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The Water Structure Model of Narten *et al.* and the Pressure Effect on Sound Absorption in Water

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The mechanism of the temperature dependence of ultrasonic absorption in water under atmospheric pressure has hitherto been studied by means of the two-state-model theory of water. For an explanation of the pressure dependence of ultrasonic absorption by the two-state model, however, we are obliged to adopt the contradictory assumption that the open-packed structure of water has a higher energy than the more close-packed one. In order to avoid this contradictory assumption inherent in the two state-model theory, we have here employed the water model recently proposed by Narten *et al.* on the basis of X-ray scattering analysis. Although the calculation based on the Narten-model succeeds in explaining the pressure dependence of the ultrasonic absorption without the above-mentioned contradictory assumption, the structual compressibility (β_{st}) thus obtained is about two times larger than the most reasonable value. The origin of this discrepancy seems to be that the Narten model of water considers the framework of the ice-1 lattice to be of infinite extent, without any boundary. By assuming the cluster-structure to be of a finite size, we can reduce β_{st} to a reasonable value in agreement with the experimental results. The water cluster is found to be about eight molecules in diameter at 4°C.

The ultrasonic absorption (α) in water is known to be higher than the classical value (α_{cl}) due to the shear viscosity (η) and the heat conductivity (k). As α_{cl} is proportional to the square of frequency (f), it is usual to write:

$$\frac{\alpha_{cl}}{f^2} = \frac{(2\pi)^2}{\rho V^3}\left(\frac{2}{3}\eta + \frac{1}{2}\frac{\gamma-1}{\gamma}\frac{k}{C_v}\right) \tag{1}$$

Here, ρ is the density; V, the sound velocity; C_v, the specific heat at a constant volume, and $\gamma(=C_p/C_v)$, the ratio of the specific heats. As $\gamma \cong 1$ in water, the term due to heat conduction can be omitted in this case. The difference being ascribed to the bulk viscosity (κ), the total absorption (α/f^2) becomes:

$$\frac{\alpha}{f^2} = \frac{(2\pi)^2}{\rho V^3}\left(\frac{2}{3}\eta + \frac{1}{2}\kappa\right) \tag{2}$$

It is known, from hypersonic measurements, that (α/f^2) in water is independent of the frequency up to the GHz ($=10^9$ Hz) range. This means that, in the general formula of relaxational viscosity absorption:

$$\alpha = \frac{2}{3}\frac{\eta}{\rho V^3}\frac{\omega^2}{1+\omega^2\tau_1^2} + \frac{1}{2}\frac{\kappa}{\rho V^3}\frac{\omega^2}{1+\omega^2\tau_2^2} \tag{3}$$

and dispersion:

$$V^2 = V_0^2 + \frac{4}{3}\frac{G}{\rho}\frac{\omega^2\tau_1^2}{1+\omega^2\tau_1^2} + \frac{K'}{\rho}\frac{\omega^2\tau_2^2}{1+\omega^2\tau_2^2} \tag{4}$$

the relaxation time for the shear viscisity (τ_1) and that for the bulk viscosity (τ_2) are sufficiently small ($\omega\tau_1 \ll 1$, $\omega\tau_2 \ll 1$ where $\omega = 2\pi f$), even in the GHz range. Here, G is the shear modulus, and K', the relaxational part of the bulk modulus related to η and κ by Maxwell's relations:

$$\eta = G\tau_1 \text{ and } \kappa = K'\tau_2 \tag{5}$$

There being relations

$$\frac{1}{\beta_0} = K_0, \quad \frac{1}{\beta_\infty} = K_\infty \tag{6}$$

between the static and instantaneous compressibilities (β_0 and β_∞), and the corresponding bulk modulus (K_0 and K_∞), we obtain as the relaxational modulus, K',

and the structual (or relaxational) compressibility, β_{st}:

$$K = K_0 + K' \text{ and } \beta_0 = \beta_\infty + \beta_{st} \quad (7)$$

The mechanism of ultrasonic absorption in water has been studied by Hall,[1] by Smith and Lawson,[2] and by Davis and Litovitz.[3] They applied the two-state-model theory of water to explain the bulk viscosity and relaxational compressibility. Hall's theory, based on the monomer-dimer model, explained the temperature dependence of sound absorption using suitably adjusted parameters to fit the experimental results (*cf.* also Davis and Litovitz[3]). In Hall's paper, it is assumed that the open-packing state of water is the lower energy state. For the explanation of the pressure dependence of the ultrasonic absorption, however, Litovitz and Carnevale,[4] calculating by means of a modification of Hall's two-state-model theory, were obliged to adopt the assumption that the open-packing structure of water has a higher free energy than the close-packing state, in contradiction to the usual physico-chemical concepts as to the structure of liquid water (*cf.* also Herzfeld and Litovitz[5]). To interpret the pressure dependence of ultrasonic absorption in water without introducing these contradictory assumptions in the two-state-model theory, we employed the water model recently proposed by Narten *et al.*[6] on the basis of their X-ray scattering analysis.

Water Structure Model Proposed by Narten *et al.* (Interstitial Model)

Samoilov[7] has proposed an interstitial model of the liquid water structure so as to explain the radial distribution function obtained from the X-ray data. Narten *et al.*, building on Samoilov's idea, formulated a model, consisting of a framework of the extended ice-1 structure, with some non-hydrogen-bonded water molecules filling some of the cavities of the network. This framework structure is very open, with ample spaces or cavities to accommodate non-hydrogen-bonded water molecules. The positions to accommodate the water molecules in the interstices are on the triad axis. The accommodated water molecules in the cavity interact with the framework molecules with less specific, although by no means negligible, force. In this model, the ice-1 framework is anisotropically extended, and both vacant lattice sites and the occupancy of the interstices by water molecules are permitted, although the vacant lattice site of the framework is practically absent up to 100°C. Accordingly, liquid water can be said to consist of two species forming both the framework and the interstitial molecules. This model, however, considers the lattice of the extended ice-1 framework to be infinite, without boundary, no cluster-structure being taken into account. Narten *et al.* found that the calculated radial distribution functions agree with the experimental results up to very high temperatures (*ca.* 200°C).

Theoretical

Acoustic pressure in an associated liquid accompanies two sorts of compression: *a*) the compression of the intermolecular distance, and *b*) the breakdown of intermolecular bonds accompanying the destruction of the open structure. The former is represented by the instantaneous compressibility, β_∞, while the latter is the origin of the structual compressibility, β_{st}. In this calculation, we assume the volume of the liquid water to be proportional to the number of framework lattice sites. This means that the dimensions of the framework remain the same, independent of whether the cavity sites are vacant or not. On this assumption, the molar volume (v) can be given by the following relations:

$$v = \frac{W}{f_1} v_{fr} \quad (8)$$

$$W = \frac{f_1 + z f_2}{f_1} \quad (9)$$

where

v_{fr}: the volume per mole of H_2O of framework
W: the fraction of water molecules in the framework positions
f_1: the occupancy of the framework sites (f_1 is 100% up to 100°C; *cf.* Narten *et al.*[6])
f_2: the occupancy of the interstitial sites
z: the number of interstitial sites per framework site

In this calculation, we will limit the temperature range at up to 100°C. Then, we obtain $f_1=1$ in Eqs. (8) and (9) from the experimental results of Narten *et al.*[6]

By substituting Eq. (8) into

$$\beta_{st} = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \quad (10)$$

we obtain:

$$\beta_{st} = W z \left(\frac{\partial f_2}{\partial p}\right)_T \quad (11)$$

where z is kept constant.

On the other hand, Narten *et al.* found both the entropy of mixing and the molar Gibbs free energy of the model from their statical thermodynamic consideration of the interstitial water model. Further, they obtained, as the free-energy change associated with the transformation of the interstitial molecule into the framework:

$$\Delta G_1^0 = \boldsymbol{RT}\left[\ln \frac{f_2}{1-f_2} - z \ln (1-f_2)\right] \quad (12)$$

We obtain from Eq. (11):

$$\left(\frac{\partial f_2}{\partial p}\right)_T = W f_2 (1-f_2) \Delta v_1^0 / \boldsymbol{RT} \quad (13)$$

1) L. Hall, *Phys. Rev.*, **73**, 775 (1948).
2) A. Smith and A. Lawson, *J. Chem. Phys.*, **22**, 351 (1954).
3) C. Davis and T. Litovitz, *ibid.*, **42**, 2563 (1965).
4) T. Litovitz and E. Carnevale, *J. Appl. Phys.*, **26**, 816 (1955).
5) K. Herzfeld and T. Litovitz, "Absorption and Dispersion of Ultrasonic Waves," Academic Press, New York and London, (1959) p. 438.
6) H. Narten, M. Danford, and H. Levy, *Discuss. Faraday Soc.*, **43**, 97 (1967).
7) O. Samoilov, "Ion no Suiwa" (Translation from Russian by W. Uehira), Chijin Shokan, Tokyo (1967).

Then, the structural compressibility is given by

$$\beta_{st} = zW^2 f_2(1-f_2)\Delta v_I^0/RT \quad (14)$$

Here $\Delta v_I^0=(\partial G_I^0/\partial p)_T$ becomes v_{fr}, because we assume that the interstitial water molecule has no effective volume. Therefore, by substituting Eq. (10), we obtain the relation:

$$\beta_{st} = \frac{zv_{fr}}{RT}\frac{f_2(1-f_2)}{(1+zf_2)^2} \quad (15)$$

It is easy to show that Eq. (15) is equivalent to the result obtained by Frank and Quist[8] on Pauling's water model:[9]

$$\beta_{st} = \frac{v_{fr}}{RT}(1-W)[W-v(1-W)] \quad (16)$$

where $v=1/z$.

We can find the temperature (t) dependence of the parameters (f_2 and W) from the data of Narten *et al.*, represented as graphs in their paper:

$$W = -4.59\times10^{-4}\ (t-4) + 0.82$$

In their paper, however, f_2 is so random that we can not find any definite relation with the temperature. We calculated f_2 from Eq. (9), by assuming z (=1/2) to be independent of the temperature.

Results of Calculations

Figure 1 shows the temperature dependence of β_{st} as obtained from Eq. (15). The results of other authors[1-4] are also shown for the sake of comparison. As may be seen, the present result gives nearly the same slope of the $\beta_{st}(t)$-curve as in previous investigations, but the value of β_{st} is about two times any previous finding (such as that of Hall *et al.*).

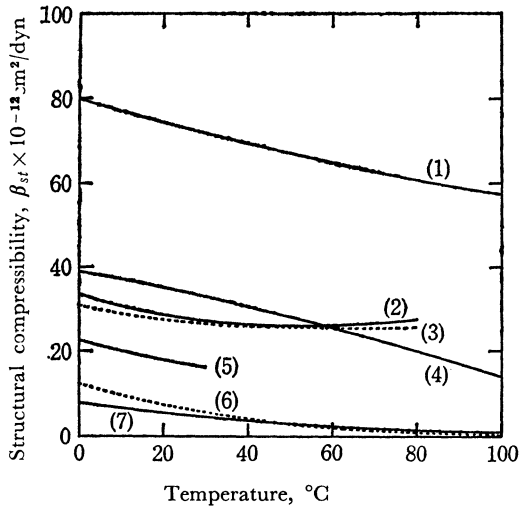

Fig. 1. Structual compressibility as function of temperature.

(1) Present study
(2) Hall
(3) Davis and Litovitz
(4) Smith and Lawson
(5) Frank and Quist
(6) Eucken[10]
(7) Némethy and Scheraga[11]

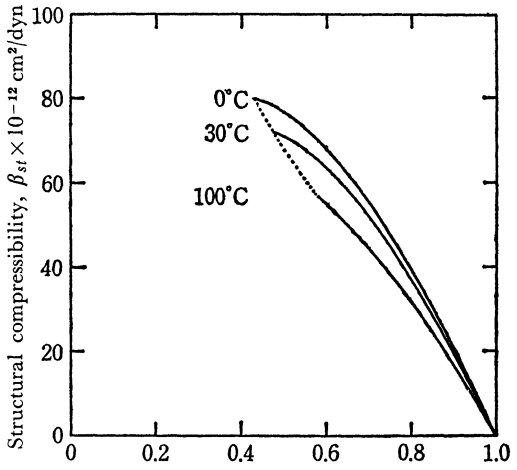

Fig. 2. β_{st} dependence of f_2 at various temperature.
---- Temperature dependence of f_2 under the atmospheric pressure.

Figure 2 shows the f_2 dependence of β_{st} at 0, 30, and 100°C. As the framework-structure part of water is destroyed with an increase in the pressure, we have to expect a monotonous increase in the occupancy of the cavity (f_2) with an increase in the pressure. On the other hand, the dotted line shows the temperature dependence of f_2 under atmospheric pressure.

Considerations and Discussion

Our results at 4°C are shown in Table 1, together with the previous ones. An obvious difference is that our value of $\beta_{st}=78.9\times10^{-12}$ cm²/dyne is much larger than that, $\beta_0(=\beta_\infty+\beta_{st})=50.2\times10^{-12}$ cm²/dyne, in water. It is necessary to remove this contradiction. If we assume a reasonable value (*cf.* Hall[1]) to be $\beta_{st}=32.2\times10^{-12}$ cm²/dyne at 4°C, which is in accordance with ultrasonic absorption measurements, we find from Eq. (16) that the apparent value, z', is 0.284 on the condition that $w=0.820$ remains the same (here we assume Eq. (17)). Then, we obtain from Eq. (9) $f_2=0.773$.

Table 1

Temp. 4°C	Present results: Narten model	Present results: Cluster model	Frank-Quist (Pauling model)	Two state model
V_{fr}	22.0	22.0	22.0	
W	0.820	0.820	0.818	
z	0.500	0.284	0.261	
f_2	0.439	0.773	(0.858)	
$\beta_{st}\times10^{-12}$	78.9	32.2	21.0	32.2[1]
				30.0[3]

The radial distribution function determined by Narten *et al.* from the X-ray scattering data is based on the lattice model up to a distance of about 10 Å,

8) H. Frank and A. Quist, *J. Chem. Phys.*, **34**, 604 (1961).
9) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, (1960) 3er. Ed.. p. 472.
10) A. Eucken, Nachr. Akad. Wiss. Göttingen, Math-Physik. Kl. p. 38 (1946); *Z. Electrochem.* **52**, 255 (1948); **53**, 102 (1949) (*cf.* Refs. 3 and 5).
11) G. Némethy and H. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962).

further distances being averaged out. It is probable that water consists of clusters of finite sizes larger than 10 Å in radius.

Here we assume that the water structure consists of clusters containing n^3 water molecules, the structure inside the cluster being the same as the Narten model. As the number of interstitices are reduced to $[(n-1)/n]^3$ times, we find that z apparently becomes $[(n-1)/n]^3$ times as large as the infinite model. Further, we assume in this cluster model that the average intermolecular distance between clusters is not affected, so the density in this model does not change. The space between the clusters is assumed not to accommodate the non-hydrogen-bonded molecules. Considering the above conditions, we obtain the following relation:

$$\left(\frac{n-1}{n}\right)^3 z = z' \tag{18}$$

where z $(=1/2)$ is the number of interstitial sites per framework site, corresponding to the Narten model without considering the cluster. If we choose $z'=0.284$, so as to bring the calculated β_{st} value in Table 1 (column (2)) into agreement with the observed value, we obtain $n=5.81$ from Eq. (18). Assuming the cluster to be spherical, the diameter of the cluster becomes about eight molecules at 4°C. In performing the above calculations at various temperatures, we find the radius (n_r) of the spherical cluster (expressed in the number of water molecules) to be dependent on the temperature as is plotted in Fig. 3. As may be seen, n_r increases with an increase in the temperature. Although this is rather unexpected, we cannot place too much weight on it, considering the very approximate nature of our hypothesis.

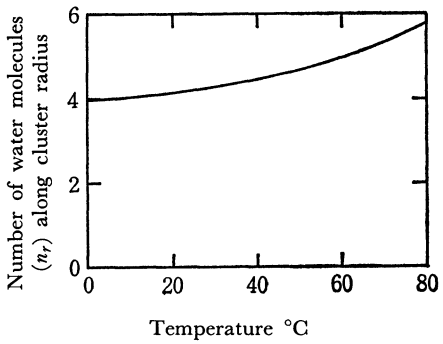

Fig. 3. n_r in dependence on temperature.