous solution of allyl alcohol can be described by the relation for a single relaxation through out the concentration range measured. In the case of the single relaxation spectrum, a trial-and-error procedure was used to obtain the ultrasonic parameters which provided the straight line of the plots of α/f^2 *vs.* $[1+(f/f_r)^2]^{-1}$. The double relaxation spectrum was analyzed by a nonlinear least-squares routine, employing a Toshiba 3400 computer. In Table 1, the obtained values of the

Table 1. Relaxation parameters, sound velocities and densitifs in aqueous solutions of *tert*-butyl and aliyl alcohols

C_a (M)	ρ (g ml^{-1})	c (m s^{-1})	f_{r1} (MHz)	f_{r2}	A_1 (10^{-17} s^2 cm^{-1})	A_2	B
2.03	0.9758	1611	87	—	104	—	49
2.28	0.9738	1610	75	—	288	—	57
2.43	0.9720	1608	69	—	507	—	35
2.49	0.9714	1607	62	—	564	—	90
2.61	0.9670	1600	62	—	639	—	121
2.99	0.9600	1570	52	4.4	962	903	184
3.35	0.9561	1550	52	5.0	1121	907	226
4.00	0.9465	1519	60	8.7	937	1145	221
5.01	0.9243	1544	74	9.3	640	1211	205
6.01	0.9005	1393	69	9.0	452	849	214
7.02	0.9741	1344	66	9.1	279	545	218
8.02	0.9527	1287	114	11.7	147	158	174
8.99	0.8273	1232	103	13.2	77	38	186
		(*tert*-butyl alcohol)					
4.03	0.9742	1584	90	—	58	—	59
4.19	0.9730	1581	90	—	68	—	61
4.69	0.9696	1570	85	—	113	—	75
5.24	0.9643	1553	80	—	134	—	94
5.97	0.9581	1532	80	—	146	—	103
6.50	0.9531	1517	80	—	149	—	103
7.01	0.9469	1498	85	—	134	—	101
7.99	0.9365	1466	85	—	100	—	99
8.73	0.9302	1442	90	—	99	—	77
9.47	0.9201	1420	100	—	82	—	70
10.1	0.9120	1399	110	—	66	—	60
		(allyl alcohol)					

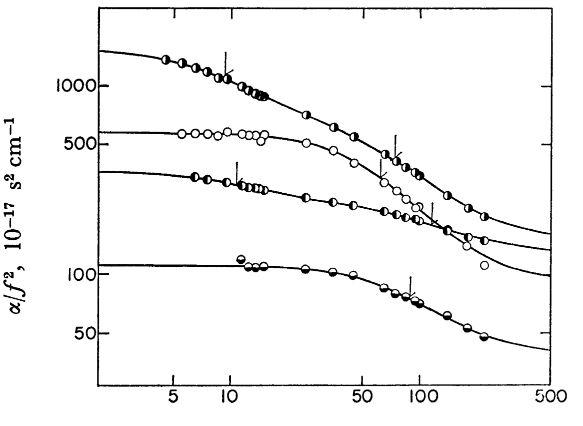

Fig. 1. Ultrasonic absorption spectra in aqueous solution of *tert*-butyl alcohol at 25 °C. The arrows show the relaxation frequencies.
◒: 2.03 M, ○: 2.61 M, ◑: 5.01 M, ◐: 8.02 M.

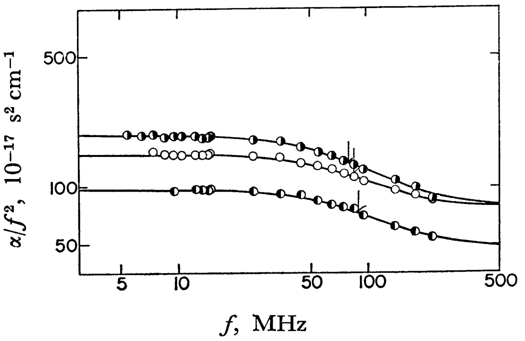

Fig. 2. Ultrasonic absorption spectra in aqueous solution of allyl alcohol.
◐: 4.19 M, ◑: 5.97 M, ○: 7.99 M.

ultrasonic parameters and the sound velocities are listed together with those of densities.

We have proposed that the excess absorptions in aqueous solution of *n*-propyl alcohol are due to the interaction between the alcohol and the water molecule, and the association and dissociation reaction of alcohol. Following this background, the excess absorption mechanisms in aqueous solutions of *tert*-butyl and allyl alcohols will be clarified. The model for the relaxation processes is as follows:

$$\mathrm{AB}_m \underset{k_{21}\searrow m\mathrm{B}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{A} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \frac{1}{n}\mathrm{A}_n \qquad (2)$$

where A is the molecule of alcohol; B that of water, and k_{ij}, the rate constant. The detailed derivations for the expressions of the relaxation frequency and the maximum excess absorption per wavelength have been described in a previous paper.[3] If the left reaction step proceeds much faster than the right one, the relaxation frequencies for each step are expressed by:

$$2\pi f_{r1} = 1/\tau_1 = k_{21}(m^2C_2^{m-1}C_3+C_2^m) + k_{12} \qquad (3)$$

$$2\pi f_{r2} = 1/\tau_2 = k_{32} + k_{23}n^2C_3^{n-1} - \frac{n^2k_{21}k_{23}C_2^mC_3^{n-1}}{k_{12}+k_{21}(m^2C_2^{m-1}C_3+C_2^m)} \qquad (4)$$

where C_2 and C_3 are the equilibrium molar concentrations of the components, B and A, respectively, and τ_i the relaxation time. The maximum excess absorption per wavelength, $\mu_{\max i}$, is given by the next equation;

$$\mu_{\max i} = \frac{1}{2}A_if_{ri}c = (\pi\rho c^2\Gamma_i/RT)(\Delta V_i-\alpha_p^\infty\Delta H_i/\rho C_p^\infty)^2 \qquad (5)$$

where ρ is density; c, the sound velocity; R, the gas constant; T, the absolute temperature; α_p^∞, the high-frequency limit of the thermal expansion coefficient; C_p^∞, 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 reaction under consideration. The Γ_i terms for the reaction expressed by Eq. (2) are:

$$\Gamma_1 = \frac{1}{V}\left(\frac{1}{C_1}+\frac{m^2}{C_2}+\frac{1}{C_3}-\frac{m^2}{C_\mathrm{T}}\right)^{-1} \qquad (6)$$

$$\Gamma_2 = \frac{1}{V}\left[\frac{n}{C_3}(n-\tau_1k_{21}nC_2^m)+\frac{n-1}{C_\mathrm{T}}(n-1+\tau_1k_{21}nC_2^m)+\frac{1}{C_4}\right]^{-1} \qquad (7)$$

where C_4 is the equilibrium concentration of the component A_n and where $C_\mathrm{T}=C_1+C_2+C_3+C_4$.

Let us first consider the excess absorption mechanisms in aqueous solution of *tert*-butyl alcohol. The excess absorption in the lower frequency range (4—14 MHz) is observed only in the concentration range of more than 2.61 M, while that in the higher frequency range (50—120 MHz) is always observed through out the concentration range measured. From these facts, the perturbation of the left equilibrium in Eq. (2) may be expected to be associated with the excess absorption mechanism in the higher frequency range. If a single water molecule interacts with a single alcohol one and if the concentration of the aggregate of alcohol, C_4, is small compared with the other components, Eq. (3) can be rewritten as:

$$2\pi f_{r1} = 1/\tau_1=k_{21}\sqrt{(C_\mathrm{a}-\beta C_\mathrm{w}+K_{12})^2+4\beta C_\mathrm{w}K_{12}} \qquad (8)$$

where K_{12} is the equilibrium constant defined by $K_{12}=k_{12}/k_{21}$; β, the mole fraction of the water monomer, and C_a and C_w the analytical concentrations of alcohol and water respectively. The introduction of the parameter, β, means that, in aqueous solutions of alcohols, an equilibrium between the monomer and hydrogen-bonded cluster of water is established and that only monomeric water molecules participate in the alcohol water interaction. Therefore, the parameter, β, might indicate the stability of the water structure.

Using the values of f_{r1}, C_a and C_w, the parameters, β, K_{12} and k_{21}, were determined so as to obtain a best fit of the data to Eq. (8). Figure 3 shows the calculated values of the relaxation frequencies, f_{r1}, for aqueous solution of *tert*-butyl alcohol along with the experimental ones. One can also evaluate the concentration dependence of the maximum excess absorption per wavelength. As has been described previously, the $\mu_{\max 1}$ is approximately proportional to $\rho c^2\Gamma_1$. The calculated values of $\rho c^2\Gamma_1V$ are shown by a solid line in Fig. 4 also with the experimental values of $\mu_{\max 1}$. In this figure, both peaks appear at almost the same concentration and the tendencies of both are identical. These facts lead to the conclusion that the excess absorption mechanism of aqueous solution of *tert*-butyl

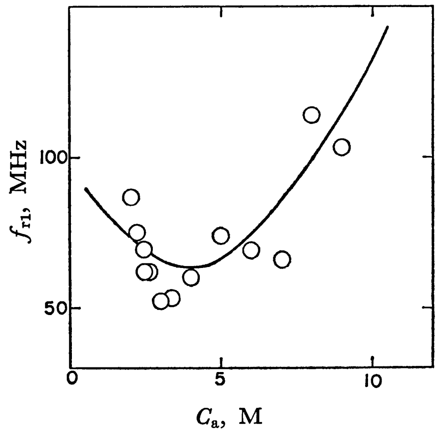

Fig. 3. Concentration dependence of the relaxation frequencies, f_{r1}, for aqueous solution of *tert*-butyl alcohol. The solid line indicates the calculated values.

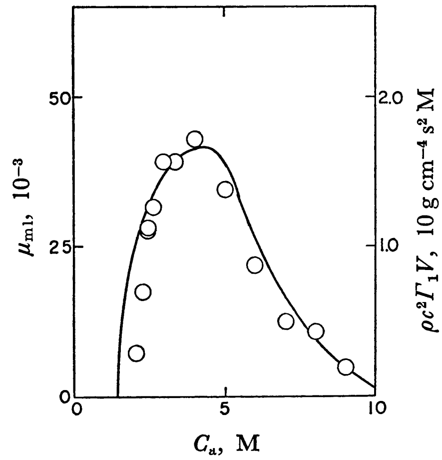

Fig. 4. The variations of $\mu_{\max 1}$ and $\rho c^2\Gamma_1 V$ with the concentration of *tert*-butyl alcohol. The solid line represents the calculated values of $\rho c^2\Gamma_1 V$. The circles are the experimental points of $\mu_{\max 1}$.

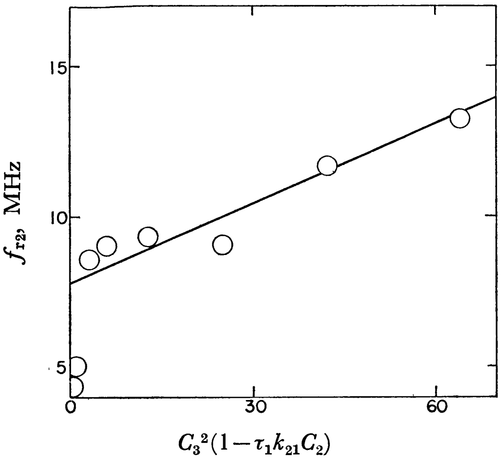

Fig. 5. The plots f_{r2} *vs.* $C_3^2(1-\tau_1 k_{21} C_2)$ for aqueous solution of *tert*-butyl alcohol at 25 °C.

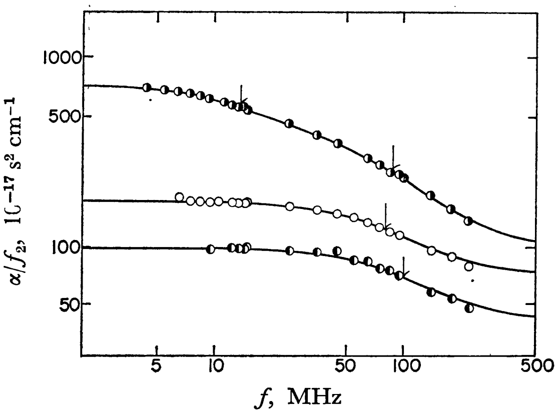

Fig. 6. Comparison of the ultrasonic absorption spectra in aqueous solution of *n*-propyl alcohol with that of allyl alcohol.

◑: 4.50 M, *n*-propyl alcohol, ○: 5.24 M, allyl alcohol, ◐: 4.19 M, allyl alcohol.

alcohol in the higher frequency range is attributed to the water alcohol interaction. Next, we will evaluate the excess absorption mechanism in the lower frequency range. Equation (4) is transformed to:

$$2\pi f_{r2} = 1/\tau_2 = n^2 k_{23} C_3^{n-1}(1-\tau_1 k_{21} C_2) + k_{32} \qquad (9)$$

The aggregation number, n, was determined so as to obtain the straight line of the plots of f_{r2} *vs.* C_3^{n-1} $(1-\tau_1 k_{21} C_2)$, and from the slope and the intercept of this line the rate constants, k_{23} and k_{32}, were determined. Figure 5 shows the plots at $n=3$, where the best fit is obtained. The kinetic parameters obtained in this way are listed in Table 2. We also estimate the concentration dependence of the maximum excess absorption per wavelength for this reaction mechanism, but the value of $\rho c^2\Gamma_2 V$ increases monotonically with the alcohol concentration.

Second, the excess absorption mechanism in aqueous solution of allyl alcohol, in which the excess absorption is not observed in the lower frequency range, will be clarified. In this solution, the association and dissociation reaction of alcohol may not be expected, about which we will discuss later. Therefore, it is sufficient to consider the perturbation of the left equilibrium as the excess absorption mechanism. For the sake of comparing the absorption spectra in aqueous solution of allyl alcohol with that of *n*-propyl alcohol, the spectra of the both solutions are shown in Fig. 6. As the behavior of the ultrasonic parameters in aqueous solution of allyl alcohol were close to those in aqueous solution of *tert*-butyl and *n*-propyl alcohols in the higher frequency range, the kinetic parameters for this mechanism in aqueous solution of allyl alcohol were also determined analogously to those obtained in the case of aqueous solution of *tert*-butyl alcohol. Figures 7 and 8 show the concentration dependence of the relaxation frequency and the maximum excess absorption per wavelength for aqueous solution of allyl alcohol. As may be seen in these figures, the calculated relaxation frequencies are very close to those of experimental values, and the position of the peak of the maximum excess absorption per wavelength appears at that of $\rho c^2\Gamma_1 V$. These results make us conclude that the excess absorption mechanism in aqueous solution of allyl alcohol is due to the perturbation of the left equilibrium expressed by Eq. (2). The kinetic para-

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_{12} (M)	k_{23} ($M^{-2} s^{-1}$)	k_{32} (s^{-1})	K_{23} (M^{-2})	β	ΔF_w (kcal)
n-Propyl alcohol[a]	1.6×10^8	6.2×10^7	2.6	2.2×10^5	6.9×10^7	0.0032	0.15	1.0
tert-Butyl alcohol	1.2×10^8	7.2×10^7	1.7	5.5×10^5	4.9×10^7	0.011	0.12	1.2
Allyl alcohol	1.5×10^8	6.3×10^7	2.4	—	—	—	0.19	0.82

a) Ref. 3.

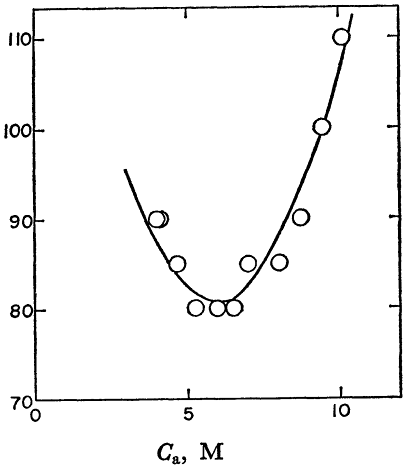

Fig. 7. Concentration dependence of the relaxation frequencies for aqueous solution of allyl alcohol.

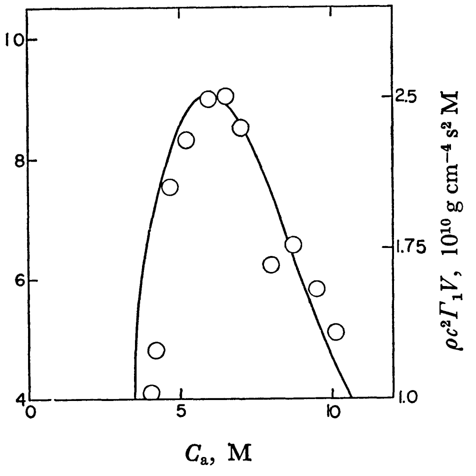

Fig. 8. The variations of μ_{max1} and $\rho c^2\Gamma_1 V$ with the concentration of allyl alcohol.

meters obtained are listed in Table 2. The parameter, β, can be related to the free energy difference between the hydrogen bonded and non-hydrogen bonded water by means of this equation; $\beta/(1-\beta)=\exp(-\Delta F_w/RT)$. In Table 2, the free energy difference in aqueous solutions of alcohols are also listed. Litovitz and his coworkers[5] have estimated the free energy difference in pure water to be 0.63 kcal at 25 °C utilizing the ultrasonic absorption technique. Therefore, the parameter, β, which is the mole fraction of monomeric water, is 0.26. Comparing this value with those obtained by the present investigation of aqueous solutions of alcohols, it is clear that all the alcohols studied here act as water structure promoters. The effect of the water structure promoter may be the result of a hydrophobic interaction. Recent investigations[6,7] of aqueous solutions of several alcohols have shown that even molecules which consist of relatively small hydrophobic groups have an ability of hydrophobic interaction. Especially, Shirahama and *et al.*[8] have found the decreasing effects of the critical micelle concentration in aqueous solutions of several alcohols and have reported that the more hydrophobic and the more concentrated the added alcohol, the more marked becomes the decrease in the critical micelle concentration. They have also shown that the hydrophobic interaction decreases in this sequence, *tert*-butyl, *n*-propyl and ethyl alcohols. The smaller the parameter, β, the more does the hydrophobic interaction increase. The results obtained in the present investigation are consistent with the above interpretation. It is well known that the presence of a double bond in a molecule weakens the hydrophobic interaction. If the aggregate of alcohol is formed by hydrophobic interaction in aqueous solutions, the absence of the excess absorption in the lower frequency range in aqueous solution of allyl alcohol can be well interpreted in terms of the decrease in the hydrophobic interaction.

In conclusion, the excess absorption mechanisms in aqueous solutions of alcohols investigated here may be attributed to the interaction of a single alcohol molecule and water molecule, and to the association and dissociation reaction of alcohol molecules. Furthermore, a decrease in the hydrophobic interaction of alcohol causes the aggregate of alcohol to disappear.

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