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Sound Velocity in Aqueous Non-Electrolyte Solutions in Relation to Water Structure

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An acoustic interferometer is employed to obtain the variation of sound velocity with concentration and temperature in hexamethylenetetramine (HMT), urea, thiourea, acetamide and *N*,*N*-dimethylformamide (DMF) and their aqueous solutions. The plot of velocity of aqueous solutions of these organic substances against temperature gives parabolic curves similar to one for pure water. In these curves, the maximum height of sound velocity is higher than that for pure water and the temperature at maximum point is lower than for water. The curves of sound velocity *vs.* concentration at various temperatures show values of maximum velocity at intermediate concentrations. The maximum value decreases with increasing temperature and finally disappears in some cases. Results show that the velocity dependency on temperature and concentration are qualitatively determined by the relative concentration of non-associated water to cluster. The sound velocity of acetamide and DMF is 1404.4 m/sec (65°C) and 1478.8 m/sec (20°C), respectively, and shows negative temperature coefficients of −2.68 m/sec/deg and −3.90 m/sec/deg, respectively.

All pure liquids, except water[1] and heavy water,[2] are found to have negative temperature coefficients of sound velocity V. Randall[1] found that water has a large positive coefficient of sound velocity at room temperature. The temperature coefficient (dV/dT) decreases to zero at 74°C and then becomes negative as for ordinary liquids. The origin of such an anomalous behaviour is sought in the structure of water.

According to the two-state model, liquid water consists of two species; a non-associated, close-packing-state water, and a bulky, associated state or cluster. According to the molecular view of the acoustic compression of water, compression of the former state is attributed to the compression of the free space among non-associated water molecules, while the compressibility of the latter part mainly results from the breaking of the hydrogen bonds and accordingly the partial destruction of the associated bulky structure. The structural sound absorption in pure water is explained along these lines by Hall.[3] The amount of the cluster part of water decreases with increasing temperature, resulting in a decrease of the structural part of the compressibility, while an increase in molecular distance with temperature rise accompanies an increase in ordinary compressibility. These opposing effects make the compressibility curve a minimum at an intermediate temperature, or the maximum of the sound velocity at a slightly different temperature.

Sound velocity in aqueous solutions is a function of both temperature T and concentration c, *i.e.*,

1) R. Randall, *Bur. Standards J. Res.*, **8**, 79 (1932).
2) M. Pancholy, *J. Acous. Soc. Amer.*, **25**, 1003 (1953).
3) L. Hall, *Phys. Rev.*, **73**, 775 (1948).

$V=V(T, c)$. Temperature dependence of sound velocity $V=V(T)$ at constant concentration and concentration dependence of sound velocity $V=V(c)$ at constant temperature are the two main aspects. An aqueous solution of any substance, either organic[4,5] or inorganic,[4,5] shows parabolic $V(T)$-curves similar to that of water. When the substance is dissolved in water, a part of the clusters in solution is decreased and the peak temperature T_m (temperature for velocity maximum V_m) is lowered, the peak velocity V_m becoming greater than that of pure water. The concentration dependence of sound velocity $V(c)$ in aqueous solutions, however, has hitherto been studied only in some primary alcohols, amines, amides, ketones, carboxylic acids and heterocyclic compounds.

In the present study, sound velocity in aqueous solutions of HMT, urea, thiourea, acetamide, and DMF is measured and the dependence on concentration and temperature is studied with the purpose of elucidating the molecular mechanism of the sound propagation in aqueous solutions.

Experimental

Materials. HMT, urea (mp 133.6°C), thiourea (mp 181.3°C) and acetamide (mp 83.1°C) were purified by recrystallization from absolute alcohol, from reagent grade products. The melting point of HMT was not measurable because of sublimation. DMF (bp 152.8—153.6°C) was purified from reagent grade product by drying with anhydride sodium sulfate and distillation.

Apparatus. A crystal-controlled ultrasonic interferometer with frequency of 5 MHz was used to measure the sound velocity. One hundred standing waves were counted. Solutions in the measuring cell were immersed in an oil bath. The temperature was kept constant within ±0.1°C.

Results and Discussions

The sound velocity in solutions of HMT, urea, thiourea, acetamide and DMF is plotted against temperature in Figs. 1—5. It should be noted that for dilute solutions the $V(T)$-curves change in a systematic manner with concentration keeping the parabolic form nearly the same as that for water. We see that the peak velocity V_m becomes higher than that of pure water with increasing concentration, and at the same time the temperature corresponding to peak velocity (T_m) becomes lower than that for pure water. In concentrated solutions, a small amount of remaining

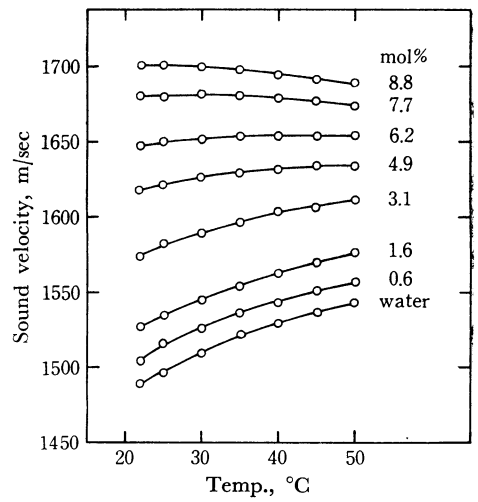

Fig. 1. Sound velocity *vs.* temperature of aqueous HMT solutions at various concentrations.

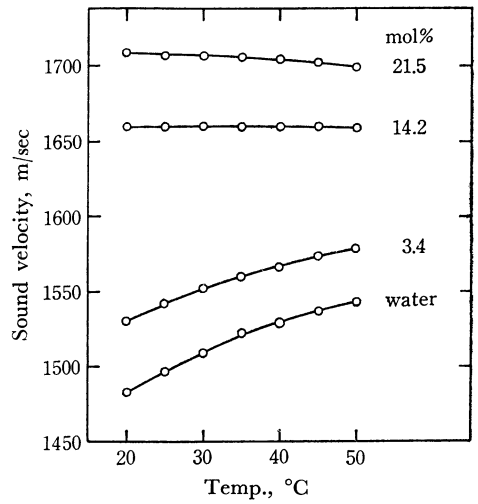

Fig. 2. Sound velocity *vs.* temperature of aqueous urea solutions at various concentrations.

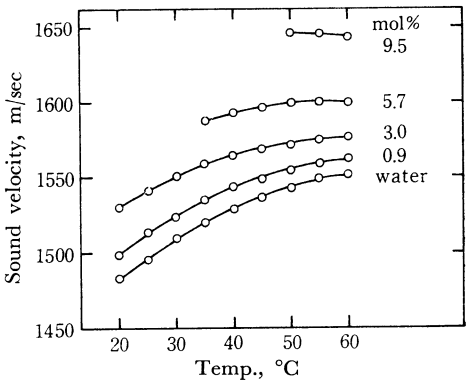

Fig. 3. Sound velocity *vs.* temperature of aqueous thiourea solutions at various concentrations.

4) J. Saneyoshi, K. Kikuchi and O. Nomoto, "Tyo-onpa Gizitu Binran," *Nikkan Kogyo Sinbunsya, Tokyo* (1966), pp. 1254—1267.

5) W. Schaaffs, Landolt-Börnstein, Zahlenwerte und Funktionen. Gruppe II, Band 5, "Molekularakustik," Springer-Verlag, Berlin, Heidelberg, New York (1967), pp. 89—125.

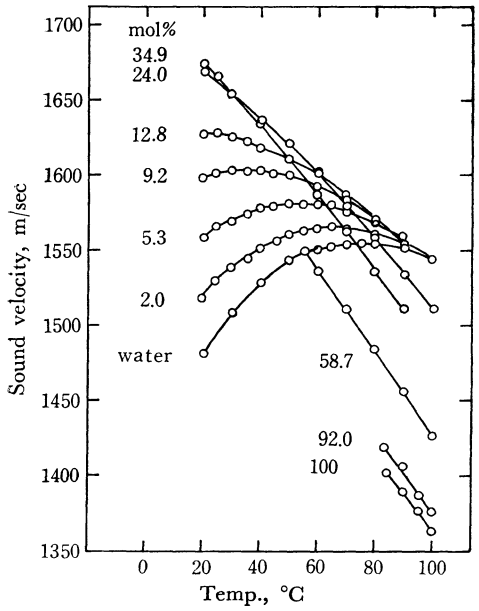

Fig. 4. Sound velocity *vs.* temperature of aqueous acetamide solutions at various concentrations.

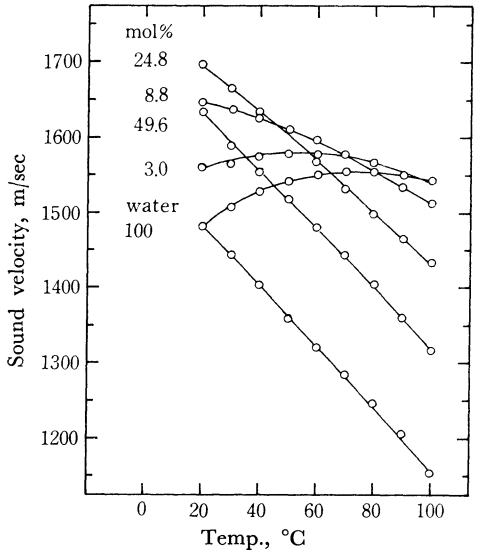

Fig. 5. Sound velocity *vs.* temperature of aqueous DMF solutions at various concentrations.

water makes the sound velocity considerably higher than that of pure solute (acetamide or DMF), the $V(T)$-curves becoming linear as in pure liquids (Figs. 4 and 5).

It is to be expected that a small amount of water in high-concentration solutions is almost in non-associated state, so that structural compressibility is absent. This makes the sound velocity in "non-associated water" much higher than in ordinary water, accompanying the great rise in velocity in highly concentrated solutions.

By extrapolating the sound velocity for pure water from that in the high-concentration region we obtain $V_2=2140$ m/sec and 2160 m/sec respectively, from acetamide solutions and DMF-solutions at 20°C, if the thermodynamic Kudriavtsev equation[6] for the sound velocity in ideal mixtures

$$V^2 = \mu\frac{M_1}{\bar{M}}V_1^2 + (1-\mu)\frac{M_2}{\bar{M}}V_2^2$$

is used. Here V_1, M_1 and μ mean sound velocity, molecular weight, and molar fraction of the first component, respectively, and V_2,M_2 and $(1-\mu)$ are the corresponding quantities for the second component. $\bar{M}=\mu M_1+(1-\mu)M_2$ is the average molecular weight. This value of V_2 is appreciably higher than the usual sound velocity for pure water (1483 m/sec at 20°C) and represents the sound velocity of virtual non-associated water.

The sound velocity V_1 in pure acetamide and DMF is found to be 1404.4 m/sec (85°C) and 1478.8 m/sec (20°C), respectively. The temperature coefficients of sound velocity in these substances are found to be -2.68 m/sec/deg and -3.90 m/sec/deg, respectively. Reported values for DMF (20°C) are $V_1=1497$ m/sec, $dV_1/dT=-4.0$ m/sec/deg[7] and $V_1=1478$ m/sec, $dV_1/dT=-3.62$ m/sec.[8]

Parshad[9] found that when alcohol is added to water, the peak temperature (74°C in pure water) becomes lower with increasing concentration. Willard[10] studied the relation between velocity and concentration in the same system and found that the shapes of curves are parabolic as for water. He assumed that for $V(T)$-curves in aqueous solutions over a wide temperature range parabolas shifted in a systematic manner with concentration are obtained. Even when we cannot find an actual velocity peak, we can determine the height and temperature of the hypothetical peak outside the measured range, by assuming that the shape of the $V(T)$ curve for solution remains the same with that of pure water, and by shifting the latter curve along the both coordinate-axes T and V till the both curves do overlap. (The hypothetical velocity peak sometimes comes below melting point.)

We assumed that the shift of the peak temperature is determined by the increment of non-associated water molecules exclusively add that this increment depends on the total surface area of solute molecules in water, considering that larger the surface area, the larger the number of single water

6) B. B. Kudriavtsev, *Soviet Physics-Acoustics*, **2**, 36 (1956).

7) I. Larionov, A. Dmitrieva and V. Goryatchoko, *Primenenie Ultraakustiki*, **2**, 75 (1958).

8) W. Schaaffs, Landolt-Börnstein, "Molekularakustik," Springer Verlag, Berlin, Heidelberg, New York (1967), p. 18.

9) R. Parshad, *Indian J. Phys.*, **15**, 323 (1941).

10) W. Willard, *J. Acous. Soc. Amer.*, **19**, 234 (1947).

molecules which might be oriented in the neighbourhood of the solute resulting in the breaking of clusters. Assuming the solute molecules to be hard spheres with surface area $S_0=k_0(M/\rho N)^{2/3}$, the total surface area of the solute in 100 g aqueous solution of p wt% becomes

$$S_t = k\frac{p}{(\rho^2 M)^{1/3}},$$

where k_0 and k are constants, and N, ρ, and M are the Avogadro number, density and the molecular weight of the solute, respectively. In Fig. 6, the peak temperatures in solutions are plotted against $p/(\rho^2 M)^{1/3}$, a quantity proportional to the total surface area S_t. As can be seen, a simple linear relation exists between the peak temperature and surface area up to about 30 wt%. This shows, at least qualitatively, the validity of our assumption that the shift of the peak temperature is determined by the relative concentration of non-associated water molecules.

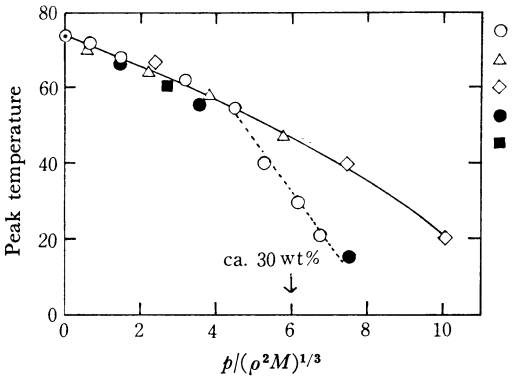

Fig. 6. Peak Temperature *vs.* $p/(\rho^2 M)^{1/3}$.
○ HMT, △ thiourea, ◇ urea, ● acetamide, ■ DMF

In Figs. 7—11 the sound velocity is plotted against molar fraction for aqueous solutions of HMT, urea, thiourea, acetamide and DMF over the whole range of concentration (up to the solubility limit in the case of HMT, urea and thiourea), and at temperatures 20—100°C. In case of sufficient solubility, these $V(c)$-curves exhibit maximum each at a fixed concentration, the maximum value gradually decreasing and shifting towards lower concentration with increasing temperature.

As seen in Figs. 10 and 11, the $V(c)$-curve at 100°C has no longer a maximum but exhibits a nearly linear relation. The aqueous solution hitherto investigated, which exhibit maximum in the $V(c)$-curve are those of primary alcohols, amines, amides, ketones, carboxylic acids and heterocyclic compounds. These compounds are known to be water-soluble non-electrolytes with radicals OH, NH_2, NH, CO, COOH and C_5H_5N, *etc.*, with tendency to form a hydrogen-bonded

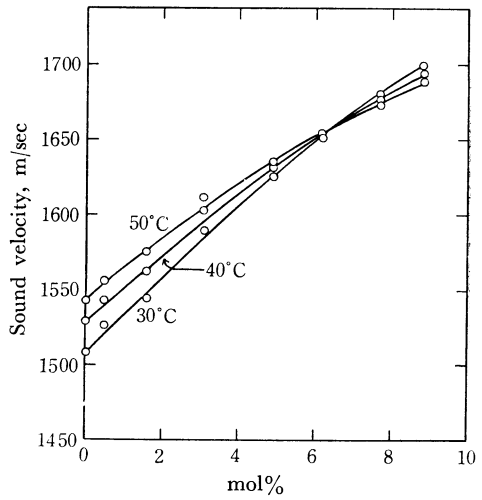

Fig. 7. Sound velocity *vs.* concentration of aqueous HMT solutions at various temperatures.

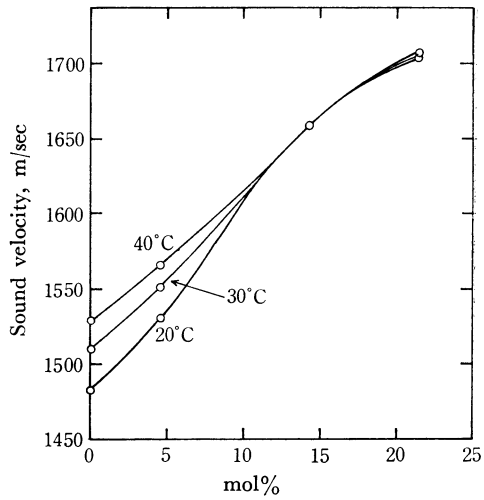

Fig. 8. Sound velocity *vs.* concentration of aqueous urea solutions at various temperatures.

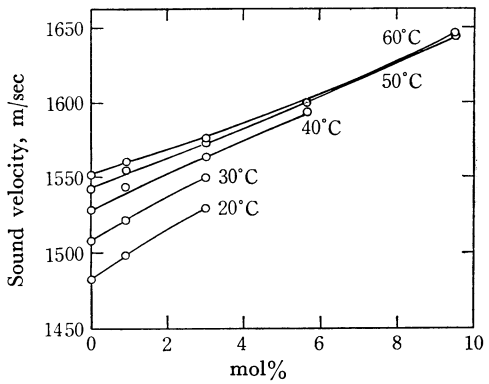

Fig. 9. Sound velocity *vs.* concentration of aqueous thiourea solutions at various temperatures.

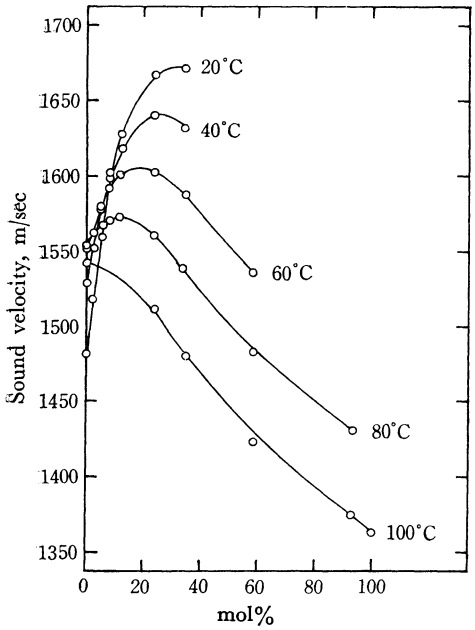

Fig. 10. Sound velocity *vs.* concentration of aqueous acetamide solutions at various temperatures.

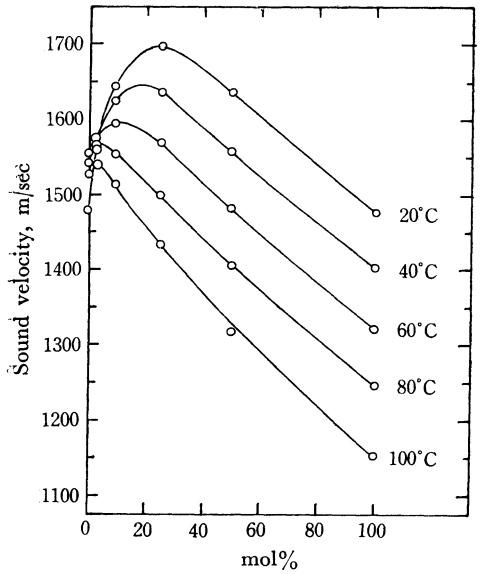

Fig. 11. Sound velocity *vs.* concentration of aqueous DMF solutions at various temperatures.

structure with water. By addition of these substances to water, it is to be expected that the available number of single water molecules decreases, so that the clusters of associated water molecules may dissolve to some extent until a new equilibrium is established.

Figure 12 gives the viscosity curves in the system water-DMF at various temperatures. The viscosity curves of aqueous solutions, especially primary alcohols[11,12] and carboxylic acids,[12,13] when plotted as functions of concentration at various temperatures, also show the maximum each at a fixed concentration, the maximum becoming lower and slightly shifting towards higher concentration with increasing temperature. It should be noticed that the direction of the shift of the viscosity peak is opposite that of the velocity peak. Recent data by Kikuchi and Oikawa[14] show no shift of viscosity peak with temperature. At any rate, the shift of viscosity peak is smaller than that of the sound velocity-peak.

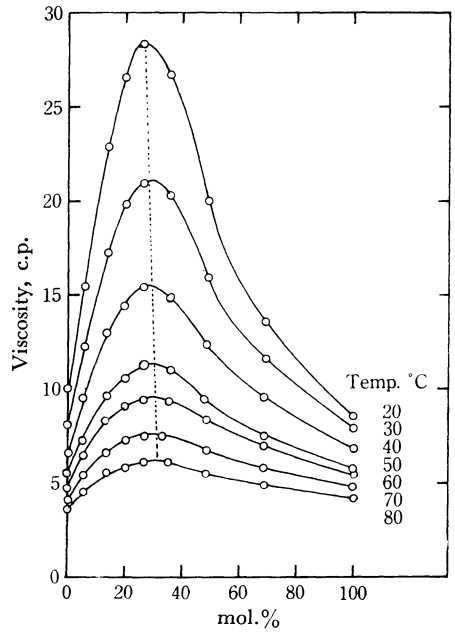

Fig. 12. Viscocity vs. concentration of aqueous DMF solutions at various temperatures. The dotted line shows the position of maximum viscocity (Larionov *et al.*[7]).

The maximum viscosity dependent on concentration is attributed to the molecular complex formation[12,15] among non-associated water molecules and the solute molecules. The viscosity maximum mighy shift towards higher concentration with temperature rise because of the increase in coordination number in the neighbourhood of the solute due to the increased fraction of the single water molecules, favouring complex formation at higher concentrations.

11) C. Bingham and F. Jackson, *Bull. Nat. Bur. Standards*, **14**, 59 (1917).
12) T. Ishikawa, "Kongoeki Nendo no Riron," Maruzen, Tokyo (1968).
13) J. Traube, *Ber.*, **19**, 871 (1886).
14) M. Kikuchi and E. Oikawa, *Nippon Kagaku Zasshi*, **88**, 19 (1967).
15) E. Hatschek, "The Viscosity of Liquids," Bell, London (1928), Chap. IX.

The solute-water-complex itself, however, does not influence sound velocity so much, because the complex is presumably of the same density and compressibility as the constituent parts before complex formation(solutes plus single-water molecules), approximately. The existence ratio of the single water molecules and clusters, however, changes with complex formation, and this gives rise on a shift towards lower concentration of the velocity peak with temperature rise.

We conclude that the maximum velocity observed for some aqueous solutions at a certain concentration at constant temperature does not correspond to the decrease in comressibility resulting from solute-water association, but is attributed to the balance between the relative magnitudes of the structural compressibility of the water-clusters and the ordinary compressibility of non-associated water molecules and solutes. Parshad[16] and Yasunaga *et al.*[17] attained analogous conclusions by adding small amounts of salt to ethanol-water system at constant temperature.

16) R. Parshad, *J. Acous. Soc. Amer.*, **21**, 175 (1949).
17) T. Yasunaga, N. Tatumoto and M. Miura, This Bulletin, **37**, 867 (1963).