

## Theoretical Calculation of Hydration Number and Activity Coefficients of Salts in Concentrated Electrolyte Solutions

by

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### 진한 전해질 용액 중에서 염의 수화수와 활성도 계수에 관한 이론적 연구

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#### ABSTRACT

The extension of the theory of the electrolyte solution to the calculation of the hydration number and the mean activity coefficient of some 1 : 1 electrolytes in the concentrated solutions has been made.

In this derivation, the hydration number has been calculated from the equation of the dielectric constant proposed by Hobbs, Jhon, and Eyring, and the mean activity coefficient from the theoretical formula developed by Jhon and Eyring.

The agreement between theory and experiment over a wide concentration range is quite satisfactory.

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#### INTRODUCTION

The theory of the activity coefficients of salts in solutions was developed by Debye & Hückel(1) and extended by Bjerrum(2) Guggenheim(3) Davies(4) and Fuoss &

Onsager(5).

Recently, Samoilov(6) studied theoretically the hydration of ions in aqueous solutions and Khomutov(7) calculated the mean activity coefficients of salts by a semiempirical formula using the second approximation of the Debye-Hückel

theory and the simple electrostatic theory of solvation proposed by Born.

In this paper, we propose a equation of dielectric constant for obtaining the hydration number of salts, and calculate the mean activity coefficients of salts in the concentrated electrolyte solutions from the theoretical formula which is based on the statistical thermodynamical considerations.

## THEORY

### A) Hydration Number

According to the domain theory of the dielectric constant of H-bonded liquids proposed by Hobbs, Jhon, and Eyring(8) the dielectric constant of water is given by

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{3\epsilon} = 4\pi \frac{N}{V} \left( \frac{n^2 + 2}{3} \right)^2 \left( \frac{V_s}{V} \cdot \frac{\mu^2 \cos^2 \theta}{kT} + \frac{V - V_s}{V} \cdot \frac{\mu^2}{3kT} \right) \quad (1)$$

Here  $n$  is the refractive index appropriate to electronic and atomic polarizability,  $\epsilon$  is dielectric constant,  $N$  is Avogadro's number,  $V_s$  is the molar volume of the solid,  $V$  is the molar volume of the liquid at temperature  $T$ ,  $k$  is the Boltzmann constant, and  $\mu$  the value of the permanent dipole moment characteristic of the isolated molecule.

This theory is successfully extended to mixtures(9)

Now, we apply the Eq(1) to the electrolyte solutions.

When the solute (salts) are dissolved into water, the dielectric constants of solutions are decreased.

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

Salt hydration in solution has become considered as a combination of a certain number of water molecules with the salts, and, for each salt, has been described in terms of a so-called hydration number.

The number of moles of hydrated water per each mole of solute in solution is  $\frac{m'}{55.51} \sum_{i=1}^i \frac{K_i}{1+K_i} n_i$ , in which  $n_i$  is the number of site of the ion of  $i$ -th kind and  $K_i$  is the equilibrium constant between water adsorbed on site produced by the ion of  $i$ -th kind and free water.

For the derivation of the dielectric constant of the electrolyte solutions, we assume that the fraction of the hydrated water in solution is not contributed to the orientation polarizability calculation since these small islands with an ion are difficult to rotate to the field direction.

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

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

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{3\epsilon} = 4\pi N \frac{\rho \left( 1 - \frac{m'M}{1000 + m'M} \right)}{18.016} \left( \frac{n^2 + 2}{3} \right)^2 \left( \frac{V_s}{V} \cdot \frac{\mu^2 \cos^2 \theta}{kT} + \frac{V - V_s}{V} \cdot \frac{\mu^2}{3kT} \right) \left( 1 - \frac{m'}{55.51} \sum_{i=1}^i \frac{K_i}{1+K_i} n_i \right) \dots \dots \dots (2)$$

where  $M$  is gram molecular weight of salt,  $\sum_{i=1}^2 \frac{K_i}{1+K_i} n_i$  is the hydration number,  $\rho$  is the density of the solution, and  $m'$  is molality, respectively.

**B) Activity Coefficient**

From statistical theories, the concentration dependence of the activity coefficients of electrolytes is accordance with experimental results only in dilute solution.

And the agreement between experimental and theoretical activity coefficients is only for certain uni-univalent electrolytes observed up to concentration 0.1-0.5M (10).

The author propose a method of allowing for the influence of salt hydration on activity coefficients by introducing into the statistical mechanical equations.

The energy effects caused by the electrostatic interaction of salts and by their hydration are considered independently.

The former effect is taken into account by the theoretical term derived by Jhon and Eyring (11) from the Debye-Hückel theory.

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

In conformity with the proposed method of allowing for the two types of interaction, the chemical potential  $\mu_i$  of the salt in solution at a mole fraction  $N_i$  can be expressed as follows:

$$\mu_i = \mu_i^\circ + RT \ln N_i f_i \dots\dots\dots(3)$$

The mean activity coefficient,  $f_i$ , of salts is

$$f_i = f_{D-H} \cdot f_{hy} \dots\dots\dots(4)$$

The first term is given by Eq. (20) in Appendix,

$$f_{D-H} = \text{Exp} \left\{ \frac{V}{8\pi} \left[ \frac{1}{(1+a\kappa)} \left( \kappa^3 - \frac{1}{a^3} \right) + \frac{1}{a^3} (1+a\kappa) - \frac{2}{a^3} \ln(1+a\kappa) \right] \right\} \dots\dots\dots 5$$

The second hydration term is formulated as follows:

$$f(S \cdot H_2O + H_2O) = f_{H_2O}(K_1) \frac{K_1}{1+K_1} \dots\dots\dots(6)$$

$$f(S \cdot H_2O + H_2O) = f_{H_2O}(K_2) \frac{K_2}{1+K_2} \dots\dots\dots(7)$$

Where  $K_1$  is the equilibrium constant between water adsorbed on site produced by cation and free water and  $K_2$  is the equilibrium constant between water adsorbed on site produced by anion and free water.

If we assume that  $n_1$  and  $K_1$  are equal to  $n_2$  and  $K_2$  respectively, the hydration term of hydrated water on the average is given by

$$f_{hy} = (K_i) \frac{K_i}{1+K_i} 2n_i m' \dots\dots\dots(8)$$

in which  $K_i$  is the equilibrium constant between water adsorbed on site produced by salt and free water.

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

$$f_i = \left\{ (K_i) \frac{K_i}{1+K_i} 2n_i m' \right\} \cdot \text{exp} \left\{ \frac{V}{8\pi} \left( \frac{1}{(1+a\kappa)} \left( \kappa^3 - \frac{1}{a^3} \right) + \frac{1}{a^3} (1+a\kappa) - \frac{2}{a^3} \ln(1+a\kappa) \right) \right\} \dots\dots\dots(9)$$

**CALCULATIONS AND RESULTS**

**A) Hydration Number**

For convenience in actual calculations,

the Eq. (2) may be rearranged to give

$$\sum_{i=1}^z \frac{K_i}{1+K_i} n_i = \frac{55.51}{m'} \left[ 1 - \frac{(\epsilon - n^2)(2\epsilon + n^2)}{3\epsilon} \right. \\ \left. \left\{ 4\pi N \frac{\rho \left( 1 - \frac{m'M}{1000 + m'M} \right)}{18.016} \cdot \left( \frac{n^2 + 2}{3} \right)^2 \right. \right. \\ \left. \left. \left( \frac{V_s}{V} \cdot \frac{\mu^2 \cos^2 \theta}{kT} + \frac{V - V_s}{V} \cdot \frac{\mu^2}{3kT} \right) \right\} \right] \quad (10)$$

Putting the known values of  $\epsilon$  (12, 13)  $n^2$  (14),  $\rho$  (14, 15, 16) for electrolyte solutions and  $V_s$ ,  $V_{H_2O}$  (17) for water at a given temperature and molality into Eq.

(10), we obtain the values of  $\sum_{i=1}^z \frac{K_i}{1+K_i} n_i$ , the hydration number of the salts in solutions.

In the calculation  $\cos^2 \theta$  is taken as 0.964(8) and  $\mu$  as 1.83 debye (18).

The results obtained are compared in Table 1 with the experimental values by Robinson's (19), Miller's (20), and Wada's methods (21).

TABLE 1. The Comparison of the Hydration Numbers.

Salt	Calcd	Robinson's (19)	Miller's (20)	Wada's (21)
LiCl	8.92	6.5	12.3	12.0
NaCl	7.08	3.5	7.3	6.7
NaBr	7.43	4.15	8.2	7.7
NaI	7.71	5.05	8.9	9.1
KCl	5.60	1.9	4.2	4.2
KI	6.05	2.45	5.1	4.8
RbCl	4.89	1.2	3.5	4.0

## B) Activity Coefficient

The mean activity coefficients of elect-

rolyte solutions have been calculated by means of Eq. (9) for concentrations of 0.1-4M sodium chloride and 0.1-2M with the other halides.

In the calculation, we have to determine the values of  $\kappa$ , Debye-Hückel parameter and  $a$ , the ionic radii of hydrated salt.

In order to determine the value of  $\kappa$ , we used the equation described in the Ref. (22),

*i. e.*

$$\kappa = \frac{50.29}{(\epsilon T)^{1/2}} I^{1/2} \text{ \AA}^{-1}, \text{ where } I = \frac{1}{2} \sum m_i Z_i^2.$$

And we assumed that the ionic radii of hydrated salts are given as

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

Putting the values of  $\sum_{i=1}^z \frac{K_i}{1+K_i} n_i$  and the known values of  $V_{salt}$  (23, 24) and  $V_{H_2O}$  (17), we obtain the value of  $a$ . And we determined the value of  $K_i$  from the number of hydration. Thus, we have

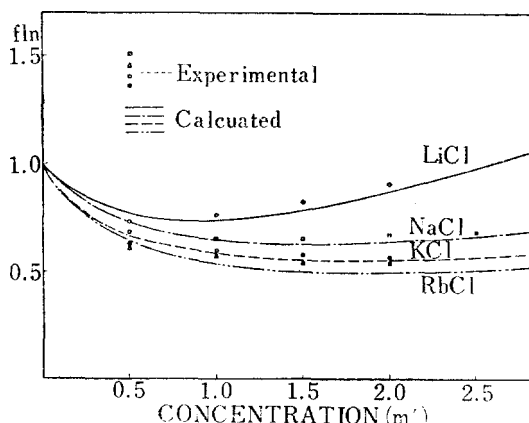


Fig. 1. Activity coefficients of alkali metal chlorides at various concentration; experimental data from ref. (19)

calculated the mean activity coefficient of salts in concentrated electrolyte solutions.

The calculated mean activity coefficients are compared with experimental values (19) in Fig. 1 and 2.

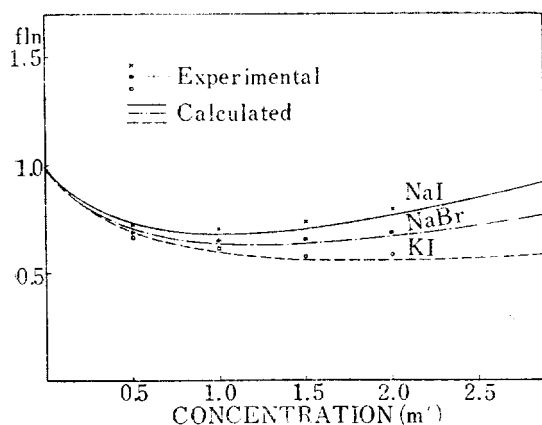


Fig. 2. Activity coefficients of alkali metal bromide and iodides at various concentration; experimental data from ref. (19).

## DISCUSSION

The above results for hydration number and activity coefficients of salts in concentrated electrolyte solutions provide the validity of Samoilov's (6) and Hückel's view (25) that concentration dependence of  $\epsilon$  must be taken into account.

Combining the completed Debye-Hückel term proposed by Jhon and Eyring (11) with the electrostatic theory of ionic hydration, we are able to deduce a formula (9) for the dependence of ionic activity coefficients on ionic strength, dielectric constant, and ionic radii in solution.

Mean activity coefficients calculated from the theory proposed by authors agree with

experimental values for sodium chloride over the concentration range 0.1-4M and for 0.1-2M LiCl, NaBr, NaI, KCl, KI, and RbCl.

And the significant deviation for the activity coefficient of LiCl in solution between theory and experiment may be explained as the remarkable difference between the size of the hydrated cation and that of the hydrated anion.

Both two effects of the electrostatic interaction and the ionic hydration are independently contributed to the activity coefficients of the salts.

From the Table I, we can correlate the values of the hydration number of salts one another-i. e., the size of the hydrated ionic radii of salts is  $\text{LiCl} > \text{NaI} > \text{NaBr} > \text{NaCl} > \text{KI} > \text{KCl} > \text{RbCl}$ , more precisely,  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$  and  $\text{Cl}^- \approx \text{Br}^- \approx \text{I}^-$ .

And our results obtained from Eq. (10) of the dielectric constant of electrolyte solution are quite satisfactory compared with experimental results.

For further test of the validity of this approach, consideration should be given to 1:2 and 2:2 salt systems in aqueous solutions, if the experimental data of dielectric constants for such a system are provided.

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## APPENDIX

**Derivation of Helmholtz Free Energy Term from Debye-Hückel's theory**

Gibb's Free Energy is written as

$$\begin{aligned} \frac{G}{kT} &= \frac{1}{kT} \sum_i N_i \mu_i \dots\dots\dots(1) \\ &= \frac{1}{kT} \sum_i N_i kT (l_n A_i^3 + l_n \rho_i + l_n r_i) \\ &= \sum_i N_i l_n A_i^3 \rho_i + \sum_i N_i l_n r_i \\ &= \sum_i N_i l_n A_i^3 \rho_i + \sum_i \left( -\frac{N_i Z_i^2 e^2 \kappa}{2\epsilon kT(1+a\kappa)} \right) \dots\dots\dots(2) \end{aligned}$$

Where

$$\kappa^2 = \frac{4\pi e^2}{\epsilon kT} \sum_i \rho_i Z_i^2 \dots\dots\dots(3)$$

Hence,

$$\begin{aligned} \sum_i \left( -\frac{N_i Z_i^2 e^2 \kappa}{2\epsilon kT(1+a\kappa)} \right) \\ &= -\frac{e^2 \kappa}{2\epsilon kT(1+a\kappa)} \sum_i N_i Z_i^2 \\ &= -\frac{4\pi e^2 \kappa V}{8\pi \epsilon kT(1+a\kappa)} \sum_i \rho_i Z_i^2 \\ &= -\frac{\kappa^3 V}{8\pi(1+a\kappa)} \dots\dots\dots(4) \end{aligned}$$

Therefore,

$$\frac{G}{kT} = \sum_i N_i l_n A_i^3 \rho_i - \frac{\kappa^3 V}{8\pi(1+a\kappa)} \dots\dots\dots(5)$$

And

$$\begin{aligned} V \left( \frac{\partial P}{\partial V} \right)_{N,T} &= \left( \frac{\partial G}{\partial V} \right)_{N,T} \\ &= -\frac{kT}{V} \sum_i N_i - kT \left\{ \frac{\kappa^3}{8\pi(1+a\kappa)} \right. \\ &\quad \left. + \frac{3V\kappa^2}{8\pi(1+a\kappa)} \left( \frac{\partial \kappa}{\partial V} \right)_{N,T} \right. \\ &\quad \left. + \frac{aV\kappa^3}{8\pi(1+a\kappa)^2} \left( \frac{\partial \kappa}{\partial V} \right)_{N,T} \right\} \dots\dots\dots(6) \end{aligned}$$

$$\begin{aligned} \partial \kappa \left( \frac{\partial \kappa}{\partial V} \right)_{N,T} &= \frac{4\pi e^2}{\epsilon kT} \sum_i \left( -\frac{N_i Z_i^2}{V^2} \right) \\ &= -\frac{\kappa^2}{V} \dots\dots\dots(7) \end{aligned}$$

$$\left( \frac{\partial \kappa}{\partial V} \right)_{N,T} = -\frac{\kappa}{2V} \dots\dots\dots(8)$$

Therefore,

$$\begin{aligned} V \left( \frac{\partial P}{\partial V} \right)_{N,T} &= -\frac{kT}{V} \sum_i N_i - \frac{\kappa^3 kT}{8\pi(1+a\kappa)} \\ &\quad \left( 1 - \frac{3}{2} + \frac{a\kappa}{2(1+a\kappa)} \right) \dots\dots\dots(9) \\ &= -\frac{kT}{V} \sum_i N_i - \frac{\kappa^3 kT}{8\pi(1+a\kappa)} \\ &\quad \left( -\frac{1}{2} + \frac{a\kappa}{2(1+a\kappa)} \right) \end{aligned}$$

$$= -\frac{kT}{V} \sum_i N_i + \frac{\kappa^3 kT}{16\pi(1+a\kappa)^2} \dots\dots\dots(10)$$

Multiply above equation by  $dV/V$  and integrate from  $p$  to 0, and  $V$  to  $\infty$ , keep  $N, T = \text{constant}$ ,

$$\begin{aligned} \int_P^0 dp &= \int_V^\infty -\frac{kT}{V^2} dV \sum_i N_i \\ &\quad + \int_V^\infty \frac{\kappa^3 kT}{16\pi(1+a\kappa)^2 V} dV \dots\dots\dots(11) \end{aligned}$$

$$\frac{P}{kT} = \sum_i \rho_i + \int_V^\infty \frac{\kappa^3}{16\pi(1+a\kappa)^2 V} dV \dots\dots\dots(12)$$

$$\kappa^2 = \frac{\kappa'^2}{V}, \quad V = \frac{\kappa'^2}{\kappa^2} \dots\dots\dots(13)$$

$$dV = -\frac{2\kappa'^2}{\kappa^3} d\kappa$$

 $\kappa = 0$ , as  $V = \infty$ 

Therefore,

$$\begin{aligned} \frac{P}{kT} &= \sum_i \rho_i + \int_\kappa^0 \frac{\kappa^3}{16\pi(1+a\kappa)^2 \cdot \frac{\kappa'^2}{\kappa^2}} \\ &\quad \left( -\frac{2\kappa'^2}{\kappa^3} d\kappa \right) \dots\dots\dots(14) \\ &= \sum_i \rho_i + \int_\kappa^0 -\frac{\kappa^2}{8\pi(1+a\kappa)^2} d\kappa \\ &= \sum_i \rho_i - \frac{1}{8\pi} \left\{ \frac{1}{a^3} (1+a\kappa - 2l_n(1+a\kappa)) \right. \end{aligned}$$

$$\begin{aligned}
 & \left. - \frac{1}{1+a\kappa} \right\}^0 \\
 & = \sum_i \rho_i + \frac{1}{8\pi a^3} \left( 1+a - \kappa 2l_n(1+a\kappa) \right. \\
 & \quad \left. - \frac{1}{(1+a\kappa)} \right) \dots \dots \dots (15)
 \end{aligned}$$

Helmholtz Free Enrgy is

$$\frac{A}{kT} = \frac{G}{kT} - \frac{PV}{kT} \dots \dots \dots (16)$$

$$\begin{aligned}
 & = \sum_i N_i l_n A_i^3 \rho_i - \frac{\kappa^3 V}{8\pi(1+a\kappa)} - \sum_i \rho_i V \\
 & \quad - \frac{V}{8\pi a^3} \left( 1+a\kappa - 2l_n(1 \right. \\
 & \quad \left. + a\kappa) - \frac{1}{(1+a\kappa)} \right) \\
 & = \sum_i N_i \left( l_n A_i^3 \rho_i - 1 \right) - \frac{\kappa^3 V}{8\pi(1+a\kappa)} \\
 & \quad - \frac{V}{8\pi a^3} \left( 1+a\kappa - 2l_n(1 \right. \\
 & \quad \left. + a\kappa) - \frac{1}{(1+a\kappa)} \right) \\
 & \dots \dots \dots (17)
 \end{aligned}$$

$$\begin{aligned}
 \frac{A}{kT} & = \sum_i N_i l_n \left( \frac{A_i^3 \rho_i}{e} \right) \\
 & \quad - \frac{V}{8\pi} \left\{ \frac{\kappa^3}{(1+a\kappa)} + \frac{1}{a^3} + \frac{\kappa}{a^2} \right. \\
 & \quad \left. - \frac{2}{a^3} l_n(1+a\kappa) - \frac{1}{(1+a\kappa)} \right\} \dots (18)
 \end{aligned}$$

Then, the extra term due to Debye-Hückel's theory is

$$\begin{aligned}
 \frac{A_{D-H}}{kT} & = - \frac{V}{8\pi} \left\{ \frac{\kappa^3}{1+a\kappa} + \frac{1}{a^3} + \frac{\kappa}{a^2} \right. \\
 & \quad \left. - \frac{2}{a^3} l_n(1+a\kappa) - \frac{1}{a^3(1+a\kappa)} \right\} \\
 & \dots \dots \dots (19)
 \end{aligned}$$

And the partition function for the term from Debye-Hückel's theory is

$$\begin{aligned}
 f_{D-H} & = \text{Exp} \left\{ \frac{V}{8\pi} \left[ \left( \frac{1}{1+a\kappa} \right) \left( \kappa^3 - \frac{1}{a^3} \right) \right. \right. \\
 & \quad \left. \left. + \frac{1}{a^3}(1+a\kappa) - \frac{2}{a^3} l_n(1+a\kappa) \right] \right\} (20)
 \end{aligned}$$

where  $a$  is the ionic radii.

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