Studies of the Hydration and the Structure of Water and Their Roles in Protein Structure. II. The Hydration of Electrolytes by Ultrasonic Interferometry and Its Temperature Dependence

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In a previous paper[1] of this series, we studied the effective volumes of ions, the magnitudes of electrostriction and the numbers of the hydration water of the ions of various 1-1 electrolytes. From the results we establisehd the existence of clathrates not only around the lithium ion, but also around the ions of rubidium, cesium, bromide and iodide, perhaps as a secondary hydration shell.

The present paper will primarily report on the numbers of hydration for various strong electrolytes as measured by the method of ultrasonic interferometry.

There are several methods to determine numbers of hydration, for example, by compressibility,[2] diffusion,[3] viscosity[4] or the dielectric constant[5]. Each is based on a different characteristic, and the significance of each character in relation to hydration is specific. Consequently, the numbers of hydration water calculated by these different methods are very different.

In the present work the method of compressibility was used. In this method there are mainly two ways to estimate the numbers of hydration water: (1), the compressibility of hydration water is assumed to be zero[2,6-13] and (2), it is assumed to be equal to that of ice.[14,15]

It is uncertain whether or not the compressibility of the solute is nearly zero. In reports on macromolecules, such as proteins, the compressibility of the solute has sometimes been disregarded[12,13] and sometimes not.[16,17] However, for small ions it may always be possible to neglect the compressibility of the solute.[2,6]

The Significance of the Compressibility of the Solution

If a part of the solvent (expressed in volume fraction), v_0, changes to v_2 as a result of hydration, the compressibility of the solution, β, may be derived as follows:

$$\beta = V_1\beta_1 + V_0\beta_0 - v_0\beta_0 + v_2\beta_2 \tag{1}$$

where v_1, V_0 and V_2 are the volume fractions of the solute, solvent and hydrated water respectively, and β_1, β_0 and β_2 are the compressibilities of the solute, solvent and hydrated water respectively. The partial specific volume of the solute, $\bar{v}$, is given as $V_1/c=\bar{v}$, where c is the weight concentration of the solute. If it can be assumed that $v_0=v_2$, the following equation is obtained from Eq. 1 and is valid under the experimental conditions:

$$\frac{\beta_0-\beta}{c} - \bar{v}\beta_0 = \bar{v} - \beta_1 + \frac{v_2}{c}(\beta_0-\beta_2) \equiv K \tag{2}$$

The adiabatic compressibility is determined experimentally by measuring the sound velocity, u, and the density, d, from the relation:

$$\beta = \frac{1}{u^2 d} \tag{3}$$

Therefore, the left side of Eq. 2 can be determined experimentally.

Experimental

The sound velocity in the solution was measured with an ultrasonic interferometer at a frequency of 5 Mc./sec. Details of the method for measuring the wavelength have been given by Passynski.[2]

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The values for the density of solutions were obtained by the pycnometer method developed by Lipkin et al.[18] The concentrations of the solutions were determined by measuring their densities. Measurements were made from 15 to 50°C at intervals of 5°C.

Results and Discussion

As may be seen from Eq. 2, to estimate the number of hydration it is necessary to assume the compressibilities of both the solute, β_1 and hydrated water, β_2. However, in aqueous solutions of strong electrolytes the compressibility of the solute is probably zero, as has been assumed by many authors.[2,6] Therefore, only the compressibility of hydrated water is uncertain in the calculation of the number of hydration from Eq. 2.

In an aqueous electrolyte solution, the strong electric field produced by the ion orientates the water molecules and causes the volume of the water to decrease. This is called the electrostriction effect.[19] This effect is probably exhibited mainly in the primary hydration shell of most 1-1 electrolytes. However, as has been described in the previous paper[1] of this series, there is a clathrate around the ions, perhaps as a secondary hydration shell. It is probably unreasonable to disregard the compressibilities of these water molecules in the secondary hydration shell or of those in the clathrate, which consists of water molecules bound mutually with hydrogen bonds. Shiio[14,15] considered the compressibility of all the hydrated water molecules in aqueous solutions of amino acids, proteins and saccharides to be the same as that of ice (18×10^{-12} cm^2/dyn.) in connection with a term, the iceberg of hydration.[20]

As has been described above, there are still some unsolved problems with regard to the compressibility of hydrated water. However, for the purpose of comparing different electrolytes, we temporarily assumed that the compressibilities of both solute and hydrated water were zero and determined the numbers of hydration on the basis of this assumption.

Figure 1 shows the numbers of hydration for various strong electrolytes in aqueous solutions and their dependence on the temperature. These numbers were obtained using Eq. 2, while the values for the partial specific volume, v, of 1-1 electrolytes are from the previous paper. In the case of 1-2 electrolytes, the apparent partial specific volumes were used. Figure 1 shows that in all these electrolyte solutions the numbers of hydration decrease with an increase in the temperature. In solutions of 1-1 electrolytes, the numbers

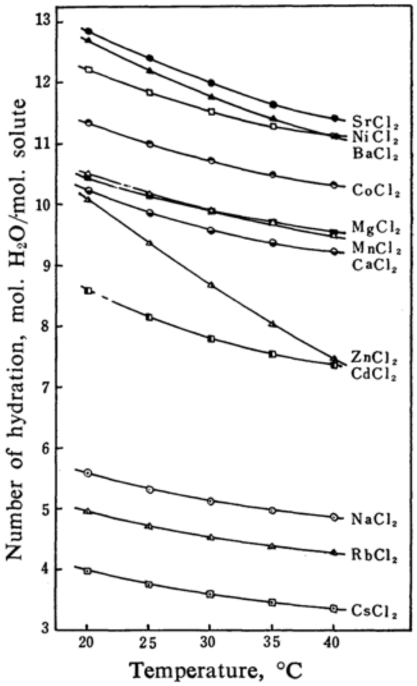

Fig. 1. Numbers of hydration for various 1-1 and 1-2 electrolytes and their dependence on the temperature (assuming that the compressibilities of both solute and hydrated water are zero).

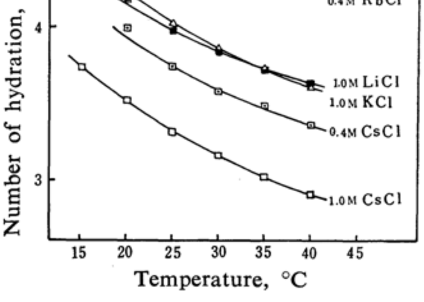

Fig. 2. Numbers of hydration for various 1-1 electrolytes and their dependences on the temperature and concentration.

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of hydration are different from each other at the same temperature, but they decrease in parallel with each other with an increase in the temperature. The same is true for solutions of 1-2 electrolytes also. This phenomenon is significant in contrast to the results obtained for the amino acids to be described in a subsequent paper. As may be seen from Fig. 2, the hydration numbers are also dependent on the concentration. Therefore, the number of hydration should be determined at an infinite dilution. However, since many authors[2,6,21-23] have determined these numbers for various concentrations and since the measurement of these numbers is not the main purpose of this paper, their concentration dependence was not studied.

Table I summarizes the numbers of hydration of various electrolytes at 20 and 40°C. As may be seen from this table, for most electrolytes the change in the number of hydration with the temperature for 1-1 electrolytes is about two-thirds of that for 1-2 electrolytes. That is to say, the change with the temperature is proportional to the number of ions in the solution. This can be explained as follows: the states of hydrated water which are built up in a strong electric field are not affected simply by the change in the temperature but also by the exchange reaction velocity between the unhydrated and hydrated water molecules.

The numbers of hydration of various electrolytes at 20°C (when their compressibilities are assumed to be zero) decrease in the following order:

$$\mathrm{Sr^{2+}>Ba^{2+}>Ni^{2+}>Co^{2+}>Mn^{2+}>Mg^{2+}>}$$
$$\mathrm{Ca^{2+}>Cd^{2+}>Na^{+}>Rb^{+}>K^{+}>Li^{+}>Cs^{+}}$$

This finding contradicts the results obtained from the dielectric constants,[5] entropy,[19] viscosity,[4] and so on. The disagreement may be due to differences between the definitions of hydration.

TABLE I. HYDRATION NUMBERS OF VARIOUS ELECTROLYTES IN AQUEOUS SOLUTIONS AT 20 AND 40°C (ASSUMING THAT THE COMPRESSIBILITIES OF BOTH SOLUTE AND HYDRATED WATER ARE ZERO)

Salt	Concn. mol./l.	Number of hydration mol. H_2O/mol.		
		20°C	40°C	Δv_2
LiCl	0.99	4.20	3.65	0.55
NaCl	0.99	5.15	4.45	0.70
KCl	1.00	4.25	3.60	0.65
RbCl	0.42	4.95	4.25	0.70
CsCl	1.00	3.50	2.90	0.60
$MgCl_2$	0.50	10.45	9.50	0.95
$CaCl_2$	0.45	10.25	9.20	1.05
$SrCl_2$	0.30	12.85	11.40	1.45
$BaCl_2$	0.22	12.70	11.10	1.60
$CdCl_2$	0.33	8.60	7.35	1.25
$MnCl_2$	0.31	10.50	9.45	1.05
$CoCl_2$	0.42	11.35	10.30	1.05
$NiCl_2$	0.38	12.25	11.10	1.15

TABLE II. COMPARISON OF β_c, THE COMPRESSIBILITY CHANGE OF THE SOLVENT, WITH $V^e{}_c$, THE VOLUME OF WATER DECREASED BY ELECTROSTRICTION (GIVEN IN THE PREVIOUS PAPER) AT 20°C

Salt	Concn. mol./l.	β_c	$V^e{}_c$	β_c/V^c_e
LiCl	0.989	0.340	0.305	1.11
NaCl	0.992	0.415	0.538	0.77
KCl	0.997	0.347	0.426	0.81
RbCl	0.415	0.171	0.156	1.10
CsCl	1.001	0.289	0.303	0.95

The values for K in Eq. 2 were compared with the $V^e{}_c$, the volume of water decreased by the electrostriction, given in the previous paper.[1] The results for 1-1 electrolytes at 20°C are summarized in Table II, where c is the molal concentration of the electrolyte. β_c, the compressibility change of the solvent, is given as

$$\beta_c = K \times c$$

As may be seen from this table, the $\beta_c/V^e{}_c$ value for sodium and potassium chloride is about 0.8, but the values for lithium, rubidium and cesium chloride are larger (0.95~1.1) than for sodium and potassium chloride. This suggests that the compressibility of hydration water varies with the states of the hydration water, as for instance, in the primary and secondary hydration shells. In the previous paper of this series, we suggested that there are hydration water molecules around such ions as lithium, rubidium and cesium, as clathrates with nearly the same density as pure water. Though this hydration water probably does not affect the volume change, it may affect the compressibility of the solvent to some extent (causing a change from zero, for example, to that of ice.) In consequence, the compressibility of an electrolyte solution is not in proportion to the electrostriction effect.

Summary

The numbers of hydration of various 1-1 and 1-2 electrolytes in aqueous solutions and their

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dependence on the temperature have been determined by the method of ultrasonic interferometry. The relation between the hydration and the compressibility of aqueous electrolyte solutions has been discussed and further evidence obtained for the existence of the clathrates as hydration shells, as was suggested in the previous paper.

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