Studies on Hydration by Ultrasonic Interferometer. V. The Change of Hydration of Inorganic Electrolytes with Temperature

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Introduction

We have already calculated the amount of hydration of ions from the compressibility of their solution, on the assumption that the hydration shells together with the ions themselves are incompressible under the pressure of an ultrasonic wave[1], and confirmed that the results obtained were satisfactory, since they were in accord with the other known facts on hydration[2].

As the reaction of ionic hydration is exothermic, temperature rise is supposed to cause the dehydration of ions. This is always true for a salt crystal having water of crystalization and we can expect that this also applies for the ionic hydration in the aqueous solution. The present study was undertaken to confirm this for several simple electrolytes in solution, using an ultrasonic interferometer for the measurement of the hydration.

Experimental Method

The ultrasonic interferometer used to measure the sound velocity and the method of calculation of hydration from the sound velocity was the same as in the first report[1]. The ultrasonic frequency used was 406.927 kc./sec.

Experimental Results and Discussions

The samples used were the aqueous solutions of 1N NaCl. The sound velocity was measured at the temperature ranging from 0°C to 60°C for water and the aqueous solution of NaCl. The curves obtained for water and NaCl solution ran parallel to each other as shown in Fig. 1.

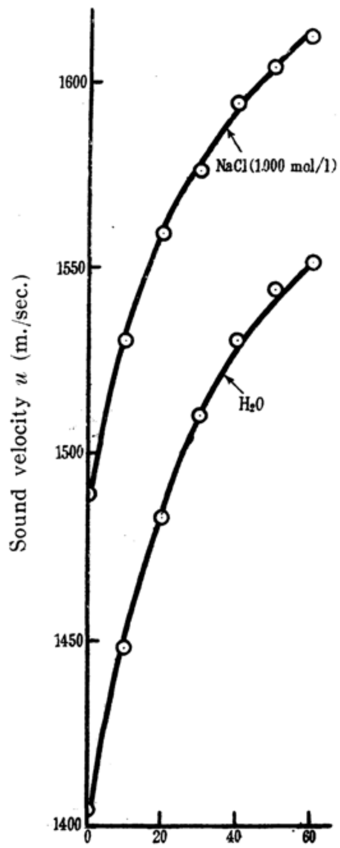

Fig. 1. Change of sound velocity with temperature.

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1) T. Yasunaga and T. Sasaki, *J. Chem. Soc. Japan*, 72, 87 (1951).

2) T. Yasunaga and T. Sasaki, *J. Chem. Soc. Japan*, 72, 89, 366 (1951); T. Sasaki, T. Yasunaga and H. Hujiwara, *J. Chem. Soc. Japan*, 73, 181 (1952).

TABLE I

Temperature °C	0	10	20	30	40	50	60
U (m./sec.)	1489.9	1528.0	1558.5	1576.6	1594.3	1604.0	1613.5
d (g./cc.)	1.0458	1.0441	1.0413	1.0396	1.0378	1.0338	1.0292
β (10^{-7} cgs)	43.08	41.02	39.54	38.70	37.91	37.60	37.33
V (cc./mol.)	137.8	125.9	116.7	106.6	106.5	99.6	103.5

We then calculated the compressibility from the sound velocity and density, and computed the amount of hydration of ions as the volume of incompressible water which was shown in Table I.

The amount of hydration decreases with increasing temperature as shown in Fig. 2.

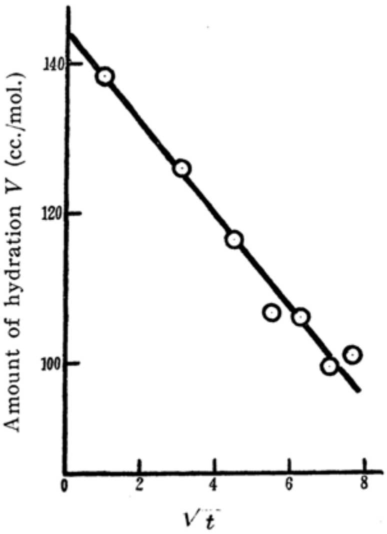

Fig. 2. Change of amount of hydration with temperature (1 N NaCl solution).

As the hydration reaction is exothermic, being caused by the mutual interaction between the ion and water dipoles, this temperature dependence is just what we expect. The relation is best expressed by

$$V_t = V_o - 6\sqrt{t}, \qquad (1)$$

where V_t is the volume of hydration water per mole solute at t°C and V_o, the value of V at 0°C. In this connection, we have already obtained a similar empirical formula for the change of the amount of hydration with concentration in a previous report[3], namely,

$$V_c = V_o - 36\sqrt{C}, \qquad (2)$$

where V_c denotes the volume of hydration water per mole solute at the concentration C and V_o, the value of V_c at the infinite dilution. We can see that temperature and concentration affect the hydration in exactly the same manner. Further, we calculated so called electrostriction, namely, the volume change due to the dissolution of salt in water at various temperatures as we did in a previous paper[4]. Fig. 3 shows the result.

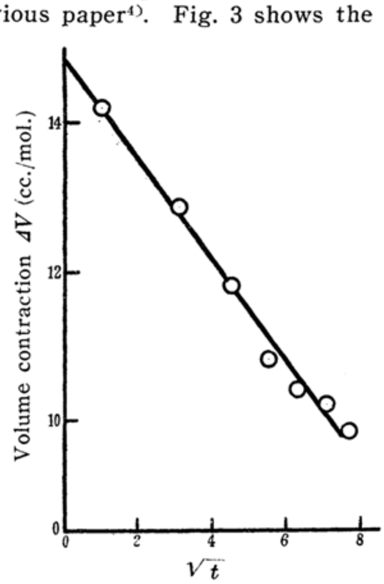

Fig. 3. Change of volume contraction with temperature (1 N NaCl solution).

In a previous paper[5] we have already confirmed a proportionality between the amount of hydration and the volume change at constant temperature and concentration for various electrolytes. From Figs. 2 and 3 we

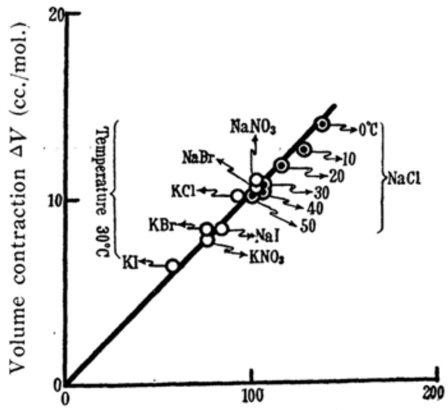

Fig. 4. Relation between amount of hydration and volume contraction.

3) T. Yasunaga and T. Sasaki, *J. Chem. Soc. Japan*, **72**, 89 (1951).

4) T. Yasunaga and T. Sasaki, *J. Chem. Soc. Japan*, **70**, 379 (1949).

5) T. Sasaki, T. Yasunaga and H. Hujiwara, *J. Chem. Soc. Japan*, **73**, 181 (1952).

can also obtain a proportionality between them even for the change of temperature at constant concentration. They are shown in Fig. 4.

It is confirmed that these two straight lines coincide with each other. In other words, the amounts of hydration and volume contraction show a unique proportionality irrespective of whether it is produced by the change of the temperature or the nature of electrolyte, and is expressed by

$$\Delta V/V=0.10.$$

Again, this fact shows, as reported in a previous paper[3], that ΔV and V are closely related to each other and are reasonably assumed to be the measure of hydration. If we assume that water of volume V is compressed by ΔV due to hydration, the mean pressure of hydration of about 4000 atmospheres is obtained, which is necessary to produce this volume contraction. The theoretical calculation for the relation between V and ΔV will be given in the next paper.

Summary

Sound velocity was measured at the temperature ranging from 0° to 60°C for water and the aqueous solutions of NaCl.

The amount of hydration was calculated from the sound velocity data for NaCl, which was shown to change linearly with the square root of temperature.

Volume contraction due to the dissolution of NaCl was also calculated at various temperatures which was found to change proportionally with the amount of hydration. The proportionality constant (0.10) was the same as obtained when the nature of the salt was changed. The mean hydration pressure was estimated to be about 4000 atmospheres.

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