Studies of the Hydration and the Structure of Water and Their Roles in Protein Structure. I. The Effective Volumes of 1-1 Electrolytes in Aqueous Solutions and the Electrostriction of Water[1]

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Recently several reports[2-8] on the conformation of proteins have drawn attention to the properties and structure of water from the viewpoint of the stabilization of hydrophobic bonds. However, although there is a considerable literature on the properties and structure of water, there are still many problems to be solved.[7-15]

In a series of studies, of which this is the first report, we propose to give information on the hydration and the structure of water and to elucidate the role of water in maintaining the conformation of proteins. As a basis for a consideration of these problems, the present paper is devoted primarily to the hydration of electrolytes.

There have been numerous investigations[16-25] in different ways of the hydration of electrolytes in aqueous solutions. However, in all cases the results have been obtained in terms of various differing assumptions and there are large discrepancies between the results obtained.[17,18,26,27] In addition, the state of the water of hydration is unknown. If the effective volumes of ions in aqueous solutions were known, various questions concerning the state and number of molecules of the water of hydration could be resolved. This problem is especially important in the case of uni-univalent (1-1) electrolytes.[23,28] This paper will report on the effective volumes of ions and the magnitudes of the electrostriction of the solvent as analyzed from a measurement of their density at various concentrations in aqueous salt solutions. The state of the water around the ions will also be discussed.

The volumes of inorganic salts in aqueous solutions are apparently smaller than the volumes in their respective crystals, due to the contraction of the solvent by electrostatic attraction between ions and water dipoles. However, the volume of lithium iodide in solution is greater than that of its crystals.[29] To obtain details on the magnitude of electrostriction, it is necessary to know the effective volumes of salts in solution rather than in crystals.

Calculation

The values for densities in aqueous salt solutions used in the calculations are quoted from the International Critical Table.

The reciprocal of the density (d_m) of a solution which contains m g. of the solute in 100 g. of the solution corresponds to the volume (V_m) of 1 g. of the solution. Therefore, the volume (V_c) of a solution containing 100 g. of water and c g. of solute can be written as follows:

$$V_c=\frac{100}{d_m}\times\frac{100}{100-m} \tag{1}$$

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$$=c\bar{v}+\frac{100}{d_o}-V^e{}_c \tag{2}$$

where $\bar{v}$ is the effective specific volume of salt in the solution; $V^e{}_c$, the volume of water decreased by electrostriction, and d_o, the density of pure water. c is given by:

$$c=\frac{100m}{100-m} \tag{3}$$

On changing the concentration, c, from c_i to c_j, we find:

$$\bar{v}_{i,j}=\frac{V_{c_i}-V_{c_j}}{c_i-c_j}=\frac{\mathrm{d}V}{\mathrm{d}c} \tag{4}$$

$$=\bar{v}-\frac{V^e{}_{c_i}-V^e{}_{c_j}}{c_i-c_j}=\bar{v}-\frac{\mathrm{d}V^e}{\mathrm{d}c} \tag{5}$$

where $\bar{v}_{i,j}$ corresponds to the apparent specific volume of the salt at a given concentration range. If $V^e{}_{c_i}$ becomes equivalent to $V^e{}_{c_j}$ with an increase in the concentration or if $\mathrm{d}V^e/\mathrm{d}c=0$, $\bar{v}_{i,j}$ will correspond to the effective specific volume of the salt in solution, because all the solvent water will be attracted by ions at a high concentration. In consequence, the volume of water (100 g.) may approach a constant $(100/\mathrm{d}_o-V^e{}_{max})$ with an increase in the concentration of the solute, as is shown by curve B in Fig. 1.

Next, with regard to the correlation between V_c and the concentration of salt, the relation given in Eqs. 6 holds true empirically.

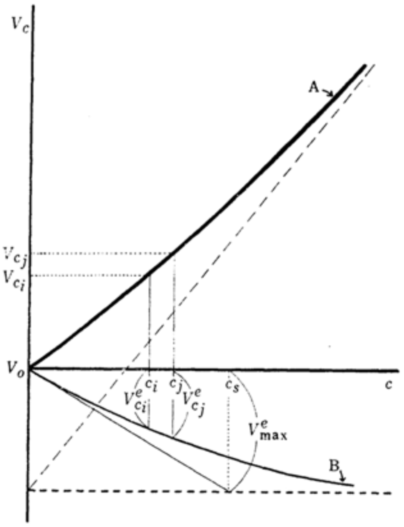

Fig. 1. Schematic representation of the volumes of the solution and the solvent plotted against the concentration of salt.
Curve A: volumes of solutions containing 100 g. of water.
Curve B: volumes of the solvent.
$V^e{}_{c_i}$ and $V^e{}_{c_j}$ represent the volumes of water decreased by electrostriction.

$$V_c=c\bar{v}+\frac{100}{d_o}-(1-e^{-kc})V^e{}_{max} \tag{6-a}$$

$$=c\bar{v}+\frac{100}{d_o}-(1-r^c)V^e{}_{max} \tag{6-b}$$

$$V_M=M\bar{v}_{mol}+\frac{1000}{d_o}-10(1-e^{-k'M})V^e{}_{max} \tag{6-c}$$

where M in Eq. 6-c indicates the molal concentration of salt and $\bar{v}_{mol}$ is the effective molar volume of salt in the solution. V_M is the volume of a solution containing 1000 g. of water and M moles of solute. The three parameters, $\bar{v}$, r and $V^e{}_{max}$, in Eq. 6-b were determined by the method of least squares on an electronic computer.

Further, from Eq. 5, the difference between $\bar{v}_{i,j}$ at an infinite dilution or the apparent specific volume, $\bar{v}_o$, of a salt, and its effective specific volume, $\bar{v}$, corresponds to the magnitude of electrostriction, v^e, per 1 g. of salt at an infinite dilution, which can be obtained from Eq. 8:

$$v^e=\bar{v}-\bar{v}_o \tag{7}$$

$$=kV^e{}_{max} \tag{8}$$

Results and Discussion

Figure 1 gives a schematic representation of the volumes of the solution and the solvent in the aqueous solution of a strong 1-1 electrolyte. The volume of the solution does not increase linearly with the concentration on account of the electrostriction of the solvent. This phenomenon may be due to the extremely rapid exchange reaction between hydrated and unhydrated water or to the overlap of hydrated water layers. In consequence, two curves, for the volumes of the solution (V_c) and of the solvent (V_s) respectively, are drawn under the following conditions;

$$\frac{\mathrm{d}V_c}{\mathrm{d}c}>0 \quad \text{and} \quad \frac{\mathrm{d}^2V_c}{\mathrm{d}c^2}>0$$

and

$$\frac{\mathrm{d}V_s}{\mathrm{d}c}<0 \quad \text{and} \quad \frac{\mathrm{d}^2V_s}{\mathrm{d}c^2}>0$$

Using Eq. 6-b, we analyzed these curves for the solutions of 1-1 electrolytes and determined the effective specific volumes, $\bar{v}$, of salt in an aqueous solution and the maximum volumes, $V^e{}_{max}$, of water decreased by the electrostriction; then, from Eqs. 7 and 8, the apparent specific volumes, $\bar{v}_o$, and the magnitudes of electrostriction, v^e, were calculated. The values obtained are listed in Table I.

For the least square calculation, we used the densities, d_m*(obeserved)*, quoted from the

TABLE I. VARIOUS CALCULATED SPECIFIC VALUES FOR AQUEOUS 1-1 ELECTROLYTE SOLUTIONS AT 20°C

Salt	m_c	r (in Eq. 6-b)	v	V^e_{max} ml.	v^e	v_o
LiCl	14	0.881023	0.5046	0.740	0.0936	0.4110
LiBr	18	0.900352	0.3076	0.280	0.0294	0.2782
LiI	30	0.915110	0.2751	0.118	0.0105	0.2646
NaCl	16	0.935300	0.4036	1.688	0.1129	0.2907
NaBr	18	0.937087	0.2714	0.669	0.0435	0.2279
NaI	18	0.950911	0.2541	0.447	0.0225	0.2316
KCl	16	0.920720	0.4390	0.934	0.0771	0.3619
KBr	18	0.933030	0.3200	0.515	0.0357	0.2843
KI	18	0.950652	0.2936	0.432	0.0218	0.2718
RbCl	18	0.929748	0.3029	0.512	0.0373	0.2656
RbBr	24	0.956536	0.2635	0.642	0.0285	0.2350
RbI	24	0.967556	0.2545	0.533	0.0176	0.2370
CsCl	18	0.953201	0.2606	0.548	0.0263	0.2343
CsBr	18	0.929158	0.2309	0.204	0.0150	0.2159
CsI	30	0.938835	0.2311	0.155	0.0098	0.2213

TABLE II. COMPARISON OF THE OBSERVED AND CALCULATED RESULTS
THE EXAMPLE SHOWS THE VALUES FOR A SOLUTION OF SODIUM CHLORIDE AT 20°C

m	c	M	Observed		Calculated		Δd_m
			d_m	V_c, ml.	d_m	V_c, ml.	
0	0	0	0.99823	100.177_3			0
2	2.041	0.349	1.01246	100.785_0	1.01246	100.785_3	0
4	4.167	0.713	1.02680	101.447_9	1.02680	101.448_0	0
6	6.383	1.082	1.04127	102.166_6	1.04127	102.166_5	0
8	8.696	1.488	1.05589	102.942_2	1.05589	102.942_0	0
10	11.111	1.901	1.07068	103.776_2	1.07068	103.776_0	0
12	13.636	2.332	1.08566	104.670_3	1.08566	104.670_4	0
14	16.278	2.786	1.10085	105.626_6	1.10085	105.627_1	0
16	19.048	3.259	1.11626	106.648_6	1.11627	106.648_4	0.00001
18	21.951	3.757	1.13190	107.740_3	1.13193	107.736_9	0.00003
20	25	4.279	1.14779	108.904_9	1.14788	108.895_6	0.00009
22	28.205	4.825	1.16395	110.146_6	1.16415	110.128_0	0.00020
24	31.579	5.402	1.18040	111.469_8	1.18074	111.437_9	0.00034
26	35.135	6.015	1.19717	112.878_8	1.19768	112.830_0	0.00051

International Critical Table, of the solutions at the concentration, m, of salt from zero to that, m_c, described in Table I at intervals of 2 g. Within this concentration range, all the data, d_m*(observed)*, agree completely with the results, d_m*(calculated)*, calculated from Eqs. 6-b and 1 using the parameters obtained. As an example, the results calculated for a solution of sodium chloride are shown in Table II.

As may be seen from Table II, however, at very high concentrations d_m*(calculated)* values deviate slightly from d_m*(observed)* values. This phenomenon may be interpreted as follows.

Instead of Eq. 2, as a function of the molal concentration of salt Eq. 9 is obtained:

$$V_M = M\bar{v}_{mol} + \frac{1000}{d_o} - V^e{}_M \tag{9}$$

The volume of water decreased by the electrostriction, $V^e{}_M$*(observed)*, at any given concentration of salt is obtained from Eq. 9; also, $V^e{}_M$*(calculated)* can be calculated from Eq. 6-c as:

$$V^e{}_M = 10(1 - e^{-k'M})V^e{}_{max} \tag{10}$$

In Fig. 2, $V^e{}_M$*(observed)* and $V^e{}_M$*(calculated)* are plotted against the molal concentration of some 1-1 electrolytes in solutions taken as typical examples. As may be seen from this figure, $V^e{}_M$*(observed)* deviates from $V^e{}_M$*(calculated)* at high concentrations; this may be caused by the change in the effective volume of salt in a solution as a result of the formation of ion pairs. In consequence, $\bar{v}_{i,j}$ in Eq. 5 at high concentrations may approach the specific volume of salt in the crystal state. In fact, for most

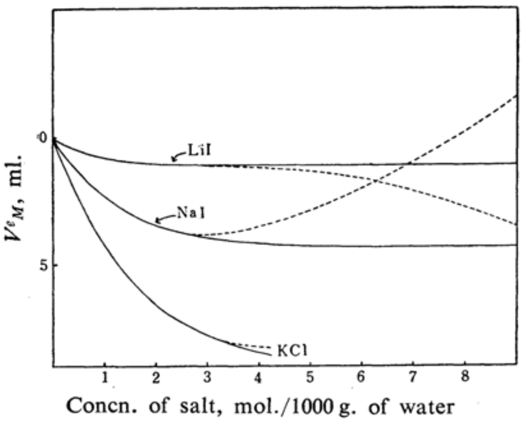

Fig. 2. Volume of water decreased by the electrostriction, V^e_M, plotted against the molal concentration of a few 1-1 electrolytes at 20°C as examples.
—— V^e_M*(calculated)*
- - - V^e_M*(observed)*

of the electrolytes calculated this expectation is realized.

On the other hand, if the hydration is related only to the shrinkage of the solvent due to electrostatic attraction, the lithium ion, which has the smallest ionic radius of all univalent cations, should have the largest electrostriction effect. However, in contrast, as may be seen from Fig. 3, which shows the curves for V^e_M*(calculated)* obtained from Eq. 10 plotted against the molal concentration of salt, and v^e_{mol} in Table III, which represents the magnitude of the molal electrostriction, the order of the molal electrostriction of univalent cations was found to be as follows:

$$Na^+ > K^+ > Rb^+ > Cs^+ > Li^+$$

Therefore, the behavior of the lithium ion in an aqueous solution seems to be unusual. It is well known that the lithium ion in an aqueous solution has an abnormal viscosity[19,22] and compressibility[16] compared with other univalent ions. Frank and Wen[20] and Kaminsky[22], therefore, suggested that there is a clathrate around the lithium ion; our results support this conception. One of these results is described in the present paper; the other will be reported in subsequent papers.

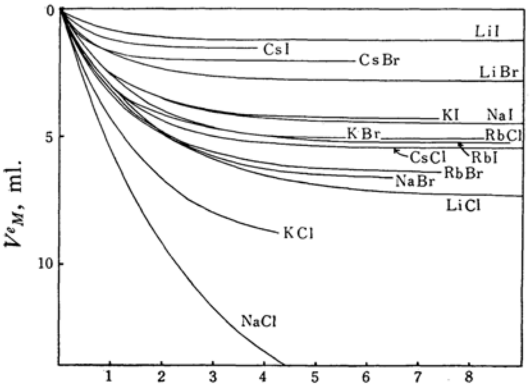

Fig. 3. Volume of water decreased by the electrostriction, V^e_M*(calculated)* obtained from Eq. 10, plotted against the molal concentration of the salt at 20°C.

There have been several reports on the clathrate structures of water around inert gases,[30,31] hydrocarbons[3,7,32,33] and ions[20,25,34–36]. A clathrate consists of water molecules bound mutually with hydrogen bonds and has a lower density than pure water.[7,8] If these conceptions are valid, then it becomes much easier to understand why v^e_{mol} and V^e_{max} are small for lithium salts. Hydration water seems to exist partly as a clathrate around the lithium ion, the density of which is low.

As may be seen from Table III, the effective molar volumes for various 1-1 electrolytes in aqueous solutions are stoichiometrically additive. The existence of this stoichiometric relation suggests that the results are accurate.

On the other hand, as may be seen from Fig. 3, the volume of the water of solutions

TABLE. III. VARIOUS CALCULATED MOLAR VALUES FOR 1-1 ELECTROLYTE SOLUTIONS AND THE NUMBER OF MOLECULES OF WATER OF HYDRATION, N, AT 20°C

Salt	k' (in Eq. 6-c)	$\bar{v}_{mol}$ ml.	v^e_{mol} ml.	$\bar{v}_{0(mol)}$ ml.	N mol. H_2O/ mol. solute
LiCl	0.536	21.4	3.97	17.4	30
LiBr	0.912	26.7	2.55	24.2	51
LiI	1.187	36.8	1.40	35.4	66
NaCl	0.391	23.6	6.60	17.0	22
NaBr	0.669	27.9	4.48	23.4	37
NaI	0.754	38.1	3.37	34.7	42
KCl	0.616	32.7	5.75	27.0	34
KBr	0.825	38.1	4.25	33.9	46
KI	0.841	48.8	3.63	45.2	47
RbCl	0.880	36.6	4.51	32.1	49
RbBr	0.734	43.6	4.72	38.9	38
RbI	0.701	54.1	3.73	50.4	28
CsCl	0.806	43.9	4.42	39.5	45
CsBr	1.565	49.1	3.18	46.0	87
CsI	1.640	60.0	2.54	57.5	96

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of lithium bromide and iodide decreases very little as a result of electrostriction. Thus, the difference in density between pure and hydrated water is apparently small. Therefore, the results support the theory that the hydration water around the lithium ion, perhaps in the secondary hydration shell, exists as a clathrate of a lower density.

Another point of interest shown in Fig. 3 is that the curves for $V^e{}_M$ in rubidium salt and cesium salt solutions decreased very little, as in lithium salt solutions. This suggests very strongly that there is a clathrate around the rubidium and cesium ions, too. Further evidence for this conception will be given in subsequent papers in this series. Furthermore, Fig. 3 indicates the presence of a clathrate around the bromide and iodide ions, too.

Studies were made of the number of the molecules of the water of hydration of ions. The curve shown in Fig. 3 converges to the constant, $V^e{}_{max}$, which corresponds to the decrease in the volume of water when it is completely hydrated to the ions. Values for $V^e{}_{max}$ for various electrolytes obtained from Eq. 6 are listed in Table I. As may be seen from Fig. 1, the tangent of curve B at an infinite dilution intersects the constant, $V^e{}_{max}$, at the concentration c_s. The relation between these is represented as follows:

$$\frac{V^e{}_{max}}{v^e} = c_s \tag{11}$$

$$\frac{100}{c_s} = H_s \tag{12}$$

where H_s is the weight (g.) of water hydrated to 1 g. of the solute. The value of c_s agrees with the reciprocal of k in Eq. 6-a. The number of the molecules of the water of hydration of ions, N, is obtained by the following equation:

$$N = \frac{H_s}{18} \times (\mathit{molecular\ weight\ of\ solute}) \tag{13}$$

The values of N are listed in Table III. As may be seen from this table, the hydration numbers of ions are quite large, even though this estimation cause something of an error. The hydration number includes the primary hydration water molecules which are orientated towards the ions and affected by the electrostriction effect. However, the number is so great that it is not possible to explain the properties of 1-1 electrolytes by this effect alone. Therefore, there are probably clathrates around the ions.

In addition, it is of interest to draw attention to the significance of Pauling's model of the structure of water with regard to clathrate compounds.[13,15,37] In this model the number of water molecules per unit is about the same as the number of hydration of ions and the diameter acting as a cavity is the same as in a primary hydration shell.

The character of the clathrate formation of ions will be supported by experiments by means of nuclear magnetic resonance spectrometry and ultrasonic interferometry to be described in subsequent papers. The other strong evidence for the existence of a clathrate around ions is that of various reports[20,33-35] on the clathrate around tetraalkylammonium ions.

Summary

The effective volumes, the apparent volumes and the magnitudes of electrostriction for various 1-1 electrolytes in aqueous solutions have been determined from an analysis of the densities of solutions at various concentrations. The molar values thus obtained are stoichiometrically additive. The state of water molecules around ions and particularly the existence of clathrates around various univalent ions, such as lithium, rubidium, cesium, bromide and iodide, and the numbers of hydration water have also been discussed.

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