

A Study on the Hydration of Ion*

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石田美雄：イオンの水和の研究

Introduction

If the ultrasonic velocity V in the ionic solution is measured, its adiabatic compressibility β can be obtained from the formula $\beta = 1/dV^2$, where d is the density of the solution. It is known that β decreases linearly with the concentration of the solution in the range of low concentration. The reason is that incompressible hydration spheres are formed by the concrete attachment of water molecules to ion. By means of this fact, some researchers (1),(2) tried to draw inferences on the state of hydration in the ionic solution.

The dielectric constant of the ionic solution has a similar character, since it decreases linearly with the concentration, when referred to the data published by Hasted, Ritson and Collie (3). It is because hydration spheres formed by the attachment of water molecules to ion have the dielectric constant reduced to the optical value. Therefore, knowledges on the state of hydration can be deduced also by the measurement of the dielectric constant of the ionic solution.

The present author, however, has found that the volume of the hydration sphere determined by the compressibility measurement, which may be called *acoustic hydration sphere*, does not necessarily coincide with that by the dielectric measurement, that is, *dielectric hydration sphere*. From this fact, the author acquired the idea of the hydration sphere which has the double-shell structure around the ion and tried to calculate the hydration energy of ion based on this model.

The hydration energy of ion is defined as the change in free energy occurring when an ion at rest in vacuum is introduced into the water. We will look back at the trials of calculation based on some other models. Born derived electrostatically the formula for the hydration energy G_s , as:

$$G_s = \frac{\epsilon - 1}{2\epsilon} \frac{z^2 e^2}{a} ,$$

assuming that the single atomic ion of valence z is a charged conducting sphere of charge ze and radius a , and the surrounding water is a continuum whose dielectric constant is ϵ . This formula gives, however, values greater than those obtained from experiments. The reason will be that the formula would lose its applicability in the immediate neighborhood of the ion.

Then, Bernal and Fowler (4) admitted that the Born's formula would hold good outside the sphere of radius R_s , but inside the sphere they tried to derive a part of hydration energy by calculating the electrostatic mutual interaction between water molecules and an ion, assuming a special arrangement of water molecules around an ion and a certain charge distribution in the

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water molecules. Since the arrangement of water molecules they assumed is the closest polyhedral packing, the number of water molecules around an ion (so-called coordination number n) is determined only by the ionic radius. They adopted $n = 4$ for alkali metal ions and halogen ions, and $n = 6$ for alkali earth metal ions, and they gave a formula for the hydration energy as:

$$U_h = \frac{\epsilon - 1}{2\epsilon} \frac{z^2 e^2}{R_z} + n p_z P(r) - u_w \quad ,$$

where R_z is the radius of the virtual sphere depending only on z , $P(r)$ the potential energy of a water molecule due to a charge ze at distance $r + r_w$ (r and r_w being the radii of the ion and the water molecule respectively), p_z a correction factor to $P(r)$, which is considered to be nearly constant for the same value of z , and u_w the electrostatic energy of a water molecule in the pure water.

Eley and Evans (5) have published the formula which is essentially equal to B-F formula but better in the agreement with the experimental values. Latimer, Pitzer and Slansky (6), on the other hand, insist that the simple Born equation gives satisfactory results, if an adequate correction is put in regarding the ionic radius.

The present author has improved the B-F formula by use of the double-shell model for hydration of ion. The procedure will be reported here.

Consideration of the Acoustic Hydration

First, the method to derive the molal volume ϕ_β of acoustic hydration sphere is stated. Between the compressibility and the concentration of the ionic solution, the relation:

$$\beta = \beta_1 + AC + BC^{\frac{3}{2}} \quad (1)$$

holds (7), where β and β_1 are compressibilities of the solution and the pure water respectively, C the molal concentration of the solution, and A and B the constants peculiar to the ionic pair constituting the solute. If we write V [cc] for the volume of the solution containing one mole of solute, the molal concentration C of the solution can be represented by $C = 1000/V$. Further in V , if we write V_1 for the volume of the water which is not affected by ion, V_2 for the volume of the solute itself and V_h for the volume of the compressed water in the hydration sphere, we get:

$$\beta V = \beta_1 V_1 \quad , \quad (2)$$

$$V = V_1 + V_2 + V_h \quad (3)$$

$$\text{and} \quad \phi_\beta = V_2 + V_h \quad . \quad (4)$$

Especially the relation (2) comes from the assumption that $V_2 + V_h$ is incompressible. From the relations (1), (2), (3) and (4), the formula

$$\phi_\beta = -\frac{1000A}{\beta_1} - \frac{1000B}{\beta_1} C^{\frac{1}{2}} \quad (5)$$

can be derived. If we denote the value of ϕ_β at the infinite dilution by $\phi_{\beta 0}$, we get

$$\phi_{\beta 0} = -\frac{1000A}{\beta_1} \quad , \quad (6)$$

putting $C \rightarrow 0$ in the formula (5).

Next, the method to obtain the coordination number n_p for the ionic pair, that is, the number of water molecules contained in the hydration sphere of the solute is stated. The coordination number n_p is expressed by the relations:

$$n_p = \frac{V_h}{M_1/\rho_h} = \frac{V'_h}{M_1/\rho_1} \quad , \quad (7)$$

where M_1 is the molecular weight of the water, ρ_h and ρ_1 are densities of the compressed and the

ordinary water respectively, and V'_h the relaxational volume of hydration water, that is, the volume which the compressed hydration water would show under the ordinary pressure, released from the ionic attraction. In order to calculate n_p , it is easier to seek V'_h than V_h and ρ_h . From the relation between masses, we have:

$$\rho V = \rho_1 V_1 + \rho_h V_h + M_2 \quad (8)$$

where ρ is the density of the solution and M_2 the molecular weight of the solute. From the formula (1), the relations (7) and (8), the formula:

$$V'_h = \frac{1000}{C} \frac{\rho - \rho_1}{\rho_1} - \frac{M_2}{\rho_1} - \frac{1000A}{\beta_1} - \frac{1000B}{\beta_1} C^{\frac{1}{2}} \quad (9)$$

can be obtained. If we denote the relaxational volume of hydration water at infinite dilution with V'_{ho} , we get:

$$V'_{ho} = \frac{1000}{\rho_1} \lim_{C \rightarrow 0} \frac{\rho - \rho_1}{C} - \frac{M_2}{\rho_1} - \frac{1000A}{\beta_1} \quad (10)$$

putting $C \rightarrow 0$ in (9). Then, the coordination number n_p can be obtained by using V'_{ho} instead of V'_h in (7). Values of several quantities of the acoustic hydration for some ionic pairs are tabulated in the Table I.

Table I. Several Values of acoustic hydration.

solute	t°C	$A \times 10^{12}$ [C.G.S]	Φ_{β_0} [cc]	V'_{ho} [cc]	n_p	Experimenter
HCl	30	- 1,825	41,4	22,6	1,2	Present author (8)
LiCl	25	- 4,480	100,0	82,0	4,5	Szaláy (9)
NaCl	30	- 6,076	137,3	119	6,6	Yasunaga (2)
NaI	20	- 5,497	120,8	86	4,7	Freyer (10)
KCl	30	- 5,314	120,1	99	5,4	Yasunaga
K I	20	- 5,463	120,0	74	4,1	Freyer
MgCl ₂	30	-10,70	242,6	221	12	Present author
BaCl ₂	25	-12,62	282,3	255	14	Bachem (11)

Consideration of the Dielectric Hydration

Hasted *et al* measured the dielectric constant of the ionic solution at various concentrations by use of microwaves whose wavelengths are 10cm and 3cm. The results show that the dielectric constant decreases linearly with the concentration. They expressed this relation by the formula $\epsilon = \epsilon_w + 2\bar{\delta}C$ and discussed on the hydration depending upon $\bar{\delta}$. The present author treated the data by another expression. When there exist many spheres of dielectric constant ϵ_2 and of the same radius a in the medium of dielectric constant ϵ_1 , the dielectric constant of the synthetic medium is expressed by

$$\epsilon = \epsilon_1 + n \frac{4\pi a^3}{3} (\epsilon_2 - \epsilon_1) \frac{1 + 2\epsilon_1}{\epsilon_2 + 2\epsilon_1} \quad (11)$$

where n is the number of spheres per unit volume (12). As to the dielectric hydration sphere, its dielectric constant ϵ_2 is considered to be equal to the optical dielectric constant of the water, since the water molecules in such a sphere do not respond to the change of the electric field on account of the ionic attraction. If we express the molal volume of the sphere at infinite dilution as ϕ_0 and the molal concentration of the solution as C , we get $\phi_{e0} = \frac{4\pi a^3 N}{3}$, where N is the Loschmidt's

number and $C=1000n/N$. Therefore, the formula (11) can be reduced to:

$$\varepsilon = \varepsilon_1 - \frac{C}{1000} \phi_{\varepsilon 0} (\varepsilon_1 - u^2) \frac{1 + 2\varepsilon_1}{u^2 + 2\varepsilon_1}, \quad (12)$$

where u is the refractive index of the water. We treated the data of Hasted *et al* by using the expression (12) and got the values of $\phi_{\varepsilon 0}$ for some ionic pairs. They are put in the Table II, together with the values of $\phi_{\varepsilon 0}$ in the Table I for comparison. From the Table II we can say that:

Table II. Molal volumes of hydration sphere.

solute	t°C	$\Phi_{\varepsilon 0}$ [cc]	t°C	$\Phi_{\beta 0}$ [cc]	$\Phi_{\varepsilon 0} - \Phi_{\beta 0}$
HCl	25	258	30	41	217
LiCl	25	182	25	100	82
NaCl	21	134	30	137	- 3
KCl	25	130	30	120	10
MgCl ₂	25	393	25	243	150
BaCl ₂	25	363	25	282	81

- 1) $\phi_{\varepsilon 0}$ is approximately equal to $\phi_{\beta 0}$ for NaCl and KCl,
- 2) $\phi_{\varepsilon 0}$ is greater than $\phi_{\beta 0}$ for the others.

From the above facts, the author got the idea of the double-shell model for the hydration of ion. That is, in the first shell which is conceived referring to $\phi_{\beta 0}$, the water molecules respond to neither the change of the pressure nor the change of the electric field, while those in the second shell which is conceived referring to $(\phi_{\varepsilon 0} - \phi_{\beta 0})$ do respond to the change of the pressure but not of the electric field.

Construction of the Double-Shell Model

In order to develop the idea, it is necessary to seek the volume of the hydration sphere referring to an individual ion, instead of that referring to an ionic pair. Since NaCl and KCl are considered not to have the second shells, it is convenient to take them as standards. In order to divide their values of $\phi_{\beta 0}$ into the values concerning cation and anion respectively, they are usually divided according to the mobility of each ion. If we denote the volumes of hydration sphere concerning cation and anion by ϕ_+ and ϕ_- , we get by the Stokes' law:

$$\left. \begin{aligned} u_+ \sqrt[3]{\phi_+} &= u_- \sqrt[3]{\phi_-} \\ \phi_+ + \phi_- &= \phi_{\beta 0} \end{aligned} \right\} \quad (13)$$

where u_+ and u_- are the mobilities of respective ions. Because the mobility of each ion is proportional to its equivalent conductance which is given in some chemical tables, we can get the values of ϕ_+ and ϕ_- . Further, if we write V_{n+} and V_{n-} for the volumes of the compressed water in ϕ_+ and ϕ_- , we obtain:

$$\left. \begin{aligned} V_{n+} &= \phi_+ - N \frac{4}{3} \pi r_{x+}^3 \\ V_{n-} &= \phi_- - N \frac{4}{3} \pi r_{x-}^3 \end{aligned} \right\} \quad (14)$$

where r_{x+} and r_{x-} are the radii of cation and anion respectively, which have been given by Pauling. If the relaxational volumes corresponding to V_{n+} and V_{n-} are denoted by V'_{n+} and V'_{n-} respectively, the relations:

$$\left. \begin{aligned} V'_{n+} / V'_{n-} &= V_{n+} / V_{n-} \\ V'_{n+} + V'_{n-} &= V'_{n0} \end{aligned} \right\} \quad (15)$$

should hold. Since the values of the right-hand side of the relations (15) are already known, we can get the values of V'_{h+} and V'_{h-} . Dividing the values by the molal volume of water, we can calculate the number of water molecules attaching to cation and anion, that is, the coordination number n_1 for each ion of the first shell.

Now, we divide practically the values of $\phi_{\beta 0}$ for NaCl, NaI, KCl and KI given in the Table I by the relation (13) and get

$$\phi_{\text{Na}^+} = 97, \quad \phi_{\text{K}^+} = 63, \quad \phi_{\text{Cl}^-} = 40, \quad \text{and} \quad \phi_{\text{I}^-} = 44,$$

by averaging two values got for an ion. We calculate n_1 from these values by the relations (14) and (15) and get $n=3$ for K^+ , $n=4$ for Na^+ , $n=2$ for Cl^- and $n=1$ for I^- . The coordination numbers n_1 for the remaining cations can be got by subtracting 2, that is, n_1 of Cl^- from the value of n_p in the Table I. The coordination number n_2 of the second shell for cation can also be obtained through dividing $(\phi_{\varepsilon 0} - \phi_{\beta 0})$ by the molal volume of the water. The reason is that the value of $(\phi_{\varepsilon 0} - \phi_{\beta 0})$ for metallic chloride consists of only the contribution from the cation, since Cl^- has not the second shell. We have summarized n_1 and n_2 thus obtained in the Table III.

Table III. Coordination numbers of ion and effective radii of the shell.

ion	n_1	n_2	$R_{\text{eff}} [\text{\AA}]$
H^+	0	12	4.42
Li^+	3	5	3.86
Na^+	4	0	3.38
K^+	3	0	2.29
Mg^{2+}	8	8	4.99
Ba^{2+}	10	4	4.82
Cl^-	2	0	2.51

Further, R_{eff} 's in the table are the effective radii of the second shells, outside which the Born's formula holds. The value for cation coming from the metallic chloride can be calculated by:

$$N \frac{4}{3} \pi R_{\text{eff}}^3 = \phi_{\varepsilon 0} - \phi_{\text{cl}^-}, \quad (16)$$

where the value of ϕ_{cl^-} is 40 as given before.

Now, we will describe the geometrical picture of water molecules attaching to an ion on the basis of the data given in the Table III. Since the first shell is incompressible, the disposition of water molecules around an ion should be the closest polyhedral packing, that is, water molecules are situated at vertices of the regular polyhedron whose centre coincides with the centre of the ion. Therefore, five kinds of the packing are possible according to the types of regular polyhedron. We deduce polyhedrons the first shell of each ion may take, on the basis of n_1 of each ion, and

Table IV. Possible polyhedral packing of the first shell.

ion	n_1	polyhedron	n_s	$a [\text{\AA}]$	$r_x [\text{\AA}]$
Li^+	3	tetrahedron	4	0.311	0.60
Na^+	4	"	4	0.311	0.95
K^+	3	"	4	0.311	1.33
Mg^{2+}	8	hexahedron	8	1.01	0.65
Ba^{2+}	10	icosahedron	12	1.34	1.35
Cl^-	2	—	—	—	1.81

show them together with the fictitious saturated coordination number n_s in the Table IV. It can be said that the first shells of Na^+ and Mg^{2+} are saturated, those of Li^+ , K^+ and Ba^{2+} , however, lack one or two water molecules and that of Cl^- is greatly unsaturated. In the table, the value denoted by a has the following meaning. When water molecules which are assumed as spheres of radii r_w are arranged one by one on vertices of the regular polyhedron whose edge length is $2r_w$, the length a is the radius of the spherical void enclosed by such a group of water molecules. If we take $r_w = 1.38 \text{ \AA}$, we can calculate the values of a for respective regular polyhedrons. The value of ionic radius r_x is shown also in comparison with a in the table. In the case when $a < r_x$, an ion and molecules can contact, but water molecules cannot contact between themselves. On the contrary, in the case when $a > r_x$ —for Mg^{2+} only at present—water molecules can contact between themselves but an ion and water molecules cannot contact. Therefore, Mg^{2+} exists in the void, leaving some room.

Next, as to the way of attachment of a water molecule to an ion, some assumptions should be made concerning the charge distribution in the water molecule. The author has adopted the model presented by Bernal-Fowler and simplified it as follows. The water molecule is a sphere whose radius is 1.38 \AA , and an oxygen atom O is situated at the centre of the sphere. The distance ρ between oxygen atom O and hydrogen atom H is 0.96 \AA and the angle $\angle \text{HOH}$ is 105° . Further, there exist the effective charges $+e'$ on H and $-2e'$ on O. We should take e' as $\frac{1}{2}e$, in order to conform to the experimental value of dipole moment of water molecule. The ways of the attachment of water molecule to an ion are shown in Fig. 1.

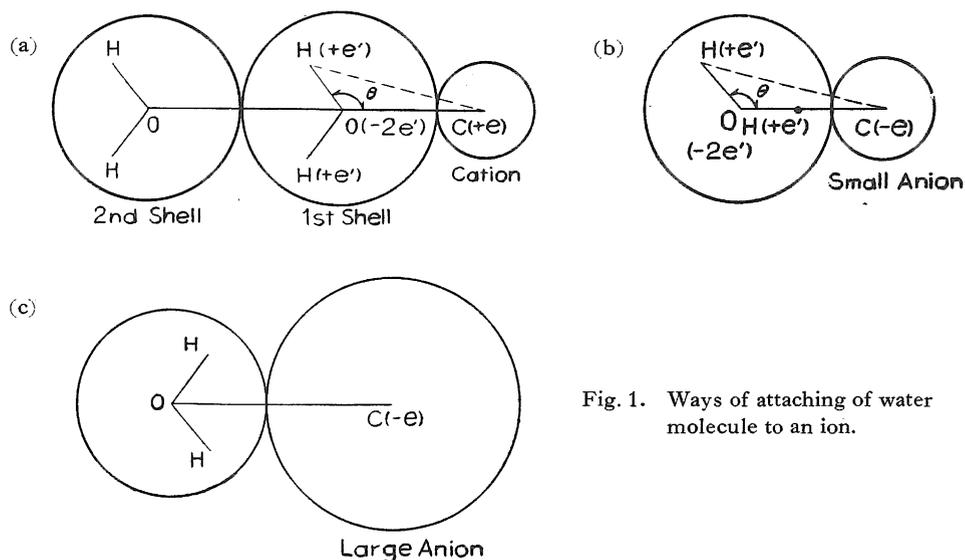


Fig. 1. Ways of attaching of water molecule to an ion.

Fig. 1 (a) shows the way of two water molecules in the first and the second shells attaching to a cation. Two types of attachment as shown in Fig. 1 (b) and (c) are considered about an anion. However, Cl^- possibly takes the type (b) on account of the fact that it is greatly unsaturated. Regarding the water molecule in the second shell, it is natural to consider the second-shell molecule being on a straight line connecting the first-shell molecule and the ion as shown in Fig. 1 (a). If it is true, the relation $n_2 \leq n_1$ should hold. It is possible to sketch the whole view in this way of thinking for the cases of Mg^{2+} and Ba^{2+} . However, in the case of Li^+ in which $n_2 > n_1$, it becomes

difficult to do so. Therefore, it might be better to think that the second-shell molecules are free within a special zone than that they are fixed at certain positions.

Calculation of the Hydration Energy of Ion

Now, the hydration energy of ion will be calculated here on the basis of the double-shell model. The Born's formula holds outside the sphere of radius R_{eff} , but a special consideration should be given to the inside of the sphere. Then, regarding the whole hydration energy U_h , the author has given the formula:

$$U_h = \frac{\epsilon_1 - 1}{2\epsilon_1} \frac{z^2 e^2}{R_{eff}} + n_1 P_1 + n_2 P_2 - (n_1 + n_2) u_w, \quad (17)$$

instead of the B-F formula. In the expression, the first term means the Born's formula, P_1 is the mutual potential energy between a water molecule in the first shell and an ion, P_2 that between a water molecule in the second shell and an ion, and u_w the energy which a water molecule should have in the pure water. Since the water at room temperature has a quasi-crystalline structure by hydrogen-bond, u_w is, in another meaning, the energy liberated by break of hydrogen-bond when a water molecule enters the shell.

We assume that the forces acting between an ion and a water molecule are the Coulomb's force and the quantum mechanical repulsive force, neglecting the force between the water molecules in the shell. From Fig. 1 (a), we get the expression for P_1 concerning a univalent cation as:

$$P_1 = \frac{2e'e}{R} - \frac{2e'e}{\sqrt{R^2 + \rho^2 + 2R\rho \cos \theta}} - \frac{b}{R^n}, \quad (18)$$

where $R = r_w + r_x$, ρ is the O-H distance. The first and second terms are Coulomb's potentials, and the last term is the quantum mechanical repulsive potential with b a constant for each ion. We take 9 for the value of n from the analogy to the ionic crystal. Since the potential energy of the system becomes minimum at the position of the figure, we can get the value of b from the expression $\frac{\partial P_1}{\partial R} = 0$ and calculate the value of P_1 . From Fig. 1 (b), we get the expression for P_1 concerning a univalent anion as:

$$P_1 = \frac{ee'}{R - \rho} + \frac{ee'}{\sqrt{R^2 + \rho^2 + 2R\rho \cos \theta}} - \frac{2ee'}{R} - \frac{b}{R^n}. \quad (19)$$

For the case of divalent cation— Ba^{2+} at present—, the value of P_2 can be calculated by the expression (18), taking the radius of ion to be $r_x + 2r_w$. For the case of Mg^{2+} , where the relation $a > r_x$ holds as stated before, the calculation should be performed by use of the expression (18), assuming the radius of ion to be $a + 2r_w$. A question arises in the case of the second shell of Li^+ . Though it is not considered that all of the water molecules of the second shell of Li^+ have the positions as shown in Fig. 1 (a), the calculation has been done, assuming it for convenience' sake.

The evaluation of u_w will be considered lastly. It has been clarified by the X-ray study that a water molecule has four nearest neighbors forming the tetrahedral connection as shown in Fig. 2 by the hydrogen-bond whose energy is measured as 4.5 [kcal/mol]. Thus a water molecule should have its share of bond energy as large as 9.0 [kcal/mol], as it is true in the case when the tetrahedral connections continue infinitely, as in the ice. It is known from the data on the ultrasonic absorption (13) that the water at the room temperature consists of groups of 8000 water molecules. Now it comes into question, how many molecules of 8000 water molecules are unsaturated, not having four nearest neighbors.

Fig. 2 shows a group of 17 molecules which are picked up far to the second nearest neighbors centring the molecule denoted by C. The number of unsaturated molecules in this case is 12, making the ratio to the whole 0.705. Since the ratio is equal to that of the surface area to the volume, when the group of molecules are assumed to form a sphere, it decreases inversely proportionally to the radius of the sphere. The radius of the small group shown in Fig. 2 has been given as 4.51 Å by the X-ray study of the water (14). On the other hand, the radius of the group of 8000 molecules can be calculated as 3.95×10^{-7} cm from the density of ice, 0.92 [g/cm³]. Therefore, the ratio of the latter group is evaluated as 0.081. Since it can be said that 91.9% molecules in the group have each their four nearest neighbors, the value of u_w can be evaluated as 8.3 [kcal/mol]. At last, we reached the stage to calculate the hydration energy of ion by the formula (17) and the calculated values are summarized in the Table V together with related values.

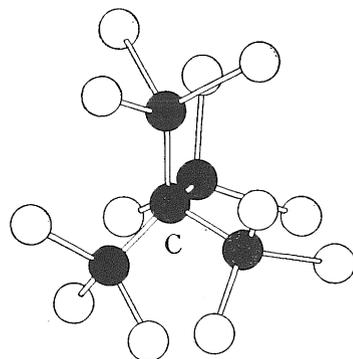


Fig. 2. A group of water molecules.

Table V. Calculated hydration energies of ion [kcal/g-ion].

ion	Born's term	P_1	P_2	U_h
H ⁺	37.1	0	—	—
Li ⁺	42.5	33.8	10.2	128.5
Na ⁺	48.5	26.6	0	121
K ⁺	56.2	19.3	0	81.1
Mg ²⁺	131	47.5	9.65	455
Ba ²⁺	136	37.0	9.79	429
Cl ⁻	65.3	9.36	0	67.4

Comparison with Experiments

The values of the hydration energy calculated above will be compared with experimental values. Between the lattice energy of the ionic crystal $[MX_\nu]$ and the hydration energy of ion, there exists the relation:

$$U_h(M^+) + \nu U_h(X^-) = W + L \quad , \quad (20)$$

where $U_h(M^+)$ and $U_h(X^-)$ are the hydration energies related to cation and anion produced when the ionic crystal $[MX_\nu]$ is dissolved into the water, W is the lattice energy of the crystal and L the integral heat of solution of the crystal. The lattice energy W can be calculated by the relation:

$$W = Q + S_M + I_M + \nu/2 \cdot D_{x_2} - \nu E_x \quad , \quad (21)$$

which was got from the Born-Harber's cycle. In the expression, Q is the heat of formation, S_M the heat of sublimation, I_M the heat of ionization, E_x the electron affinity and D_{x_2} the heat of dissociation. Since the values of the terms in the right-hand side of the relation (21) are all given by experiments, we can get the experimental value of the lattice energy. In the Table VI, the value of left-hand side of (20) obtained by the calculation is compared with the value of right-hand side obtained by the experiments.

Table VI. Comparison of hydration energy with the lattice energy.

solute	$U_h(M^+) + \nu U_h(X^-)$	W	L	$W + L$
LiCl	196	203.6	- 8.6	195.0
NaCl	188	183.1	+ 1.0	184.1
KCl	148.5	165.5	+ 4.2	169.7
MgCl ₂	590	623.5	-36.3	587.2
BaCl ₂	564	523.5	-2.6	520.9

There is another comparison with the experiments. Benjamin and Gold 15) published a table of heats, entropies and Gibbs free energies of hydration at 25° C of simple ions, relative to hydrogen ion, which was compiled from the recent thermodynamic data. Randles 16) also, has measured the outer or Volta potential differences between the mercury and the aqueous solutions. From the results the real hydration energies of alkali metal ions and halide ions have been calculated. In the Table VII, the calculated values of the present author and Bernal-Fowler were compared with their values. In the column of Benjamin-Gold in the table, the absolute values of Gibbs free energy of hydration are given, taking the value of hydrogen ion as 260 [kcal/g-ion].

Table VII. Hydration energies of ion [kcal/g-ion] by several researchers.

ion	present author	Benjamin-Gold	Randles	Bernal-Fowler
Li ⁺	128.5	121.6	122.1	131
Na ⁺	121	97.7	98.2	114
K ⁺	81.1	80.1	80.6	94
Mg ²⁺	455	454.5	—	495
Ba ²⁺	429	—	—	350
Cl ⁻	67.4	74.0	70.7	67

Discussion

The present theory may be divided into two parts, one is the method to determine the coordination number and the other the method to calculate the hydration energy.

In the first place, concerning the coordination number, the present theory is featured by the double-shell model. Bockris (17) has shown in his review article of ionic hydration that there is large discrepancy between the results of various experimental methods, illustrating the data on sodium ion, and suggested that different experimental methods give measures of different types of hydration. As the methods are roughly divisible into two classes, one giving lower values of coordination number (<10) and the other giving higher values (>10) for sodium ion, it is probable, he said, that the former give a measure of primary hydration and the latter a measure of total hydration which is the sum of the primary and the secondary hydrations. The way of thinking in the present theory is very similar to his. The *secondary hydration*, however, which corresponds to anomalously high value of coordination number (>10) for sodium ion is quite different from our *second shell* which vanishes for sodium ion. Both the acoustic hydration and the dielectric hydration in this paper are in the category of the primary hydration. It may be said that the author made clear the fine structure of the primary hydration.

Secondly, regarding the formula to determine the hydration energy, the present theory has advantages over the B-F theory with respect to the following points.

1) *Limit of application of Born's term*

The radius R_z in the B-F theory was determined as to agree with the experimental value and has not a physical origin. Moreover, since R_z has the same value referring to ions of the same z , the individuality of ion is neglected. On the other hand, $R_{z,j}$ in the present theory has a clear derivation and shows the individuality of ion of the same z .

2) *Interaction between ion and water molecule*

In the B-F theory, $P(r)$ has been got considering only the Coulomb's force and the influence of other forces was included in the correction factor p_z which was so determined as to conform to the experimental value. In the present theory, P_1 and P_2 were calculated considering both the Coulomb's force and the quantum mechanical repulsive force. Of course, the latter force which appears in the theory of ionic crystal is the force acting between ions. Therefore, it is assumed in the present theory that the force of the same type acts also between an ion and a water molecule.

3) *Evaluation of u_w*

In the B-F theory, u_w was calculated as the Coulomb's potential between two water molecules which are tetrahedrally connected and given as 31.0 [kcal/g-ion], whose value differs considerably from the one got in the present theory. The reason will be that the concept of hydrogen-bond was not yet established and there were no experimental values of it in the year of 1933.

In conclusion, since the radius of hydrogen ion is not given, the hydration energy of H^+ cannot be calculated by the present theory or by the B-F theory. We can say, however, according to the present theory, that 12 water molecules around a hydrogen ion form a shell whose radius is 4.42 Å. And the shell responds to the change of pressure but not of the electric field. It is said in chemistry that H^+ in water makes an ion $(H_3O)^+$, combining with a water molecule. It does not necessarily mean that H^+ combines eternally with a specified water molecule. It is probable to consider that H^+ can be combined with any one of 12 water molecules for a short time and the shell presents some amount of cohesion energy as a result. It will be a future problem to derive a formula for cohesion energy on the basis of such thought.

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