A New Model for the Calculation of Theromodynamic Functions of Simple Salts in Aqueous Soutions

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Thermodynamic functions for simple salts in aqueous solutions have been calculated using a simple model based on the Born theory. A structural treatment of ion-solvent interactions has been considered. It takes into consideration ion-dipole, ion-quadrupole and ion-induced-dipole interactions as well as the Born-type interactions. A formula for the calculation of the effective ion-water separation in solution is proposed. Calculated values of the change in Gibbs free energy, enthalpy and entropy of hydration showed good agreement with experiment.

INTRODUCTION

The thermodynamics of ions in solutions has been widely considered from both theoretical and experimental standpoints[1–15]. On the theoretical side, several models for the calculation of ion-ion interaction in solution have been given [1–6]. Ion-solvent interactions have also been considered by many investigators[7–14]. The first theory of solvation energy, due to Born[7], regarded ions as rigid spheres in a continuous dielectric medium. The free energy of solvation, ΔG_{solv}, was regarded as the electrostatic potential energy in the solvent less than that in vacuum. However, ΔG_{solv} values calculated according to this theory are too high when compared with experiment. Webb[8] introduced two corrections to the Born theory: (a) the dielectric constant is less than that in the bulk of the solution; (b) the solvent undergoes compression near the ion and thus allowance must be made for the work used up in this process. The results for the free energy of hydration of individual cations obtained in this way are closer to experiment, but the agreement is nevertheless still poor.

The first attempt of a structural calculation of the heat of hydration was made by Bernal and Fowler[9] on the basis of the theory of tetrahedral coordination in water. The ion-dipole interaction in the primary hydration sheath and the electrostatic energy of one water molecule, in addition to the Born term, have been considered. Values obtained from this method are smaller by about 42 kJ/mole than the experimental ones.

Eley and Evans[10] used a model similar to that of Bernal and Fowler but subjected it to a more rigorous treatment. They considered the formation of a tetrahedral ion-water complex through the removal of a tetrahedral group of five water molecules from the bulk of the solution. Values obtained by this method agree better with experiment and are compared in Tables 1 and 3 with those obtained in the present work.

TABLE 1

EXPERIMENTAL[12] AND CALCULATED ENTROPIES OF HYDRATION FOR VARIOUS IONS AT 25°C IN J MOL^{-1} K^{-1}. ALSO SHOWN, THE CALCULATED EFFECTIVE RADII FOR IONS.

Ion	r_e(A°)	$-\Delta S_i$(exp)	ΔS_i^*(calc)	$-\Delta S_i^\#$(calc)
Li$^+$	2.59	121.9	122.5	146
Na$^+$	2.75	110.6	103.5	119
K$^+$	3.08	75.00	73.18	92.5
Rb$^+$	3.15	62.84	67.94	84.5
Cs$^+$	3.14	59.87	68.66	—
F$^-$	2.51	132.3	132.0	149
Cl$^-$	3.05	75.35	75.52	103
Br$^-$	3.26	59.87	60.42	65.7
I$^-$	3.65	36.82	38.91	38.1
Mg^{2+}	2.48	312.9	321.5	304
Ca^{2+}	2.77	256.4	250.4	259
Sr^{2+}	2.83	249.7	236.2	—
Al^{3+}	2.42	533.7	532.8	436

* The present work.
# Calculated by Eley and Evans, (reference 10).

The entropy of hydration, ΔG_{hyd}, can be calculated using various theories. The simplest approach is by differentiation of the free energy of hydration, ΔG_{hyd}, as expressed by the Born equation, with respect to temperature. This approach yields the correct sign and order of ΔS_{hyd}, but is in poor agreement with experiment. Two alternate approaches are commonly used. The first, based on compressibilities, was considered by Webb[8] and Latimer[15]. Here, ΔS_{hyd} can be well accounted for if it is considered to arise from a decrease of the entropy of water near the ion. Such a decrease is brought about by compression of the solvent in the high field of the ion. The agreement with experiment is to within 10–30% for simple ions. The second approach, based on statistical mechanics, was carried out by Eley and Evans[10]. Here, the presence of an ion in water restricts the degrees of freedom of water molecules in the primary hydration sheath causing entropy loss. Better agreement with experiment is obtained from this approach than from the first one. However, the complexity involved in the calculations limits it use.

In the present work, a model is presented for the calculation of ΔG_{hyd}, and ΔS_{hyd} and enthalpy of hydration, ΔH_{hyd}. This model employs newly developed empricical formulae for the calculation of distances between species in aqueous solutions. The values obtained from this model are compared with experiment as well as with those obtained from other models. It is observed that this model provides better agreement with experiment than the models previously outlined.

THEORETICAL

When a solid ionic crystal dissolves, energy changes may be thought to occur in several steps. Firstly, the crystalline substance is broken up giving rise to free "gaseous" positive and negative ions. The energy used up in this step is the lattice

energy, U_g. Secondly, the ions are surrounded by water molecules forming hydrated ions. This process leads to the evolution of the total heat of hydration of the cation ΔH_c and the anion ΔH_a. The energy of ion-ion interaction, ΔH_{I-I}, is significant, especially at high ionic concentratioin. The total energy change for hydration is thus given by

$$\Delta H_{hyd} = -U_g + (\Delta H_c + \Delta H_a) + \Delta H_{I-I} \qquad (1)$$

In the present work ΔH_{hyd} will be calculated from ΔG_{hyd} and ΔS_{hyd}.

The free energy of hydration for an ion-water interaction is defined as the change in free energy during the transfer of an ion from a point in vacuum at infinite distance from the solution to the bulk. The total free energy change for ion-water interaction is given by[16]

$$\Delta G_{I-water} = W_{BC} + W_{I-Q} + W_{I-I-D} \qquad (2)$$

Where, W_{BC} is the born charging contribution to the free energy. This is the sum of the work of discharging an equivalent sphere in vacuum and the work of charging it in water. It is given by[16]

$$W_{BC} = -\frac{N_A(z_i e_o)^2}{2(r_i + 2r_w)}\left(1 - \frac{1}{\varepsilon}\right) \qquad (3)$$

where z_i is the ionic charge, ε is the dielectric constant of water, r_i is the ionic radius, r_w is the radius of a water molecule. The term $(r_i + 2r_w)$ represents the radius of the hydrated ion.

W_{I-Q} is the ion-quadruple contribution and is obtained by treating water molecules as electric quadrupoles, rather than dipoles. Thus the ion-quadruple interaction must be used instead the ion-dipole interaction. W_{I-Q} is given by[16]

$$W_{I-Q} = W - \frac{N_A n z_i e_o \mu_w}{(r_i + r_w)^2} \pm \frac{N_A n z_i e_o P_w}{2(r_i + r_w)^3} \qquad (4)$$

where W is a constant whose magnitude is *ca.* 84 kJ/mole for cations and 126 kJ/mole for anions, n is the number of water molecules involved in the primary hydration sheath, P_w is the quadrupole moment for a water molecule, and μ_w and r_w are the dipole moment and radius of water, respectively. The (+) in the (±) is for cations and the (−) is for anions.

W_{I-I-D} is the ion-induced-dipole interaction in the primary hydration sheath and is given by[16]

$$W_{I-I-D} = -\frac{N_A n \alpha (z_i e_o)^2}{2(r_i + r_w)^4} \qquad (5)$$

where α is the deformation polarizability of a water molecule.

The actual distance between the center of an ion and the center of a water molecule is not simply the sum of the ionic and water radii, $(r_i + r_w)$. The actual distance, r_{iw}, may be less or larger depending on the magnitude of the attractive force between the ion and water. This force depends on the ionic charge and size.

The term $(r_i + r_w)$ must thus be replaced by r_{iw}. In the present work, the following formula is proposed for the evaluation of r_{iw}

$$r_{iw} = (r_i + r_w) + \frac{0.21}{z_i r_i}(CF) \qquad \text{for cations}$$

$$= 2.49(r_i)^{0.4} \qquad \text{for anions} \qquad (6)$$

where CF is a correction factor given by

$$CF = 1 \qquad \text{for univalent cations}$$

$$= (0.65/r_i) \qquad \text{for di-and trivalent cations}$$

The total work of hydration is then given by

$$W_{I-water} = \Delta G_{I-water}(\text{cation}) = 83.68 - \frac{4N_A z_i e_o \mu_w}{r_{iw}^2} + \frac{4N_A z_i e_o P_w}{2r_{iw}^3}$$
$$- \frac{N_A(z_i e_o)^2}{2(r_{iw} + r_w)}(1 - \frac{1}{\varepsilon}) - \frac{4N_A \alpha(z_i e_o)^2}{2r_{iw}^4} \qquad (7)$$

$$W_{I-water} = \Delta G_{I-water}(\text{anion}) = 125.5 - \frac{4N_A z_i e_o \mu_w}{r_{iw}^2} - \frac{4N_A z_i e_o P_w}{2r_{iw}^3}$$
$$- \frac{N_A(z_i e_o)^2}{2(r_{iw} + r_w)}(1 - \frac{1}{\varepsilon}) - \frac{4N_A \alpha(z_i e_o)^2}{2r_{iw}^4} \qquad (8)$$

It should be noted that this work is equal to the Gibbs free energy and cannot be directly compared with the experimental heat of hydration. The Gibbs free energy of hydration, ΔG_i, for an ion i is related to the heat of hydration by the relation

$$\Delta G_i = \Delta H_i - T\Delta S_i \qquad (9)$$

where ΔS_i is the ionic entropy of hydration, it is given by

$$\Delta S_i = S_i' - S_{g,i} \qquad (10)$$

where S_i' is the partial ionic entropy of the ion in the solution and $S_{g,i}$ is the ionic entropy in the gas phase. For monoatomic ions, S_i' is given by an empirical function of ionic radius[17]

$$S_i' = (3/2) R \ln M + 154.6 - 1130\frac{z_i}{r_e^2(A°)} \qquad (11)$$

where M is the molar mass of the ion and r_e is its effective radius.

In the present work, the following empirical formula for r_e is proposed:

$$r_e = r_i + C_1 \frac{r_1 \pm (C_2 - r_i)^3}{r_i} \qquad (12)$$

where, as before, the (+) in the (±) refers to cations and the (−) to anions and C_1 and C_2 are constants with the following values:

$$C_1 = 1.80 \qquad C_2 = 1.0 \qquad \text{for univalent cations.}$$

$$C_1 = 1.83 \qquad C_2 = 0.7 \qquad \text{for divalent cations.}$$

$$C_1 = 1.92 \qquad C_2 = 0.6 \qquad \text{for trivalent cations.}$$

$$C_1 = 1.15 \qquad C_2 = 1.3 \qquad \text{for univalent anions.}$$

The ionic entropy in the gas phase may be calculated from the Sackur-Tetrode equation[18]. For a monoatomic gas the entropy is determined only by the translational degrees of freedom. At 1 atm and 25°C it is given by

$$S_{g,i} = (3/2) R \ln M + 108.7 \tag{13}$$

equation (10) thus becomes

$$\Delta S_i = 45.90 - 1130 \frac{Z_i}{r_e^2(A°)} \tag{14}$$

Equations (6), (7), (8), (12) and (14) can be used to calculate the heat of hydration for individual ions. However, to calculate the heat of hydration for a salt, composed of cations and anions, the sum of the heats of hydration for individual ions must be used instead, and it must be adjusted to account for ion-ion interaction. This is especially important at high ionic strengths. This additional term is given by

$$\Delta G_{I-I} = 2.303 \, \nu RT \log \gamma \tag{15}$$

where ν is the sum of numbers of cations and anions in the salt and γ is the mean activity coefficient for the salt, given by[6]

$$\log \gamma = -Z_+|Z_-| \frac{B\sqrt{I}}{1 = (a/r_a)} + CI - D\sqrt{I} \tag{16}$$

where Z_+ and Z_- are the charges of the cation and anion respectively, I is the ionic strength, B is a temperature dependent constant, r_a is the thickness of the ionic atmosphere that depends on both the temperature and the ionic strength, a is the distance of closest approach between ions in solution and C and D are empirical constants.

The net change in the Gibbs free energy throughout the hydration of a salt is given by

$$\Delta G_{hyd} = \Sigma \, \Delta G_{I-water} + \Delta G_{I-I} \tag{17}$$

and the accompanying enthalpy change during the hydration process is given by

$$\Delta H_{hyd} = \Delta G_{hyd} + T\Delta S_{hyd} \tag{18}$$

where ΔS_s is the total entropy change through the hydration process. It is the sum of the contributions of individual ion entropies, such that

$$\Delta S_{hyd} = \Sigma_i \Delta S_i \tag{19}$$

RESULTS AND DISCUSSION

The entropy changes accompanying the hydration of individual ions were calculated using equations (12) and (14). Table 1 shows these values for various ions along with the experimental values for comparison. The agreement between

the calculated values and those derived from experiment is remarkably good and is better than that obtained by Eley and Evans[10] using a tedious statistical-mechanical model.

TABLE 2

EXPERIMENTAL[12] AND CALCULATED ENTROPIES (IN PARENTHESES) OF HYDRATION FOR VARIOUS SALTS AT 25°C IN J MOL^{-1} K^{-1}.

cation/Anion	F^-	Cl^-	Br^-	I^-
Li^+	−254.3	−197.3	−181.8	−158.7
	(−254.5)	(−198.0)	(−182.9)	(−161.4)
Na^+	−243.0	−186.0	−170.5	−147.4
	(−235.5)	(−178.9)	(−163.9)	(−142.4)
K^+	−207.3	−150.3	−134.9	−111.8
	(−205.2)	(−148.7)	(−133.6)	(−112.1)
Rb^+	−195.2	−138.2	−122.7	−99.66
	(−199.9)	(−143.5)	(−128.4)	(−106.9)
Cs^+	−192.2	−135.2	−119.7	−96.69
	(−200.7)	(−144.2)	(−129.1)	(−107.6)
Mg^{2+}	−577.6	−463.6	−432.6	−386.5
	(−585.5)	(−472.5)	(−442.3)	(−399.3)
Ca^{2+}	−521.1	−407.1	−376.1	−330.0
	(−512.6)	(−399.6)	(−369.4)	(−326.4)
Sr^{2+}	−514.3	−400.4	−369.4	−323.3
	(−501.8)	(−387.2)	(−357.0)	(−314.0)
Al^{3+}	−930.7	−759.8	−713.3	−644.2
	(−928.8)	(−759.3)	(−714.0)	(−649.5)

TABLE 3

EXPERIMENTAL[12] AND CALCULATED GIBBS ENERGIES DUE TO ION-WATER INTERACTIONS, $\Delta G_{I-water}$, FOR VARIOUS ION IN KJ MOL^{-1}.

Ion	$-\Delta G_{exp}$	$-\Delta G^*_{calc}$	$-\Delta G^\#_{calc}$
Li^+	472.7	458.1	515
Na^+	372.7	382.8	448
K^+	300.3	304.3	351
Rb^+	277.7	279.5	314
Cs^+	245.3	248.4	—
F^-	473.3	476.1	339
Cl^-	356.2	355.1	218
Br^-	342.2	328.7	197
I^-	295.7	295.4	—
Mg^{2+}	1830	1858	2000
Ca^{2+}	1518	1505	1720
Sr^{2+}	1372	1379	—
Ba^{2+}	1242	1203	1390
Al^{3+}	4505	4505	4100

* The present work.

Calculated by Eley and Evans, (reference 10).

The entropy change for the hydration of a salt is taken as the sum of entropies for individual ions forming the salt. Table 2 shows experimental and calculated entropies of hydration for various salts.

To calculate the Gibbs free energy change of hydration, energy changes due to both ion-solvent interaction and ion-ion interactions must be considered. Ion-solvent interaction were calculated for various ions using equations (6), (7) and (8). The results are shown in Table 3. The Gibbs energy due to ion-ion interactions for various salts in aqueous medium, calculated at 25°C using equations (15) and (16), are presented in Table 4.

TABLE 4

ACTIVITY COEFFICIENTS AND GIBBS FREE ENERGIES DUE TO ION-ION INTER-
ACTIONS, ΔG_{I-I}, FOR VARIOUS SALTS IN AQUEOUS SOLUTIONS. VALUES ARE
IN J Mol^{-1} CALCULATED AT 25°C AND A CONCENTRATION OF 1 m.

Salt	γ	$-\Delta G_{I-I}$	Salt	γ	$-\Delta G_{I-I}$
LiF	0.66	2059	NaF	0.56	2870
LiCl	0.90	518.8	NaCl	0.66	3682
LiBr	1.01	−50.21	NaBr	0.69	1841
LiI	1.27	−1188	NaI	0.73	1556
KF	0.55	2962	RbF	0.56	2870
KCl	0.61	2452	RbCl	0.59	2619
KBr	0.62	2368	RbBr	0.60	2536
KI	0.65	2134	RbI	0.61	2452
MgF_2	0.34	8017	CaF_2	0.29	9201
$MgCl_2$	0.58	4054	$CaCl_2$	0.50	5151
$MgBr_2$	0.68	2862	$CaBr_2$	0.54	4581
MgI_2	0.87	1033	CaI_2	0.72	2452
SrF_2	0.27	13540	BaF_2	0.25	10300
$SrCl_2$	0.47	5611	$BaCl_2$	0.43	6272
$SrBr_2$	0.54	4581	$BaBr_2$	0.50	5151
SrI_2	0.68	2866	BaI_2	0.62	3552
AlF_3	0.27	12970			
$AlCl_3$	0.52	6485			
$AlBr_3$	0.60	5063			
AlI_3	0.73	3117			

ΔG_{hyd} for various salts were calculated using equation (17) and are shown in Table 5 along with the experimental values.

TABLE 5

EXPERIMENTAL[12] AND CALCULATED (IN PARENTHESES) VALUES OF THE
NET GIBBS ENERGIES OF HYDRATION, ΔG_{hyd}, FOR VARIOUS SALTS
IN KJ MOL^{-1} AT 25°C.

Cation/Anion	F^-	Cl^-	Br^-	I^-
Li^+	−946.0 (−936.2)	−828.8 (−813.7)	−815.0 (−786.8)	−768.4 (−752.3)
Na^+	−845.9 (−681.8)	−728.7 (−741.6)	−714.9 (−713.4)	−668.4 (−679.8)
K^+	−773.5 (−783.4)	−656.3 (−661.9)	−642.5 (−635.5)	−596.0 (601.9)
Rb^+	−750.9 (−758.5)	−633.7 (−637.3)	−619.9 (−610.8)	−573.3 (−577.4)
Mg^{2+}	−2777 (−2818)	−2543 (−2572)	−2525 (−2518)	−2422 (−2450)
Ca^{2+}	−2464 (−2467)	−2230 (−2221)	−2202 (−2167)	−2109 (−2098)
Sr^{2+}	−2318 (−2341)	−2084 (−2095)	−2056 (−2041)	−1963 (−1797)
Ba^{2+}	−2189 (−2165)	−1955 (−1919)	−1927 (−1865)	−1834 (−1797)
Al^{3+}	−5925 (−5946)	−5573 (−5577)	−5532 (−5496)	−5392 (−5394)

TABLE 6

EXPERIMENTAL[12] AND CALCULATED (IN PARENTHESES) VALUES OF THE
HEAT OF INTERACTION BETWEEN A SALT AND WATER IN KJ MOLE^{-1} AT 25°C.

Cation/Anion	F^-	Cl^-	Br^-	I^-
Li^+	−1028* (−1012)	−893.7 (−872.7)	−879.5 (−841.3)	−821.1 (−800.5)
Na^+	−918.5* (−931.9)	−784.4 (−794.9)	−770.2 (−762.2)	−712.3 (−722.2)
K^+	−833.9* (−844.5)	−699.8 (−706.2)	−685.5 (−675.1)	−627.7 (−635.3)
Rb^+	−809.1* (−818.1)	−675.0* (−680.0)	−660.7* (−649.1)	−602.9* (−609.3)
Mg^{2+}	−2952* (−2993)	−2684* (−2713)	−2655* (−2650)	−2539* (−2569)
Ca^{2+}	−2619 (−2621)	−2351 (−2340)	−2323 (−2278)	−2207 (−2196)
Al^{3+}	−6202 (−6223)	−5799 (−5803)	−5757 (−5709)	−5583 (−5588)

* Obtained from experimental values of ΔG and ΔS.

The inclusion of the ion-ion interaction term in the calculation, even though relatively small, emphasizes that the value of the Gibbs free energy of hydration, and hence that of heat of hydration, has a non-linear dependence on the salt concentration. At relatively low concentrations, the activity coefficient, γ, is less than unity and the energy due to ion-ion interaction enhances the stability of the ion in solution. However, at high concentrations, $\gamma \gg 1$, and ion-ion interactions destabilize the ion making ΔG_i and ΔH_i less negative.

Values of ΔH_{hyd} for various salts were calculated at 25°C using equations (18) and (19). The results are shown in Table 6 along with the experimental values for comparison.

In conclusion, this is a relatively simple method that provides excellent agreement (within 3%) with experiment. It may thus form the basis of a reliable method for the calculation of thermodynamic function of ions in solution.

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