ON THE HYDRATION NUMBERS AND ACTIVITY COEFFICIENTS OF SOME SALTS PRESENT IN SEA WATER

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ABSTRACT

The hydration numbers of some salts present in sea water have been calculated by a simple model for the equation of the dielectric constant, and the mean activity coefficients from the theoretical formula proposed by Jhon and Eyring.

The validity of the theory for the electrolyte solution is tested by evaluating the hydration numbers and the mean activity coefficients of some 1 : 1, 1 : 2, 2 : 1 and 1 : 3 electrolytes in sea water.

The results show good agreement with the observations.

INTRODUCTION

The study of hydration numbers and mean activity coefficients for salts in concentrated solutions may be useful in understanding properties and structures of sea water, which contains NaCl, KCl, NaI, KI, NH_4Cl, $MgCl_2$, $BaCl_2$, $LaCl_3$, Na_2SO_4, etc.

The experiment and semi-empirical theory of hydration on the salt have been studied by Stokes & Robinson (1), Miller (2), and Samoilov (3).

And the theory of activity coefficients of salts in solutions was developed by Debye & Hückel (4), Bjerrum (5), Guggenheim (6), Davies (7), and Fuoss & Onsager (8).

While, Khomutov (9) obtained the rational activity coefficients of salts in solutions from a semi-empirical formula using the second approximation of the Debye-Hückel theory and the simple electrostatic theory of solvation.

Recently, Jhon and Eyring (10) proposed a theory of electrolyte solution based on the Significant Structure Theory of Liquid (11) and applied successfully to the concentrated electrolyte solut-

ions.

Very recently, Sung and Jhon (12) have developed a model for the equation of dielectric constant to obtain the hydration number of salts in solution from the domain theory of dielectric constant of hydrogen-bonded liquid proposed by Hobbs, Jhon, and Eyring (13).

The model was applied with success to some 1 : 1 electrolytes, and calculated the hydration numbers and the mean activity coefficients for NaCl over the concentration range 0.1—4.0 M and for 0.1—2.0 M LiCl, NaBr, NaI, KCl, KI, and RbCl.

In this paper, a further validation of the model and theory is tested for some salts (uni-univalent, uni-divalent, uni-trivalent, and di-univalent type salts) present in sea water.

HYDRATION NUMBERS OF SALTS IN SEA WATER

According to Hobbs, Jhon, and Eyring (13), the dielectric constant of water or hydrogen-bonded liquids is given by

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{3\epsilon} = 4\pi \frac{N}{V} \cdot \left(\frac{n^2 + 2}{3} \right)^2$$

$$\cdot \left(\frac{V_s}{V} \cdot \frac{\mu^2 G}{kT} + \frac{V-V_s}{V} \cdot \frac{\mu^2}{3kT} \right) \quad (1)$$

Here $G = \cos^2\theta$, ϵ and n are the dielelectric constant and index of refraction, respectively, and N is Avogadro's number, k is the Boltzmann constant, μ is the value of the permanent dipole moment characteristic of the isolated molecule, V_s is the molar volume of the solid, and V is the molar volume of the liquid at the temperatue T.

The application of this theory is extended to some mixtures of hydrogen-bonded fluids (14).

In the aqueous electrolyte solution which the salts are dissolved into water, the dielectric constants of the solutions are less than those of pure water.

These phenomena suggest us that the hydration occurs between the salts and water molecules in the solution, i.e., the solvation is the result of interactions between solute and solvent.

In these cases, the numbers of hydration are considered as a combination of a certain number of water molecules with the salts.

To derive the dielectric constants cf the electrolyte solutions, we are taken into account that the fraction of the hydrated water in solution is not contributed to the orientating polarizability since these small islands with an ion are difficult to rotate to the field direction.

The number of moles of hydrated water per each mole of solute in the solution is $\dfrac{m'}{55.51} \sum\limits_{i=1}^{n}$ $\dfrac{K_i}{1+K_i} n_i$, in which K_i is the equilibrium constant between water adsorbed on sites produced by the ion of ith kind and free water and n_i is the number of sites of the ion of ith kind.

And, the actual molar volume of water is used in the equation.

Then, the dielectric constant of the electrolyte solution is given by

$$\frac{(\epsilon-n^2)(2\epsilon+n^2)}{3\epsilon} = 4\pi N \frac{\rho \left(1 - \dfrac{m'M}{1,000+m'M} \right)}{18.016}$$

$$\cdot \left(\frac{n^2+2}{3} \right)^2 \cdot \left(\frac{V_s}{V} \cdot \frac{\mu^2 G}{RT} + \frac{V-V_s}{V} \cdot \frac{\mu^2}{3RT} \right)$$

$$\cdot \left(1 - \frac{m'}{55.51} \sum_{i=1}^{n} \frac{K_i}{1+K_i} n_i \right) \quad (2)$$

Where ρ is the density of the aqueous electrolyte solution, $\sum\limits_{i=1}^{n} \dfrac{K_i}{1+K_i} n_i$ is the hydration number of the salt, m' and M are the molality of the solution and the gram molecular weight of the salt, respectively.

Rearranging eq. (2) for convenience in actual calculations, we obtain

$$\sum_{i=1}^{n} \frac{K_i}{1+K_i} n_i = \frac{55.51}{m'} \left(1 - \frac{(\epsilon-n^2)(2\epsilon+n^2)}{3\epsilon} \cdot \right.$$

$$\left\{ 4\pi N \frac{\rho \left(1 - \dfrac{m'M}{1,000+m'M} \right)}{18.016} \cdot \left(\frac{n^2+2}{3} \right)^2 \right.$$

$$\left. \left. \cdot \left(\frac{V_s}{V} \cdot \frac{\mu^2 G}{RT} + \frac{V-V_s}{V} \cdot \frac{\mu^2}{3RT} \right) \right\} \right) \quad (3)$$

In the calculation, the following values were used: $G = 0.964$ (13) and $\mu = 1.830$ debye (15).

And putting the experimental values of ϵ (16, 17, 18), n^2 (18), ρ (18, 19), V_S and V_{H_2O}(20) for water at a given temperature, and molality, m' into eq.(3), we obtain the value of $\sum\limits_{i=1}^{n} \dfrac{K_i}{1+K_i} n_i$, the hydration number of the salts in the sea water.

The calculated results of the hydration number are compared with the observed values (21) in Table 1.

Table 1. The comparison of the hydration numbers.

Salts	Calcd.	Obsd.
NH₄Cl	9. 1	—
MgCl₂	10. 8	10. 5
BaCl₂	12. 2	12. 7
LaCl₃	12. 4	—
Na₂SO₄	10. 1	—

ACTIVITY COEFFICIENT OF SALTS IN SEA WATER

The theoretical activity coefficients of the concentration dependence of salts in aqueous solutions are in good agreement with the observations only for certain uni-univalent electrolyte up to concentration 0.1—0.5 M (22).

To obtain the activity coefficients of salts in the concentrated electrolyte solution, the authors (12) proposed a method allowing for the influence of ionic hydration by resulting from the firm bonding of a definite quantity of water on the salts.

The energy effects caused by the electrostatic interaction of ions and by their hydration are discussed independently.

The former effect is taken into account by means of the theoretically derived equation by Jhon and Eyring (10) from the Debye-Hückel theory.

The latter effect is regarded as resulting from the change in hydration number with variation in the concentration.

In the solution, the chemical potential μ_i of the ions i at a mole is given by

$$\mu_i = \mu_i^\circ + RT l_n a_i \qquad (4)$$
$$a_i = N_i f_i \qquad (5)$$

Where μ_i, a_i, N_i, and f_i are chemical potential at unit activity, activity, mole fraction, and activity coefficient for component i, respectively.

The mean activity coefficient, f_i, of salts is

$$f_i = f_{D-H} \, f_{hyd.} \qquad (6)$$

Where

$$f_{D-H} = E_{x,p} \left\{ \frac{V}{8\pi} \left(\frac{1}{(1+a\kappa)} \left(\kappa^3 - \frac{1}{a^3} \right) \right. \right.$$
$$\left. \left. + \frac{1}{a^3} (1 + a\kappa) - \frac{2}{a^3} l_n(1+a\kappa) \right) \right\} \qquad (7)$$

$$f_{hyd.} = (K_i)^{\sum\limits_{i=1}^{n} \frac{K_i}{1+K_i} n_i m'} \qquad (8)$$

Where a, κ, n_i and K_i are the ionic radii of the hydrated salts, Debye-Hückel parameter, the site numbers of ions, and the equilibrium constant

between water adsorbed on site produced by salt and free water.

Therefore, the logarithm of the mean activity coefficient of the salt in solution is given by as follows:

$$l_n f_i = \left\{ \frac{V}{8\pi} \frac{1}{(1+a\kappa)} \left(\kappa^3 - \frac{1}{a^3} \right) + \frac{1}{a^3} (1+a\kappa) \right.$$
$$\left. - \frac{2}{a^3} l_n(1+a\kappa) \right\} \cdot \left\{ \sum_{i=1}^{n} \frac{K_i}{1+K_i} n_i m' l_n K_i \right\} \qquad (9)$$

In the calculation, we have to determine the values of a, the ionic radii of the hydrated salts and κ, Debye-Hückel parameter.

In order to determine the value of κ, we used the equation described in the reference (22),

$$\kappa = \frac{50.29}{(\epsilon T)^{1/2}} I^{1/2} \text{ Å}^{-1}, \quad \text{Where } I = \frac{1}{2} \Sigma m_i Z_i^2$$

And we assumed that the ionic radii of the hydrated salts in aqueous solution is given as

$$a = \left\{ \frac{3}{4\pi} \cdot \frac{\left[V_{salt} + \left(\sum_{i=1}^{n} \frac{K_i}{1+K_i} n_i \right) V_{H_2O} \right]}{2} \right\}^{1/3}$$

Putting the values of $\sum_{i=1}^{n} \frac{K_i}{1+K_i} n_i$ and the experimental values of V_{salt} (19) and V_{H_2O} (20), we determine the value of a, the ionic radii of the hydrated salts.

The determined values of a and n_i are listed in Table 2.

Table 2. The numbers of site and ionic radii of salts.

Salts	Number of Site	Ionic Radii of Hydrated Salts	Ionic Radii of Salts
NaCl	7.3	3.14(Å)	2.81[a](Å)
NaI	8.0	3.29	3.23
KCl	6.0	3.18	3.14
KI	6.4	3.31	3.30
NH$_4$Cl	9.5	3.39	3.19
MgCl$_2$	7.7	4.24	4.16[b]
BaCl$_2$	8.5	4.67	4.62
LaCl$_3$	13.5	4.79	4.67
Na$_2$SO$_4$	7.8	4.46	4.35

(a) Data are taken from reference 19.
(b) Data are taken from reference 25.

And we determined the value of K_i from the numbers of hydration.

Then, we can calculated the mean activity coe-

fficients of salts in the aqueous solutions.

The obtained mean activity coefficients are compared with experiments (24) in Figure 1.
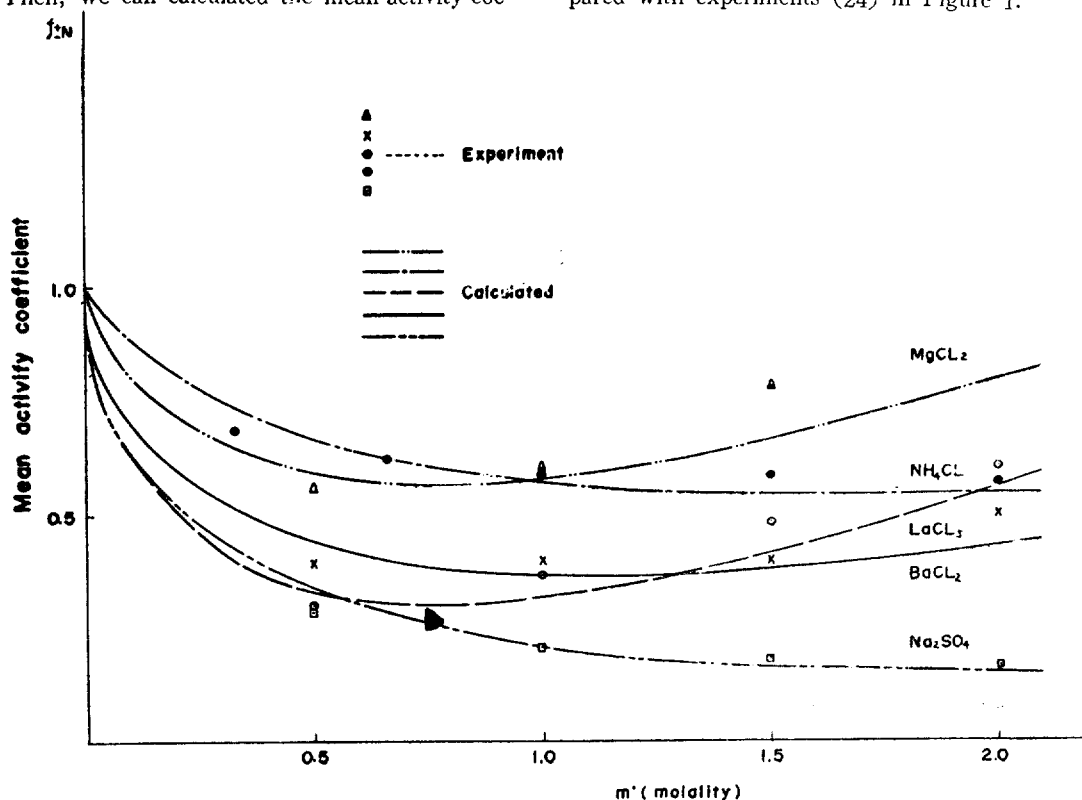

Fig. 1. Activity coefficients of uni-univalent, uni-divalent, uni-trivalent, and di-univalent electrolytes at various concentration: experimental data from ref. (24).

DISCUSSION

As may be seen from Figure 1, the mean activity coefficients calculated by means of the proposed theory show good agreement with experimental values over the concentration range 0.1— 2.0 M.

This facts confirm the correctness of Hückel's view (26) that the concentration dependence of ϵ must be considered. The free energy variation of ionic hydrations with water is one reason for the variation in the mean activity coefficient.

With the combination of the exact Debye-Hückel equation and the theory of ionic hydration derived by Jhon and Eyring (10), we can deduce a formula (9) depending upon the ionic strength, diel-

ectric constnat, equilibrium constant, and the ionic radii of the hydrated salts in aqueous solutions.

From the above results, we conclude that the mean activity coefficients of salts have been independently contributed by both two effects of the electrostatic interaction and the ionic hydration.

In the Table 2, the ionic radii and the numbers of site are compared with the observations. These values are very reasonable.

Judging from Table 1 and the previous results (12), the numbers of hydration of various salts at the certain temperature increase in following order:

$LaCl_3 > BaCl_2 > MgCl_2 > Na_2SO_4 > NH_4Cl > NaI$
$> NaBr > NaCl > KI > KCl.$
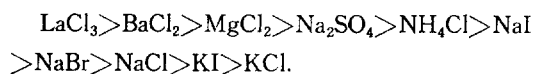
These results are quite satisfactory with the experiments.

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