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The Ultrasonic Velocity and the Absorption of Aqueous *t*-Butyl Alcohol Solutions in Relation to the Structures of Water and Solutions

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The adiabatic compressibility *vs.* concentration curves in aqueous solutions of *t*-butyl alcohol (*t*-Bu) over a certain temperature range have a common intersection at a fixed concentration (μ_c^β). The sound absorptions of solutions are nearly constant and are independent of the concentration up to a concentration (μ_i^α) nearly the same as the μ_c^β. On the basis of the value of $\mu_c^\beta(\cong\mu_i^\alpha)$, the properties and the dissolved state of *t*-Bu in liquid water discussed in terms of the liquid clathrate hydrate model. At this concentration, the liquid clathrate hydrate of *t*-Bu consists of 18-hedron, containing 32 water molecules for each *t*-Bu molecule. For higher concentrations than μ_c^β, the breakdown of the liquid clathrate hydrate by the addition of excess *t*-Bu occurs, accompanied by an increase in the number of clusters.

In previous papers,[1,2] the sound velocity (V), the density (ρ), and the adiabatic compressibility (β) in aqueous solutions of nonelectrolytes have been investigated as functions of the concentration (μ: mole fraction). For each aqueous solution, it has been found that the V-μ curves and β-μ curves have common intersections at the fixed concentrations of μ_c and μ_c^β respectively, the sound velocity (V_c) and the compressibility (β_c) at these concentrations being independent of the temperature over a certain range (ΔT_c^V and ΔT_c^β) respectively.

From the temperature dependency of the β-μ curves in these systems, it can be concluded that the structural unit termed "liquid clathrate hydrate" with a composition of μ_c^β or $r_c^\beta=$(water/solute) does exist for various aqueous systems.

A number of papers have been published on the ultrasonic absorption (α) in aqueous solutions of nonelectrolytes—alcohol homologs,[3-6] substituted alcohols,[7,8] urea and its derivatives,[9] acetone,[3] dioxane,[3,10,11] dioxolane,[12] amines,[13,14] *etc.*; the main interest is, however, the behavior of an absorption peak in the α-μ curve. Blandamer *et al.* have pointed out that the sound absorption for some aqueous systems—alcohols,[4,5] substituted alcohols,[7] dioxolane,[12] amine[13]—in a lower concentration range is

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[1] H. Endo, This Bulletin, **46**, 1106 (1973).

[2] H. Endo, *ibid.*, **46**, 1586 (1973).

[3] C. J. Burton, *J. Acoust. Soc. Amer.* **20**, 186 (1948).

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[13] M. J. Blandamer, N. J. Hidden, and M. C. R. Symons, *ibid.*, **66**, 316 (1970).

[14] R. N. Barfield and W. G. Schenider, *J. Chem. Phys.*, **31**, 488 (1959).

relatively insensitive to the compositions of the solutions (see also Thamsen[8]). Above this concentration, the value of α increases rapidly, reaches a maximum, and then gradually decreases to a lower value of α. According to Blandamer *et al.*,[4,5,7,12,13] this behavior of the α-μ curve in the lower concentration range is attributable to the formation of a clathrate in a solution. In one group of theories, the absorption peaks are explained in terms of a chemical relaxation process (*cf.* Andrea *et al.*[15]) involving the formation and decomposition of associated complexes, but the behavior of the α-μ curve in the lower concentration range can not be interpreted in terms of this mechanism.

In the present work, the acoustical properties of an aqueous solution of *t*-Bu have been studied both for the sound velocity and the absorption. It was found that the concentration (μ_1^α) at the sudden increase of the α-μ curve corresponds to μ_c^β. On the basis of this result, we will report that the low-concentration absorption-behavior of a *t*-Bu solution can also be explained on the basis of the liquid clathrate hydrate model used for the explanation of the behavior of β.

Experimental

Materials. Water was purified by two distillations. In order to purify the *t*-Bu, the reagent-grade product was refluxed with calcium oxide and then distilled.

Ultrasonic Apparatus. The ultrasonic pulse method was used for the absorption measurement. The absorption coefficients were determined at 60 MHz, and the mean value of 5~9 measurements was used. A crystal-controlled ultrasonic interferometer operating at a frequency of 5 MHz was used for the velocity measurements. The experimental error for the absorption data was about ±2%, and the overall accuracy of the sound velocity data was within ±0.2 m/s.

Measurements of Viscosity and Density. The viscosity coefficient (η) was measured for aqueous solutions by means of a modified Ostwald capillary viscometer. The density measurement was made by means of an Ostwald-type pycnometer. All the measurements were carried out between 20° and 50 °C at 5.0±0.1 °C intervals.

Classical Absorption Coefficient (α_η). The α_η at frequency (f) was calculated by the relation:

$$\alpha_\eta/f^2 = \frac{8\pi^2\eta}{3\rho V^3}$$

Results

Ultrasonic Velocity. In Fig. 1, the sound velocity is plotted against the mole fraction for aqueous solutions of *t*-Bu. The intersection point of V-μ curves for various temperatures converges to one point ($\mu_c^V = 0.032$), at which V_c is constant (=1601 m/s) in this temperature range (20—35 °C). The parameters, V_c, μ_c^V, v_c^V, r_c^V, and ΔT_c^V, were obtained from Fig. 1; they are summarized in the left-hand half of Table 1. Here the notations used were the same as those used in Refs. 1 and 2.

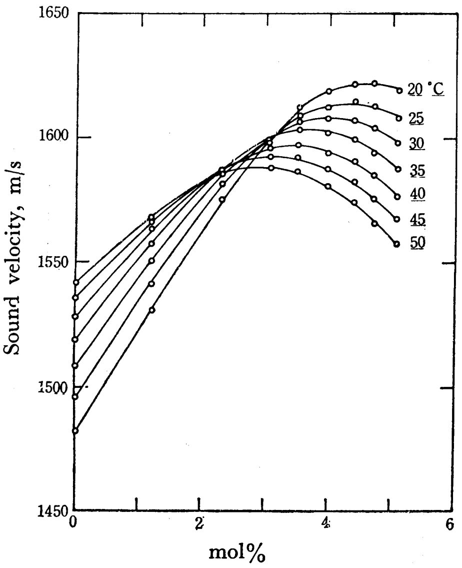

Fig. 1. Concentration dependence of sound velocity.

Table 1. Data concerning V-μ curve and β-μ curve of aqueous *t*-Bu solutions

	Sound velocity		Adiabatic compressibility
V_c	1601 m/s	β_c	40.0×10^{-12} cm²/dyn
μ_c^V	3.2 mol%	μ_c^β	3.0 mol%
v_c^V	14.7 vol.%	v_c^β	13.9 vol.%
r_c^V	30	r_c^β	32
ΔT_c^V	20—35 °C	ΔT_c^β	20—35 °C

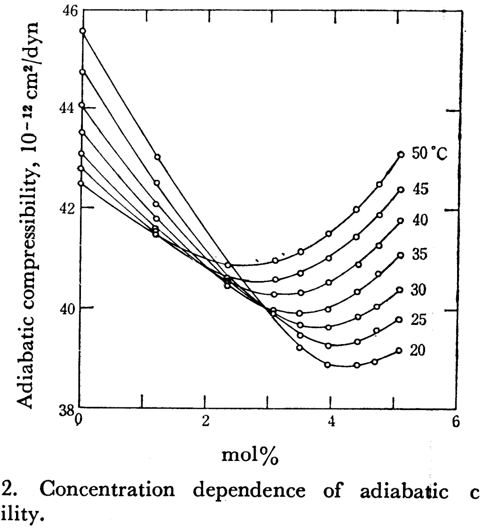

Fig. 2. Concentration dependence of adiabatic compressibility.

Adiabatic Compressibility. In Fig. 2, the adiabatic compressibility is plotted against the mole fraction for aqueous solutions of *t*-Bu. It is found that the β-μ curves at various temperatures intersect at one common point ($\mu_c^\beta = 0.030$), at which β_c is constant ($=40.0\times10^{-12}$ cm²/dyn). The values of β_c, μ_c^β, r_c^β, v_c^β, and ΔT_c^β are shown in the right-hand half of Table 1. The behavior of the V-μ and β-μ curves for various temperatures is similar to that of other nonelectrolytes.[1,2]

Viscosity and Classical Absorption Coefficients. The

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[15] J. H. Andreae, P. D. Edmonds and J. F. McKellar, *Acustica*, **15**, 74 (1965).

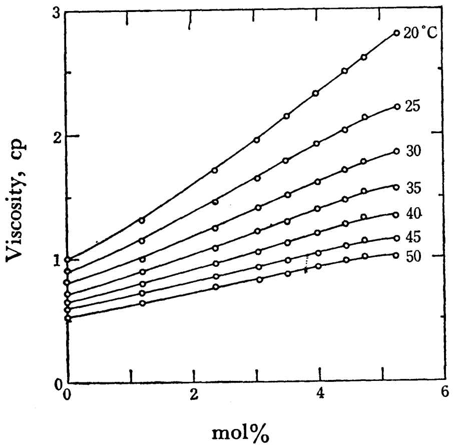

Fig. 3. Concentration dependence of viscosity.

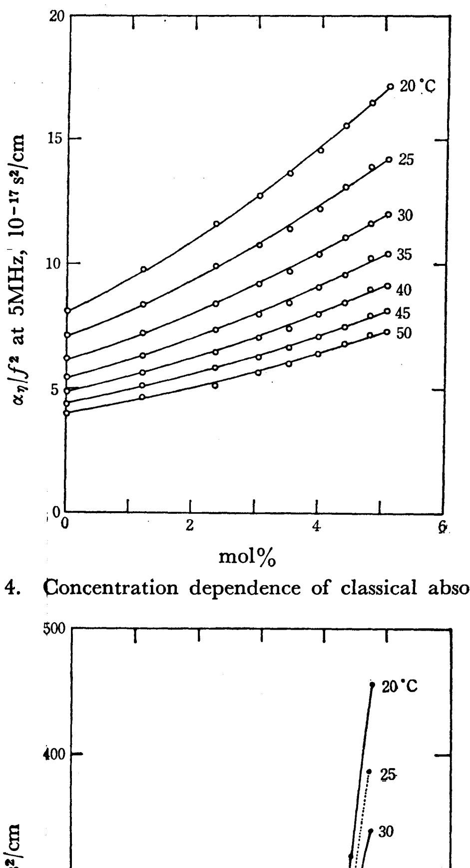

Fig. 4. Concentration dependence of classical absorption.

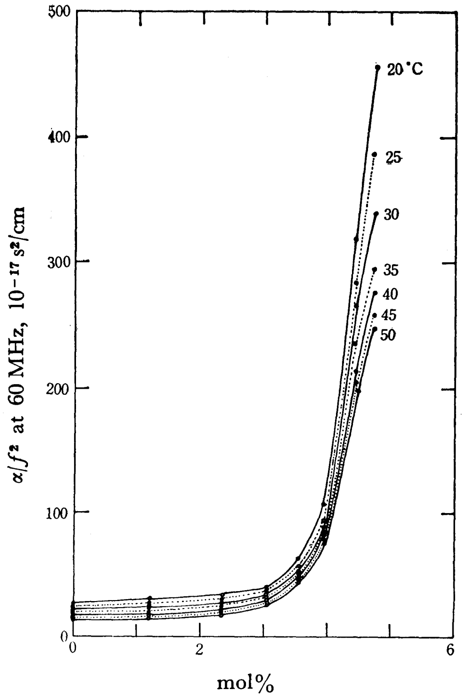

Fig. 5. Concentration dependence of sound absorption.

η-μ curves are shown in Fig. 3. The values of η at various temperatures increased monotonously with an increase in the concentration. The classical absorption coefficients (α_η/f^2) are shown in Fig. 4. The behavior of the α_η/f^2-μ curves at various temperatures is almost like that of the η-μ curves.

Ultrasonic Absorption Coefficients. The α/f^2-μ curves are given in Fig. 5. It is seen that α/f^2 was relatively insensitive to the change in μ in a low concentration range, and that it increased suddenly at a definite concentration. This limiting concentration is denoted by $\mu_{\rm I}^{\alpha}$. It is seen that $\mu_{\rm I}^{\alpha}\cong 0.03$ mole fraction for the 20—35 °C temperature range, and that it decreases slightly in the higher temperature range ($\mu\cong 0.02$ for 40—50 °C). In the 20—35 °C temperature range, the value of $\mu_{\rm I}^{\alpha}$ for the α/f^2-μ curves coincides with that of $\mu_{\rm c}^{\beta}$ for the β-μ curves. The behavior of the excess absorption ($\Delta\alpha/f^2=\alpha/f^2-\alpha_\eta/f^2$) is not significantly different from that of α/f^2 alone.

Discussion

The experimental results shown above can be interpreted in terms of the same model of aqueous nonelectrolyte solutions as was employed in previous papers.[1,2] In our model, $\mu_{\rm c}^{\beta}$ corresponds to the concentration where $d\beta_{\rm st}/dT$ ($\beta_{\rm st}$=structural compressibility) becomes zero. Solute molecules are accommodated in water clusters without changing their size and ice-1 structure up to this concentration. Therefore, the $\beta_{\rm st}$ of the solution decreases with an increase in the concentration up to this point, thus keeping the water-cluster structure intact. On the other hand, the β_∞(instantaneous compressibility) is constant and $d\beta_\infty/dT=0$ up to this concentration in order to keep the number of water cluster constant. We have seen[1,2] that the ratio $r_{\rm c}^{\beta}$(=water/solute) at this concentration, $\mu_{\rm c}^{\beta}$, corresponds to the specific molecular ratios for some clathrate-making substances, and we assumed that the "liquid clathrate hydrate" exists at this composition. Here, the $\beta_{\rm st}$ of the "water-solute-cluster" at the composition of $r_{\rm c}^{\beta}$ is small, but this value is not zero since the size of this "water-solute-cluster" is significantly larger than that of this structure unit. Beyond this concentration, the number of clusters increases, resulting in a decrease in their mean size. This increase in the number of clusters takes place slowly, accompanying a decrease in $\beta_{\rm st}$ up to the concentration of $d\beta/d\mu=0$, at which the "water-solute-cluster" is destroyed separately. This is also accompanied by an increase in the β_∞($d\beta_\infty/dT>0$).

Now that the $r_{\rm c}^{\beta}$ for *t*-Bu—water system becomes 32, as was observed for tetra-ethyl ammonium chloride, the shape of the clathrate was assumed to be 18-hedron. (The solid clathrate hydrate of this composition of the *t*-Bu—water system is not known, but a "double hydrate" with help gas (H_2S) of the 16X8Y136H_2O (X=H_2S and Y=*t*-Bu) composition is known).

The above finding, that the ultrasonic absorption remains nearly constant, that it is not very different from that of water in the lower concentration range, and that it increases rather rapidly from a certain concentration $\mu_{\mathrm{i}}^{\alpha}(\cong\mu_{\mathrm{c}}^{\beta})$, is of prime importance in elucidating the mechanism of the ultrasonic absorption in aqueous nonelectrolyte systems. This behavior is not explicable on the basis of the reaction-type theory[14,15) between a solute and solvent molecules. It can, however, be explained easily, at least qualitatively, on the basis of the "entropy of mixing"-type diffusion-theory[16,17) of sound absorption in aqueous systems if we employ the same model of the aqueous systems as was employed previously[1,2) in explaining the behavior of the sound velocity and the adiabatic compressibility. According to this theory,[16,17) the excess sound absorption in aqueous nonelectrolytes arises from the irreversible entropy production caused by the diffusion of solutes into the groups of water molecules produced by the collapse of water-clusters under sound pressure. If we assume that the solute molecules are all incorporated in water-clusters up to the concentration of μ_{c}^{β} as has been assumed previously,[1,2) almost no diffusion can be expected when some of the clusters are collapsed under the sound pressure, because the collapse of clusters does not accompany a local concentration change. This explains the initial concentration-independent part of the absorption curves. The increase in ultrasonic absorption beyond $\mu_{\mathrm{c}}^{\beta}(\cong\mu_{\mathrm{i}}^{\alpha})$ is to be expected, because free solute molecules or smaller clusters of different compositions are present at higher concentrations, as has been assumed previously.[1,2)

We[1,2) ourselves have also previously pointed out that when V_{c} and β_{c} are plotted as functions of $v_{\mathrm{c}}^{\mathrm{V}}$ and v_{c}^{β} respectively, the various solutes can be classified into three groups according to the shapes of the curves. Here, $v_{\mathrm{c}}^{\mathrm{V}}$ and v_{c}^{β} indicate the volume fractions corresponding to $\mu_{\mathrm{c}}^{\mathrm{V}}$ and μ_{c}^{β} at 20 °C respectively.

The first group (I) consists of the urea-homolog series, hexamethylenetetramine, and glycerine. The molecules of the solutes belonging to this group collaborate in making the framework of water constituent part of liquid water. The sound velocity, V_{c}, and $v_{\mathrm{c}}^{\mathrm{V}}$ and the adiabatic compressibility, β_{c}, at v_{c}^{β} for this series of solutes are represented by:

$$V_{\mathrm{c}} = 403\,v_{\mathrm{c}}^{\mathrm{V}} + 1547 \quad (\mathrm{m/s})$$

$$\beta_{\mathrm{c}} = (45.6-42.7\,v_{\mathrm{c}}^{\beta})\times 10^{-12} \quad (\mathrm{cm^2/dyn})$$

respectively.

The second group (II) consists of formamide, acetamide, and the alcohol homolog series except for the lowest-molecular-weight substances in each homolog. These solutes only fill up the cavity of the liquid water structure. The V_{c} *vs.* $v_{\mathrm{c}}^{\mathrm{V}}$ and β_{c} *vs.* v_{c}^{β} relations for this group are represented, respectively, by:

$$V_{\mathrm{c}} = 1143\,v_{\mathrm{c}}^{\mathrm{V}} + 1390 \quad (\mathrm{m/s})$$

$$\beta_{\mathrm{c}} = (77.5-236.7\,v_{\mathrm{c}}^{\beta})\times 10^{-12} \quad (\mathrm{cm^2/dyn})$$

The third group (III) consists of the lowest-molecular-weight substances in each homolog series. This group will presumably have intermediate properties between Groups (I) and (II).

Notice that *t*-Bu, although of the alcohol homolog series, belongs to Group (I).

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17) O. Nomoto, *ibid.*, **12**, 300 (1957).