Ionic Hydration in an Aqueous Electrolyte Solution and Its Parameter[*]

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It is well-known that ion-solvent interaction in aqueous solutions plays an important rôle in various properties and phenomena[1-4], such as the adsorption, surface tension, mobility, viscosity, diffusion, compressibility and activity coefficient, as well as the swelling, salting-out and other lyotropic phenomena. A concept of ionic hydration has been introduced as an important factor in attempting to explain these phenomena, and the amount or the intensity of hydration has been determined by various methods, such as measurements of the compressibility[5-8], the activity[9-11], the diffusion[12] and the dielectric constant[13,14]. All these quantities measure in some way the ion-solvent interaction or the hydration properties, but each of these different methods measures a different extent of ionic hydration. It is desirable, therefore, to establish a common and basic parameter concerning ionic hydration.

The dissolution of an electrolyte in water causes a volume contraction and a decrease in compressibility due to the interaction between the ions and water molecules. The magnitude of these changes can, therefore, be used as a measure of the hydration. We have already noticed[8,15,16] that the volume contraction is proportional to the amount of hydration water calculated from the compressibility data and that the proportionality constant is independent of the temperature and the nature of the electrolyte. For the explanation of this fact, we can refer to the studies of Webb[17] and Bernal and Fowler[18], who have calculated the mutual interaction between water molecules and ions. However, the lack of data necessary for calculation, especially the lack of knowledge about the hydrostatic pressure in the immediate vicinity of an ion in an aqueous solution, made a similar calculation impossible in the present case. Therefore, we adopted another method of calculation, one similar to

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Harned and Owen's19) and based upon the empirical equation of Tait, which gives the compressibility of water under pressure. Thus we obtained the quantity which may be proposed as a common parameter of hydration.

Tait's Equation and its Applicability to Water.—Tait's equation is applicable to many pure liquids in either of the form:

$$\beta_1^{(p)}V_1^{(p)}\equiv-(\partial V_1^{(p)}/\partial P)_T=0.4343C/(B+P) \tag{1}$$

or in its integrated form:

$$V_1^{(p_0)}-V_1^{(p)}=C\log\{(B+P)/(B+P_0)\} \tag{2}$$

where β_1 is the isothermal compressibility; V_1, the molar volume of water (solvent); P, the pressure; T, the absolute temperature, and B and C, constants dependent only upon the temperature and the nature of the liquid. The superscript (p) indicates the properties under the external pressure, P, and P_0 is the standard pressure, which may be taken as one bar.

According to Carl20) and Gibson21), Eq. 1 is applicable to water up to about $P=10000$ bar; the former author has also shown that the value of $0.4343C/V_1^{(p_0)}$ is independent of the temperature. The values of B, C and $0.4343C/V_1^{(p_0)}$ for water at temperatures ranging from 20 to 50°C, calculated from Bridgman's data22) by the present authors, are shown in Table I. The average value of $0.4343C/V_1^{(p_0)}$ is somewhat different from the value obtained by Carl (0.1243)20) and that obtained by Gibson (0.1368)23).

TABLE I. CONSTANTS OF TAIT'S EQUATION FOR WATER

Temp., °C	B, bar	C, ml./mol.	$0.4343C/V_1^{(p_0)}$
20	2897	2.394	0.1327
25	2978	2.430	0.1345
30	3039	2.459	0.1359
40	2998	2.405	0.1325
50	3019	2.430	0.1333
		Average	0.1338

The Molar Volume of the Solute in a Solution.—The molar volume of the solute was calculated by a method similar to that of Harned and Owen19). According to Tammann24), water in an electrolyte solution behaves like a substance under a constant effective pressure which is higher than the atmospheric one by P_e. This state is called electrostriction by Nernst25). The volume contraction and the decrease in the compressibility of a solution produced by the addition of an electrolyte to it are ascribed exclusively to the changes in the respective properties of the solvent water. The volume, $\varphi_1^{(p)}$, occupied by one mole of water in an electrolyte solution under an external pressure, P, is, therefore, the molar volume of pure water under the pressure $(P+P_e)$. Thus, from Eq. 2 we obtain:

$$V_1^{(p)}-\varphi_1^{(p)}=C\log\{(B+P+P_e)/(B+P)\} \tag{3}$$

A solution containing n_1 mol. of water and one mole of solute has the volume

$$V^{(p)}=n_1\varphi_1^{(p)}+\varphi_2^{(p)} \tag{4}$$

where $\varphi_2^{(p)}$ is the contribution to the volume of the solution made by one mole of solute in the state of solution.

From Eqs. 2, 3 and 4, we obtain

$$V^{(p)}=n_1V_1^{(p_0)}-n_1C\times\log\{(B+P+P_e)/(B+P_0)\}+\varphi_2^{(p)} \tag{5}$$

Putting $P=P_0$, we get

$$V^{(p_0)}=n_1V_1^{(p_0)}-n_1C\times\log\{(B+P_0+P_e)/(B+P_0)\}+\varphi_2^{(p_0)} \tag{6}$$

By the differentiation of Eq. 5 with respect to pressure at a constant temperature and composition, we obtain:

$$\beta^{(p)}V^{(p)}\equiv-(\partial V^{(p)}/\partial P)_T=0.4343Cn_1/(B+P+P_e)-(\partial\varphi_2^{(p)}/\partial P)_T \tag{7}$$

where β is the isothermal compressibility of the solution.

As the last term of Eq. 7 is negligible at moderate pressures and concentrations for an electrolyte solution21), we obtain from Eqs. 1 and 7:

$$(B+P_0+P_e)/(B+P_0)=n_1\beta_1^{(p_0)}V_1^{(p_0)}/\beta^{(p_0)}V^{(p_0)} \tag{8}$$

and from Eqs. 6 and 8:

$$\varphi_2^{(p_0)}=V^{(p_0)}-n_1V_1^{(p_0)}+n_1C\log(n_1\beta_1^{(p_0)}V_1^{(p_0)}/\beta^{(p_0)}V^{(p_0)}) \tag{9}$$

By Eq. 9 we can calculate $\varphi_2^{(p_0)}$ from the isothermal compressibilities and the densities of both solution and solvent water. The isothermal compressibility can be determined by the sound velocity measurement7).

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TABLE II. THE MOLAR VOLUME OF ELECTROLYTES IN THE STATE OF SOLUTION AND IN SUPER-COOLED LIQUID STATE

Electrolyte	$[\varphi_2^{(p_0)}]$ ml./mol.	V_2 ml./mol.	Temp. °C	Reference for sound velocity*
LiCl	27.7	24.21	25	C
$LiNO_3$	36.3	36.08	25	C
NaCl	31.2	29.99	20	F
	29.5	30.04	25	C
NaBr	34.9	35.35	20	F
NaI	42.7	43.83	20	F
NaOH	15.7	19.2	25	C
KCl	39.3	38.06	20	F
	38.0	38.12	25	C
KBr	43.3	44.21	20	F
KI	52.3	52.90	20	F
NH_4Cl	40.5	—	25	C
$MgCl_2$	44.9	50.57	20	T-S
	42.9	50.62	25	C
$CaCl_2$	46.2	47.0	20	T-S
$Ca(NO_3)_2$	61.4	—	25	C
$BaCl_2$	56.6	56.2	20	T-S
	55.6	56.2	30	T-S
	56.2	56.2	40	T-S
Na_2CO_3	41.2	46.15	20	T-S
	35.8	46.18	25	C
Na_2SO_4	56.8	57.16	20	T-S
K_2SO_4	70.1	70.89	25	C
$(NH_4)_2SO_4$	76.6	—	25	C
$CuSO_4$	29.5	—	25	C
$MgSO_4$	35.2	—	25	C

* C: Corey[26) F: Freyer[27)
T-S: Present authors

The values of $\varphi_2^{(p_0)}$ obtained were nearly independent of the concentration. The values at an infinite dilution are shown in Table II as $[\varphi_2^{(p_0)}]$. According to the view that the solute merely melts on going into a solution and occupies the same volume as that of the super-cooled liquid[21), the molar volume of a molten electrolyte at a high temperature was calculated and was extrapolated to the temperatures corresponding to those at which $[\varphi_2^{(p_0)}]$ was calculated. The values obtained are listed in the third column of Table II as V_2. The two values, obtained from independent methods, exhibit a satisfactory agreement except for a few cases which require further study. This result strongly supports the view that the solute in a solution behaves as a super-cooled liquid so far as its contribution to the volume of the solution is concerned. This means that the aqueous electolyte solution behaves ideally when we use as the molar volume of water the value under the pressure (P_0+P_e) instead of that under P_0.

Rosen[28) also calculated the molar volume of alkali halides in the solution state from the density of the solution on a principle similar to, but by using an equation of state different from ours. Thus he obtained the same result as did Scott[29), who actually calculated the value by the extrapolation of the apparent molar volume. Both of these authors have given values slightly smaller than ours.

The Parameter of Hydration

Before we discuss the common parameter of hydration, it is pertinent to list some useful quantities relating to the amount of hydration, which will itself be discussed in a later section.

Effective Pressure. — Following Tammann's principle[24) mentioned above, Eucken[30) has calculated the "Hydratationsdruck" the measure of the intensity of solute-solvent interaction for some electrolytes and non-electrolytes such as alcohol and sugar, by comparing the effects of pressure and solute on the specific volume of the solvent water. However, the effective pressure, P_e, or electrostriction, which can be calculated by Eq. 8, expresses more clearly the intensity of the ionic hydration. P_e is further correlated with the molar concentration of water (C_1) and solute (C_2) in a solution in a manner similar to van der Waals' cohesive pressure in gases as follows[31):

$$P_e = LC_1C_2 \qquad (10)$$

where L is a constant representing the electrostriction or clectrostatic attraction under unit concentration.

Volume Contraction. — A number of investigators have examined the volume change which takes place when a solute dissolves into a solvent[1,2,15,17). This is also one of the simplest quantities representing the intensity of hydration and is directly related to the effective pressure mentioned above. The present authors define the volume contraction of the system, ΔV, due to the dissolution of one mole of solute by

$$\Delta V \equiv n_1 V_1^{(p_0)} + \varphi_2^{(p_0)} - V^{(p_0)} \qquad (11)$$

From Eqs. 6 and 11, we obtain

$$\Delta V = n_1 C \log\{(B+P_0+P_e)/(B+P_0)\} \qquad (12)$$

Eq. 12 enables the calculation of ΔV from the value of P_e. Here the volume contraction is ascribed exclusively to the change in the volume of the solvent water.

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The Amount of Hydration Water.—An entirely different method has been adopted to give a parameter of hydration based on the incompressible hydration shell model[5-8].

If we assume, as is usual with inorganic ions, that the hydration shells, together with the central solute ions, are incompressible, the volume of water, V_h, bound to one mole of solute in solution, reduced to the atmosphere pressure of P_0, is given by

$$V_h = (n_1 \beta_1^{(p_0)} V_1^{(p\ )} - \beta^{(p_0)} V^{(p_0)}) / \beta_1^{(p_0)} = -K_2/\beta_1^{(p_0)} \tag{13}$$

where K_2 is the apparent molal compressibility of the solute. The value of V_h may be calculated from the compressibility and density data. We can also give the average hydration number of water molecules for a pair of solute ions by

$$h = V_h / V_1^{(p_0)} \tag{14}$$

The evaluation of V_h and h has been attempted by several authors[5-8,15,16].

The Correlation between L, ΔV and V_h, and the Parameter of Hydration

In order to discuss the correlation between the above three quantities, L, ΔV and V_h, the

TABLE III. VARIOUS PARAMETERS FOR HYDRATION OF ELECTROLYTE

Electrolyte	$[\Delta V]$ ml./mol.	$[V_h]$ ml./mol.	$[h]$	$[h^*]$	Temp. °C	Reference for sound velocity*
LiCl	10.3	77	4.24	4.38	25	C
$LiNO_3$	7.25	54	2.98	3.40	25	C
NaCl	14.3	107	5.96	6.41	20	F
	12.1	90	4.98	5.45	25	C
NaBr	11.5	87	4.82	5.46	20	F
NaI	8.06	61	3.37	4.03	20	F
NaOH	20.4	152	8.40	8.90	25	C
KCl	12.4	93	5.17	5.50	20	F
	10.8	80	4.44	4.80	25	C
KBr	9.51	72	3.97	4.39	20	F
KI	6.99	53	2.92	3.40	20	F
KCN	—	—	—	4.23	25	C
$KClO_3$	—	—	—	3.82	25	C
NH_4Cl	3.64	27	1.50	1.83	25	C
$NH_4(CH_3CO_2)$	—	—	—	2.20	25	C
$MgCl_2$	27.6	208	11.5	11.8	20	T-S
	25.2	187	10.4	10.8	25	C
$Mg(NO_3)_2$	20.4	151	8.38	9.32	25	C
$CaCl_2$	27.0	203	11.3	11.8	20	T-S
$Ca(NO_3)_2$	18.5	137	7.60	8.43	25	C
$NiCl_2$	—	—	—	11.5	25	C
$CoCl_2$	—	—	—	11.6	25	C
$Co(NO_3)_2$	—	—	—	9.91	25	C
$Co(CH_3CO_2)_2$	—	—	—	14.7	25	C
$BaCl_2$	30.2	227	12.6	13.3	20	T-S
	28.1	207	11.4	12.4	30	T-S
	26.7	201	11.1	11.7	40	T-S
$Ba(OH)_2$	—	—	—	18.4	25	C
$AlCl_3$	—	—	—	13.6	25	C
$Al(NO_3)_3$	—	—	—	14.4	25	C
Na_2CO_3	45.7	345	19.1	20.3	20	T-S
	38.2	284	15.7	16.9	25	C
Na_2SO_4	43.6	329	18.2	18.8	20	T-S
K_2CO_3	—	—	—	16.7	25	C
K_2SO_4	34.9	259	14.4	15.3	25	C
$K_2Cr_2O_7$	—	—	—	10.8	25	C
$(NH_4)_2SO_4$	22.7	169	9.34	9.90	25	C
$MgSO_4$	35.8	266	14.7	15.4	25	C
$CoSO_4$	—	—	—	15.5	25	C
$CuSO_4$	32.1	239	13.2	14.0	25	C

* Same as in the footnote of Table II.

density, $d^{(p_0)}$ and the isothermal compressibility, $\beta^{(p_0)}$, of a dilute solution at atmospheric pressure are expressed as follows:

$$d^{(p_0)}=d_1^{(p_0)}+aC_2 \quad \text{and} \quad \beta^{(p_0)}=\beta_1^{(p_0)}+bC_2$$

where a and b are constants characteristic of the electrolyte and where the higher terms of concentration are disregarded. Putting these relations into Eqs. 10, 12 and 13, and extrapolating C_2 to zero, we get the following relations:

$$[L]=(B+P_0)(V_1^{(p_0)}/1000)^2[h] \tag{15}$$

$$[\varDelta V]=0.4343C[h] \tag{16}$$

$$[V_\mathrm{h}]=-[K_2]/\beta_1^{(p_0)}=V_1^{(p_0)}[h] \tag{17}$$

where $[L]$, $[\varDelta V]$, $[V_\mathrm{h}]$, $[K_2]$ and $[h]$ denote L, $\varDelta V$, V_h, K_2 and h at an infinite dilution respectively, and

$$[h]=(1000d_1^{(p_0)}/M_1)(a/d_1^{(p_0)}-b/\beta_1^{(p_0)}) -M_2/M_1 \tag{18}$$

where M_1 and M_2 are the molecular weights of the solvent and of the solute respectively. It is noticeable that each of the three quantities contains a common factor $[h]$ multiplied by a different coefficient which depends only upon the nature of water. Therefore, they vary proportionally to each other and to $[h]$; namely, they change proportionally with the change in the nature of the solute provided that the solvent and temperature are kept unchanged. It is quite legitimate, therefore, to take the quantity $[h]$ as a common parameter of hydration. The quantities of $[\varDelta V]$, $[V_\mathrm{h}]$ and $[h]$ for several electrolytes are listed in Table III.

An important conclusion evidently follows from Eqs. 16 and 17; that is,

$$[\varDelta V]/[V_\mathrm{h}]=0.4343C/V_1^{(p_0)} \tag{19}$$

As is seen in Table I, the values of $0.4343C/V_1^{(p_0)}$ for water are independent of the temperature, their average being 0.1338. This, together with Eq. 19, explains the previously-mentioned facts[8,15,16] that the volume contraction due to the dissolution of the electrolyte is about 10% of the volume of hydration water for the same electrolyte and that this value does not change with the temperature or the nature of the solute. There, the volume of hydration water (called V_h^*) was calculated from the data of adiabatic compressibility instead of from those of isothermal compressibility in Eq. 13, and the volume contraction (called $\varDelta V^*$) was calculated by using V_2 instead of $\varphi_2^{(p_0)}$ in Eq. 11. Figure 1 shows the plots of $[\varDelta V^*]$ against $[V_\mathrm{h}]$, together with the theoretical straight line of Eq. 19. Agreement is satisfactory.

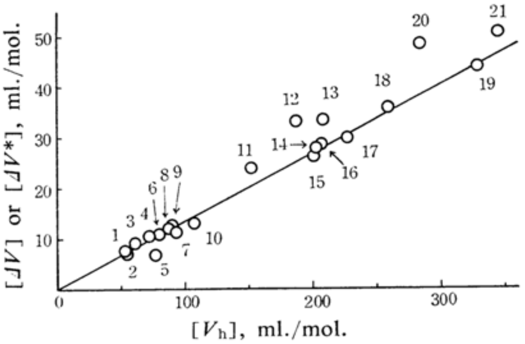

Fig. 1. Correlation between $[\varDelta V^*]$ and $[V_\mathrm{h}]$.

1	KI (20)	2	$LiNO_3$(25)
3	NaI (20)	4	KBr(20)
5	LiCl (25)	6	KCl(25)
7	KCl(20)	8	NaBr(20)
9	NaCl (25)	10	NaCl(20)
11	NaOH(25)	12	$MgCl_2$(25)
13	$MgCl_2$(20)	14	$CaCl_2$(20)
15	$BaCl_2$(40)	16	$BaCl_2$(30)
17	$BaCl_2$(20)	18	K_2SO_4(25)
19	Na_2SO_4(20)	20	Na_2CO_3(25)
21	Na_2CO_3(20)		

The numbers in bracket indicate temperature (°C) and solid line expresses Eq. 19.

It is further noticed in Table III that the value of $[h]$ decreases with the increase in temperature, as can be seen in the case of barium chloride. A similar temperature change was found for sodium chloride in the temperature range from 0 to 60°C[8]. The hydration reaction proves, therefore, to be exothermic in nature.

Stokes and Robinson[9] and Miller[11] modified the Debye-Hückel equation for the activity in a solution of strong electrolytes and expressed the effect of ion-solvent interaction by the term "hydration number". Though their numerical values agree as a whole with ours, their results are not staisfactory in that the hydration numbers increase with the increasing size of the anion and in that the law of the additive contribution of individual ions to the total hydration number does not hold.

Glueckauf[10] calculated hydration numbers with a model similar to that of Stokes and Robinson by means of volume fraction instead of mole fraction statistics; he found values about half as large as those of Stokes and Robinson. In his results, the anomalies of anions are less remarkable, and the additivity law holds fairly well. However, since his hydration numbers for anions are relatively small and since the variation among anions is not so distinct, it does not fully explain the difference in the contribution of each anion to the various phenomena involved in hydration. The superiority of the $[h]$ parameter in comparison with the hydration numbers cited above is shown by the fact that it varies significantly among ions and is directly proportional to such quantities as [L], [ΔV] and [V_h].

The values of [V_h^*] are somewhat greater than those of [V_h], and the ratio [V_h^*]/[V_h] is roughly constant, being 1.08±0.14 for the electrolytes listed in Table III. The former can, therefore, be used in place of the latter after due precautions. This is rather fortunate, since the accurate data necessary for the calculation of isothermal from adiabatic compressibility are often lacking. Conventional hydration numbers, [h^*], calculated from the value of [V_h^*] are also listed in the fifth column of Table III.

Summary

Tait's equation for water and Harned and Owen's treatment of an electrolyte solution, together with sound velocity data, enabled the calculation of the molar volume of electrolytes in the solution state. The results agreed fairly well with the molar volume of the super-cooled molten electrolyte extrapolated to room temperature.

The concentration coefficient of electrostrictive pressure, $L=P_e/C_1C_2$, the volume contraction due to the dissolution of one mole of solute, ΔV, and the volume of hydration water per mole of solute, V_h, as an incompressible part of water have been evaluated. We have found a common variable, [h], for L, ΔV and V_h, and it has been proposed that this variable can be used as a parameter of hydration expressing the mole number of hydration water per mole of electrolyte. A conventional hydration number, [h^*], was also proposed.

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