Ultrasonic Velocity and Compressibility in Aqueous Solutions of Alkali Metal Chlorides

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The ultrasonic velocity of aqueous solutions of alkali metal chlorides was measured by the use of the sing-around technique at 0.5 and 1 mol kg^{-1} over the temperature range from 30 to 85 °C; compressibilities of the solutions were also determined. It was found that the ultrasound velocity *versus* temperature curves show a maximum, while the compressibility *versus* temperature ones show a minimum. Both maxima and minima appear at lower temperatures than that observed for pure water. The maximum shifted values were found for Na$^+$ ion. The results were explained by the dynamic structure of the water around the ions.

One of the abnormal properties of water is the variation of ultrasound velocity with temperature in water. That is, the propagation velocity of ultrasound in normal liquids falls off with increasing temperature; however, for water the ultrasonic velocity attains a maximum value of 1557 m s^{-1} at a temperature of 74 °C, and only above this temperature does the ultrasound velocity diminish. The adiabatic compressibility of water shows a minimum at 64 °C. These phenomenon are due to the peculiar liquid structure of water.

The temperature of maximum sound velocity in water is changed by the presence of ions,[1-3] since the water structure is affected by the ions. Thus, from the effects upon the ultrasound velocity and the compressibility of water by the ions it is possible to obtain some information with regard to the ion–water interactions.

There have been several studies of the ultrasound velocity in aqueous electrolyte solutions. However, only a few systematic investigations[1-3] have been reported so far over a sufficiently wide range of concentration and temperature.

We have, therefore, attempted to measure the ultrasound velocity of aqueous solutions of alkali metal chlorides over a wide range of temperature; the adiabatic compressiblities of these solutions were also determined. The results are discussed on the basis of the dynamic structure of water around cations.

Experimental

Alkali metal chlorides (G. R., E. Merck Co.) were used without further purification.

Sound velocity was measured by the "sing-around" technique, using an apparatus (Choonpa Kogyo Co.) at 5 MHz. Procedures of the measurement of the sound velocity are described elesewhere.[4] Ultrasound velocity in the solutions was determined at 5 °C intervals over a temperature range from 30 to 85 °C and at 1 °C intervals in case of need. The constancy of temperature was ±0.01 °C.

Adiabatic compressibility κ was calculated by the following relation:

$$\kappa = 1/u^2 d, \tag{1}$$

where u is the velocity of ultrasound and d the density of the solution. Values of the densities at the experimental temperature and concentration were calculated from the following polynomials of the concentration or temperature:

$$d = d_0 + \sum_{i=1}^{5} a_i m^i \tag{2}$$

and

$$d = d_0 + \sum_{i=1}^{5} b_i t^i, \tag{3}$$

where d_0 is the density of pure water, m the molality, and t the temperature (°C). Values of the coefficients a_i and b_i in the polynomials were determined from the densities of solution of alkali metal chlorides,[5] using a HITAC 8400.

Results and Discussion

The temperature dependence of ultrasonic velocities in aqueous solutions of alkali metal chlorides are shown in Figs. 1 and 2 at salt concentrations 0.5 and 1 mol kg^{-1}. Only the ultrasound velocity in CsCl solution is lower than that in water over all the range of temperature at both concentrations. The difference of the sound velocities in the salt solutions and water increases with increasing concentration. The temperature of maximum sound velocity, T_{vm}, varies according to the kinds of salts and their concentrations, and shifts to lower temperatures than 74 °C.

At any temperature the sound velocity in the salt

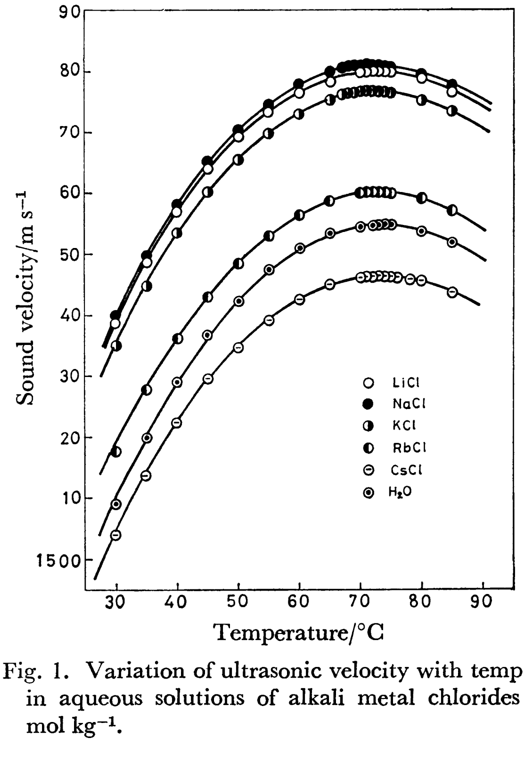

Fig. 1. Variation of ultrasonic velocity with temperature in aqueous solutions of alkali metal chlorides at 0.5 mol kg^{-1}.

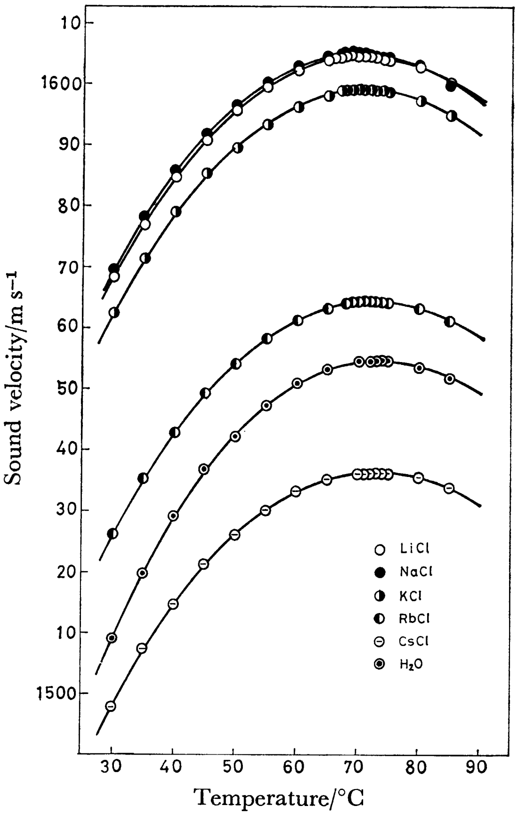

Fig. 2. Variation of ultrasonic velocity with temperature in aqueous solutions of alkali metal chlorides at 1 mol kg^{-1}.

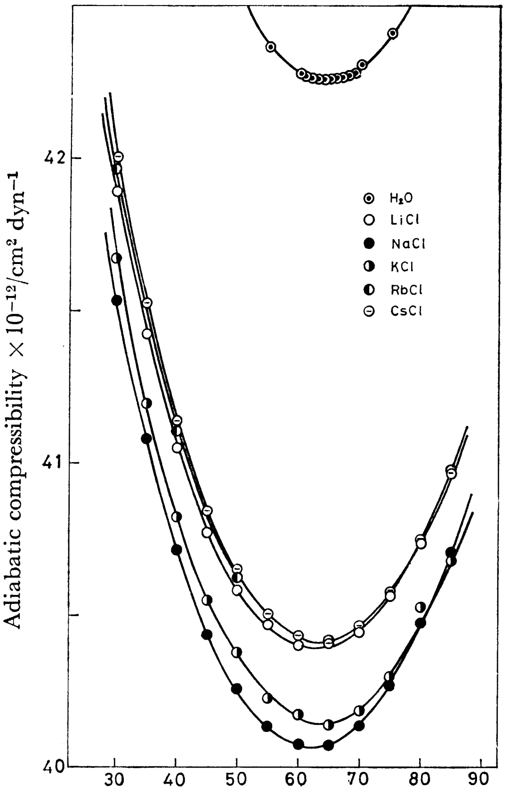

Fig. 3. Variation of adiabatic compressibility with temperature of aqueous solutions of alkali metal chlorides at 0.5 mol kg^{-1}.

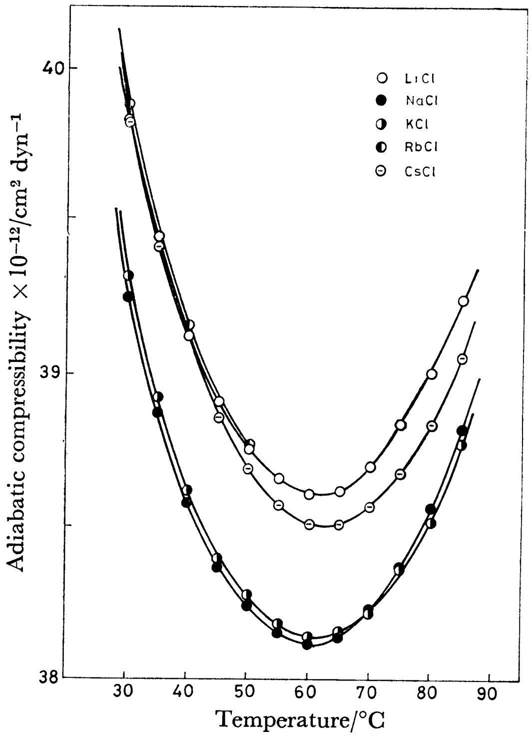

Fig. 4. Variation of adiabatic compressibility with temperature in aqueous solutions of alkali metal chlorides at 1 mol kg^{-1}.

solutions decreases in the order:

$$\mathrm{NaCl} > \mathrm{LiCl} > \mathrm{KCl} > \mathrm{RbCl} > \mathrm{CsCl}$$

but above 70 °C the velocity in the 1 mol kg^{-1} solution of LiCl becomes larger than that in NaCl solution.

The temperature dependence of the compressibilities are shown in Figs. 3 and 4. The compressibilities of RbCl solution at temperature higher than 50 °C could not be calculated, since the values of densities in the temperature range were not found in the literature.

All the values of compressibilities for the salt solutions are smaller than that of water and the order of magnitude differes in different concentrations. Below 70 °C the compressibility of NaCl solution is the lowest at each concentration. Judging from the fact that the values of compressibilities for LiCl, RbCl, and CsCl solutions do not differ markedly from one another, the large density of CsCl solution is thought to account for the fact that the sound velocity in CsCl solution is smaller than that in water. From the above-mentioned results, it seems difficult to connect directly the sound velocity and compressibility with the structure of solutions.

According to Hirata and Arakawa,[6] the compressibility of water is equal to $\kappa_\infty + \kappa_{\mathrm{relax}}$ under our experimental conditions, where κ_∞ and κ_{relax} are the instantaneous and the relaxational parts of the compressibility, respectively.[7] As the temperature rises, κ_∞ increases due to thermal motion but κ_{relax} decreases due to thermal rupture of water structure. The competition between these two opposing tendencies leads to the compressibility minimum at 64 °C and the sound velocity maximum at 74 °C.

An ion affects the thermal motion of the water molecules around it. Thus the temperature of the

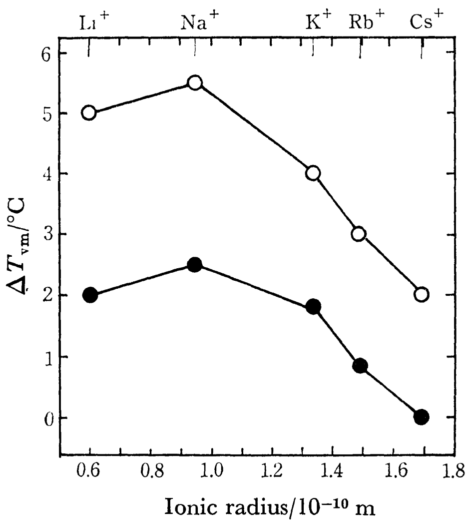

Fig. 5. Relation between ΔT_{vm} and ionic radius.
-●- 0.5 mol kg^{-1}; -○- 1 mol kg^{-1}.

compressibility minimum(T_{cm}) and the sound velocity maximum(T_{vm}) must reflect the change of water structure due to the presence of the ions. Because the chlorine ion is common to all the salts treated in the present study, the relative effects of the cations can be compared.

Figure 5 shows the relation between the ionic radius and $\Delta T_v = T^\circ_{vm} - T_{vm}$, where T°_{vm} is 74 °C. Figure 6 shows the relation between the ionic radius and $\Delta T_{cm} = T^\circ_{cm} - T_{cm}$, where T°_{cm} is 64 °C. These results show a maximum at the Na$^+$ ion. The curves shift to nearly parallel accordingly to the concentration or the kind of anion.

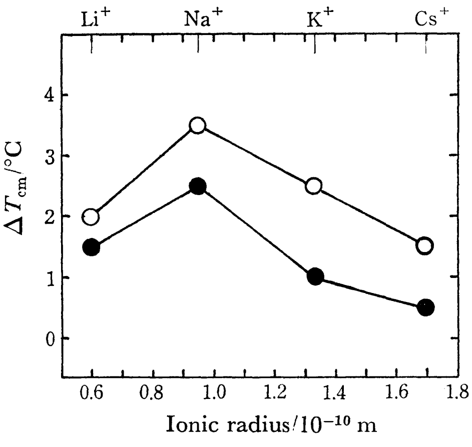

Fig. 6. Relation between ΔT_{cm} and ionic radius.
-●- 0.5 mol kg^{-1}; -○- 1 mol kg^{-1}.

Eigen and Mass[8)] measured "the absorption-volume of particle" $Q \cdot \lambda$ in the reaction of alkali metal nitrilotriacetate and alkali metal acetylenediaminetetraacetate complex in aqueous solutions. $Q \cdot \lambda$ is a parameter which characterizes the chemical equilibrium. $Q \cdot \lambda$ *versus* the frequency of the ultrasound curve shows a maximum. The values of $(Q \cdot \lambda)_{max}$ were greatest at Na$^+$ ion. Hindeman[9)] measured the chemical shifts of protons in aqueous solutions of alkali metal halides. The absolute value of the chemical shift for the cations shows a maximum at Na$^+$ ion.

There are many thermodynamic properties which do exhibit a maximum at Na$^+$ ion. Desnoyers and Jolicoeur[10)] proposed a possible explanation; these maxima may appear because "the strength of ion–solvent interactions decreases with increasing size of the ions, but the coordination number of the ion increases with increasing size." According to X-ray analysis and neutron scattering, the coordination numbers of alkali metal ions are 4 for Li$^+$, Na$^+$, and K$^+$ ions,[11)] and 8 for Cs$^+$ ion.[12)] The above suggestion leaves something to be desired. In order to explain the above results, it is necessary to consider the state of the water molecules around the ion more deeply.

The compressibility of the solution will be discussed, since it is a fundamental thermodynamic quantity. Attention will be directed to the concentration range, at which the cospheres of the cation and the anion do not overlap.

The compressibility of an aqueous electrolyte solution is smaller than that of pure water. This is ascribed to two effects:[6)] (1) the decrease of compressibility caused by the introduction of incompressible ions, and (2) the change of water structure around the ion. Among the effects, the contribution of effect (1) is larger, and depends more on the concentration rather than on the kind of ions (see Figs. 3 and 4). Recently, Subrahmanyan and Moorthy[13)] showed that if these are no interactions between water and solutes, T_{cm} is always lower than T°_{cm}. What they called the dilution effect corresponds to effect (1). Thus, we have the following relation, taking account of effects (1) and (2):

$$T_{cm} = T^{id}_{cm} + T^{ion}_{cm} \tag{4}$$

$$\Delta T_{cm} = T^\circ_{cm} - (T^{id}_{cm} + T^{ion}_{cm}) \tag{5}$$

where T^{id}_{cm} and T^{ion}_{cm} are the contribution by the dilution effect and the ion–water interaction, respectively, and $T^{id}_{cm} > T^{ion}_{cm}$. The value of T^{id}_{cm} is about constant in the case of the alkali metal ions if the concentration is constant, and so ΔT_{cm} depends mainly on T^{ion}_{cm}.

The Na$^+$ ion is a weak structure-making ion. According to Samoilov,[14)] τ_i/τ_o for Na$^+$ ion is 1.3 at 25 °C, where τ_i and τ_o are the mean residence times of a water molecule in the immediate neighborhood of the ion in the aqueous solution and in the immediate vicinity of a water molecule in pure water, respectively. Since the coordination number of the water molecule around Na$^+$ ion is 4, the water structure around Na$^+$ ion is like that of pure water. No disordered water molecules exist outside the reoriented water molecules around an Na$^+$ ion. Therefore, T^{ion}_{cm} for Na$^+$ ion is very small and the decrease of the compressibility of the NaCl solution is mainly caused by the dilution effect.

The alkali metal ions do not change the water structure so much. The structure-breaking ion make the thermal motion of water molecules more intense, but the structure-making ions show a contrary effect. Samoilov[14)] proved that the surface density of the distribution of water molecule around the ion decreases with increasing the ionic radius. The surface densities of K^+, Rb^+, and Cs^+ ions are smaller than that of pure water. Therefore, the structure-breaking ion causes the compressibility of the solution to increase in comparison with that of NaCl solution, as seen in Figs. 3 and 4. The value of $T^{\text{ion}}_{\text{cm}}$ increases and so ΔT_{cm} decreases with increasing size of the ions in the case of K^+, Rb^+, and Cs^+ ions. Nomoto and Endo[3)] found that ΔT_{vm} of NH_4I solution is zero up to the concentration of 25 wt%. Both NH_4^+ and I^- ions are the structure-breaking ions. They mentioned that neither ion destroys the water structure markedly and both expand the water lattice.

Water molecules adjacent to Li^+ ion strongly reorient around it; according to Passynski,[15)] they should be regarded as incompressible. The disordered water molecules exist outside these reoriented water molecules.[16)] The Li^+ ion with immobile water molecules, therefore, behaves like a structure-breaking ion in the case of the acoustic and some thermodynamic phenomena. This model is supported by the fact that the compressibilities of the LiCl, RbCl, and CsCl solutions have values close to each other.

Now we shall call attention to fact that the compressibilities of the solutions are divided into two groups. In the first group, as mentioned above, are the compressibilities of the solutions of LiCl, RbCl, and CsCl. These cations interact strongly with water molecules, though there is a difference in that Li^+ ion is a structure maker but Rb^+ and Cs^+ ions are structure breakers. The second group includes the compressibilities of the solutions of NaCl and KCl. Na^+ and K^+ ions interact weakly with water molecules, and their effects are directly opposite to each other. In the case of the alkali metal–chelate complex, the reactions are divided into two groups in the same way (Ref. 7, Fig. 3).

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