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A Theory of Ion Association as a Complement of the Debye-Hückel Theory*

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The classical Debye-Hückel theory of strong electrolyte solutions was re-examined in order to explain ion association. Regarding a symmetrical electrolyte in very dilute solutions, a more precise expression was derived for excess chemical potential due to electrostatic ion-ion interactions. This expression has, in addition to the Debye-Hückel term, a supplementary term resulting from a more proper account of the energy of the interactions of ions existing near each other. If the concept of ion association is taken as a complement of the Debye-Hückel theory, the contribution to the chemical potential of the electrolyte from ion association should correspond to the supplementary term. The following equation was thus obtained for the ion-association constant:

$$K=(8\pi Na^3/1000)\sum_{n=1}^{\infty} b^{2n+2}/[(2n+2)!\ (2n-1)]$$

This equation is in agreement with that derived by Ebeling on the basis of the cluster theory and has an asymptotic representation (at $b\rightarrow\infty$) in common with Bjerrum's. For practical b values, the present equation has the merit that it gives moderate K values, decreasing monotonously with an increase in the a value, and eliminates the disadvantages of Fuoss's result, giving a minimum K value at $b=3$, and of Bjerrum's, giving $K=0$ at $b\leqq 2$.

Debye and Hückel[1)] have been successful in explaining the behavior of ions in dilute solutions of strong 1 : 1 electrolytes. For polyvalent ions, however, their theory was not satisfying, and the theoretical prediction evidently deviates from the experimental results even for dilute solutions.

Gronwall, LaMer, and Sandved[2)] made an attempt to improve the Debye-Hückel theory by solving the Poisson-Boltzmann equation more accurately. However, the accurate solutions obtained by them and by other authors[3)] were found to lack self-consistency.[4,5)]

On the other hand, Bjerrum[6)] introduced the concept of so-called ion association to explain the deviation of the experimental results from the Debye-Hückel theory. Thereafter, many other theories of ion association have been proposed by Denison and Ramsey,[7)] Gilkerson,[8)] Fuoss,[9)] Ebeling,[10)] and other authors.[11)] These theories of ion association, with the probable exception of Ebeling's theory, have been based on specific models of the ion-pair.

Although evidence can be given for the formation of ion-pairs in solution, the geometrical configurations of the ion-pairs can hardly be specified. There may be solvent-separated ion-pairs in addition to contact ion-pairs.[12)] If, as in Bjerrum's theory, all pairs of oppositely charged ions within a certain critical distance of each other are regarded as ion-pairs, some arbitrariness will be involved in the choice of the critical distance. Moreover, there seems to be a chance that fast-moving unassociated ions momentarily exist within the critical distance of each other. Thus, no geometrical models of the ion-pairs can be free from arbitrariness.

In our opinion, a theory of ion-association dealing with ion-pairs must be complementary to the theory describing the behavior of free ions (usually, the Debye-Hückel theory). We therefore re-examined the Debye-Hückel theory to see what correction could be made to improve the theory. Then, relating the correction to ion association, we obtained a theoretical expression for the ion-association constant of symmetrical electrolytes. The expression includes no arbitrary parameters except for the one representing the closest distance of approach of ions, and incidentally, it is in agreement with the expression derived by Ebeling on the basis of the cluster theory.

We shall describe the derivation of the expression for ion-association constants and compare the results with those deduced by other authors.[6,7,9,10)]

Symbols

a	closest distance of approach of ions
b	Bjerrum's parameter [Eq. (14)]
c	concentration of electrolyte
e	elementary charge
k	Boltzmann's constant
n_i	number of i-type ions in V cm^3 of solution
q	$=z^2s/2$
r	distance from central ion
s	$=e^2/\varepsilon kT$
y	activity coefficient
z_i	charge number of i-type ion
z_j	charge number of central j-ion
z	absolute value of charge number of ions of symmetrical electrolytes
A	constant to be determined from condition of electrical neutrality [Eqs. (11) and (13)]
G^{el}	Gibbs free energy of electrostatic interactions between ions
K	ion-association constant
N	Avogadro's number
R	gas constant
T	absolute temperature
V	volume of solution
α	degree of association
γ	Euler's constant ($\gamma=0.5772\cdots$)
ε	dielectric constant of solvent
κ	reciprocal thickness of ionic atmosphere [Eq. (4)]
λ	charging parameter
μ	chemical potential per mole of electrolyte
μ^{el}	contribution of ion-ion interactions to μ
μ_i^{el}	contribution of ion-ion interactions to chemical potential of one i-type ion

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ρ charge density
ψ electrostatic potential due to all the ions
ψ^{cloud} electrostatic potential due to all the ions except central j-ion
A_{DH}, ρ_{DH}, ψ_{DH}, and $\psi_{\text{DH}}^{\text{cloud}}$
approximate expressions for A, ρ, ψ, and ψ^{cloud} respectively, under Debye-Hückel conditions

Boltzmann Distribution and Poisson Equation. In the following discussions, the solvent is considered to be a continuous medium of a dielectric constant, ε, and the ions to be rigid spheres. The ion-ion interactions are assumed to be purely electrostatic.

If a particular ion is selected as the center of a coordinate system, the Boltzmann distribution law gives the charge density, ρ, as a function of the radial coordinate, r:

$$\rho(r) = \sum_i \frac{n_i z_i e}{V} \exp\left(-\frac{z_i e\psi(r)}{kT}\right) \tag{1}$$

where n_i is the number of i-type ions in V cm^3 of the solution, $z_i e$ the charge of the i-type ions, and $\psi(r)$ the electrostatic potential. We shall use in the following the subscripts 1 and 2 to denote, respectively, the cation and the anion of a single electrolyte. For a symmetrical electrolyte:

$$n_1 = n_2 \quad \text{and} \quad z_1 = -z_2 = z(z>0)$$

With n_1 and z, Eq. (1) can be rewritten as follows:

$$\rho(r) = \frac{n_1 z e}{V}\left[\exp\left(-\frac{ze\psi(r)}{kT}\right) - \exp\left(\frac{ze\psi(r)}{kT}\right)\right] \tag{2}$$

By expanding the exponential functions in Eq. (2) and introducing the parameter κ (the reciprocal thickness of the ionic atmosphere), one obtains:

$$\rho(r) = -\frac{\varepsilon\kappa^2}{4\pi}\sum_{n=0}^{\infty}\frac{1}{(2n+1)!}\left(\frac{ze}{kT}\right)^{2n}[\psi(r)]^{2n+1} \tag{3}$$

The parameter κ is defined by the expression:

$$\kappa^2 = \frac{8\pi n_1 z^2 s}{V} \tag{4}$$

or by the general expression:

$$\kappa^2 = \frac{4\pi\sum_i n_i z_i^2 e^2}{V\varepsilon kT} = \frac{4\pi s\sum_i n_i z_i^2}{V} \tag{5}$$

where s is a parameter with the dimension of length** and is defined by:

$$s = \frac{e^2}{\varepsilon kT}$$

The potential, $\psi(r)$, and the charge density, $\rho(r)$, are related to each other by the Poisson equation:

$$\frac{1}{r^2}\cdot\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\psi(r)}{\mathrm{d}r}\right) = -\frac{4\pi\rho(r)}{\varepsilon}$$

Debye-Hückel Approximation. For a very dilute solution, Debye and Hückel[1)] simplified Eq. (3), ignoring the terms with $n \geqq 1$ under the condition of $|ze\psi(r)/kT| \ll 1$:

$$\rho(r) \simeq \rho_{\text{DH}}(r) = -\frac{\varepsilon\kappa^2}{4\pi}\psi_{\text{DH}}(r) \tag{6}$$

where the subscript DH indicates that the Debye-Hückel condition is assumed to be satisfied. Then they solved the Poisson equation and derived the expression:

$$\psi_{\text{DH}}(r) = A_{\text{DH}}\frac{\exp(-\kappa r)}{r} \tag{7}$$

The constant, A_{DH}, can be determined by means of the condition of electrical neutrality:

$$\int_a^{\infty} 4\pi r^2\rho(r)\mathrm{d}r = -z_j e \tag{8}$$

where $z_j e$ is the charge of the central j-ion and a is the closest distance of approach of ions. Equation (8) was solved with Eqs. (6) and (7) to give:

$$A_{\text{DH}} = \frac{z_j e\exp(\kappa a)}{\varepsilon(1+\kappa a)} \tag{9}$$

The potential, $\psi(r)$, is in general represented by the sum of the potential due to the j-ion, $z_j e/\varepsilon r$, and the potential due to all the other ions, $\psi^{\text{cloud}}(r)$. With the Debye-Hückel approximation,

$$\psi^{\text{cloud}}(r) \simeq \psi_{\text{DH}}^{\text{cloud}}(r) \left(=\psi_{\text{DH}}(r) - \frac{z_j e}{\varepsilon r}\right)$$
$$= \frac{z_j e}{\varepsilon r}\left[\frac{\exp(\kappa a - \kappa r)}{1+\kappa a} - 1\right]$$

Since the j-ion is present inside a cavity with a radius of a surrounded by an ionic cloud, the potential, $\psi^{\text{cloud}}(r)$, at the j-ion is given by the potential, $\psi^{\text{cloud}}(r)$, at $r=a$:

$$\psi^{\text{cloud}}(a) \simeq \psi_{\text{DH}}^{\text{cloud}}(a) = -\frac{z_j e\kappa}{\varepsilon(1+\kappa a)} \tag{10}$$

Contribution of the Ions Existing in the Vicinity of the j-ion to the Potential, $\psi^{\text{cloud}}(a)$. The contribution of the ions existing in the vicinity of the j-ion to the potentials, $\psi(r)$, $\psi^{\text{cloud}}(r)$, and $\psi^{\text{cloud}}(a)$, was ignored in the Debye-Hückel approximation. More exact expressions for these potentials including the ignored contribution can be derived by using a closer approximation to the original equation [Eq. (3)] for the charge distribution. In Eq. (3), the Debye-Hückel-type expression [a modification of Eq. (7)]:

$$\psi(r) = A\frac{\exp(-\kappa r)}{r} \tag{11}$$

can be used as an approximation to $\psi(r)$. A is a constant to be determined from the conditions of electrical neutrality. Since, for our purposes in this paper, we are primarily interested in the potential, $\psi^{\text{cloud}}(a)$, we shall describe below only the derivation of the potential, $\psi^{\text{cloud}}(a)$, of a closer approximation.

The time-averaged number of i-type ions in a unit volume at a certain distance, r, from the j-ion is given by the Boltzmann distribution law. Thus, their contribution to the potential at the j-ion can be expressed by:

$$\frac{1}{\varepsilon r}\cdot\frac{n_i z_i e}{V}\exp\left(-\frac{z_i e\psi(r)}{kT}\right)$$

The superposition of the contributions of the ions (except the j-ion) of all types in the whole space gives the potential at any one place within the distance

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** In an aqueous solution at 25.0 °C with $\varepsilon = 78.30_3$, s has a value of 7.157 Å.

$r \leqq a$ due to the ionic cloud, $\psi^{\mathrm{cloud}}(a)$:

$$\psi^{\mathrm{colud}}(a) = \int_a^\infty \frac{1}{\varepsilon r} \sum_i \left[\frac{n_i z_i e}{V} \exp\left(-\frac{z_i e \psi(r)}{kT} \right) \right] 4\pi r^2 \mathrm{d}r$$

or

$$\psi^{\mathrm{colud}}(a) = \frac{4\pi}{\varepsilon} \int_a^\infty r\rho(r) \mathrm{d}r$$

Using Eq. (11) for $\psi(r)$, one obtains:

$$\begin{aligned}\psi^{\mathrm{cloud}}(a) &= -\kappa^2 \sum_{n=0}^{\infty} \frac{1}{(2n+1)!} \left(\frac{ze}{kT} \right)^{2n} A^{2n+1} \\ &\quad \times \int_a^\infty \frac{\exp[-(2n+1)\kappa r]}{r^{2n}} \mathrm{d}r \\ &= -\kappa A \exp(-\kappa a) \\ &\quad - (\kappa a)^2 \sum_{n=1}^{\infty} \frac{\exp[-(2n+1)\kappa a]}{(2n+1)!(2n-1)a^{2n+1}} \left(\frac{ze}{kT} \right)^{2n} A^{2n+1} \\ &\quad + (\kappa a)^3(\cdots\cdots) + \cdots\cdots \end{aligned} \tag{12}$$

(For details of the calculation of the integral, see the footnote.***) The constant A in Eq. (12) is determined by the condition of electrical neutrality [Eq. (8)] as follows. The whole charge in all the volume outside the sphere of radius a is given by:

$$\begin{aligned}&\int_a^\infty 4\pi r^2 \rho(r) \mathrm{d}r \\ &= -\varepsilon\kappa^2 \sum_{n=0}^{\infty} \frac{1}{(2n+1)!} \left(\frac{ze}{kT} \right)^{2n} A^{2n+1} \int_a^\infty \frac{\exp[-(2n+1)\kappa r]}{r^{2n-1}} \mathrm{d}r \\ &= -\varepsilon(1+\kappa a) A \exp(-\kappa a) \\ &\quad - \varepsilon(\kappa a)^2 \left\{ -\frac{\ln(3\kappa a)+\gamma}{6a^2} \left(\frac{ze}{kT} \right)^2 A^3 \right. \\ &\quad \left. + \sum_{n=2}^{\infty} \frac{\exp[-(2n+1)\kappa a]}{(2n+1)!\,(2n-2)a^{2n}} \left(\frac{ze}{kT} \right)^{2n} A^{2n+1} \right\} \\ &\quad + (\kappa a)^3 (\cdots\cdots) + \cdots\cdots \end{aligned}$$

where γ is Euler's constant ($\gamma = 0.5772\cdots$.) Since this charge must be equal to $-z_j e$, the constant A becomes:

$$\begin{aligned} A = \frac{z_j e \exp(\kappa a)}{\varepsilon(1+\kappa a)} &\left\{ 1 - (\kappa a)^2 \left[-\frac{\ln(3\kappa a)+\gamma}{6} b^2 \left(\frac{z_j}{z} \right)^2 \right. \right. \\ &\left. \left. + \sum_{n=2}^{\infty} \frac{b^{2n}(z_j/z)^{2n}}{(2n+2)!\,(2n-1)} \right] \right\} \end{aligned} \tag{13}$$

where the $(\kappa a)^3$ and higher-order terms are disregarded. b is Bjerrum's parameter and is defined by:

$$b = \frac{|z_1 z_2| s}{a} = \frac{|z_1 z_2| e^2}{\varepsilon k T a} \tag{14}$$

or, for a symmetrical electrolyte,

$$b = \frac{z^2 s}{a} \tag{15}$$

By substituting Eq. (13) into Eq. (12) and by disregarding the $(\kappa a)^3$ and higher-order terms, one obtains:

$$\psi^{\mathrm{Cloud}}(a) = -\frac{z_j e \kappa}{\varepsilon(1+\kappa a)} - (\kappa a)^2 \frac{z_j e}{\varepsilon a} \sum_{n=1}^{\infty} \frac{b^{2n}(z_j/z)^{2n}}{(2n+1)!\,(2n-1)} \tag{16}^\dagger$$

The second term on the right-hand side has been added as the first correction term to the Debye-Hückel expression [Eq. (10)].

The Gibbs Free Energy of the Electrostatic Interactions between Ions, G^{el}. According to the Debye charging process,[1] G^{el} can be evaluated as the electric work of charging up all the ions simultaneously from zero to their actual values at the same relative rate:[4,5]

$$G^{\mathrm{el}} = \int_0^1 \sum_j z_j e \psi^{\mathrm{cloud}}(a, \lambda z, \lambda\kappa) \mathrm{d}\lambda \tag{17}$$

where the summation is made over all the ions in V cm^3 of the solution, λ denotes the fraction of their final charges which the ions have at any stage of the integration, and $\psi^{\mathrm{cloud}}(a, \lambda z, \lambda\kappa)$ is given by:

$$\begin{aligned}\psi^{\mathrm{cloud}}(a, \lambda z, \lambda\kappa) &= -\frac{\lambda z_j e \lambda\kappa}{\varepsilon(1+\lambda\kappa a)} \\ &\quad - (\lambda\kappa a)^2 \frac{\lambda z_j e}{\varepsilon a} \sum_{n=1}^{\infty} \frac{(\lambda^2 b)^{2n}}{(2n+1)!\,(2n-1)} \end{aligned}$$

This expression is obtained by substituting $\lambda z_j e$ and λze for $z_j e$ and ze respectively in Eq. (16). Then the right-hand side of Eq. (17) can be calculated as follows:

$$\begin{aligned} G^{\mathrm{el}} &= -\frac{\sum_j z_j^2 e^2 \kappa}{\varepsilon} \int_0^1 \frac{\lambda^2}{1+\lambda\kappa a} \mathrm{d}\lambda \\ &\quad - \frac{\sum_j z_j^2 e^2}{\varepsilon a} (\kappa a)^2 \sum_{n=1}^{\infty} \frac{b^{2n}}{(2n+1)!\,(2n-1)} \int_0^1 \lambda^{4n+3} \mathrm{d}\lambda \\ &= -\frac{\sum_i n_i z_i^2 e^2}{3\varepsilon} \kappa\tau(\kappa a) \\ &\quad - \frac{\sum_i n_i z_i^2 e^2}{2\varepsilon a} (\kappa a)^2 \sum_{n=1}^{\infty} \frac{b^{2n}}{(2n+2)!\,(2n-1)} \end{aligned} \tag{18}$$

where

$$\tau(x) = \frac{3}{x^3} \left[\ln(1+x) - x + \frac{1}{2} x^2 \right]$$

The relation, $\sum_j z_j^2 e^2 = \sum_i n_i z_i^2 e^2$ (where i denotes the type of ion), is used in the last step of the calculation.

Contribution of Ion-Ion Interactions to the Chemical Potential of an Ion of Type i, μ_i^{el}. We have two ways for the derivation of μ_i^{el} as follows:

A) Derivation of μ_i^{el} from G^{el} (According to the Debye Charging Process). μ_i^{el} can be defined by the equation:

$$\mu_i^{\mathrm{el}} = \frac{\partial G^{\mathrm{el}}}{\partial n_i} \tag{19}$$

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$$\begin{aligned} -\int_a^\infty \frac{\exp[-(2n+1)\kappa r]}{r} \mathrm{d}r &= \ln[(2n+1)\kappa a] + \gamma \\ &\quad - (2n+1)\kappa a + \frac{[(2n+1)\kappa a]^2}{2 \cdot 2!} - \cdots\cdots \\ &\quad \cdots\cdots + \frac{[-(2n+1)\kappa a]^p}{p \cdot p!} + \cdots\cdots \end{aligned}$$

$$\begin{aligned} \int_a^\infty \frac{\exp[-(2n+1)\kappa r]}{r^m} \mathrm{d}r &= \frac{\exp[-(2n+1)\kappa a]}{(m-1)a^{m-1}} \\ &\quad \times \left\{ 1 + \frac{-(2n+1)\kappa a}{(m-2)} + \frac{[-(2n+1)\kappa a]^{m-2}}{(m-2)!} \right\} \\ &\quad + \frac{[-(2n+1)\kappa a]^{m-1}}{(m-1)!\,a^{m-1}} \int_a^\infty \frac{\exp[-(2n+1)\kappa r]}{r} \mathrm{d}r \end{aligned}$$

(when $m \geqq 2$)

† The $(\kappa a)^2$ term in Eq. (13) contributes only to the $(\kappa a)^3$ and higher-order terms, which are ignored in Eq. (16); therefore, the use of A_{DH} [Eq. (9)] instead of A [Eq. (13)] leads to the same result.

Using Eq. (18) and Eq. (5), Eq. (19) becomes:

$$\begin{aligned}\mu_i^{\rm el} = &-\frac{z_i^2e^2\kappa}{2\varepsilon(1+\kappa a)} - kT(\kappa a)^2\sum_{n=1}^{\infty}\frac{b^{2n+1}}{(2n+2)!\,(2n-1)}\\ &+\frac{kT(\partial V/\partial n_i)}{24\pi a^3}(\kappa a)^3\sigma(\kappa a)\\ &+\frac{kT(\partial V/\partial n_i)}{8\pi a^3}(\kappa a)^4\sum_{n=1}^{\infty}\frac{b^{2n}}{(2n+2)!\,(2n-1)}\end{aligned} \qquad (20)$$

where

$$\begin{aligned}\sigma(x) &= \frac{3}{x^3}\left[-2\ln(1+x)+(1+x)-\frac{1}{1+x}\right]\\ &= 1-3\cdot\frac{2}{4}x+3\cdot\frac{3}{5}x^2-3\cdot\frac{4}{6}x^3+3\cdot\frac{5}{7}x^4-\cdots\end{aligned}$$

The Debye-Hückel approximation corresponds to the first and third terms on the right-hand side of Eq. (20).[4,5] For a very dilute solution, the second term is more important than the third term.

B) Direct Derivation of $\mu_i^{\rm el}$ *(According to the Güntelberg Charging Process).* $\mu_i^{\rm el}$ is the electrostatic work done when a single ion of the i type is added to an assembly consisting of the rest of the ions and the solvent. If we disregard the work due to the volume change $(\partial V/\partial n_i)$, which is negligibly small compared with the other electric work in dilute solutions, $\mu_i^{\rm el}$ can be evaluated as the electric work of increasing the charge of the particular ion from zero to z_ie in the solution.[4,5] Thus, according to Güntelberg, one has:

$$\mu_i^{\rm el} = \int_0^1 z_ie\psi^{\rm cloud}(a,\ \lambda z_i)\,{\rm d}\lambda \qquad (21)$$

where $\psi^{\rm cloud}(a,\ \lambda z_i)$ is given by Eq. (16), with the substitution of λz_i for z_j:

$$\begin{aligned}\psi^{\rm cloud}(a,\ \lambda z_i) = &-\frac{\lambda z_ie\kappa}{\varepsilon(1+\kappa a)}\\ &-(\kappa a)^2\frac{\lambda z_ie}{\varepsilon a}\sum_{n=1}^{\infty}\frac{\lambda^{2n}b^{2n}}{(2n+1)!\,(2n-1)}\end{aligned}$$

By integration, Eq. (21) becomes:

$$\mu_i^{\rm el} = -\frac{z_i^2e^2\kappa}{2\varepsilon(1+\kappa a)} - kT(\kappa a)^2\sum_{n=1}^{\infty}\frac{b^{2n+1}}{(2n+2)!\,(2n-1)} \qquad (22)$$

This equation can also be derived from the Debye charging process, if $(\partial V/\partial n_i)$ is so small or if the solution is so dilute that the $(\kappa a)^3$ and $(\kappa a)^4$ terms can be ignored [see Eq. (20)].

A more involved expression for $\mu_i^{\rm el}$ was derived by Gronwall *et al.*[2] from a more accurate solution of the Poisson-Boltzmann equation. However, these authors' expression has disadvantages in that it is too complicated to be applied to actual systems and involves the inconsistency that the two charging processes give different expressions for $\mu_i^{\rm el}$.[4,5] This inconcistency can be avoided only for very dilute solutions, where the correction terms derived by these authors can in practice be expressed by the first two terms of the progression in Eq. (22). Kaneko[3] made another correction to the Debye-Hückel theory. Although his expression for $\mu_i^{\rm el}$ involves the same kind of problem as mentioned above, his expression is consistent with Eq. (22) for very dilute solutions. By advancing the approximation, we might obtain a more accurate result for solutions of moderate concentration, but the difficulties encountered by Gronwall *et al.* and Kaneko will remain. Therefore, no further efforts will be made to derive an expression for the $\mu_i^{\rm el}$ of a closer approximation than Eq. (22). Although Eq. (22) in itself is valid only for solutions of sufficiently low concentrations, an attempt will be made to extend the application of Eq. (22) up to higher concentrations by connecting it with the concept of ion association.

Concept of Ion Association and the Derivation of the Ion-Association Constant. It is a common practice to attribute deviations from the Debye-Hückel theory to ion association. The ion-association equilibrium for a symmetrical electrolyte is expressed by:

$$\begin{array}{lccccc} & \rm M & + & \rm A & \rightleftarrows & \rm MA\\ \text{concentration} & c(1-\alpha) & & c(1-\alpha) & & c\alpha\end{array} \qquad (23)$$

where c denotes the concentration of the electrolyte and α the degree of association. When the ion-association equilibrium is assumed, the cation, M, and the anion, A, are usually considered to be free ions in the sense that they behave as predicted by the Debye-Hückel theory. The activity coefficients, $y_{\rm M}$ and $y_{\rm A}$, of the ions, M and A, respectively are given by:

$$\ln y_{\rm M} = \ln y_{\rm A} = -\frac{z^2e^2\kappa}{2\varepsilon kT(1+\kappa a)} \qquad (24)$$

Now, the chemical potential μ of the electrolyte is:

$$\begin{aligned}\mu = \mu_{\rm M}^0 + \mu_{\rm A}^0 + 2RT\ln c + RT\ln(y_{\rm M}y_{\rm A})\\ + 2RT\ln(1-\alpha)\end{aligned} \qquad (25)$$

where $\mu_{\rm M}^0$ and $\mu_{\rm A}^0$ represent the chemical potentials of the two ionic species, M and A, respectively in the standard state. The contribution of ion-ion interactions to the chemical potential of the electrolyte, $\mu^{\rm el}$, is equal to the last two terms of Eq. (25). Using Eq. (24) and considering $\alpha \ll 1$ in very dilute solutions, one obtains:

$$\begin{aligned}\mu^{\rm el} &= RT\ln(y_{\rm M}y_{\rm A}) + 2RT\ln(1-\alpha)\\ &\simeq -\frac{Nz^2e^2\kappa}{\varepsilon(1+\kappa a)} - 2RT\alpha\end{aligned} \qquad (26)$$

where N is the Avogadro number.

Since $\mu_i^{\rm el}$ given by Eq. (22) is the contribution of ion-ion interactions to the chemical potential of an ion of the i type, $\mu_i^{\rm el}$ multiplied by the total number of ions, $2N$, gives $\mu^{\rm el}$:

$$\begin{aligned}\mu^{\rm el} &= 2N\mu_i^{\rm el}\\ &= -\frac{Nz^2e^2\kappa}{\varepsilon(1+\kappa a)} - 2RT(\kappa a)^2\sum_{n=1}^{\infty}\frac{b^{2n+1}}{(2n+2)!\,(2n-1)}\end{aligned} \qquad (27)$$

A comparison of Eqs. (26) and (27) leads to:

$$\alpha = (\kappa a)^2\sum_{n=1}^{\infty}\frac{b^{2n+1}}{(2n+2)!\,(2n-1)} \qquad (28)$$

The equilibrium constant, K, of the ion-association reaction [Eq. (23)] is given by:

$$K = \frac{\alpha y_{\rm MA}}{c(1-\alpha)^2y_{\rm M}y_{\rm A}} \qquad (29)$$

where $y_{\rm MA}$ is the activity coefficient of the ion-pair MA. In very dilute solutions, Eq. (29) can be written as:

Table 1. Values of the sum $\sum_{n=1}^{\infty}\frac{b^{2n+2}}{(2n+2)!\,(2n-1)}$ (abbreviated to $\sum$) and its limiting expression $\frac{\exp(b)}{2b}$

b	$\log \sum$	$\log \frac{\exp(b)}{2b}$	b	$\log \sum$	$\log \frac{\exp(b)}{2b}$	b	$\log \sum$	$\log \frac{\exp(b)}{2b}$	b	$\log \sum$	$\log \frac{\exp(b)}{2b}$
0.1	−5.3802	0.7424	3.6	0.9118	0.7061	12.5	4.2388	4.0307	50.0	19.7518	19.7147
0.2	−4.1759	0.4848	3.7	0.9634	0.7377	13.0	4.4263	4.2309	55.0	21.8783	21.8448
0.3	−3.4713	0.3521	3.8	1.0139	0.7695	13.5	4.6158	4.4316	60.0	24.0090	23.9785
0.4	−2.9712	0.2706	3.9	1.0633	0.8017	14.0	4.8069	4.6330	65.0	26.1433	26.1152
0.5	−2.5831	0.2171	4.0	1.1117	0.8341	14.5	4.9997	4.8349	70.0	28.2804	28.2545
0.6	−2.2659	0.1814	4.1	1.1592	0.8668	15.0	5.1939	5.0373	75.0	30.4201	30.3960
0.7	−1.9974	0.1579	4.2	1.2058	0.8998	15.5	5.3893	5.2402	80.0	32.5620	32.5394
0.8	−1.7648	0.1433	4.3	1.2516	0.9330	16.0	5.5859	5.4436	85.0	34.7058	34.6846
0.9	−1.5593	0.1356	4.4	1.2965	0.9664	16.5	5.7836	5.6473	90.0	36.8512	36.8312
1.0	−1·3754	0.1333	4.5	1.3408	1.0001	17.0	5.9822	5.8515	95.0	38.9981	38.9792
1.1	−1.2088	0.1353	4.6	1.3843	1.0340	17.5	6.1817	6.0561	100.0	41.1463	41.1284
1.2	−1.0565	0.1409	4.7	1.4272	1.0681	18.0	6.3819	6.2610	110.0	45.4462	45.4300
1.3	−0.9162	0.1496	4.8	1.4694	1.1023	18.5	6.5828	6.4662	120.0	49.7500	49.7351
1.4	−0.7861	0.1609	4.9	1.5111	1.1368	19.0	6.7844	6.6718	130.0	54.0570	54.0433
1.5	−0.6649	0.1743	5.0	1.5522	1.1715	19.5	6.9865	6.8777	140.0	58.3667	58.3541
1.6	−0.5512	0.1897	5.2	1.6329	1.2413	20.0	7.1892	7.0838	150.0	62.6789	62.6670
1.7	−0.4443	0.2068	5.4	1.7117	1.3118	21.0	7.5960	7.4969	160.0	66.9930	66.9820
1.8	−0.3432	0.2254	5.6	1.7889	1.3828	22.0	8.0046	7.9110	170.0	71.3090	71.2986
1.9	−0.2475	0.2454	5.8	1.8646	1.4545	23.0	8.4147	8.3260	180.0	75.6265	75.6167
2.0	−0.1564	0.2665	6.0	1.9391	1.5266	24.0	8.8261	8.7418	190.0	79.9455	79.9362
2.1	−0.0696	0.2888	6.2	2.0124	1.5992	25.0	9.2386	9.1584	200.0	84.2657	84.2568
2.2	0.0134	0.3120	6.4	2.0848	1.6723	26.0	9.6523	9.5756	250.0	105.8817	105.8746
2.3	0.0929	0.3361	6.6	2.1563	1.7458	27.0	10.0669	9.9936	300.0	127.5161	127.5102
2.4	0.1693	0.3611	6.8	2.2271	1.8197	28.0	10.4824	10.4121	350.0	149.1630	149.1580
2.5	0.2427	0.3868	7.0	2.2973	1.8939	29.0	10.8987	10.8311	400.0	170.8191	170.8147
2.6	0.3134	0.4132	7.5	2.4709	2.0811	30.0	11.3157	11.2507	450.0	192.4822	192.4783
2.7	0.3818	0.4402	8.0	2.6428	2.2702	32.0	12.1517	12.0912	500.0	214.1508	214.1472
2.8	0.4478	0.4678	8.5	2.8142	2.4611	34.0	12.9900	12.9335	600.0	257.5004	257.4975
2.9	0.5117	0.4960	9.0	2.9860	2.6534	36.0	13.8303	13.7773	700.0	300.8626	300.8600
3.0	0.5737	0.5247	9.5	3.1590	2.8470	38.0	14.6723	14.6224	800.0	344.2338	344.2315
3.1	0.6339	0.5539	10.0	3.3336	3.0419	40.0	15.5159	15.4687	900.0	387.6120	387·6098
3.2	0.6924	0.5836	10.5	3.5102	3.2379	42.0	16.3608	16.3161	1000.0	430.9955	430.9934
3.3	0.7494	0.6136	11.0	3.6890	3.4348	44.0	17.2070	17.1645			
3.4	0.8049	0.6441	11.5	3.8700	3.6327	46.0	18.0543	18.0138			
3.5	0.8590	0.6749	12.0	4.0533	3.8313	48.0	18.9026	18.8639			

$$K \simeq \frac{\alpha}{c} \tag{30}$$

By noticing that $c=1000n_1/NV$, $\kappa^2=8\pi n_1 z^2 s/V$ [Eq. (4)], and $b=z^2s/a$ [Eq. (15)], Eqs. (30) and (28) give:

$$K=\frac{8\pi Na^3}{1000}\cdot\frac{b^{2n+2}}{(2n+2)!\,(2n-1)} \quad \text{when } b\to\infty \tag{31}$$

The sum of the progression terms is shown in Table 1 for a variety of b values and is compared with the corresponding value of $\exp(b)/2b$. Obviously, it approaches $\exp(b)/2b$ with an increase in the b value, so that the ion-association constant becomes:

$$K \simeq \frac{4\pi Na^3}{1000}\frac{\exp(b)}{b} \quad \text{when } b\to\infty \tag{32}$$

This is in agreement with the limiting case ($b\to\infty$) of the Bjerrum theory.[6,13]

Comparison of This Theory with Other Theories of Ion Association. In this work the Debye-Hückel treatment was extended and correction terms were derived on the assumption that the solution is very dilute. By using these results and by assuming the ion-association equilibrium, we obtained an expression for the ion-association constant [Eq. (31)] which includes no arbitrary parameters except for a. (The other parameter, b, is a function of a.) Although the same expression for K was previously derived by Ebeling[10] from the cluster theory, the much simpler method of derivation given above will make the thermodynamical understanding of the ion association easier and clearer.

We shall now compare our results with those of the Bjerrum theory,[6] in which the ion-association constant is given by:

$$K = \frac{4\pi N}{1000}(z^2s)^3Q(b) \tag{33}$$

$$Q(b) = \int_2^b \frac{\exp(x)}{x^4}\mathrm{d}x$$

In the derivation of this equation, Bjerrum assumed a so-called "critical distance of ion association,"

TABLE 2. THERMODYNAMIC PARAMETERS FOR ION-PAIR FORMATION

Parameter	Yokoyama-Yamatera, Ebeling, and Bjerrum ($b\rightarrow\infty$)	Fuoss	Denison-Ramsey
K	$\frac{4\pi Na^3}{1000}\cdot\frac{\exp(b)}{b}$	$\frac{4\pi Na^3}{3000}\exp(b)$	$\exp(b)$
ΔG°	$-RT\left(\ln\frac{4\pi Na^3}{1000b}+b\right)$	$-RT\left(\ln\frac{4\pi Na^3}{3000}+b\right)$	$-bRT$
ΔS°	$R\ln\frac{4\pi Na^3}{1000b}-bRT\frac{\partial\ln\varepsilon}{\partial T}$	$R\ln\frac{4\pi Na^3}{3000}-bRT\frac{\partial\ln\varepsilon}{\partial T}$	$-bRT\frac{\partial\ln\varepsilon}{\partial T}$
ΔH°	$-bRT^2\left(\frac{\partial\ln\varepsilon}{\partial T}+\frac{1}{T}\right)$	$-bRT^2\left(\frac{\partial\ln\varepsilon}{\partial T}+\frac{1}{T}\right)$	$-bRT^2\left(\frac{\partial\ln\varepsilon}{\partial T}+\frac{1}{T}\right)$

$q(=z^2s/2)$, and regarded a pair of oppositely charged ions within the crirical distance of each other as an ion-pair, and an ion with no other ions within the critical distance, as a free ion.†† In the present theory, an ion-pair is treated as a chemical species of unknown geometrical configuration, and the ion-association constant is derived from a thermodynamical consideration of the ion-ion interaction. A comparison between $\rho(r)$, the time-averaged charge distribution around an ion due to the Boltzmann distribution law [Eq. (1)], and $\rho_{\mathrm{DH}}(r)$, the charge distribution assumed by the Debye-Hückel theory, shows that the latter underestimates the charge distribution in the vicinity of an ion. The excess (negative) free energy arising from the interaction of the ion with the additional opposite charge in excess of $\rho_{\mathrm{DH}}(r)$ is regarded as resulting from the ion-pair formation, assuming that a free ion is such an ion as is described by the Debye-Hückel theory [Eq. (24)].

For very large values of b ($b\rightarrow\infty$), both expressions, (31) and (33), can be approximated by Eq. (32). This probably results from the fact that an approximate classification of ions into free ions and contact ion-pairs can be made at large b values. With a decrease in the value of b, the discrepancy between the ion-association constants predicted by Eqs. (31) and (33) gradually increases. The greatest discrepancy is found at $b\leqq 2$ (*i.e.*, $a\geqq q$), where the Bjerrum theory gives $K=0$, while the present theory predicts a definite value for K. This situation is illustrated by Fig. 1, where log K for 2 : 2 electrolytes in aqueous solutions at 25.0 °C is plotted against a in accordance with Eqs. (31) and (33). According to our opinion that the ion association is a working hypothesis for interpreting the deviation of the behavior of actual electrolyte solutions from that predicted by the Debye-Hückel theory, the ion-association constants should have finite values even at $b\leqq 2$, corresponding to non-zero values of the second term on the right-hand side of Eq. (22).

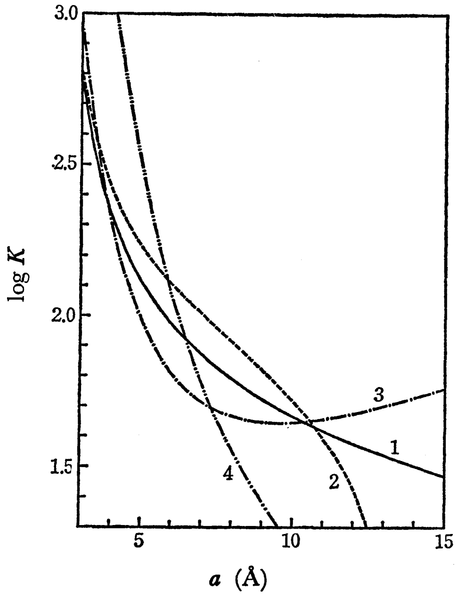

Fig. 1. Theoretical log K values for 2 : 2 electrolytes in aqueous solutions at 25.0 °C.

1: Present theory and Ebeling's theory (——)
2: Bjerrum's theory (—–—)
3: Fuoss's theory (—·—)
4: Denison-Ramsey's theory (—··—)

The Fuoss 1958 theory⁹⁾ is different from the Bjerrum theory in that a pair of ions in physical contact is meant by ion-pair. Although it gives a clearer idea of ion-pairs, it seems to be less adequate for complementing the Debye-Hückel theory. Fuoss's expression for the ion-association constant (Table 2) gives a minimum value of K at a certain value of a and then increasingly large values with an increase in a, as is shown in Fig. 1. For usual values of a, however, it gives K values not very much different from those predicted by the present theory. This seems to be a reason why the Fuoss theory gives a good explanation of the experimental results.

Denison and Ramsey⁷⁾ proposed the expression for the ion-association constant:

$$K=\exp(b)$$

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†† Guggenheim[5,14)] and other authors[15)] introduced another parameter, d, as a variable critical distance or the distance defining the association, and made a generalization of Bjerrum's expression [Eq. (33)] using:

$$Q(b)=\int_{d/s}^{b}\frac{\exp(x)}{x^4}\mathrm{d}x$$

Thus, they introduced flexibility in the critical distance of the Bjerrum theory. In addition, the parameter d can be considered to be the closest distance of approach of free ions and can be used in place of a in the Debye-Hückel expression (24).

in preference to the Fuoss theory. Their theory is based on the assumption of the Born thermodynamic cycle for the dissociation of an ion-pair, and is similar to the Fuoss theory[9] in that the contact ion-pair is assumed. However, the ion-association constants predicted by Denison-Ramsey's expression decrease with an increase in a, similarly to those predicted by the present theory.

The Gibbs free-energy change, $\Delta G°$, the enthalpy change, $\Delta H°$, and the entropy change, $\Delta S°$, for ion-pair formation were derived from the theoretical expressions for the ion-association constant; they are shown in Table 2, where Eq. (31) for the present and Ebeling's theories[10] and Eq. (33) for the Bjerrum theory[6] are approximated by the limiting equation (32). The thermodynamic parameters derived from Eq. (32) are not very different from those from Fuoss's and Denison-Ramsey's expressions; indeed, the formulas for $\Delta H°$ are identical with each other. (It should be noted that this remark is concerned with the limiting case of a large value of b.)†††

In a subsequent paper,[16] the ion-association constants predicted by the theories will be compared with the experimental results obtained from measurements of the electric conductivity and the osmotic coefficient.

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††† At a large value of b, contact ion-pairs predominate over other kinds of ion-pairs in contributing to the chemical potential arising from ion-ion interactions. This seems to be the reason why all the theories give similar results in the limiting case.

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