The Studies on the Hydration Energy and Water Structures in Dilute Aqueous Solution

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Thermodynamic properties of dilute aqueous solutions are influenced by the interactions between ions and water molecules as well as the change of the water structure around the ion. To obtain hydration energies of monoatomic ions and local water structures around the ions, we make use of the discrete-continuum method. The calculated values for the hydration energies of ions are in good agreement with experimental values. The hydration energies of monoatomic cations can be qualitatively correlated with the sum of the successive ionization potentials from its atomic state to the ionic state. From their correlations, we can classify various ions as three groups. It is also found that the main factors which determine the stability of water structures around the ions are the charges and dimensions of ions.

The properties of aqueous electrolyte solution in chemical processes are strongly influenced by ions and their surrounding water molecules.[1–3)] In particular, we would like to chemically classify various ions into three groups by correlating the hydration energies of ions with the sum of successive ionization potentials from its atomic state to ionic state[4)] and into two groups by comparing the intermolecular interaction energies among water molecules in aqueous solution with those in pure water.[5–7)]

Recent progresses in the ab initio quantum mechanical method,[8–11)] statistical thermodynamics,[12,13)] and the simulation using computer technology[14–17)] have given the remarkable information for local water structures around ions.

In order to understand the local water structures around ions, we have calculated hydration energies of ions using the empirical potential function.[18–22)] Earlier theoretical approaches calculating thermodynamic properties of aqueous solution can be divided into the discrete[23–25)] and continuum methods.[10,14,15)] Since it is possible to make accurate studies of solvation effects using relatively small clusters[16)] and it takes much computing time to include all water molecules in calculation, we make use of the discrete-continuum method.[13,18)] In this method, the water molecules interacting strongly with an ion are discretely treated, while the remaining water molecules are considered as a polarizable dielectric continuum.

Especially, if the interaction energies of water molecules oriented by the electric field of an ion are compared with those of pure water molecules, the enhancement of the water structure around the ion can be quantitatively known. The foci of our studies are to understand the experimental observation on aqueous ionic solution according to the characteristics of ions.

Model System. I) Hydration Scheme: According to the idea presented by Frank and Wen,[5)] the environment of a dissolved ion is divided into three regions. As shown in Fig. 1, the ion is discretely surrounded by several water molecules within the first hydration shell, the second hydration shell water and bulk water are treated as the dielectric continuum. Dielectric saturation is assumed to occur in the secondary hydration shell water, but the dielectric constant of bulk water is equal to that of pure water.

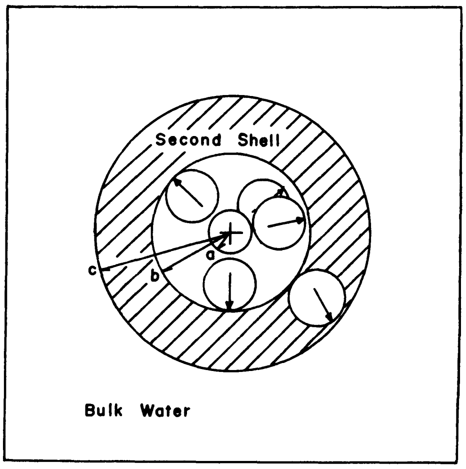


Fig. 1. Schematic diagram to indicate that an ion is enveloped by the first hydration shell (b), the second hydration shell (c), and the bulk water which is equivalent to pure water.

One of the arrangements of water molecules in the first hydration shell can be assumed to be either one of the tetrahedral, trigonal bipyramidal, and octahedral structure, which have been shown by ab initio calculations.[10)] As the water molecules are discretely added outside the first hydration shell according to the hydration number, geometrical features could be recognized by the results of Monte Carlo simulations[17)] for aqueous solutions of alkali metal and halide ions.

The hydration schemes of water molecules in the first hydration shell around the ion are determined by the given hydration number and can be defined by the variables θ_w and Φ_w which are shown in Fig. 2.

II) Water Molecule. The water molecule is taken to be isotropic polarizable sphere which ignores the detailed charge distribution and has the permanent off-centered dipole.[20)] Multipoles higher than the di-

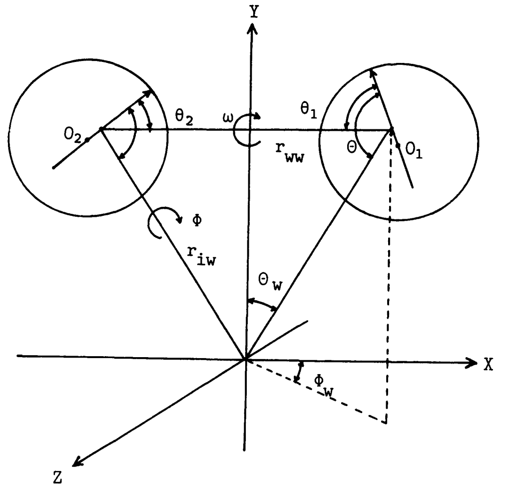
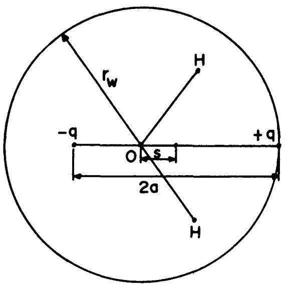


Fig. 2. Geometric features for the water dipole around the point charge. The distance between O_1 and O_2 is equal to the distance between oxygens of water molecules.



$r_w = 1.45$ Å

$2a = 2.00$ Å

$S = 0.45$ Å

Fig. 3. Permanent electrostatic distribution in water from gas phase calibration data (since $\mu=1.85\times10^{-18}$ esu cm, $q=\mu/2a=0.1926e$).

pole are not considered in this work, because its inclusion for potential functions is arbitrary and the use of multipoles would not alter the final results significantly. The model of water molecule[20] is described by estimating three parameters, namely the length of the off-centered dipole (2a), the amount by which the dipole is off-centered(s) and the van der Waals radius of water molecule (r_w).

The water model and the values of the parameters used in this work are shown in Fig. 3. The parameters are empirically obtained by fitting the oxygen–oxygen distance and the energy of water dimer.[26–28] The computed results are -21.25 kJ mol^{-1} and 2.77 Å for the dimerization energy and oxygen–oxygen distance, respectively.

The value of the permanent dipole moment of water molecule is used as 1.85D ($1\text{D} = 3.325\times10^{-30}$ Cm) which is experimentally determined.[29]

For the polarizability of water, there are important contributions to the static polarizability, α_w, from intra- and intermolecular motions. It should be noted that we have used the value of α_w which includes the electronic polarizability of water ($=1.44\times10^{-24}$ cm^3) as well as the small increment of 0.16×10^{-24} cm^3 according to the effect of intramolecular motions.[26,30]

III) Ion. The ions in solution are taken to be charged conducting spheres. The choice of X-ray crystallographic radii for ions brings out a good approximation to the respective radii of the bare ions in solution.[21] Since ion–solvent interaction energies in a strong polar solvent are similar to those between cations and anions in crystals, it is reasonable that the ion in the solution may be compressed to its crystallographic radius.[31] We have used the effective ionic radii which are measured according to the coordination number of ion.[32] The coordination number of ion corresponds to the number of water molecules in the first hydration shell of ion. The hydration numbers in our work are taken from the X-ray diffraction data on structures of metal complexes in solution.[33] The hydration numbers of ions not included in Ref.33 are decided by fitting the hydration energies of ion.

Potential Function.[34–36] The energies of the dipole-dipole interaction, E_{dd}, and the dipole-induced dipole interaction, E_{did}, will be calculated by using Eqs. 1 and 2.

$$E_{dd} = -\frac{\mu^2}{Dr_{ww}^3}(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\omega), \tag{1}$$

$$E_{did} = -\frac{1}{2}\frac{\mu^2\alpha_w}{Dr_{ww}^6}(3\cos^2\theta_1 + 1). \tag{2}$$

Geometrical parameters for the dipole–dipole interaction are shown in Fig. 2, D is the dielectric constant, α_w is the polarizability, and μ is the permanent dipole moment of water molecule. The energies of the ion-dipole interaction, E_{id}, and the ion-induced dipole interaction, E_{iid} will be calculated by using Eqs. 3 and 4.

$$E_{id} = -\frac{q\mu}{Dr_{iw}^2}\cos\theta, \tag{3}$$

$$E_{iid} = -\frac{q^2\alpha_w}{2Dr_{iw}^4}, \tag{4}$$

where q is the ionic charge, r_{iw} is the distance between the ion and the dipole.

The dielectric constant is represented by Eq. 5.[34]

$$D = \left(\frac{\varepsilon_0-\varepsilon_1}{c-a}\right)r_{iw} + \varepsilon_1 - \left(\frac{\varepsilon_0-\varepsilon_1}{c-a}\right)a, \tag{5}$$

where D means the dielectric constant at the distance separated from the ion, ε_1 and ε_0 denote the dielectric constant at the surface of ion, and that of bulk water, respectively. a and c are the radius of ion and the distance from a point charge to bulk water, respectively.

The nonbonded interaction energies, E_{nb}, between

Table 1. The Radii, the Sum of True Ionization Potentials, and Polarizabilities for the Water Molecule and the Ions

Specie	R/Å[a)]	$\sum I$/eV[b)]	α/Å^3[c)]	Specie	R/Å[a)]	$\sum I$/eV[b)]	α/Å^3[c)]
H_2O	1.45	12.59	1.60	Zn^{2+}	0.88	67.08	0.94
Li^+	0.93	80.93	0.03	Mn^{2+}	0.97	46.38	1.30
Na^+	1.17	52.42	0.21	Fe^{2+}	0.92	54.70	1.00
K^+	1.49	35.97	0.87	Co^{2+}	0.89	58.41	1.10
Rb^+	1.64	31.47	1.98	Ni^{2+}	0.83	60.97	1.00
Cs^+	1.83	27.01	3.34	Cu^{2+}	0.87	64.86	1.00
Be^{2+}	0.59	181.43	0.01	Ag^+	1.29	29.07	2.25
Mg^{2+}	0.86	102.82	0.12	Tl^+	1.64	26.53	4.30
Ca^{2+}	1.14	68.89	0.90	Hg^{2+}	1.16	63.39	5.20
Sr^{2+}	1.32	60.35	1.42	Pb^{2+}	1.33	44.02	4.20
Ba^{2+}	1.49	50.72	2.40	Al^{3+}	0.68	173.25	0.07
F^-	1.19	3.34	0.95	Sc^{3+}	0.89	117.57	1.10
Cl^-	1.67	3.62	3.48	Y^{3+}	1.04	100.91	1.50
Br^-	1.82	3.37	4.82	La^{3+}	1.18	85.77	2.40
I^-	2.06	3.06	7.22	Fe^{3+}	0.79	109.52	2.20

a) From Ref. 32. b) From Ref. 41. c) From Ref. 39.

ion and water and between water molecules are calculated by using the familiar Lennard-Jones 6-12 potential and are given by Eq. 6.

$$E_{\mathrm{nb}} = -K_6(i,j)/Z_{ij}^6(1-0.5/Z_{ij}^6) \tag{6}$$

where $k_6(i,j)=C(i,j)/r_{ij}^{0\,6}$ and $Z_{ij}=r_{ij}/r_{ij}{}^0$, r_{ij}^0 is the sum of the van der Waals radii of the interacting molecules and $\dot{C}(i,j)$ is calculated by using London-Margenau formulas.[38)]

The values of effective ionization potential used in the nonbonded energy term could be obtained by multiplying the true ionization potential by a suitable coefficient.[40)] In this work, we obtained new coefficients in the process of fitting the dimerization energy of water molecule and the heat of hydration of all ions. The correction coefficients which would be used in this calculation are 4.5 for the water molecule and 3.0 for all ions.

The radii, true ionization potentials, and polarizabilities for the water molecule and all ions are summarized in Table 1.

The polarization energy for the continuous medium outside the first hydration shell is given by Eq. 7[12,24,25)]

$$E_{\mathrm{pol}} = \frac{1}{2}\left\{\left(\frac{1-\varepsilon_b'}{\varepsilon_b'}\right)\frac{q^2}{b}+\left(\frac{1-\varepsilon_0}{\varepsilon_0}\right)\frac{q^2}{c}\right\}, \tag{7}$$

where

$$\varepsilon_{\mathrm{b}}' = \varepsilon_{\mathrm{b}}\left(\frac{(1-\varepsilon_{\mathrm{b}})(1-\varepsilon_c)}{\varepsilon_c}\frac{b}{c}+1\right)^{-1}$$

and

$$\varepsilon_b = \varepsilon_m/\varepsilon_1$$
$$\varepsilon_c = \varepsilon_0/\varepsilon_m.$$

The first hydration shell of radius b is surrounded by a water layer of thickness $(c-b)$, which is immersed in the bulk water of dielectric constant ε_0. The relative permittivity ε_m between $\varepsilon_1=1$ and $\varepsilon_0=78.5$ is calculated by using Eq. 5. The thickness of the secondary layer $(c-b)$ was taken as the diameter of water molecule.

Hydration Energy Analysis.[14,20)] The energy for the process of transferring an ion from vacuum into a position inside the liquid water, ΔE_{hyd}, can be obtained from the energies of intermolecular interaction in pure water and dilute aqueous solution. The thermodynamic cycle of this process is shown in Fig. 4.[20)] The total energy of solution is composed of the ion-water interaction, E_{iw}, the water-water interaction in aqueous solution, E_{ww}, and that of the pure water, E_{ww}°. The energy of hydration is given by[14,42)]

$$\Delta E_{\mathrm{hyd}} = E_{\mathrm{iw}} + E_{\mathrm{ww}} - E_{\mathrm{ww}}^{\circ}. \tag{8}$$

The ion-water interaction energy, E_{iw}, can be divided into the contributions exclusively arising from the first shell water molecules, E_{fw}, and from the polarization of the water molecules outside the first hydration shell, E_{pol}.

$$E_{\mathrm{iw}} = E_{\mathrm{fw}} + E_{\mathrm{pol}}. \tag{9}$$

Also, the water-water interaction can be considered as being composed of three components representing the first hydration shell-first hydration shell interaction, E_{ff}, the first hydration shell-remaining water interaction, E_{fr}, and the remaining water-remaining water interaction, E_{rr}.

$$E_{\mathrm{ww}} = E_{\mathrm{ff}} + E_{\mathrm{fr}} + E_{\mathrm{rr}}. \tag{10}$$

As the reference system, the pure water was also considered as a dilute solution containing a water solute.[14,15,42)] Since the average number of hydrogen bonds per a water molecule in pure water is about 4,[44)] we considered that the water solute is surrounded with four water molecules in a tetrahedral configuration and this water cluster may be successively surrounded by the other water molecules.

The total intermolecular interaction energy in pure water is expressed as

$$E^{\circ}_{\mathrm{ww}} = E^{\circ}_{\mathrm{fw}} + E^{\circ}_{\mathrm{ff}} + E^{\circ}_{\mathrm{fr}} + E^{\circ}_{\mathrm{rr}}, \qquad (11)$$

where E°_{fw} is the interaction energy for the water solute-surrounding water molecules, E°_{ff} for the first hydration shell-first hydration shell, E°_{fr} for the first hydration shell-remaining water, and E°_{rr} for the remaining water-remaining water.

E°_{fw} is the sum of the energies of separating $n+1$ water molecules from pure water to make a room for the ion of which the hydration number is n. This value is equal to the dissociation energy in the gas phase.

$$E^{\circ}_{\mathrm{fw}} = nE^{\circ}_{\mathrm{l}}, \qquad (12)$$

where $E_{\mathrm{l}}{}^{\circ}$ is the average hydrogen bond energy which is calculated from the water cluster with the ice-like structure. The calculated value of $E_{\mathrm{l}}{}^{\circ}$ in this work is -18.24 kJ mol^{-1}.

E°_{ff} is the sum of the interaction energies between the first hydration water molecules around the water solute, which is the same as the sum of the interaction energies between the secondary neighbor water molecules in the water cluster. The interaction energy between the secondary neighbor water molecules in pure water is -1.84 kJ mol^{-1}.

E°_{fr} is the interaction energy between the water molecules in the first hydration shell and the remaining water, which is the energy forming a cavity in the supermolecule-approach.[20] E°_{fr} in Eq. 11 arises from some changes of the water structure at the second hydration shell in transferring the solvated ion into the cavity inside the bulk water. Since the nature and extent of the second hydration shell is not well understood at this time, it is very difficult to calculate the energies of E°_{fr} and E_{fr} quantitatively. If E°_{fr} in pure water is compared with E_{fr} in the ionic solution, the difference of these energies is qualitatively estimated to be about 41.84 kJ mol^{-1}.[13,20] Therefore, we can assume that the water structure in the second hydration shell is not variant in transferring of ion from vacuum into pure water.

Finally, one water molecule in vacuum has to be returned to the aqueous solution to complete the cycle by checking the thermodynamic cycle in Fig. 4. The exchange of energy involved in this process is equal to the work of condensation, ΔH_{con}. This value can be taken from the latent heat of condensation to be about 44.76 kJ mol^{-1}.[20] Thus, the total hydration energy, ΔE_{hyd}, is represented as

$$\begin{aligned}\Delta E_{\mathrm{hyd}} &= E_{\mathrm{fw}} + E_{\mathrm{pol}} - E^{\circ}_{\mathrm{fw}} + E_{\mathrm{ff}} - E^{\circ}_{\mathrm{ff}} + \Delta H_{\mathrm{con}} \\ &= E_{\mathrm{fw}} + E_{\mathrm{pol}} - E^{\circ}_{\mathrm{fw}} + \Delta E_{\mathrm{ww}} + \Delta H_{\mathrm{con}}, \qquad (13)\end{aligned}$$

where

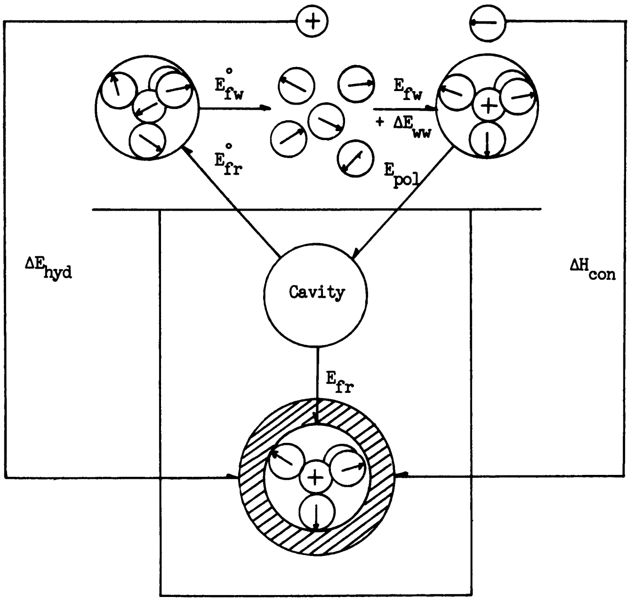


Fig. 4. The total hydration energy of ion (ΔE_{hyd}) separated into the various steps.

$$\Delta E_{\mathrm{ww}} = E_{\mathrm{ff}} - E^{\circ}_{\mathrm{ff}}. \qquad (14)$$

ΔE_{ww} is the energy which indicates the change of local water structures around the ion. Therefore, the phenomena of structure making and breaking of ions can be explained by the quantity of these values.

Free Energy Analysis.[3] The free energy of hydration of an ion at constant volume and pressure is given by

$$\Delta F_{\mathrm{hyd}} \simeq \Delta E_{\mathrm{hyd}} + T\Delta S_{\mathrm{hyd}}. \qquad (15)$$

The entropy of hydration for the ion is given by

$$\Delta S_{\mathrm{hyd}} = \Delta S_{\mathrm{f}} + S_{\mathrm{pol}}, \qquad (16)$$

where ΔS_{f} is the contribution from the water molecules in the first hydration shell and estimated by Frank and Evans.[45,46] The second term is the contribution from the water molecules outside the first hydration shell and is given by[12,25]

$$S_{\mathrm{pol}} = -\frac{q^2}{2}\left\{\frac{(b-c)}{bc}\frac{1}{\varepsilon_{\mathrm{m}}^2}\left(\frac{\partial\varepsilon_{\mathrm{m}}}{\partial T}\right)_p - \frac{1}{c}\frac{1}{\varepsilon_0^2}\left(\frac{\partial\varepsilon_0}{\partial T}\right)_p\right\}, \qquad (17)$$

where q is the ionic charge, $(\partial\varepsilon_{\mathrm{m}}/\partial T)_p$ is the temperature variation of the local relative permittivity and $(\partial\varepsilon_{\mathrm{o}}/\partial T)_p$ is that of the bulk dielectric constant. Of the parameters, the values of $(\partial\varepsilon_{\mathrm{m}}/\partial T)_p$ and $(\partial\varepsilon_{\mathrm{o}}/\partial T)_p$ for water are $-0.00160\ \mathrm{K}^{-1}$ and $-0.3595\ \mathrm{K}^{-1}$, respectively.[25]

Results and Discussion

The hydration energies of ions are obtained by one by one optimizing r_{iw}, θ, and ϕ which indicate the position of water molecules around the ion. The calcu-

Table 2. The Hydration Energies and the Free Energies of Ions[a)]

Ion	n	$R_{i\text{-}o}$[b)]	$-E_{iw}$	$-E_{pol}$	$-\Delta E_{ww}$	$-\Delta E_{hyd}$	$-\Delta F_{hyd}$	$-\Delta H_{exp}$[c)]
Li^+	4	1.80	514.2	132.6	27.2	623.8	584.1	558.6
Na^+	4	2.21	351.9	123.0	3.3	427.6	397.1	443.9
K^+	5	2.61	335.1	114.6	−3.8	372.0	351.5	360.2
Rb^+	5	2.90	312.5	109.2	−6.3	341.8	325.1	338.9
Cs^+	5	3.06	284.5	106.7	−8.8	308.4	292.0	314.6
Ag^+	6	2.59	515.9	115.1	4.2	537.2	504.6	513.4
Tl^+	5	2.94	348.5	108.8	−7.1	376.6	356.9	364.0
Be^{2+}	4	1.49	2257.7	564.4	−184.5	2587.8	2470.2	2563.1
Mg^{2+}	5	1.85	1603.3	525.5	−8.8	2046.4	1961.5	1998.3
Ca^{2+}	6	2.27	1262.7	486.2	32.2	1683.6	1615.0	1668.6
Sr^{2+}	6	2.45	1082.0	471.1	10.5	1466.1	1399.1	1520.9
Ba^{2+}	6	2.63	946.8	457.3	1.3	1307.9	1255.2	1378.6
Zn^{2+}	6	2.10	1592.8	501.7	50.6	2047.6	1962.3	2046.0
Mn^{2+}	6	2.19	1466.5	493.3	42.3	1904.1	1822.1	1841.0
Fe^{2+}	6	2.13	1532.2	498.7	48.5	1981.5	1898.3	1946.0
Co^{2+}	6	2.13	1586.2	498.7	48.5	2035.9	1943.9	1996.2
Ni^{2+}	6	2.09	1686.2	502.5	51.0	2141.8	2046.8	2105.0
Cu^{2+}	6	2.11	1615.4	500.8	49.8	2068.6	1984.5	2100.0
Hg^{2+}	6	2.51	1492.0	466.5	10.9	1872.3	1806.2	1823.8
Pb^{2+}	6	2.57	1133.4	461.9	5.9	1503.3	1451.0	1480.7
Al^{3+}	5	1.67	3960.6	1224.7	−313.4	4798.2	4659.3	4665.2
Sc^{3+}	6	2.07	2844.3	1134.7	51.9	3933.0	3810.0	3897.0
Y^{3+}	6	2.20	2439.7	1108.3	41.0	3491.1	3368.6	3583.2
La^{3+}	6	2.34	2122.5	1080.7	23.0	3128.8	3022.1	3296.2
Fe^{3+}	6	2.07	3220.4	1134.7	51.9	4309.5	4168.5	4430.0

a) All energies have units of kilojoule per mol. b) $R_{i\text{-}o}$ is the calculated distance between ion and oxygen and has unit of Å . c) The experimental results are taken from the compilation of Rosseinsky[47)] and Smith.[48)]

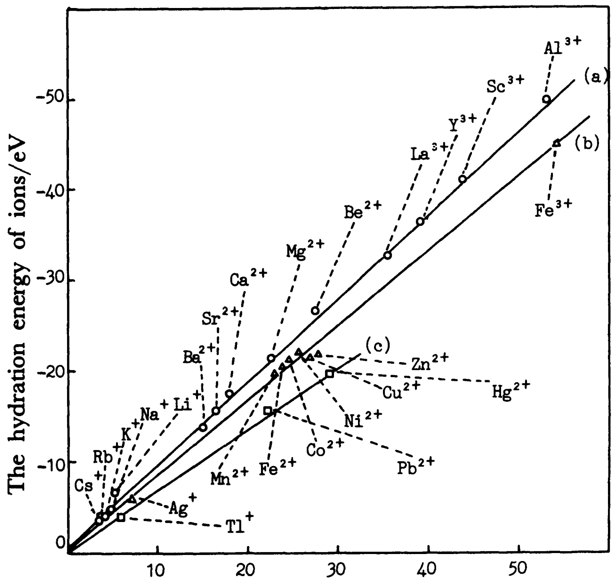


Fig. 5. The relation between ΔE_{hyd} and $\sum I$ at 25 °C.

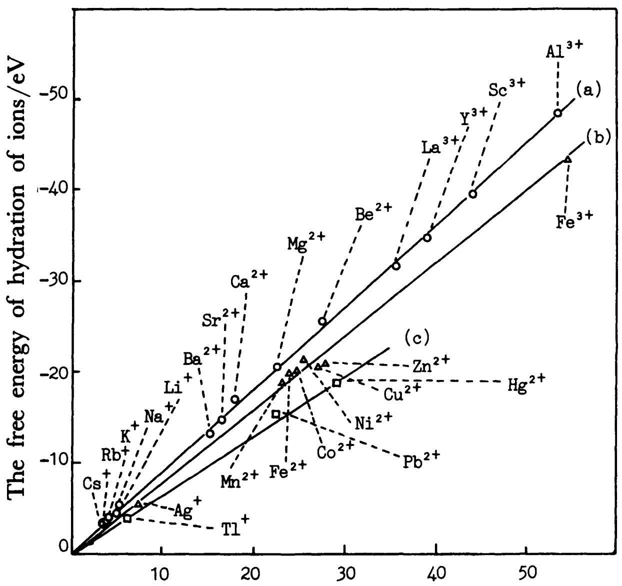


Fig. 6. The relation between ΔF_{hyd} and $\sum I$ at 25 °C.

lated hydration energies and free energies of ions are summarized in Table 2. Comparing the calculated hydration energy with the experimental data, ΔH_{exp}, the difference of energies may be about ±42 kJ mol^{-1}. From the calculated results, the hydration energies of monoatomic cations can be qualitatively correlated with the sum of the successive ionization energies from its atomic state to the ionic state.[4)] From inspecting the plots in Figs. 5 and 6, we classify the cations into three groups in terms of the hydration energy and free energy of ion, respectively. In Table 3, since the correlation coefficients for linearity of the plots in Figs. 5 and 6 are about 1.0, the present classification can be proven.[49)]

The cationic species are classified as group(a) belonging to IA-IIIA groups including Al^{3+} in IIIB group, group(b) belonging to VIA-IIB groups, and group(c) belonging to IIB-IVB groups in the periodic table. This classification is in good agreement with the result obtained by Matsuda and Notoya.⁴⁾

It is interesting to empirically investigate the chemical characteristics of each group. The present classification of cationic species originates from the consideration of the different shape of nonbonded energy curve between ion and water. The contributive components for interaction between ion and water molecule are given in Table 4. In the same charge ions, it is found that the nonbonded term in the potential energy plays an essential role in classifying the ionic species. The variations of the nonbonded energy term between ion and one water molecule depending on the ion-oxygen distance are minutely represented in Fig. 7. The ions of group(c) have the stronger nonbonded energy than those of groups(a) and (b). It is mainly due to the low ionization potential of two electrons in 6s configuration. The lower ionization potential and larger polarizability the ion has, the larger nonbonded energy the ion has. The ions of group(c) have been considered as soft acids in the principle of hard and soft acids and bases.⁵⁰⁾

Table 3. The Slopes and Interceptions for Each Group

	Group	a a)	b a)	σ^2 b)	ρ b)
ΔE_{hyd}	a	0.93	0.06	0.49	1.00
	b	0.82	0.06	1.22	1.00
	c	0.68	−0.11	0.30	1.00
ΔF_{hyd}	a	0.90	−0.13	0.42	1.00
	b	0.80	−0.38	1.26	0.98
	c	0.66	−0.18	0.35	1.00

a) The slopes a and interceptions b for each group are calculated by the least square method. b) σ^2 and ρ represent the variance of the fit and the correlation coefficient, respectively.

In the case of the ions of group(b), their 3d electrons are distributed among 3d orbitals. For Mn^{2+} with five 3d electrons and Zn^{2+} with a completely filled 3d shell, the hydration energies mainly depend on the electrostatic energy term in the potential energy, since their polarizabilities and radii are small.

Since the ions of group(a) have no 3d electrons and are small in size and low in the polarizability (relatively large core charges, less shielded nucleus), the ions have the large electrostatic energies and low nonbonded energies (see Fig. 7). From the above results, the ions of group(a) have been recognized as the hard acids in the principle of hard and soft acids and bases.

The interaction energies among water molecules around an ion are expressed as ΔE_{ww} in Tables 4 and 5. Since the water molecule in our model is an isotropically polarizable sphere including only dipole, the geometric approach¹⁵⁾ for a hydrogen bonding is not reasonable. Therefore, comparison of the interaction energies among water molecules around the ion with those around the water solute in pure water gives the information about enhancement of the structures of water molecules in the first hydration shell. The intermolecular interaction energy changes due to the

Table 4. The Contributive Components for Interactions between Ion and Water Molecules and between the Water Molecules a)

Group b)	Ion	$-E_{\mathrm{id}}$	$-E_{\mathrm{iid}}$	E_{ni} c)	E_{dd}	$-E_{\mathrm{did}}$	$-E_{\mathrm{nw}}$ c)	$-E_{\mathrm{iw}}$	ΔE_{ww}
a	Li^+	422.6	173.2	81.6	20.9	2.5	56.5	514.2	−27.2
	Na^+	302.5	88.7	39.3	12.6	0.8	25.9	351.9	−3.3
	K^+	285.8	63.2	13.8	15.1	0.8	26.8	335.1	3.8
	Rb^+	238.1	43.9	−30.5	8.8	0.4	13.0	312.5	6.3
	Cs^+	217.1	36.4	−30.5	7.5	0.4	9.6	284.5	8.8
	Be^{2+}	1136.8	1254.4	133.5	32.2	5.9	−146.9	2257.7	184.5
	Mg^{2+}	1010.9	793.7	201.3	37.7	5.0	41.8	1603.3	8.8
	Ca^{2+}	867.3	487.0	91.6	36.4	3.3	92.9	1262.7	−32.2
	Sr^{2+}	763.2	377.0	58.2	30.1	2.1	66.1	1082.0	−10.5
	Ba^{2+}	676.6	296.2	25.5	22.6	1.3	44.4	946.8	−1.3
	Al^{3+}	1784.9	2474.0	298.3	48.1	8.4	−255.6	3960.6	313.4
	Sc^{3+}	1515.9	1487.0	158.6	45.6	5.0	120.0	2844.3	−51.9
	Y^{3+}	1370.7	1216.3	147.3	39.3	3.8	103.3	2439.7	−41.0
	La^{3+}	1236.8	989.9	104.2	33.9	2.9	81.6	2122.5	−23.0
b	Ag^+	347.3	77.8	−90.4	23.4	1.7	48.1	515.9	−4.2
	Zn^{2+}	987.0	630.5	24.3	44.4	4.6	117.6	1592.8	−50.6
	Mn^{2+}	920.9	548.5	3.3	39.7	3.8	105.4	1466.5	−42.3
	Fe^{2+}	964.0	601.7	33.5	42.7	4.6	114.2	1532.2	−48.5
	Co^{2+}	964.0	601.7	−20.5	42.7	4.6	114.2	1586.2	−48.5
	Ni^{2+}	994.5	640.6	−51.0	44.8	5.0	118.4	1686.2	−51.0
	Cu^{2+}	979.1	620.5	−15.9	43.5	4.6	116.3	1615.9	−49.8
	Fe^{3+}	1515.9	1487.0	−217.6	45.6	5.0	120.1	3220.4	−51.9
c	Tl^+	232.6	41.8	−74.1	8.4	0.4	12.1	348.5	7.1
	Hg^{2+}	732.6	347.3	−412.5	25.1	1.7	56.5	1492.0	−10.9
	Pb^{2+}	703.7	320.5	−109.2	23.8	1.7	49.8	1133.4	−5.9

a) All energies have units of kilojoule per mol. b) a, b, and c mean the groups of ions. c) E_{ni} and E_{nw} represent the nonbonded energies between ion and water molecules and between the water molecules, respectively.

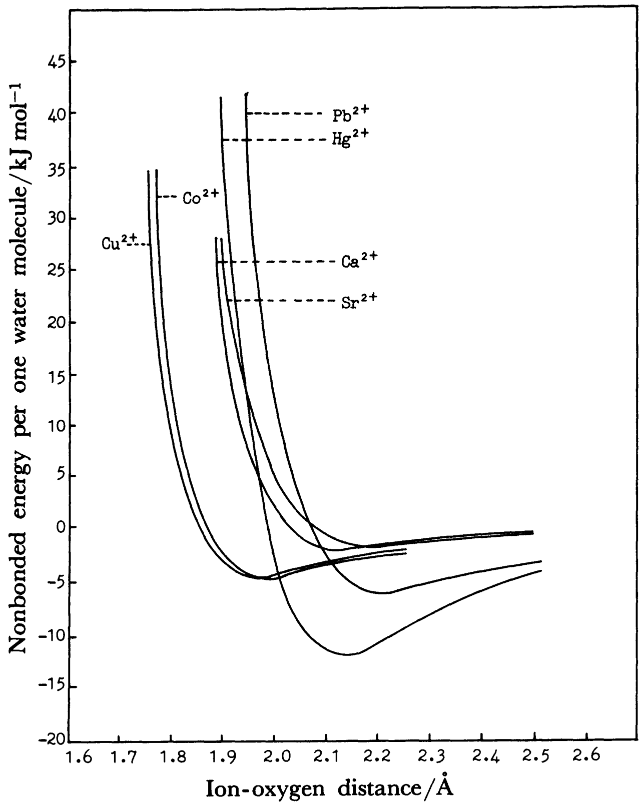


Fig. 7. The nonbonded energy term between ion and one water molecule according to the ion–oxygen distance.

Table 5. The Hydration Energies of Anions[a)]

Ion	n	$R_{i\text{-}o}$[b)]	$-E_{iw}$	$-E_{pol}$	ΔE_{ww}	$-\Delta E_{hyd}$
F^-	5	2.99	420.9	125.5	18.0	454.8
Cl^-	6	3.57	354.8	113.4	7.5	363.6
Br^-	6	3.60	322.6	113.0	7.5	330.5
I^-	6	3.78	274.1	109.6	7.9	278.2

a) All energies have units of kilojoule per mol. b) $R_{i\text{-}o}$ is the calculated distance between ion and oxygen and has unit of Å.

structure making and breaking ions are represented as the negative and positive values from Eq. 14, respectively.

In alkali metal ions, Li^+ and Na^+ are the structure making ions of which the surrounding water molecules are more stable than the pure water. On the other hand, K^+, Rb^+, and Cs^+ are the structure breaking ions. Here, it is found that the water structure around the ion was gradually broken according to the increment of the ionic radius. This result correspondes to the tendency of the B-coefficient of the Jones-Dole equation in electrolyte solution.[51)] Compared with the alkali metal ions, the halide ions have the structure breaking effect which arises from the expansion of the first hydration shell due to the change of the direction of dipole.

Since multiple charged ions, such as Zn^{2+}, Ni^{2+}, and Fe^{3+}, strongly attract the surrounding water molecules, the distances among water molecules in the first hydration are shorter than that in pure water and the water structure around these ions are enhanced. Therefore, these ions are structure making ions.

On the other hand, since Be^{2+}, Mg^{2+}, and Al^{3+} are very small ions and the interactions between ion and water molecules are very strong, the ion and surrounding water molecules are close to the aquo complex compounds. In these ions, it is difficult to explain the structure enhancement by only water molecules in the first hydration shell.

Jorgensen's Monte Carlo calculation suggested that structure makers may not be explained by a pronounced increase in solvent-solvent hydrogen bonding.[14)] The structure making effect in our method can be explained not by the increment of hydrogen bonding but by the comparison of average energy in the first hydration shell of an ion in aqueous solution with those of pure water. Although the formation of the first hydration shell represents a significant change in water structure, the contribution to the total hydration energy of the ion is not remarkable.

Our calculation leads to conclusions that the classification of ions into three groups is accomplished by the values of the nonbonded energy which involves the sum of ionization potential and polarizability of the ions. And the main factors which determine whether the ions will be structure makers or structure breakers in aqueous solution are the interaction energy of the ions with water molecules in the first hydration shell and the dimension of the ions characterized by the polarizability.

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References

1) B. E. Conway and R. G. Barradas, Ed., "Chemical Physics of Ionic Solutions," John Wiley, New York (1966).

2) "Ionic Processes in Solution," ed by R. W. Gurney Dover Publ. Co., New York (1962).

3) F. Franks, "Water. A Comprehensive Treatise," Plenum Press, New York (1973). Vol. 3.

4) A. Matsuda and R. Notoya, "Thermodynamical Empirical Rules for Solvation of Monoatomic Cations," Research Institute for Catalysis, Hokkaido University (1982).

5) H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).

6) M. Kaminsky, *Discuss. Faraday Soc.*, **24**, 171 (1957).

7) O. Y. Samoilov, *Discuss. Faraday Soc.*, **24**, 141 (1957).

8) B. M. Rode, R. Fujikura, and S. Fujiwara, *Bull. Chem. Soc. Jpn.*, **53**, 1965 (1980).

9) E. Clementi, H. Kistenmacher, W. Kolos, and S. Romano, *Theor. Chim. Acta*, **55**, 257 (1980).

10) H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **61**, 799 (1974).

11) S. Fujiwara and R. M. Rode, *Bull. Chem. Soc. Jpn.*, **52**, 3221 (1979).

12) D. L. Beveridge and G. W. Schnuelle, *J. Phys. Chem.*, **78**, 2064 (1974).

13) G. W. Schnuelle and D. L. Beveridge, *J. Phys. Chem.*, **79**, 2566 (1975).

14) J. Chandrasekhar, D. C. Spellmeyer, and W. L. Jorgensen, *J. Am. Chem. Soc.*, **106**, 903 (1984).

15) M. Mezei and D. L. Beveridge, *J. Chem. Phys.*, **74**, 622 (1981).

16) M. Rao and B. J. Berne, *J. Phys. Chem.*, **85**, 1498 (1981).

17) F. T. Marchese and D. L. Beveridge, *J. Am. Chem. Soc.*, **106**, 3713 (1984).

18) A. D. Buckingham, *Discuss. Faraday Soc.*, **24**, 151 (1957).

19) B. T. Gowda and S. W. Benson, *J. Phys. Chem.*, **86**, 847 (1982).

20) J. O' M. Bockris and A. K. N. Reddy, "Modern Electrochemistry," Plenum Press, New York (1970), Vol. 1, p. 45.

21) S. Goldman and R. G. Bates, *J. Am. Chem. Soc.*, **94**, 1476 (1972).

22) I. Eliezer and P. Krindel, *J. Chem. Phys.*, **57**, 1884 (1972).

23) K. J. Laidler and J. S. Muirhead-Gould, *Discuss. Faraday Soc.*, **40**, 953 (1965).

24) M. H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. 1*, **74**, 1604 (1978).

25) M. H. Abraham, J. Liszi, and L. Mêszáros, *J. Chem. Phys.*, **70**, 2491 (1979).

26) J. C. Owicki, L. L. Shipman, and H. A. Scheraga, *J. Phys. Chem.*, **79**, 1794 (1975).

27) O. Matsuoka, E. Clementi, and M. Yoshimine, *J. Chem. Phys.*, **64**, 1351 (1976).

28) T. R. Dyke, K. M. Mack, and J. S. Muenter, *J. Chem. Phys.*, **66**, 498 (1977).

29) S. A. Clough, Y. Beers, G. P. Klein, and L. S. Rothman, *J. Chem. Phys.*, **59**, 2254 (1973).

30) S. Nir, S. Adams, and R. Rein, *J. Chem. Phys.*, **59**, 3341 (1973).

31) B. E. Conway, *J. Solution Chem.*, **7**, 721 (1978).

32) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).

33) H. Ohtaki, "X-ray Diffraction Studies on the Structures of Metal Complexes in Solution," Tokyo Institute of Technology, Nagatsuta (1981).

34) A. D. Buckingham, "Intermolecular Interactions: From Diatomics to Biopolymers," ed by B. Pullman, John Wiley, New York (1978), p. 1.

35) A. J. Hopfinger, "Conformational Properties of Macromolecules," Academic Press, New York (1973), p. 38.

36) J. O. Hirshfelder and W. J. Meath, "Intermolecular Forces," ed by J. O. Hirshfelder, John Wiley, New York (1967), p. 3.

37) M. J. Moon, M. S. Jhon, and Y. K. Kang, *Bull. Korean Chem. Soc.*, **4**, 133 (1983).

38) T. M. Reed and K. E. Gubbins, "Applied Statistical Mechanics," McGraw-Hill, New York (1973), p. 138.

39) J. R. Tessman and A. H. Kahn, *Phys. Rev.*, **92**, 890 (1953).

40) K. S. Pitzer, *Advan. Chem. Phys.*, **2**, 59 (1959).

41) J. E. Huheey, "Inorganic Chemistry, "Haper and Row, New York (1978), p. 40.

42) A. Warshel, *Chem. Phys. Lett.*, **55**, 454 (1978).

43) W. L. Jorgensen, *J. Am. Chem. Soc.*, **103**, 335 (1981).

44) F. H. Stillinger, *Science*, **209**, 451 (1980).

45) H. S. Frank, *J. Chem. Phys.*, **13**, 493 (1945).

46) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

47) D. R. Rosseinsky, *Chem. Rev.*, **65**, 467 (1965).

48) D. W. Smith, *J. Chem. Educ.*, **54**, 540 (1977).

49) K. J. Johnson, "Numerical Methods in Chemistry," Marcel Dekker, New York (1980), p. 241.

50) R. F. Nalewajski, *J. Am. Chem. Soc.*, **106**, 944 (1984).

51) E. R. Neightingale, Jr., "Chemical Physics of Ionic Solution," ed by B. E. Conway, and R. G. Barradas, John Wiley, New York (1966), p. 87.