報告番号 甲第 974 号

主論文

THEORETICAL AND EXPERIMENTAL STUDIES
OF
ION ASSOCIATION

イオン会合の
理論的および実験的研究

横山晴彦

HARUHIKO YOKOYAMA

THEORETICAL AND EXPERIMENTAL STUDIES
OF
ION ASSOCIATION

HARUHIKO YOKOYAMA

Dissertation

for

the Degree of Doctor of Science

Submitted to

Faculty of Science

Nagoya University

1975

CONTENTS

LIST OF THE MOST IMPORTANT SYMBOLS

A	constant to be determined from condition of electrical neutrality [Eq.(2.11) and (2.13)]
A_{DH}	approximate expression for A under Debye-Hückel conditions
a	closest distance of approach of ions
b	Bjerrum's parameter [Eq.(2.14)]
c	molar concentration of electrolyte
D	absorbance
e	elementary charge
G^{el}	Gibbs free energy of electrostatic interactions between ions
h	hydration parameter [Eq.(3.11)]
I	ionic strength
K	ion-association constant
K_{q}	formation constant for quadrupoles
K_{t}	formation constant for triple-ions
k	Boltzmann's constant
m	molal concentartion of electrolyte
n_i	number of i-type ions in V cm^3 of solution
P	variable defined by Eq.(4.8)
Q	variable defined by Eq.(4.8)
q	$= z^2 s/2$
R	gas constant
r	distance from central ion
r_{M}	crystallographic radius of M ion
r_{A}	crystallographic radius of A ion

s	$= e^2/\varepsilon kT$
T	absolute temperature
V	volume of solution
y	activity coefficient on molar concentration scale
z	absolute value of charge number of ions of symmetrical electrolytes
z_i	charge number of i-type ion
z_j	charge number of central j-ion
α	degree of association
β	$=[M_2A]/[MA]=[MA_2]/[MA]$
γ	activity coefficient on molality scale
γ'	Euler's constant ($\gamma' = 0.5772 \cdots\cdot$)
δ	$=[(MA)_2]/[MA]$
ε	dielectric constant of solvent
κ	reciprocal thickness of ionic atmosphere [Eq. (2.4)]
Λ	equivalent conductivity of electrolyte
Λ_0	limiting equivalent conductivity of electrolyte
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
ρ	charge density
ρ_{DH}	approximate expression for ρ under Debye-Hückel conditions
$\sigma_D(\%)$	standard deviation of D in percentage
σ_Λ	standard deviation of Λ

σ_{ϕ}	standard deviation of ϕ
ϕ	molal osmotic coefficient of electrolyte
ϕ_{DH}	molal osmotic coefficient expected by the Debye-Hückel theory [Eq.(3.4)]
ψ	electrostatic potential due to all the ions
ψ_{DH}	approximate expression for ψ under Debye-Hückel conditions
ψ^{cloud}	electrostatic potential due to all the ions except central j-ion
ψ^{cloud}_{DH}	approximate expression for ψ^{cloud} under Debye-Hückel conditions

CHAPTER 1

Introduction

The Debye-Hückel theory[1) can, in many cases, explain the various characteristics of strong electrolyte solutions. However, the electrolyte solutions containing highly charged ions, or those in the solvents of low dielectric constants, often show a deviation from the Debye-Hückel prediction; this deviation has often been interpreted as a result of ion association. The concept of ion association has first been introduced by Bjerrum,[2) who has presented a theoretical expression for the ion-association constant and has shown that the experimental data could be well explained by considering ion association. However, the Bjerrum theory has a disadvantage that an arbitrary assumption has been made in the derivation of the theoretical ion-association constant. After the Bjerrum theory, several authors[3-8) have proposed various theories of ion association on the basis of different concepts of ion association; however, problems do not seem to be solved completely. On the other hand, many experimental studies of ion association have been made and the ion-association constants have been determined on a variety of electrolyte solutions. It has often happened that the obtained values of ion-association constants depend on the experimental method used and on the manner of analysis of the data. This is also a problem to be solved.

The main purpose of the present study is to clarify theoretically and experimentally what is ion association. Theoretically, the Debye-Hückel theory is re-examined and then ion association is discussed from the point of view that the concept of ion association is a practical and useful convention to complement the Debye-Hückel theory.

Experimentally, the ion association constants for some 2 : 2 electrolytes have been determined by means of vapor-pressure osmometry and spectrophotometry. In connection with the analysis of the data, it is examined how the values assumed for the closest distance of approach of ions influence the values of the ion-association constants and how the results from the different kinds of experiments are related to each other and to the theory.

This dissertation consists of three main subjects. First, in Chapter 2, a theoretical expression including no arbitrary parameters except the one representing the closest distance of approach of ions is derived for the ion-association constant of symmetrical electrolytes. Secondly, in Chapter 3, the osmotic coefficients of aqueous solutions of some 2 : 2 electrolytes measured with a vapor-pressure osmometer are presented. Discussion is made as to the manner of analysis of the data. The *best* values of the ion-association constant and the closest distance of approach of ions are obtained with the help of the theoretical expression of the ion-association constant obtained in Chapter 2. Finally, in Chapter 4, a spectrophotometrical investigation of simple and mixed electrolyte solutions is made to give the ion-association constants, which are compared with those obtained by means of other experimental methods.

CHAPTER 2

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

2.1. Introduction

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[9)] 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[10)] were found to lack self-consistency.[11,12)]

On the other hand, Bjerrum[2)] 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,[4)] Gilkerson,[5)] Fuoss,[3)] Ebeling,[6)] and other authors.[7,8)] These theories of ion association, with 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.[13-17)] 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.$^{2-4,6)}$

2.2. 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:

$$\rho(r) = \sum_i \frac{n_i z_i e}{V} \exp\left(-\frac{z_i e\psi(r)}{kT}\right) \qquad (2.1)$$

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:

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

With n_1 and z, Eq.(2.1) can be rewritten as follows:

$$\rho(r) = \frac{n_1 z e}{V}\left[\exp\left(-\frac{ze\psi(r)}{kT}\right) - \exp\left(\frac{ze\psi(r)}{kT}\right)\right] \tag{2.2}$$

By expanding the exponential functions in Eq.(2.2) and introducing the parameter κ (the reciprocal thickness of the ionic atmosphere), one obtains:

$$\rho(r) = -\frac{\varepsilon\kappa^2}{4\pi}\sum_{n=0}^{\infty}\frac{1}{(2n+1)!}\left(\frac{ze}{kT}\right)^{2n}[\psi(r)]^{2n+1} \tag{2.3}$$

The parameter κ is defined by the expression:

$$\kappa^2 = \frac{8\pi n_1 z^2 s}{V} \tag{2.4}$$

or by the general expression:

$$\kappa^2 = \frac{4\pi \sum_i n_i z_i^2 e^2}{V\varepsilon kT} = \frac{4\pi s \sum_i n_i z_i^2}{V} \tag{2.5}$$

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:

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

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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.

2.3. Debye-Hückel Approximation

For a very dilute solution, Debye and Hückel$^{1)}$ simplified Eq.(2.3), ignoring the terms with $n \geq 1$ under the condition of $|ze\psi(r)/kT| << 1$:

$$\rho(r) \simeq \rho_{\mathrm{DH}}(r) = -\frac{\varepsilon\kappa^2}{4\pi}\psi_{\mathrm{DH}}(r) \qquad (2.6)$$

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:

$$\psi_{\mathrm{DH}}(r) = A_{\mathrm{DH}}\frac{\exp(-\kappa r)}{r} \qquad (2.7)$$

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

$$\int_a^\infty 4\pi r^2\rho(r)\,dr = -z_je \qquad (2.8)$$

where z_je is the charge of the central j-ion and a is the closest distance of approach of ions. Equation (2.8) was solved with Eqs.(2.6) and (2.7) to give:

$$A_{\mathrm{DH}} = \frac{z_je\exp(\kappa a)}{\varepsilon(1+\kappa a)} \qquad (2.9)$$

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

$$\psi^{\mathrm{cloud}}(r) \simeq \psi^{\mathrm{cloud}}_{\mathrm{DH}}(r) \quad \left(= \psi_{\mathrm{DH}}(r) - \frac{z_je}{\varepsilon r}\right)$$

$$= \frac{z_je}{\varepsilon r}\left[\frac{\exp(\kappa a-\kappa r)}{1+\kappa a} - 1\right]$$

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

$$\psi^{\text{cloud}}(a) \simeq \psi^{\text{cloud}}_{\text{DH}}(a) = -\frac{z_j e\kappa}{\varepsilon(1+\kappa a)} \tag{2.10}$$

2.4. 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.(2.3)] for the charge distribution. In Eq.(2.3), the Debye-Hückel-type expression [a modification of Eq.(2.7)]:

$$\psi(r) = A\,\frac{\exp(-\kappa r)}{r} \tag{2.11}$$

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 (ecept the *j*-ion) of all types in the whole space gives the potential at any one place within the distance $r \leq a$ due to the ionic cloud, $\psi^{\text{cloud}}(a)$:

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

or

$$\psi^{\text{cloud}}(a) = \frac{4\pi}{\varepsilon} \int_a^\infty r\rho(r)\,dr$$

Using Eq.(2.11) for $\psi(r)$, one obtains:

$$\begin{aligned}\psi^{\text{cloud}}(a) &= -\kappa^2 \sum_{n=0}^{\infty} \frac{1}{(2n+1)!} \left(\frac{ze}{kT}\right)^{2n} A^{2n+1} \int_a^\infty \frac{\exp[-(2n+1)\kappa r]}{r^{2n}}\,dr \\ &= -\kappa A \exp(-\kappa a) \\ &\quad - (\kappa a)^2 \sum_{n=1}^{\infty} \frac{\exp[-(2n+1)\kappa a]}{(2n+1)!\,(2n-1)\,a^{2n+1}} \left(\frac{ze}{kT}\right)^{2n} A^{2n+1} \\ &\quad + (\kappa a)^3(\cdots\cdots) + \cdots\cdots \qquad (2.12)\end{aligned}$$

(For details of the calculation of the integral, see the footnote.**)

** $$-\int_a^\infty \frac{\exp[-(2n+1)\kappa r]}{r}\,dr = \ln[(2n+1)\kappa a] + \gamma' - (2n+1)\kappa a + \frac{[(2n+1)\kappa a]^2}{2\cdot 2!} - \cdots\cdots + \frac{[-(2n+1)\kappa a]^p}{p\cdot p!} + \cdots\cdots$$

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

(when $m \geqq 2$)

The constant A in Eq.(2.12) is determined by the condition of electrical neutrality [Eq.(2.8)] as follows. The whole charge in all the volume outside the sphere of radius a is given by:

$$\int_a^\infty 4\pi r^2 \rho(r)\,dr = -\varepsilon\kappa^2 \sum_{n=0}^{\infty} \frac{1}{(2n+1)!}\left(\frac{ze}{kT}\right)^{2n} A^{2n+1} \int_a^\infty \frac{\exp[-(2n+1)\kappa r]}{r^{2n-1}}\,dr$$

$$= -\varepsilon(1+\kappa a)A\exp(-\kappa a)$$

$$-\varepsilon(\kappa a)^2\left\{-\frac{\ln(3\kappa a)+\gamma'}{6a^2}\left(\frac{ze}{kT}\right)^2 A^3\right.$$

$$\left.+\sum_{n=2}^{\infty}\frac{\exp[-(2n+1)\kappa a]}{(2n+1)!\,(2n-2)\,a^{2n}}\left(\frac{ze}{kT}\right)^{2n} A^{2n+1}\right\}$$

$$+(\kappa a)^3(\cdots\cdots)+\cdots\cdots$$

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

$$A = \frac{z_j e\exp(\kappa a)}{\varepsilon(1+\kappa a)}\left\{1-(\kappa a)^2\left[-\frac{\ln(3\kappa a)+\gamma'}{6}\,b^2\left(\frac{z_j}{z}\right)^2\right.\right.$$

$$\left.\left.+\sum_{n=2}^{\infty}\frac{b^{2n}(z_j/z)^{2n}}{(2n+2)!\,(2n-1)}\right]\right\} \qquad (2.13)$$

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

$$b = \frac{|z_1 z_2|s}{a} = \frac{|z_1 z_2|e^2}{\varepsilon kTa} \qquad (2.14)$$

or, for a symmetrical electrolyte,

$$b = \frac{z^2 s}{a} \qquad (2.15)$$

By substituting Eq.(2.13) into Eq.(2.12) and by disregarding the $(\kappa a)^3$ and higher-order terms, one obtains:

$$\psi^{\text{cloud}}(a) = -\frac{z_j e\kappa}{\varepsilon(1+\kappa a)} - (\kappa a)^2\frac{z_j e}{\varepsilon a}\sum_{n=1}^{\infty}\frac{b^{2n}(z_j/z)^{2n}}{(2n+1)!\,(2n-1)} \qquad (2.16)^{***}$$

The second term on the right-hand side has been added as the first correction term to the Debye-Hückel expression [Eq. (2.10)].

2.5. 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:$^{11,12)}$

$$G^{\mathrm{el}} = \int_0^1 \sum_j z_j e\, \psi^{\mathrm{cloud}}(a,\lambda z,\lambda\kappa)\,d\lambda \tag{2.17}$$

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:

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

This expression is obtained by substituting $\lambda z_j e$ and $\lambda z e$ for $z_j e$ and ze respectively in Eq. (2.16). Then the right-hand side of Eq. (2.17) can be calculated as follows:

$$G^{\mathrm{el}} = -\frac{\sum_j z_j^2 e^2 \kappa}{\varepsilon} \int_0^1 \frac{\lambda^2}{1+\lambda\kappa a}\,d\lambda$$

$$- \frac{\sum_j z_j^2 e^2}{\varepsilon a} (\kappa a)^2 \sum_{n=1}^{\infty} \frac{b^{2n}}{(2n+1)!\,(2n-1)} \int_0^1 \lambda^{4n+3}\,d\lambda$$

$$= -\frac{\sum_i n_i z_i^2 e^2}{3\varepsilon} \kappa\tau(\kappa a) - \frac{\sum_i n_i z_i^2 e^2}{2\varepsilon a} (\kappa a)^2 \sum_{n=1}^{\infty} \frac{b^{2n}}{(2n+2)!\,(2n-1)} \tag{2.18}$$

*** The $(\kappa a)^2$ term in Eq. (2.13) contributes only to the $(\kappa a)^3$ and higher-order terms, which are ignored in Eq. (2.16); therefore, the use of A_{DH} [Eq. (2.9)] instead of A [Eq. (2.13)] leads to the same result.

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.

2.6. 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:

2.6.1. Derivation of μ_i^{el} from G^{el} (According to the Debye Charging Process)

μ_i^{el} can be defined by the equation:

$$\mu_i^{\text{el}} = \frac{\partial G^{\text{el}}}{\partial n_i} \tag{2.19}$$

Using Eq. (2.18) and Eq. (2.5), Eq. (2.19) becomes:

$$\mu_i^{\text{el}} = -\frac{z_i^2 e^2 \kappa}{2\varepsilon(1+\kappa a)} - kT(\kappa a)^2 \sum_{n=1}^{\infty} \frac{b^{2n+1}}{(2n+2)!\,(2n-1)} + \frac{kT(\partial V/\partial n_i)}{24\pi a^3}(\kappa a)^3 \sigma(\kappa a)$$
$$+ \frac{kT(\partial V/\partial n_i)}{8\pi a^3}(\kappa a)^4 \sum_{n=1}^{\infty} \frac{b^{2n}}{(2n+2)!\,(2n-1)} \tag{2.20}$$

where

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

The Debye-Hückel approximation corresponds to the first and third terms on the right-hand side of Eq. (2.20).[11,12] For a very dilute solution, the second term is more important than the third term.

2.6.2. Direct Derivation of μ_i^{el} (According to the Güntelberg Charging Process)

μ_i^{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, μ_i^{el} can be evaluated as the electric work of increasing the charge of the particular ion from zero to $z_i e$ in the solution.11,12) Thus, according to Güntelberg, one has:

$$\mu_i^{\mathrm{el}} = \int_0^1 z_i e\, \psi^{\mathrm{cloud}}(a,\lambda z_i)\,\mathrm{d}\lambda \tag{2.21}$$

where $\psi^{\mathrm{cloud}}(a,\lambda z_i)$ is given by Eq.(2.16), with the substitution of λz_i for z_j:

$$\psi^{\mathrm{cloud}}(a,\lambda z_i) = -\frac{\lambda z_i e\kappa}{\varepsilon(1+\kappa a)} - (\kappa a)^2\,\frac{\lambda z_i e}{\varepsilon a}\sum_{n=1}^{\infty}\frac{\lambda^{2n} b^{2n}}{(2n+1)!\,(2n-1)}$$

By integration, Eq.(2.21) becomes:

$$\mu_i^{\mathrm{el}} = -\frac{z_i^2 e^2 \kappa}{2\varepsilon(1+\kappa a)} - kT(\kappa a)^2\sum_{n=1}^{\infty}\frac{b^{2n+1}}{(2n+2)!\,(2n-1)} \tag{2.22}$$

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.(2.20)].

A more involved expression for μ_i^{el} was derived by Gronwall *et al.*9) 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 μ_i^{el}.11,12) 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.(2.22). Kaneko[10)] made another correction to the Debye-Hückel theory. Although his expression for μ_i^{el} involves the same kind of problem as mentioned above, his expression is consistent with Eq.(2.22) 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 μ_i^{el} of a closer approximation than Eq.(2.22). Although Eq.(2.22) in itself is valid only for solutions of sufficiently low concentrations, an attempt will be made to extend the application of Eq.(2.22) up to higher concentrations by connecting it with the concept of ion association.

2.7. 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:

$$\begin{array}{lccccc} & \mathrm{M} & + & \mathrm{A} & \rightleftharpoons & \mathrm{MA} \\ \text{concentration} & c(1-\alpha) & & c(1-\alpha) & & c\alpha \end{array} \qquad (2.23)$$

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_M and y_A, of the ions, M and A, respectively are given by:

$$\ln y_M = \ln y_A = -\frac{z^2 e^2 \kappa}{2\varepsilon k T(1+\kappa a)} \qquad (2.24)$$

Now, the chemical potential μ of the electrolyte is:

$$\mu = \mu_M^\circ + \mu_A^\circ + 2RT\ln c + RT\ln(y_M y_A) + 2RT\ln(1-\alpha) \tag{2.25}$$

where μ_M° and μ_A° 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, μ^{el}, is equal to the last two terms of Eq.(2.25). Using Eq.(2.24) and considering $\alpha \ll 1$ in very dilute solutions, one obtains:

$$\begin{aligned}\mu^{el} &= RT\ln(y_M y_A) + 2RT\ln(1-\alpha) \\ &\simeq -\frac{Nz^2e^2\kappa}{\varepsilon(1+\kappa a)} - 2RT\alpha \end{aligned} \tag{2.26}$$

where N is the Avogadro number.

Since μ_i^{el} given by Eq.(2.22) is the contribution of ion-ion interactions to the chemical potential of an ion of the i type, μ_i^{el} multiplied by the total number of ions, $2N$, gives μ^{el}:

$$\begin{aligned}\mu^{el} &= 2N\mu_i^{el} \\ &= -\frac{Nz^2e^2\kappa}{\varepsilon(1+\kappa a)} - 2RT(\kappa a)^2\sum_{n=1}^{\infty}\frac{b^{2n+1}}{(2n+2)!\,(2n-1)}\end{aligned} \tag{2.27}$$

A comparison of Eqs.(2.26) and (2.27) leads to:

$$\alpha = (\kappa a)^2\sum_{n=1}^{\infty}\frac{b^{2n+1}}{(2n+2)!\,(2n-1)} \tag{2.28}$$

The equilibrium constant, K, of the ion-association reaction [Eq.(2.23)] is given by:

$$K = \frac{\alpha y_{MA}}{c(1-\alpha)^2 y_M y_A} \tag{2.29}$$

where y_{MA} is the activity coefficient of the ion-pair MA. In very dilute solutions, Eq.(2.29) can be written as:

$$K \simeq \frac{\alpha}{c} \tag{2.30}$$

By noticing that $c = 1000n_1/NV$, $\kappa^2 = 8\pi n_1 z^2 s/V$ [Eq.(2.4)], and $b = z^2 s/a$ [Eq.(2.15)], Eqs.(2.30) and (2.28) give:

$$K = \frac{8\pi N a^3}{1000} \sum_{n=1}^{\infty} \frac{b^{2n+2}}{(2n+2)!\,(2n-1)} \qquad (2.31)$$

The sum of the progression terms is shown in Table 2.1 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:

$$K \simeq \frac{4\pi N a^3}{1000} \cdot \frac{\exp(b)}{b} \qquad \text{when } b \longrightarrow \infty \qquad (2.32)$$

This is in agreement with the limiting case ($b \rightarrow \infty$) of the Bjerrum theory.[2,18]

2.8. 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. (2.31)] 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[6] 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,[2] in which the ion-association constant is given by:

$$K = \frac{4\pi N}{1000} (z^2 s)^3 \, Q(b) \qquad (2.33)$$

$$Q(b) = \int_2^b \frac{\exp(x)}{x^4} \, dx$$

In the derivation of this equation, Bjerrum assumed a so-called "critical distance of ion association," q ($= z^2 s/2$), and regarded a pair of oppositely charged ions within the critical 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.(2.1)], and $\rho_{DH}(r)$, 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 $\rho_{DH}(r)$ 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.(2.24)].

For very large values of b ($b \to \infty$), both expressions, (2.31) and (2.33), can be approximated by Eq.(2.32). 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

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† Guggenheim[12,19)] and other authors[20-23)] introduced another parameter, d, as a variable critical distance or the distance defining the association, and made a generalization of Bjerrum's expression [Eq.(2.33)] using:

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

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 (2.24).

the value of b, the discrepancy between the ion-association constants predicted by Eqs.(2.31) and (2.33) gradually increases. The greatest discrepancy is found at $b \leqq 2$ (*i.e.*, $a \leqq q$), where the Bjerrum theory gives $K = 0$, while the present theory predicts a definite value for K. This situation is illustrated by Fig.2.1, where $\log K$ for 2 : 2 electrolytes in aqueous solutions at 25.0°C is plotted against a in accordance with Eqs.(2.31) and (2.33). 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.(2.22).

The Fuoss 1958 theory[3)] 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 2.2) 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.2.1. 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 Ramsey[4)] proposed the expression for the ion-association constant:

$$K = \exp(b)$$

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[3)] 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 2.2, where Eq.(2.31) for the present and Ebeling's theories$^{6)}$ and Eq.(2.33) for the Bjerrum theory$^{2)}$ are approximated by the limiting equation (2.32). The thermodynamic parameters derived from Eq.(2.32) are not very different from those derived 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.)[††]

[††] 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.

CHAPTER 3

Vapor-Pressure Osmometric Studies of the Ion Association of Some 2 : 2 Electrolytes in Water

3.1. Introduction

In Chapter 2, we re-examined the Debye-Hückel theory1) of strong electrolyte solutions and especially discussed ion association from the theoretical point of view. It was shown that the observed deviations from the Debye-Hückel theory could be explained without referring to ion association, but at the same time it was reported that the concept of ion association is a practical and useful convention to complement the Debye-Hückel theory. This convention can be justified at least for symmetrical strong electrolytes, irrespective of whether or not ion-pairs are actual well-defined entities.

The existing data of ion-association constants are not sufficient for comparison with our theoretical expression of ion-association constants. Except in a few cases,21,24-27) the literature gives only one set of values of the ion-association constant (K) and the closest distance of approach of ions (a). However, the K value to be obtained from the analysis of experimental results must be influenced by the choice of the value of a.21,24-27) The theoretical expression of the ion-association constant also shows a dependence of K on a, but in a different way. Thus, it is of interest to obtain ion-association constants as a function of a and to discuss what are the *best* values of the ion-association constant and the closest distance of approach. As will be described below, we measured the osmotic coefficients of aqueous solutions of some 2 : 2 electrolytes by means of a vapor-pressure osmometer. Assuming ideal Debye-Hückel behavior of the free ions, the ion-association constants were obtained with several values of a from analyses with and without taking triple-ion formation, quadrupole formation, and ion hydration into account. Ion-association constants were also obtained as functions of a by the recalculation of the available cryoscopy and conductivity data.24,26,28-33) These results will be shown and discussed in connection with the theories of ion association.2,3,34)

3.2. Experimental

3.2.1. Measurements

The osmotic coefficients of the electrolyte solutions were measured by vapor-pressure osmometry (vpo). This method has been described by many authors.35-38) Thus, a brief explanation of the apparatus and the procedure will suffice.

A Hitachi Perkin-Elmer 115 molecular-weight apparatus was used in the experiment. It has a cell surrounded by double thermostats. The cell is equipped with two thermistors covered with glass, on which liquids are dropped. The thermistors are connected with a bridge circuit, which is balanced when both thermistor tops are covered with a solvent in equilibrium with its vapor. When the solvent on one of the thermistors is replaced by a solution, the solvent vapor condenses into the solution and liberates the heat of condensation. The temperature of the solution increases until an equilibrium is reached. The change in temperature is detected by the thermistor and shown as a change in the electrical resistance, ΔR. The value of ΔR is dependent on the concentration (molality), m, and the molal osmotic coefficient, ϕ, of the solute, and can be fitted to a power series of the form:

$$\Delta R = s_1(\nu m\phi) + s_2(\nu m\phi)^2 + s_3(\nu m\phi)^3 + s_4(\nu m\phi)^4 \qquad (3.1)$$

where ν is the number of moles of ions formed from one mole of the electrolyte (for nonelectrolyte, $\nu = 1$) and where s_1, s_2, s_3, and s_4 are the coefficients to be determined experimentally. We used glucose as the standard material and measured the values of ΔR on its aqueous solutions with concentrations from 0.005 to 0.18 mol kg^{-1}. Assuming $\phi = 1$ for glucose in water at 25.0°C, we obtained $s_1 = 4925$, $s_2 = -988.7$, $s_3 = 13050$, and $s_4 = -47920$ by the method of least-squares. The obseved values of ΔR for various solutions were put into Eq.(3.1), and the osmotic coefficients (ϕ) were evaluated. We measured the osmotic coefficients (ϕ) of sodium chloride and obtained the approximate expression:

$$1 - \phi = 0.2963\, m^{1/2} + 0.1036\, m - 1.306\, m^{3/2}$$

The values of ϕ predicted by this equation at several concentrations up to 0.1 mol kg^{-1} agreed with the values from e.m.f. measurements$^{39)}$ within the range of experimental error. This shows that the assumption of $\phi = 1$ for glucose solutions is adequate.

3.2.2. Materials

A reagent-grade glucose (anhydride) was used as the standard material after having been dried at about 80°C and then kept over silica gel. A reagent-grade sodium chloride was recrystallized by concentrating its aqueous solution, and was then dried at about 600°C. A reagent-grade magnesium sulfate was recrystallized as the hydrate, $MgSO_4 \cdot 7H_2O$, from its aqueous solution below 48°C and then air-dried at room temperature. Its composition was confirmed by gravimetric analyses of magnesium as magnesium pyrophosphate and of sulfate as barium sulfate. The calcium sulfate used was dihydrate of reagent grade. The number of water of crystallization was confirmed by the dehydration at about 700°C and by the titration of the calcium ion with ethylenediaminetetraacetic acid. A stock solution of manganese sulfate was prepared by the use of a recrystallized reagent-grade hydrate. Its concentration was determined by gravimetric analysis of sulfate. Tris-(1,10-phenanthroline)ruthenium(II) sulfate hydrate, $[Ru(phen)_3]SO_4 \cdot 7H_2O$, was prepared in a manner similar to that described by Dwyer.40) The complex was synthesized by adding sodium hypophosphite as a reducing agent to a solution containing ruthenium chloride and 1,10-phenanthroline; the iodide was obtained by precipitation from the solution. Sulfate of this complex was prepared by the double decomposition of the iodide and silver sulfate, and was purified by repeated precipitations with acetone from alcoholic solutions and by a final recrystallization from an aqueous solution. It was dried over silica gel for a few days until it reached a constant weight. The number of the water of crystallization was determined to be seven —— directly by the Karl-Fischer method and by the spectrophotometric analysis of HDO in a D_2O solution of the salt,41) and indirectly by the gravimetric analysis of sulfate.

3.3. Results and Discussion

3.3.1. Ion-Pair Formation

The ΔR values were measured for some 2 : 2 electrolytes in aqueous solutions at 25.0 ± 0.03°C. The osmotic coefficients (ϕ) were calculated from ΔR with Eq.(3.1) and are shown in Table 3.1.* The measured ϕ values are plotted against the molal concentration of the solute, m, in Fig.3.1 for $MgSO_4$ and in Fig.3.2 for $CaSO_4$, together with the

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* The values of ϕ obtained for $MgSO_4$ and $MnSO_4$ around 0.1 mol kg^{-1} are, respectively, 1.6 % and 3.0 % smaller than those obtained by Robinson and Jones,42) who made isopiestic vapor-pressure measurements.

results from cryoscopic measurements.[24,26] These figures also give the ϕ *vs.* m curves predicted by the Debye-Hückel theory[1] with a few values assumed for the closest distance of approach of ions, a. None of the theoretical curves fits the experimental results. For any reasonable value of a, the experimantal ϕ values are lower than the values predicted by the Debye-Hückel theory. A decrease in ϕ is usually considered to result from ion association.[21,24-26] According to this usual convention, we shall assume an ion-association equilibrium and shall estimate the ion-association constants on the basis of an analysis of the experimental ϕ values.

The ion-association equilibrium for a symmetrical electrolyte is expressed by:

$$\begin{array}{lccccc} & \mathrm{M} & + & \mathrm{A} & \rightleftharpoons & \mathrm{MA} \\ \text{concentration} & m(1-\alpha) & & m(1-\alpha) & & m\alpha \end{array} \qquad (3.2)$$

where m denotes the molality of the electrolyte and where α is the degree of association defined by:

$$\alpha = \frac{[\mathrm{MA}]}{m}$$

The brackets indicate the concentration of a given species. The ions, M and A, having the z_1e and z_2e charges respectively, are usually considered as *free* ions in the sense that the Debye-Hückel theory can be applied to them. On the other hand, the ion-pair, MA, is presumed to behave like a non-electrolyte in dilute solutions. Therefore, the ϕ of an electrolyte solution is related to α as follows:

$$\phi = (1-\alpha)\,\phi_{DH} + \frac{\alpha}{2}$$

or (3.3)

$$\alpha = \frac{\phi_{DH} - \phi}{\phi_{DH} - 0.5}$$

where ϕ_{DH} is the molal osmotic coefficient expected by the Debye-Hückel theory and is given by:

$$\phi_{DH} = 1 - \frac{z^2 \kappa s}{6} \sigma(\kappa a) \qquad (3.4)$$

with the definition of the function $\sigma(x)$:

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

In Eq.(3.4), s is a parameter equal to $e^2/\varepsilon kT$ and the parameter κ is here expressed by the equation:

$$\kappa^2 = \frac{8\pi N}{1000} z^2 s m(1-\alpha) \qquad (3.5)$$

where $m(1-\alpha)$ represents the concentration of the free ion on the molality scale. The molality can be used in place of the molar concentration, since the difference between the two values is less than the experimental error in dilute solutions up to about 0.1 mol kg^{-1}.

The values of α, κ, and ϕ_{DH} were calculated by successive approximations in the following way. The value of κ was calculated by using Eq.(3.5), with $\alpha = 0$ provisionally. The value of ϕ_{DH} was evaluated with Eq.(3.4), and then the value of α, with Eq.(3.3). This value of α was in turn put into Eq.(3.5) in order to recalculate the value of κ. With this κ value, the values of ϕ_{DH} and α were recalculated in the same way as before. After several cycles of the successive approximation, the parameter values were fixed. The final value of α was used for the calculation of the ion-association constant, K, with the expression:

$$K = \frac{\alpha}{(1-\alpha)^2 m \gamma_M \gamma_A}$$

where γ_M and γ_A are the activity coefficients of the free ions, M and A respectively, and are given by:

$$\ln \gamma_M = \ln \gamma_A = - \frac{z^2 \kappa s}{2(1+\kappa a)} \qquad (3.6)$$

The activity coefficient of the MA ion-pair was regarded as unity.

The ion-association constants of some 2 : 2 electrolytes were calculated with several a values assumed. The results for $MgSO_4$, $CaSO_4$, $MnSO_4$, and $[Ru(phen)_3]SO_4$ are shown in Figs.3.3 to 3.6 respectively. Apparent linear relationships were observed between $\log K$ and m up to about 0.05 mol kg^{-1}; extrapolation to $m = 0$ gave different $\log K$ values, depending on the a values.

In each figure for $MgSO_4$, $CaSO_4$, and $MnSO_4$, there seems to be a specific a value at which the $\log K$ value is apparently independent of the concentration, *i.e.*, $a = 4.2$ Å for $MgSO_4$, about 4 Å for $CaSO_4$, and 3.8 Å for $MnSO_4$. However, such a situation may be incidental, since the $\log K$ values for $MgSO_4$ and $MnSO_4$ are no longer constant at concentrations higher than 0.06 mol kg^{-1}. The concentration dependence of the ion-association constant may be attributed to the effects of other ion-ion interactions and ion hydration disregarded in the analysis. Below, we shall take the triple-ion formation into consideration in order to obtain better ion-association constants.

3.3.2. Triple-Ion Formation

When an ion approaches an ion-pair, the electrostatic interaction between the charge and the dipole will cause the formation of a so-called "triple-ion." There are two possible equilibria for the formation of a triple-ion:

$$MA + M \rightleftharpoons M_2A$$

$$MA + A \rightleftharpoons MA_2$$

Assuming an equal formation constant for the M_2A and MA_2 triple-ions, one can express the concentration of each species as follows:

$$[M] = [A] = m[1-\alpha(1+3\beta)]$$

$$[MA] = m\alpha$$

$$[M_2A] = [MA_2] = m\alpha\beta$$

where β is the parameter defined by:

$$\beta = \frac{[M_2A]}{[MA]} = \frac{[MA_2]}{[MA]}$$

Thus, the formation constant for the triple-ions, K_t, is expressed by:

$$K_t = \frac{[M_2A]\gamma_{M_2A}}{[MA][M]\gamma_M} = \frac{[MA_2]\gamma_{MA_2}}{[MA][A]\gamma_A} = \frac{\beta}{[1-\alpha(1+3\beta)]m} \tag{3.7}$$

where γ_{M_2A} and γ_{MA_2} are the activity coefficients of M_2A and MA_2 and are assumed to be equal to γ_M and γ_A respectively.

With the above assumptions, the osmotic coefficient of the electrolyte can be expressed by:

$$\phi = [1-\alpha(1+2\beta)]\,\phi_{DH} + \frac{\alpha}{2} \tag{3.8}$$

where

$$\phi_{DH} = 1 - \frac{z^2\kappa s}{6}\,\sigma(\kappa a) \tag{3.9}$$

Eq.(3.9) is apparently the same as Eq.(3:4), but here the parameter κ is given by:

$$\kappa^2 = \frac{8\pi N}{1000}\,z^2 sm[1-\alpha(1+2\beta)] \tag{3.10}$$

Assuming the value of K_t for a given a value and using Eqs.(3.7) to (3.10), the values of α, β, κ, and ϕ_{DH} were calculated by successive approximations. With the α and β values thus obtained, the ion-association constant, K, was calculated according to the expression:

$$K = \frac{\alpha}{[1-\alpha(1+3\beta)]^2 m\gamma_M\gamma_A}$$

The value of K was thus obtained at each concentration, and then the K values were averaged. The osmotic coefficient was calculated for each concentration with the averaged value of K and used for the calculation of the standard deviation, σ_ϕ, defined by:

$$\sigma_\phi = \sqrt{\frac{\sum_{i=1}^{n}(\phi_{\mathrm{calcd},i} - \phi_{\mathrm{obsd},i})^2}{n-2}}$$

where n is the total number of points of the run and where ϕ_{obsd} and ϕ_{calcd} are the observed and calculated osmotic coefficients respectively. The σ_ϕ value was obtained as a function of K_t for a given a value. The K_t value giving the minimum value of σ_ϕ was regarded as the *best* value of K_t.

The K value was calculated at each concentration with the K_t value obtained above and was plotted against m. Figure 3.7 shows the results for magnesium sulfate, assuming a few a values. For each value of a, the $\log K$ value shows a very good constancy up to about 0.1 mol kg^{-1}. In the same figure, the corresponding previous plots are reproduced from Fig.3.3 in broken lines. The constant value of $\log K$ obtained here for each of the given a values is in fairly good agreement with the value obtained by extrapolation to $m = 0$ in the previous plot. This shows that a good enough estimation of the ion-association constant K can be made without taking the triple-ion formation into account. The same discussion also applies to Figs.3.8 to 3.10 for the other electrolytes.

3.3.3. Hydration

The ion hydration causes a decrease in the concentration of the water as solvent. This decrease is equal to hm, where h represents the hydration parameter given by:

$$h = \frac{h_\mathrm{M}[\mathrm{M}] + h_\mathrm{A}[\mathrm{A}] + h_\mathrm{MA}[\mathrm{MA}] + h_{\mathrm{M_2A}}[\mathrm{M_2A}] + h_{\mathrm{MA_2}}[\mathrm{MA_2}]}{m}$$

$$= (h_\mathrm{M} + h_\mathrm{A})[1-\alpha(1+3\beta)] + h_\mathrm{MA}\alpha + (h_{\mathrm{M_2A}} + h_{\mathrm{MA_2}})\alpha\beta \qquad (3.11)$$

where h_M, h_A, h_MA, $h_{\mathrm{M_2A}}$, and $h_{\mathrm{MA_2}}$ are the hydration numbers of the M, A, MA, M_2A, and MA_2 species respectively. If the ion hydration is allowed for, the molality of the solute, m', can be expressed by:

$$m' = \frac{55.51}{55.51 - hm}\, m = \frac{m}{1 - 0.0180\, hm}$$

and the expression for the osmotic coefficient ϕ becomes:

$$\phi = \frac{1}{1 - 0.0180\, hm} \{[1-\alpha(1+3\beta)]\, \phi_{DH} + \frac{\alpha}{2}\}$$

where ϕ_{DH} is given by Eq.(3.9). The ion-association constant, K, and the triple-ion formation constant, K_t, are expressed by:

$$K = \frac{\alpha}{[1-\alpha(1+3\beta)]^2 m' \gamma_M \gamma_A}$$

and

$$K_t = \frac{\beta}{[1-\alpha(1+3\beta)]m'}$$

If the value of the parameter h is given, the K and K_t values can be calculated by the procedure described before. Since it is difficult to estimate the hydration numbers, h_{MA}, h_{M_2A}, and h_{MA_2}, involved in the parameter h [Eq.(3.11)], for convenience we shall consider two extreme cases in order to learn how far the ion hydration affects the estimation of the K and K_t values.

Case (A): The hydration numbers of the ion-pair and the triple-ions are simply equal to the sums of the hydration numbers of the constituent ions.

$$\left.\begin{aligned} h_{MA} &= h_M + h_A = h_0 \\ h_{M_2A} &= 2h_M + h_A \\ h_{MA_2} &= h_M + 2h_A \end{aligned}\right\} \qquad (3.12)$$

where the parameter h_0 can be determined by the measurement of the hydration number in very dilute solutions. By using Eq.(3.12), the parameter h in Eq.(3.11) is expressed by:

$$h = h_0$$

Case (B): The hydration number of the ion-pair is equal to zero and the sum of the hydration numbers of the M_2A and MA_2 triple-ions is equal to $h_M + h_A$:

$$h_{MA} = 0$$

$$h_{M_2A} + h_{MA_2} = h_M + h_A = h_0$$

Thus, the expression for h becomes:

$$h = h_0 [1-\alpha(1+2\beta)]$$

Tentatively taking $h_0 = 15$,** the ion-association constants were calculated for the two cases, (A) and (B). The case of $MgSO_4$ with $a = 6.0$ Å will be taken as an example. The K_t values giving the minimum values of σ_ϕ are 3.1 and 2.7 mol^{-1} kg for (A) and (B) respectively. These K_t values are slightly greater than the value, 2.2 mol^{-1} kg, which was obtained by disregarding the ion hydration. However, the K values remained unchanged at 121 ± 5 mol^{-1} kg. The $\log K$ value for $MgSO_4$ with $a = 6.0$ Å is plotted against m in Fig.3.11, where the overlapping solid marks of different kinds show the unchanged K values. The $\log K$ values obtained by disregarding the triple-ion formation ($K_t = 0$) are also plotted in Fig.3.11. In each case, an apparent linear relationship is observed between $\log K$ and m up to about 0.05 mol kg^{-1}. The slopes are different from one another, indicating different K_t values. However, extrapolations of the lines to $m = 0$ give the same intercept, showing the same $\log K$ value.

The consideration of the triple-ion formation and the ion hydration resulted in no appreciable change in the ion-association constant K from that obtained by the extrapolation of the $\log K$ *vs.* m plots in

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** The literature gives various values of the hydration number of the electrolyte.43) The average value of h_0 for $MgSO_4$ is probably about 15.

Figs.3.3 to 3.6, where the triple-ion formation and the ion hydration were ignored. When the triple-ion formation and the ion hydration were allowed for, the value of K was practically constant up to about 0.1 mol kg^{-1}. On the other hand, the value of K_t was slightly dependent on the estimation of the hydration numbers of the ions. Table 3.2 gives the K values for a variety of a values, together with the K_t values. Each set of the values of a, K, and K_t can reproduce the observed osmotic coefficients within the range of experimental error. This is shown in Figs.3.1 and 3.2. In each of the figures, the best-fitting curves for different a values coalesce into a curve (the solid line).

Fuoss and Kraus[44) have proposed a theory of the triple-ion formation. Their theory predicts K_t values of 2.6 mol^{-1} kg at $a = 8.2$ Å and 3.3 mol^{-1} kg at $a = 5.7$ Å for 2 : 2 electrolytes in aqueous solutions at 25°C. These are close to the values obtained in the present work (Table 3.2).

Gardner and Glueckauf[25) have obtained K and K_t values for some 2 : 2 electrolytes by a reanalysis of the cryoscopic data given by Brown and Prue.[24) The manner of the analysis of the data was different from that described in the present article. We also reanalyzed the same and other cryoscopic data[24,26) for $MgSO_4$ and $CaSO_4$ in the manner followed in the analysis of the vpo data. The results are shown in Table 3.3. For $a = 9.25$ Å, Gardner and Glueckauf obtained $K_t = 2.6$ mol^{-1} kg and $K = 158$ mol^{-1} kg for $MgSO_4$ and $K_t = 2.7$ mol^{-1} kg and $K = 234$ mol^{-1} kg for $CaSO_4$. Their result for $CaSO_4$ is appreciably different from that given in Table 3.3, whereas for $MgSO_4$ the results are close to each other and also to the result of our vpo experiment (25°C).

3.3.4. Quadrupole Formation

In Sections 3.3.1 and 3.3.2, the triple-ion formation constant, K_t, was estimated disregarding the quadrupole formation. We shall now discuss how the correction for quadrupole formation will affect the values of K and K_t to be obtained.

The equilibrium for the formation of a quadrupole $(MA)_2$ is expressed by:

$$MA + MA \rightleftharpoons (MA)_2$$

The formation constant, K_q, is given by:

$$K_q = \frac{[(MA)_2]}{[MA]^2} = \frac{\delta}{m\alpha}$$

where δ is the parameter defined by:

$$\delta = \frac{[(MA)_2]}{[MA]}$$

Then, the osmotic coefficient becomes:

$$\phi = \frac{1}{1-0.0180\,hm}\left\{[1-\alpha(1+2\beta+2\delta)]\,\phi_{DH} + \frac{\alpha(1+\delta)}{2}\right\}$$

The experimental data are not good enough to estimate the values of K_t and K_q at the same time. Thus, some relation between K_t and K_q values has to be assumed if one is to estimate them by the analysis of the experimental data.

Defining K' as:

$$K' = \frac{[(MA)_2]}{[M_2A]\,[A]\,\gamma_{M_2A}\gamma_A} = \frac{[(MA)_2]}{[MA_2]\,[M]\,\gamma_{MA_2}\gamma_M}$$

one obtains the relation:

$$\frac{K_q}{K_t} = \frac{K'}{K}$$

K' is the ion-association constant of a kind of 2 : 2 electrolyte and can be approximated by K. Then, K_q/K_t will have a value near unity. Assuming $K_q = K_t$, we obtained the K_t, K_q, and K values for $MgSO_4$ shown in Table 3.4. The ion-association constants (K) given here are slightly greater than the corresponding values shown in Table 3.2, but the change is within the range of experimental error except when large a values are assumed. The K_t values are appreciably smaller than those shown in Table 3.2. Thus, it was found that a correction for the quadrupole formation would make the K_t values smaller than the values shown in Table 3.2, but would affect the K values very little.

3.3.5. Comparison with the Ion-Association Constants Obtained from Conductivity Experiments

The electric conductivity was measured for $MgSO_4$ solutions by Dunsmore and James28) and Katayama,29) for $CaSO_4$ solutions by Inada *et al.*,30) and for $MnSO_4$ solutions by Hallada and Atkinson31) and Petrucci *et al.*32) Although no conductivity measurements were made of $[Ru(phen)_3]SO_4$ solutions, the electric conductivities of $[Fe(phen)_3]SO_4$ solutions were measured by Kubota and Yokoi.33) They analyzed the conductivity data in order to obtain the values of the ion-association constant and the closest distance of approach. However, these results have to be revised before they can be compared with the results from vpo, since different authors used different theoretical equations for the analysis of the conductivity data.

For the reanalysis of the conductivity data, we used Fuoss-Hsia's equation45) expanded by Fernández-Prini.46) This equation gives the equivalent conductivity, Λ, for an association system as follows:

$$\frac{\Lambda}{1-\alpha} = \Lambda_0 - S[c(1-\alpha)]^{1/2} + Ec(1-\alpha)\log[c(1-\alpha)] + J_1c(1-\alpha) - J_2[c(1-\alpha)]^{3/2} \qquad (3.13)$$

where Λ_0 is the limiting equivalent conductivity, c, is the concentration of the solute on the molar scale, and α is the degree of association. The latter is related to K by:

$$K = \frac{\alpha}{(1-\alpha)^2 c y_M y_A} \tag{3.14}$$

The parameters, J_1 and J_2, as well as the activity coefficients, y_M and y_A, of the free ions, M and A, are functions of the closest distance of approach of ions, a. Since measurements of the conductivity are usually made at concentrations well below 10^{-2} mol l^{-1}, c, y_M, and y_A on the molar concentration scale can be approximated by m, γ_M, and γ_A [Eq.(3.6)] on the molality scale respectively; the other interactions, such as triple-ion formation, described in the previous sections can be ignored.

With a given value of a and a roughly estimated value of Λ_0, K was calculated for each concentration by means of Eqs.(3.13) and (3.14). With the averaged K value, the electric conductivity at each concentration was calculated and then used to calculate the standard deviation, as defined by:

$$\sigma_\Lambda = \sqrt{\frac{\sum_{i=1}^{n} (\Lambda_{\mathrm{calcd},i} - \Lambda_{\mathrm{obsd},i})^2}{n-2}}$$

where n is the total number of points of the run and where Λ_{obsd} and Λ_{calcd} are, respectively, the observed and the calculated electric conductivity at each concentration. The averaged K value depended on the assumed Λ_0 value. The best-fitting values of K and Λ_0 for a given a value were determined by the minimization of the standard deviation, σ_Λ, and are listed in Table 3.5 as a function of a for each of the electrolytes. The $\log K$ values given in Table 3.5 show a tendency similar to that observed from vpo (results in Table 3.2), and each of the K values has a magnitude similar to the corresponding one in Table 3.2.

3.3.6. Critical Discussion of the Minimum Standard Deviation as the Criterion of the *Best* Values

As a criterion of the *best* values, we used the minimum standard deviations of ϕ and Λ respectively for the determination of K and K_t from the vapor-pressure osmometric measurements and for the determination of K and Λ_0 from the conductivity data. The rather sharp minima shown by the standard deviations, σ_ϕ and σ_Λ, for each given a value made the determination of the *best* parameter values possible. In most conductivity studies, however, where the minimization of σ_Λ has been used for the simultaneous determination of the values of three parameters, K, Λ_0, and a, the minimum standard deviation is not necessarily a good criterion of the *best* parameter values. The minimum values of σ_ϕ and σ_Λ we obtained for each fixed value of a are plotted against a in Figs.3.12 and 3.13 respectively. In the latter, the results obtained for $MgSO_4$ by the use of Fuoss-Onsager's equation47) and Pitts's equation48,49) are also shown for comparison. In Fig.3.13, some of the curves have two minima, while others have a shallow minimum. The a value giving the minimum σ_Λ depends not only on the experimental data, but also on the theoretical equations used for the analysis of the data. These facts imply that the minimum standard deviation cannot be a good basis for the determination of the *best* a value. Figure 3.12 gives hardly a clue for determining the *best* a value from the vpo data. Regarding the conductivity method, a similar discussion has also been made in detail by Hanna *et al.*27,50) Thus, we shall try to estimate the *best* a and K values with the help of theories of ion association.2,3,34)

3.3.7. Estimation of the *Best* Values with the Help of Theories of Ion Association

In Chapter 2, we made a refinement of the Debye-Hückel theory[1)] on the basis of the purely electrostatic model and introduced a correction term into the Debye-Hückel expression for the chemical potential of a dissolved electrolyte. By connecting the correction term with the conventional concept of ion association, we derived the expression for the ion-association constant, Eq.(2.31), which gives the K value as a function of a. Since this theoretical K value decreases monotonously with the increase in a, and since the experimental K value increases with the increase in the assumed value of a, only one choice of a set of a and K values can satisfy both theory and experiment. Such sets of a and K values are given in Table 3.6. Each of the listed a values is somewhat greater than the sum of the crystallographic radii of the cation and the anion, $r_M + r_A$,*** and is plausible if hydration of the ions is taken into consideration. This can be taken as evidence for the validity of the theory.

Fuoss's theory[3)] of ion association could be used in place of our theory. In that case, the results for $MgSO_4$, $CaSO_4$, and $MnSO_4$ are similar to those given in Table 3.6, but no value of a would simultaneously satisfy the theory and the experiment for $[Ru(phen)_3]SO_4$ and $[Fe(phen)_3]SO_4$. This disagreement between theory and experiment may substantiate our previous criticism of Fuoss's theory of ion association described in Section 2.8.

Bjerrum's theory[2)] could also be used to determine the values of the ion-association constant and the closest distance of approach of ions, but in a manner different from the above. Since his theory regards a cation and an anion within the critical distance q ($= z^2e^2/2\varepsilon kT$) of each other as forming an ion-pair, the substitution of q for a in the Debye-Hückel expression [Eqs.(3.4) and (3.9)] should give a K value consistent with Bjerrum's theory. Such K values are given at the bottoms of Tables 3.2 to 3.5, where the values of q (14.3 Å at 25°C and 13.9 Å at 0°C) are substituted for a. In Bjerrum's theory, the parameter a characteristic of each elctrolyte is the closest distance of approach of the cation and the anion of an ion-pair, and the value can be calculated by the use of a relation between K and a. The values of a thus obtained from the vpo experimental results are 4.6_4 Å for $MgSO_4$, 4.3_6 Å for $CaSO_4$, 4.1_3 Å for $MnSO_4$, and 9.9_0 Å for $[Ru(phen)_3]SO_4$. These a values are smaller than those given in Table 3.6. Especially, the value, 9.9_0 Å, for $[Ru(phen)_3]SO_4$ is very close to the sum of the crystallographic radii of the cation and the anion, 10.0 Å. This could be taken as an indication of there being no appreciable hydration. However, in view of the fact that the salt is highly soluble in water and crystallizes as a hydrate with more than seven molecules of water, there seem to be water molecules intervening between the ions in aqueous solutions; thus, the a value of 9.9_0 Å is possibly too small. This may be caused by the unreasonable characteristic of Bjerrum's theory that the theoretical ion-association constants decrease rapidly to zero as the value of a approaches the critical distance, 14.3 Å.

[***] The values of $r_M + r_A$ given in Table 3.6 were estimated as follows. The crystallographic data of $CaSO_4 \cdot 2H_2O$ and K_2SO_4[51)] were used for the estimation of the radius, r_A, of the sulfate ion. Pauling's radius[52)] of each cation was subtracted from the distance between the metal ion and the nearest oxygen atom of the neighboring sulfate ion; the difference, 1.3_8 Å, was obtained as the radius of the oxygen atom belonging to a sulfate ion. This oxygen radius was added to the bond length between the sulfur and the oxygen atom of a sulfate

ion, 1.5_0 Å,[51,53] to obtain 2.8_8 Å as the value of r_A for the sulfate ion. Pauling's radii[52] were used as the r_M values for magnesium, calcium, and manganese ions. For $[Fe(phen)_3]^{2+}$, the data of X-ray diffraction[54] are available. They give 6.1_3 Å as the distance from the central iron atom to the most distant hydrogen atom of the coordinated 1,10-phenanthroline ligand. The r_M value of $[Fe(phen)_3]^{2+}$ was estimated as the sum of this distance, 6.1_3 Å, and the effective radius of the hydrogen atom, 0.9_5 Å, as estimated from the interatomic distance between the hydrogen atom of the ligand and the nearest oxygen atom of a tartratoantimonate ion given in the literature.[54] The r_M value for $[Ru(phen)_3]^{2+}$ was assumed to be equal to that for the iron-complex ion.

CHAPTER 4

Spectrophotometric Studies of the Ion Association of Some 2 : 2 Electrolytes in Water

4.1. Introduction

In Chapters 1 and 2, we have developed a theory of ion association and have made use of it in the experimental determinations of the *best* values of ion-association constants and the closest distance of approach of ions. With the help of the theory, consistent and plausible results have been derived from vapor-pressure osmometry and conductivity measurements on 2 : 2 electrolyte solutions. In this connection, it is of interest to see if spectrophotometric studies give results consistent with the previous ones.

The absorption spectra of ion-pairs in the ultraviolet region have often been measured on solutions of metal complex salts such as hexamminecobalt(III) salts, and analyzed to obtain the ion-association constants.17,55-57) The ion association of divalent ions has been observed between the Cu^{2+}, Hg^{2+}, $[Co(NH_3)_5Cl]^{2+}$, and UO_2^{2+} cations and the SO_4^{2-} ion,58-64) and between some metal cations such as Mg^{2+} and the $S_2O_3^{2-}$ ion.65) These are considered to be special cases where spectrophotometry can be directly applied to the determination of the ion-association constant. In most electrolyte solutions, ion-pair formation causes no appreciable change in the absorption. However, even when no absorption change occurs, the ion-association constant can be indirectly determined by means of appropriate indicators.66) For example, with the pH indicator, 2,4-dinitrophenol, the ion-association constant of $MgSO_4$ in 20 % ethanol solutions has been measured by Bale *et al.*67) This method with the pH indicator has the disadvantage, however, that the complex composition of the solution makes the analysis of the data difficult and introduces considerable uncertainty into the results.

In this Chapter, an attempt has been made to determine spectrophotometrically the ion-association constants of magnesium, calcium, manganese, and zinc sulfates, with copper sulfate as an indicator. Copper sulfate in aqueous solutions is known to show an intense ultraviolet absorption attributable to the formation of ion-pairs,58-62) whereas the other four sulfates are nearly transparent in aqueous solutions and no ion-pair formation is detected spectrophotometrically. When copper sulfate is mixed with one of the four sulfates, the ion-association of the latter can be expected to be indirectly observed through the change in absorption due to copper sulfate ion-pairs. Although spectrophotometric studies of the ion association of copper sulfate have been made by several authors,58-62) they are not sufficient for the purpose of the present investigation. Thus, a re-examination has also been made of the ion association in simple copper sulfate solutions.

4.2. Experimental

4.2.1. Measurements

The absorption measurements were made at 250 nm with a Carl Zeiss PMQII spectrophotometer equipped with a M4QIII monochromator, using 1-cm quartz cells. The slit width was 0.15 mm, resulting in a spectral-band width of 0.57 nm at 250 nm. The cells were maintained at 25.00 ± 0.05°C by the circulation of water from a thermostat to the cell holder.

Copper perchlorate solutions of 5.007×10^{-3} and 1.001×10^{-2} M were prepared by the dilution of a stock solution of 5.007×10^{-2} M copper perchlorate containing about 2×10^{-3} M perchloric acid to protect it against hydrolysis. Their absorbances, observed at 250 nm, were 0.0607 and 0.1218 respectively, which gave absorbances per mol l^{-1} of the copper ion of 12.12 and 12.16 respectively. These values are in agreement with each other within the range of experimental error; the average, 12.14, was used as the molar extinction coefficient of the free copper ions.

A stock solution of 1.000×10^{-2} M copper sulfate containing 1.01×10^{-4} M sulfuric acid was diluted with a 1.01×10^{-4} M sulfuric acid solution. Thereby, nine copper sulfate solutions with concentrations from 2×10^{-3} to 10^{-2} M at 10^{-3} M intervals were prepared; their absorbances were then measured.

A stock solution of 1.000×10^{-2} M magnesium sulfate containing 1.01×10^{-4} M sulfuric acid was mixed with the stock solution of copper sulfate, and with 1.01×10^{-4} M sulfuric acid when necessary, to make nine mixed electrolyte solutions. (The compositions of the solutions are shown in Table 4.3.) Similar mixed electrolyte solutions containing copper sulfate and another divalent metal sulfate were also prepared with calcium, manganese, and zinc sulfates in the same manner as in the case of magnesium sulfate. The absorbances of all the solutions were measured under the condition described above. Simple solutions containing no copper sulfate were also prepared by the dilution of the stock solutions, and their absorbances were measured as the blank values to be subtracted from the absorbances of the mixed electrolyte solutions. The blank values were nearly zero, or less than 0.001. All the solutions were prepared within an error of ± 0.1 % in concentration, and their transmittances were observed within an error of ± 0.05 %.

4.2.2. Materials

The copper perchlorate was prepared by dissolving basic copper carbonate in an aqueous solution containing an equivalent amount of perchloric acid. After the solution had then been concentrated on a water bath, the salt was crystallized with stirring at room temperature and recrystallized twice from its aqueous solution containing a very small amount of perchloric acid. The crystal was obtained as a hexahydrate after having been dried over phosphorus pentaoxide. Its composition was confirmed by the electrolytic analysis of the copper ion. A reagent-grade copper sulfate was recrystallized as a pentahydrate from its aqueous solution containing a very small amount of sulfuric acid; it was then air-dried at room temperature. Its composition was confirmed by the electrolytic analysis of the copper ion and by dehydration at about 220°C. The magnesium and calcium sulfates used were prepared and analyzed according to the procedure described in Section 3.2.2. The manganese sulfate used was a reagent-grade hydrate. The manganese concentration in its stock solution was determined by the titration of the manganese ion with EDTA.68) The zinc sulfate used was a heptahydrate of reagent grade. The zinc concentration in its stock solution was determined by the titration of the zinc ion with EDTA.

4.3. Results and Discussion

4.3.1. Determination of the Ion-Association Constant of Copper Sulfate

The observed absorbances (D) of aqueous copper sulfate solutions of various concentrations (c_M) containing 1.01×10^{-4} M H_2SO_4 are shown in Table 4.1, together with the absorbances per mol l^{-1} of copper sulfate (D/c_M). The corresponding values are also listed for copper perchlorate solutions containing about 2×10^{-3} M $HClO_4$. The D/c_M values of the copper sulfate solutions are very much greater than those of the copper perchlorate solutions and increase with the increase in the concentration. This phenomenon has usually been attributed to the ion association of the copper ion with the sulfate ion.58-62) In the following, the absorption data will be analyzed in order to obtain the ion-association constant.

The possible ion-association equilibria between ions in the solution are:

$$M + A \rightleftharpoons MA \tag{4.1}$$

$$H + A \rightleftharpoons HA \tag{4.2}$$

where M, A, H, HA, and MA represent Cu^{2+}, SO_4^{2-}, H^+, HSO_4^-, and $Cu^{2+}SO_4^{2-}$ respectively. Since the concentration of the sulfuric acid is as low as 1.01×10^{-4} M, the formation of the $Cu^{2+}HSO_4^-$ ion-pair was ignored. The formations of the $(Cu^{2+})_2SO_4^{2-}$ and $Cu^{2+}(SO_4^{2-})_2$ triple-ions and the $(Cu^{2+}SO_4^{2-})_2$ quadrupole were also ignored. According to vpo studies described in Chapter 3, this approximation is good enough for the present study, where the concentrations of the solutions are lower than 10^{-2} M. The formation constants, K_{MA} and K_{HA}, of $Cu^{2+}SO_4^{2-}$ and HSO_4^- respectively are given by:

$$K_{MA} = \frac{[MA]}{[M][A]y_M y_A} \tag{4.3}$$

$$K_{HA} = \frac{[HA]y_{HA}}{[H][A]y_H y_A} \tag{4.4}$$

where y_M, y_H, y_A, and y_{HA} are the activity coefficients of Cu^{2+}, H^+, SO_4^{2-}, and HSO_4^- respectively. The activity coefficient of the $Cu^{2+}SO_4^{2-}$ ion-pair was regarded as unity. The total concentrations of Cu^{2+}, SO_4^{2-}, and H^+, denoted by c_M, c_A, and c_H respectively, are related to the concentrations of the species existing in the solution as follows:

$$\left.\begin{aligned} c_M &= [M] + [MA] \\ c_A &= [A] + [MA] + [HA] \\ c_H &= [H] + [HA] \end{aligned}\right\} \qquad (4.5)$$

The absorption observed at 250 nm can be attributed to the free Cu^{2+} ion and the $Cu^{2+}SO_4{}^{2-}$ ion-pair. Thus, the absorbance, D, of each solution can be expressed by:

$$\begin{aligned} D &= \varepsilon_M[M] + \varepsilon_{MA}[MA] \\ &= \varepsilon_M c_M + (\varepsilon_{MA} - \varepsilon_M)[MA] \qquad (4.6) \end{aligned}$$

where ε_M and ε_{MA} are the molar extinction coefficients of Cu^{2+} and $Cu^{2+}SO_4{}^{2-}$ respectively. Using Eqs.(4.3), (4.5), and (4.6), one can derive the relation:

$$P = \frac{1}{\varepsilon_{MA} - \varepsilon_M} Q + \frac{1}{K_{MA}(\varepsilon_{MA} - \varepsilon_M)} \qquad (4.7)$$

where P and Q are variables defined by:

$$\left.\begin{aligned} P &= \frac{(c_A - [HA])y_M y_A}{(D/c_M) - \varepsilon_M} \\ Q &= (c_M + c_A - [MA] - [HA])y_M y_A \end{aligned}\right\} \qquad (4.8)$$

If K_{MA}, ε_M, and ε_{MA} are assumed to be constant under the present experimental conditions, a linear relationship can be expected between P and Q in Eq.(4.7). The parameters appearing in Eq.(4.8) were treated as follows.

The molar extinction coefficient of the free ion, ε_M, was assumed to be equal to the absorbance (per cm) per mol l^{-1} of copper perchlorate in dilute solutions. This assumption is justified, at least at 250 nm, since the copper perchlorate solutions at this wavelength obey Beer's law, as is shown in Table 4.1; however, this does not exclude the possibility that ion-pairs may be formed between copper ions and perchlorate ions. The concentration of the hydrogensulfate ion, [HA], is given by:

$$[\mathrm{HA}] = \frac{R_1 - \sqrt{R_1^{\,2} - 4c_\mathrm{H}(c_\mathrm{A} - [\mathrm{MA}])}}{2} \tag{4.9}$$

where R_1 is a variable defined by:

$$R_1 = c_\mathrm{H} + c_\mathrm{A} - [\mathrm{MA}] + \frac{1}{K_\mathrm{HA}y_\mathrm{A}}$$

These equations were derived from Eqs.(4.4) and (4.5) on the assumption that $y_\mathrm{HA} = y_\mathrm{A}$. This assumption is acceptable for the calculation of the P and Q values with Eq.(4.8), since, at the low acid concentration of $c_\mathrm{H} = 2.02 \times 10^{-4}$ M, [HA] is very low compared with c_A. The value of K_HA was taken from the literature.69) The $\log K_\mathrm{HA}$ value of 1.99 was obtained by many authors by means of various experimental methods. The activity coefficients, y_M and y_A, were expressed by the Debye-Hückel expression:1)

$$\log y_\mathrm{M} = \log y_\mathrm{A} = -\frac{4A_1\sqrt{I}}{1 + Ba\sqrt{I}} \tag{4.10}$$

These equations are given by rewriting Eq.(2.24). A_1 and B are constants defined by:

$$B = \sqrt{\frac{8\pi Ne^2}{1000\varepsilon kT}} = \sqrt{\frac{8\pi Ns}{1000}} \qquad (B = 0.3291 \times 10^8 \text{ at } 25.0\,^\circ\mathrm{C})$$

$$A_1 = 0.21714\,\frac{e^2}{\varepsilon kT}\sqrt{\frac{8\pi Ne^2}{1000\varepsilon kT}} = 0.21714\,sB \qquad (A_1 = 0.5115 \text{ at } 25.0\,^\circ\mathrm{C})$$

I is the ionic strength given by:

$$I = 2(c_\mathrm{M} + c_\mathrm{A} - 2[\mathrm{MA}] - [\mathrm{HA}]) + \frac{1}{2}c_\mathrm{H} \tag{4.11}$$

The values of P, Q, and K_MA were calculated by the method of successive approximations in the following way. Assuming [MA] = [HA] = 0 provisionally, the ionic strength and then the activity coefficients were estimated for a given a value. By putting the values of these parameters into Eq.(4.8), the values of P and Q were calculated for each solution. Assuming a linear relationship between the P and Q values, the coefficient of the first term, $1/(\varepsilon_{\mathrm{MA}} - \varepsilon_{\mathrm{M}})$, and the second term, $1/K_{\mathrm{MA}}(\varepsilon_{\mathrm{MA}} - \varepsilon_{\mathrm{M}})$, of the right-hand side of Eq.(4.7) were evaluated by the method of least squares; the value of K_{MA} was then obtained as the ratio between them. The K_{MA} value thus obtained was used for the calculation of the [MA], [HA], I, y_{M}, and y_{A} values by means of Eqs. (4.3)-(4.5) and (4.9)-(4.11); these values were in turn used for the recalculation of the values of P and Q. Then, by the use of these values, the value of K_{MA} was evaluated again in the same way as above. In order to obtain the final value of K_{MA}, such calculations were repeated several times until the values of $1/(\varepsilon_{\mathrm{MA}} - \varepsilon_{\mathrm{M}})$ and $1/K_{\mathrm{MA}}(\varepsilon_{\mathrm{MA}} - \varepsilon_{\mathrm{M}})$ in Eq.(4.7) became constant within 0.05 % of their respective values.

The resulting plot of P *vs.* Q is shown in Fig.4.1 for each value of the parameter a. In Table 4.2, the values of K_{MA} and $\varepsilon_{\mathrm{MA}}$ are shown for the several a values assumed. Figure 4.2 gives the plot of $\log K_{\mathrm{MA}}$ *vs.* a. For $a = 10$ Å, the result in the present work, $K_{\mathrm{MA}} = 241\ \mathrm{mol^{-1}\ l}$, is in essential agreement with that obtained by Davies *et al.*$^{60)}$ at 240 nm, $K_{\mathrm{MA}} = 250\ \mathrm{mol^{-1}\ l}$.

Table 4.2 also gives the standard deviation of D in percentage, $\sigma_D(\%)$, defined by:

$$\sigma_D(\%) = \sqrt{\frac{\sum_{i=1}^{n} [100\,(D_{\mathrm{obsd},i} - D_{\mathrm{calcd},i})/D_{\mathrm{calcd},i}]^2}{n-2}}$$

where $D_{\mathrm{obsd},i}$ and $D_{\mathrm{calcd},i}$ are the observed and calculated absorbances respectively for the ith copper sulfate solution. The value of $D_{\mathrm{calcd},i}$ was calculated by means of Eq.(4.6), where the $\varepsilon_{\mathrm{MA}}$ value given in Table 4.2 was used together with the connected K_{MA} value from which the [MA] value was derived. As is shown in Table 4.2, the $\sigma_D(\%)$ values for the a values between 4 and 14.3 Å (Bjerrum's critical distance of ion association[2)]) are as small as 0.09-0.16 %. This shows that the observed absorbances are reproducible within the range of experimental error with each set of the a, K_{MA}, and $\varepsilon_{\mathrm{MA}}$ values. The value of a which gives the minimum σ_D(%) might be regarded as the *best* value. A minimum was actually found around $a = 5$ Å. However, it is a shallow minimum; therefore, there is some uncertainty as to the *best* value of a.

4.3.2. Determination of the Ion-Association Constants of Magnesium, Calcium, Manganese, and Zinc Sulfates from Measurements of Mixed Electrolyte Solutions

The absorbances of the mixed $CuSO_4$-$MgSO_4$, $CuSO_4$-$CaSO_4$, $CuSO_4$-$MnSO_4$, and $CuSO_4$-$ZnSO_4$ solutions containing 1.01×10^{-4} M of H_2SO_4 are shown in Table 4.3. A comparison of Table 4.3 with Table 4.1 shows that the addition of a second divalent metal sulfate increases the absorbance of the solution. This increase in the absorbance is attributable to the increase in the concentration of the ion-pair, $Cu^{2+}SO_4{}^{2-}$, caused by the increase in the concentration of the sulfate ion. However, the quantity of free sulfate ions supplied by the second metal sulfate depends on the ion-association constant of the second metal ions with sulfate ions, if the concentrations of the second components are the same. In the following paragraphs, the ion-association constant of the second metal sulfate will be estimated on the basis of an analysis of the absorption data.

We shall discuss the mixed $CuSO_4$-$MgSO_4$ solutions as an example. The third ion-association equilibrium, Eq.(4.12), must be considered in addition to Eqs.(4.1) and (4.2) for copper sulfate solutions:

$$\mathrm{M'} + \mathrm{A} \rightleftarrows \mathrm{M'A} \qquad (4.12)$$

where M' represents the Mg^{2+} ion and M'A, the $Mg^{2+}SO_4{}^{2-}$ ion-pair.

The formation constant of the ion-pair, $K_{\mathrm{M'A}}$, is expressed by:

$$K_{\mathrm{M'A}} = \frac{[\mathrm{M'A}]}{[\mathrm{M'}][\mathrm{A}]y_{\mathrm{M'}}y_{\mathrm{A}}} \tag{4.13}$$

where $y_{\mathrm{M'}}$ is the activity coefficient of the free magnesium ion. The activity coefficient of the $\mathrm{Mg^{2+}SO_4{}^{2-}}$ ion-pair is regarded as unity. The total concentrations, c_{M}, c_{H}, $c_{\mathrm{M'}}$, and c_{A}, are related to the concentrations of the species existing in the solution as follows:

$$\left.\begin{aligned} c_{\mathrm{M}} &= [\mathrm{M}] + [\mathrm{MA}] \\ c_{\mathrm{H}} &= [\mathrm{H}] + [\mathrm{HA}] \\ c_{\mathrm{M'}} &= [\mathrm{M'}] + [\mathrm{M'A}] \\ c_{\mathrm{A}} &= [\mathrm{A}] + [\mathrm{MA}] + [\mathrm{M'A}] + [\mathrm{HA}] \end{aligned}\right\} \tag{4.14}$$

The concentration of the $\mathrm{Cu^{2+}SO_4{}^{2-}}$ ion-pair can be expressed by:

$$[\mathrm{MA}] = \frac{D - \varepsilon_{\mathrm{M}} c_{\mathrm{M}}}{\varepsilon_{\mathrm{MA}} - \varepsilon_{\mathrm{M}}} \tag{4.15}$$

which was obtained by rewriting Eq.(4.6). Equation (4.6) can also be used for the mixed electrolyte solutions, since magnesium sulfate as well as the other second components give absorbances as small as 0.001 or less in solutions of $c_{\mathrm{M'}} = 10^{-2}$ M; the small absorbance has been allowed for in obtaining each D value given in Table 4.3. By combining Eqs.(4.3) and (4.14), one obtains:

$$[\mathrm{M'A}] = c_{\mathrm{A}} - [\mathrm{MA}] - [\mathrm{HA}] - \frac{[\mathrm{MA}]}{(c_{\mathrm{M}} - [\mathrm{MA}])\, K_{\mathrm{MA}} y_{\mathrm{M}} y_{\mathrm{A}}} \tag{4.16}$$

The concentration [HA] is given by:

$$[\mathrm{HA}] = \frac{R_2 - \sqrt{R_2{}^2 - 4\, c_{\mathrm{H}}(\, c_{\mathrm{A}} - [\mathrm{MA}] - [\mathrm{M'A}])}}{2} \tag{4.17}$$

where R_2 is a variable defined by:

$$R_2 = c_{\mathrm{H}} + c_{\mathrm{A}} - [\mathrm{MA}] - [\mathrm{M'A}] + \frac{1}{K_{\mathrm{HA}}\, y_{\mathrm{A}}}$$

Equation (4.17) was derived from Eqs.(4.4) and (4.14) by assuming

$y_{\mathrm{HA}} = y_{\mathrm{H}}$ in the same manner as in the case of copper sulfate solutions.

Then, by the use of Eqs.(4.13)-(4.17), $K_{\mathrm{M'A}}$ can be calculated if the values of K_{HA}, K_{MA}, ε_{M}, $\varepsilon_{\mathrm{MA}}$, y_{M}, $y_{\mathrm{M'}}$, and y_{A} are known. As has been mentioned above, $\log K_{\mathrm{HA}} = 1.99$ is given in the literature[69)] and the value of ε_{M} has been experimentally determined to be 12.14 (Table 4.1). The values of K_{MA} and $\varepsilon_{\mathrm{MA}}$ have already been obtained as a function of a; they are listed in Table 4.2. By assuming that both copper and magnesium sulfates have the same a value, the activity coefficients of the free ions, y_{M}, $y_{\mathrm{M'}}$, and y_{A}, are given by the Debye-Hückel theory[1)] as follows:

$$\log y_{\mathrm{M}} = \log y_{\mathrm{M'}} = \log y_{\mathrm{A}} = -\frac{4A\sqrt{I}}{1 + Ba\sqrt{I}} \tag{4.18}$$

where the ionic strength, I, is given by:

$$I = 2\,(c_{\mathrm{M}} + c_{\mathrm{M'}} + c_{\mathrm{A}} - 2[\mathrm{MA}] - 2[\mathrm{M'A}] - [\mathrm{HA}]) + \frac{1}{2}c_{\mathrm{H}}$$

The calculation of $K_{\mathrm{M'A}}$ was done as follows. Assuming [M'A] = [HA] = 0 provisionally, the ionic strength, I, and then the activity coefficients, y_{M} and y_{A}, were evaluated for a given a value. [MA] was calculated by the use of Eq.(4.15) with the corresponding $\varepsilon_{\mathrm{MA}}$ value for the given a value. By putting these values into the right-hand side of Eq.(4.16), the value of [M'A] was obtained, and then the value of [HA] was calculated by the use of Eq.(4.17). The values of [M'A] and [HA] thus obtained were used for the recalculation of I, y_{M}, and y_{A}, after which [M'A] and [HA] were re-evaluated in the same way. Such a procedure was repeated several times until both the [M'A] and [HA] values became constant within 0.05 % of their respective values. The values of [M'A], [HA], and y_{A} thus obtained were then used to evaluate the ion-association constant, $K_{\mathrm{M'A}}$, by means of Eqs.(4.13), (4.14), and (4.18). The values of $K_{\mathrm{M'A}}$ were thus obtained for the solutions of each different composition, after which the $K_{\mathrm{M'A}}$ values were averaged. In Table 4.4, the averaged $K_{M'A}$ value of $MgSO_4$ as well as those of the other sulfates are shown for the several a values assumed.

A comparison of Table 4.4 with Table 4.2 shows that the ion-association constants ($K_{M'A}$) of $MgSO_4$, $CaSO_4$, $MnSO_4$, and $ZnSO_4$ are considerably smaller than that of $CuSO_4$ (K_{MA}) at the same a value, and that, as the assumed a value increases, $K_{M'A}$ increases in parallel with K_{MA}, with the difference kept almost constant; *i.e.*, $K_{MA} - K_{M'A} =$ 84-86 for $MgSO_4$, 68-70 for $CaSO_4$, 65-68 for $MnSO_4$, and 61-64 for $ZnSO_4$.

These results were derived from the data on the mixed aqueous solutions of copper sulfate and a second metal sulfate in question, assuming that the a value for the latter was the same as that for copper sulfate. Therefore, the results obtained for the second metal sulfates (Table 4.4) may be different from those which would be obtained from the experiments on single electrolyte solutions. This problem will be examined below.

The activity coefficient of each ionic species is expressed by:

$$\log y_i = - \frac{4A\sqrt{I}}{1 + Ba_i\sqrt{I}} \tag{4.19}$$

where the subscript i stands for the ionic species, whether M, M', or A. Rigorously speaking, the condition $a_i = a_j$ is required in order for Eq.(4.19) and a similar equation for j-ions to satisfy the thermodynamical relation:[70)]

$$\frac{\partial(\log y_i)}{\partial c_j} = \frac{\partial(\log y_j)}{\partial c_i}$$

As an approximation, however, Eq.(4.19) will be used without the condition that $a_i = a_j$.

The main ionic species existing in the mixed $CuSO_4$-$MgSO_4$ solutions are Cu^{2+}, Mg^{2+}, and $SO_4{}^{2-}$. Since the sulfate ion is the predominant anionic species, the closest distance of approach of the copper ion in the mixed electrolyte solution, a_M, can be reasonably approximated by the a value in single copper sulfate solutions. The same argument applies to $a_{M'}$ for the magnesium ion. Considering the probability of a sulfate ion colliding with each of the metal cations, we assumed the equation:

$$a_A = \frac{a_M c_M + a_{M'} c_{M'}}{c_M + c_{M'}}$$

Then the activity coefficient of each ion was calculated by the use of Eq.(4.19). The K_{MA} and ε_{MA} values were so chosen from Table 4.2 as to correspond to the assumed a_M value. Then the experimental data was analyzed in the way described above, except that different a values and, accordingly, different activity coefficients were used for different ions instead of a common a and a common activity coefficient. The values of $K_{M'A}$ were thus obtained for various combinations of the values of a_M and $a_{M'}$.

In Fig.4.3, the values of $K_{M'A}$ obtained for $MgSO_4$ are plotted against the values of $a_{M'}$, with several fixed a_M values. This figure also shows, for comparison, the plot of the results given in Table 4.4, which was obtained above with the assumption that $a_M = a_{M'} (= a_A)$ [Eq.(4.18)]. The values of $K_{M'A}$ obtained with and without this assumption [Eq.(4.18)] are close to each other when the value of $a_{M'}$ is not very different from the value of a_M; for example, $a_{M'} = 3\text{-}7$ Å for $a_M = 5$ Å and $a_{M'} = 6.5\text{-}12$ Å for $a_M = 10$ Å. This condition is probably satisfied in view of the fact that the crystallographic radius of the magnesium ion is only slightly different from that of the copper ion (see Table 4.6). Thus, the $K_{M'A}$ values given in Table 4.4 for the special case of $a_M = a_{M'}$ approximate the $K_{M'A}$ values in the general case without the assumption that $a_M = a_{M'}$, if one reads $a_{M'}$ for a.

In other words, the results obtained for $MgSO_4$ from experiments on the mixed electrolyte solutions with the assumption that $a_M = a_{M'}$ probably represent the results which would be obtained from experiments on single magnesium sulfate solutions. The same argument also applies to the cases of the other mixed electrolyte solutions investigated.

4.3.3. Comparison with the Vapor-Pressure Osmometry and the Conductivity Method

In Chapter 3, the ion association of $MgSO_4$, $CaSO_4$, and $MnSO_4$ in aqueous solutions was studied with a vapor-pressure osmometer, and the ion-association constants were obtained. The ion-association constants of these electrolytes were also obtained by reanalyzing the literature values of the conductivity[28-32] by means of Fuoss-Hsia's equation[45] expanded by Fernández-Prini.[46] In connection with the present spectrophotometric studies, the conductivity data on aqueous $CuSO_4$ and $ZnSO_4$ solutions measured by Owen and Gurry[71] were reanalyzed in the manner described in Chapter 3, and the ion-association constants were evaluated with various a values assumed. The results are shown in Table 4.5; the $\log K_{MA}$ for $CuSO_4$ is plotted against a in Fig.4.2. In the range of $a = 3.0\text{-}14.3$ Å, the ion-association constant of $CuSO_4$ derived from the conductivity data is not very different from that determined by the spectrophotometry (Table 4.2).

Figure 4.4 gives the plot of $\log K_{M'A}$ *vs.* a for $MgSO_4$ as an example of the results obtained from the spectrophotometric studies of the mixed electrolyte solutions, together with those obtained in Chapter 3 from the vapor-pressure osmometric and conductivity studies of the single electrolyte solutions. The spectrophotometric method gives slightly smaller ion-association constants than those given by the other methods.

In Fig.4.5, the log *K* values (the subscripts, MA and M'A are omitted) are plotted against the reciprocal of the crystallographic radii of the cations, with the assumption that $a = 6$ Å. The log *K* values increase in the order: $MgSO_4 < CaSO_4 < MnSO_4 < ZnSO_4 < CuSO_4$. This order is the same as that obtained by the other methods. The same tendency was also obtained with the assumption that $a = 14.3$ Å. Such a tendency in the magnitude of the ion-association constants seems to reflect some properties of the metal ions. In this connection, further discussions will be made in the next section.

4.3.4. Estimation of the *Best* Value of *a* with the Help of the Theory of Ion Association

In Chapter 2, we derived an expression for the ion-association constant [Eq.(2.31)]. The log *K* *vs.* *a* curves obtained with Eq.(2.31) are shown in Figs.4.2 and 4.4 (broken curves) and there compared with the experimental curves. The point where the experimental curve cross the theoretical curve gives experimental *a* and *K* values consistent with the theory of ion association.

The values of *a* and *K* for each electrolyte were obtained in this way; they are shown in Table 4.6. The magnitude of the ion-association constant increased with the decrease in *a* and with the decrease in the crystallographic radii of the metal ions except for the case of the magnesium ion. This general trend can be expected from electrostatic considerations. The small value of *K* and the large value of *a* for magnesium sulfate, in spite of the small crystallographic radii of the magnesium ion, can be attributed to the strong hydration of the magnesium ion.

The results given in Table 4.6 show that the differences between the *a* value of copper sulfate and those of the other electrolytes are much less than 2 Å. This satisfies the above-mentioned condition for the validity of the present treatment in deriving ion-association constants from the spectrophotometric data on the mixed electrolyte solutions.

SUMMARY

1. The Debye-Hückel theory was re-examined and a theoretical expression was derived for the ion-association constant of symmetrical electrolytes. It was shown that the concept of ion association is a practical and useful convention to complement the Debye-Hückel theory.

2. The osmotic coefficients of solutions of some 2 : 2 electrolytes were measured with a vapor-pressure osmometer. The data were analyzed to obtain the ion-association constants; the triple-ion formation and the ion hydration were considered. The values of the ion-association constants obtained depended on the assumed value of the closest distance of approach of ions, a.

3. The conductivity and cryoscopic data given in the literature were analyzed to obtain the ion-association constants as a function of a. The value of the ion-association constant obtained for a given a value only slightly depended on the experimental methods.

4. The ion-association constants of the divalent metal ions with the sulfate ion were determined as a function of a from the spectrophotometric measurements of simple and mixed aqueous electrolyte solutions. The results obtained were similar to those obtained from the vapor-pressure osmometric and conductivity measurements.

5. The criterion of minimum standard deviation was found to be unsatisfactory for the simultaneous determination of the *best* values of the ion-association constant and the closest distance of approach of ions. Their *best* values were determined with the help of the theoretical expression of the ion-association constant. The obtained *best* values of a were reasonable; this may be evidence for the validity of the theory.

TABLES AND FIGURES

Table 2.1

Values of the Sum $\sum_{n=1}^{\infty} \frac{b^{2n+2}}{(2n+2)!\,(2n-1)}$ (Abbreviated to Σ) and Its Limiting Expression $\frac{\exp(b)}{2b}$

b	$\log \Sigma$	$\log \frac{\exp(b)}{2b}$	b	$\log \Sigma$	$\log \frac{\exp(b)}{2b}$	b	$\log \Sigma$	$\log \frac{\exp(b)}{2b}$	b	$\log \Sigma$	$\log \frac{\exp(b)}{2b}$
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			

Table 2.2

Thermodynamic Parameters for Ion-Pair Formation

Paramater	Yokoyama-Yamatera, Ebeling,[6) and Bjerrum[2) ($b \to \infty$)	Fuoss[3)	Denison-Ramsey[4)
K	$\frac{4\pi N a^3}{1000}\cdot\frac{\exp(b)}{b}$	$\frac{4\pi N a^3}{3000}\cdot\exp(b)$	$\exp(b)$
$\Delta G°$	$-RT(\ln\frac{4\pi N a^3}{1000b}+b)$	$-RT(\ln\frac{4\pi N a^3}{3000}+b)$	$-bRT$
$\Delta S°$	$R\ln\frac{4\pi N a^3}{1000b}-bRT\frac{\partial\ln\varepsilon}{\partial T}$	$R\ln\frac{4\pi N a^3}{3000}-bRT\frac{\partial\ln\varepsilon}{\partial T}$	$-bRT\frac{\partial\ln\varepsilon}{\partial T}$
$\Delta H°$	$-bRT^2(\frac{\partial\ln\varepsilon}{\partial T}+\frac{1}{T})$	$-bRT^2(\frac{\partial\ln\varepsilon}{\partial T}+\frac{1}{T})$	$-bRT^2(\frac{\partial\ln\varepsilon}{\partial T}+\frac{1}{T})$

Table 3.1

Osmotic Coefficients ϕ of Some 2 : 2 Electrolytes Measured with a Vapor-Pressure Osmometer at 25.0°C

$MgSO_4$		$CaSO_4$		$MnSO_4$		$[Ru(phen)_3]SO_4$	
m (mol kg^{-1})	ϕ	m (mol kg^{-1})	ϕ	m (mol kg^{-1})	ϕ	m (mol kg^{-1})	ϕ
0.005036	0.800 ± 0.008	0.002990	0.816 ± 0.012	0.008371	0.744 ± 0.005	0.008542	0.829 ± 0.005
0.01485	0.722 ± 0.004	0.004438	0.809 ± 0.009	0.01662	0.695 ± 0.003	0.01675	0.806 ± 0.003
0.02021	0.700 ± 0.003	0.005943	0.773 ± 0.007	0.02549	0.664 ± 0.003	0.02498	0.775 ± 0.003
0.02473	0.686 ± 0.003	0.007465	0.763 ± 0.006	0.03346	0.646 ± 0.003	0.03300	0.760 ± 0.002
0.03050	0.672 ± 0.002	0.008923	0.745 ± 0.005	0.04187	0.632 ± 0.002	0.04079	0.744 ± 0.002
0.03464	0.664 ± 0.002	0.01044	0.736 ± 0.004	0.05108	0.619 ± 0.002	0.05040	0.727 ± 0.002
0.03948	0.655 ± 0.002	0.01187	0.721 ± 0.004	0.05858	0.609 ± 0.002	0.05868	0.716 ± 0.002
0.04455	0.648 ± 0.002	0.01334	0.729 ± 0.004	0.06786	0.599 ± 0.002	0.06763	0.705 ± 0.002
0.04961	0.638 ± 0.002	0.01491	0.709 ± 0.004	0.07549	0.594 ± 0.002	0.07635	0.699 ± 0.002
0.05984	0.629 ± 0.002			0.08432	0.584 ± 0.002	0.08536	0.687 ± 0.002
0.07903	0.610 ± 0.002			0.1006	0.569 ± 0.002		
0.09945	0.596 ± 0.002			0.1264	0.557 ± 0.002		
0.1490	0.573 ± 0.002						

Table 3.2

K and K_t Values of Some 2 : 2 Electrolytes Determined by the Vapor-Pressure Osmometric Measurements at 25.0°C

	$MgSO_4$				$CaSO_4$				$MnSO_4$				$[Ru(phen)_3]SO_4$			
a	K	K_t			K	K_t			K	K_t			K	K_t		
(Å)	$(\text{mol}^{-1}\text{ kg})$	$(\text{mol}^{-1}\text{ kg})$			$(\text{mol}^{-1}\text{ kg})$	$(\text{mol}^{-1}\text{ kg})$			$(\text{mol}^{-1}\text{ kg})$	$(\text{mol}^{-1}\text{ kg})$			$(\text{mol}^{-1}\text{ kg})$	$(\text{mol}^{-1}\text{ kg})$		
		$h = 0$	$h_0 = 15$			$h = 0$	$h_0 = 15$			$h = 0$	$h_0 = 15$			$h = 0$	$h_0 = 15$	
			(B)[a]	(A)[a]			(B)	(A)			(B)	(A)			(B)	(A)
4.0	72 ± 8	0	0.7	0.9	118 ± 27	0	0	0	136 ± 8	0.7	1.2	1.5				
5.0	100 ± 3	1.5	2.1	2.4	135 ± 25	1.4	1.8	2.1	159 ± 5	1.9	2.3	2.7				
6.0	121 ± 5	2.2	2.7	3.1	147 ± 24	2.8	3.3	3.5	178 ± 4	2.5	3.0	3.5				
7.0	137 ± 6	2.5	3.0	3.5	159 ± 24	3.6	4.0	4.3	192 ± 4	2.9	3.4	4.0				
8.0	150 ± 7	2.6	3.1	3.7	169 ± 24	4.0	4.4	4.7	204 ± 5	3.1	3.6	4.3	7 ± 2	20	20	21
10.0	169 ± 7	2.7	3.1	3.9	188 ± 24	4.2	4.6	5.0	222 ± 5	3.4	3.8	4.6	28 ± 3	5.1	5.9	6.5
12.0	183 ± 6	2.6	3.1	3.9	204 ± 24	4.1	4.4	4.8	235 ± 6	3.4	3.9	4.8	42 ± 3	3.2	3.7	4.3
14.3[b]	194 ± 6	2.5	2.9	3.8	219 ± 24	3.6	3.9	4.3	246 ± 8	3.4	3.8	4.8	53 ± 4	2.2	2.6	3.1

a) See the text (p. 28 and 29).

b) The critical distance of ion association at 25°C in Bjerrum's theory.[2)]

Table 3.3

K and K_t Values Determined by the Reanalysis of the Cryoscopic Data up to 0.1 mol kg^{-1} at 0°C

	$MgSO_4$ (Brown & Prue[24])				$MgSO_4$ (Isono[26])				$CaSO_4$ (Brown & Prue[24])			
a (Å)	K (mol^{-1} kg)	K_t (mol^{-1} kg)			K (mol^{-1} kg)	K_t (mol^{-1} kg)			K (mol^{-1} kg)	K_t (mol^{-1} kg)		
		$h = 0$	$h_0 = 15$			$h = 0$	$h_0 = 15$			$h = 0$	$h_0 = 15$	
			(B)[a]	(A)[a]			(B)	(A)			(B)	(A)
4.0	87 ± 15	0	0.6	0.8	81 ± 20	0	0.2	0.5	159 ± 15	2.1	2.5	2.8
5.0	114 ± 10	1.1	1.6	1.9	101 ± 18	1.0	1.5	1.8	171 ± 15	3.7	4.3	4.4
6.0	134 ± 8	1.6	2.0	2.4	117 ± 18	1.7	2.1	2.5	181 ± 14	4.9	5.3	5.6
7.0	149 ± 8	1.8	2.2	2.7	130 ± 18	2.0	2.4	2.8	191 ± 14	5.5	5.9	6.2
8.0	161 ± 8	1.9	2.3	2.9	141 ± 19	2.1	2.5	3.0	200 ± 14	6.0	6.4	6.7
10.0	179 ± 9	1.9	2.3	3.0	160 ± 19	2.1	2.5	3.1	217 ± 14	6.2	6.6	7.0
12.0	192 ± 10	1.9	2.2	3.0	174 ± 19	2.0	2.3	3.0	231 ± 14	6.1	6.5	6.9
13.9[b]	201 ± 11	1.8	2.1	3.0	184 ± 19	1.8	2.2	2.8	243 ± 14	5.9	6.2	6.6

a) See the text (p. 28 and 29).

b) The critical distance of ion association at 0°C in Bjerrum's theory.[2]

Table 3.4

K and K_t Values of $MgSO_4$ Obtained with the Assumption of $K_q = K_t$ at 25.0°C (vpo)

a (Å)	K (mol^{-1} kg)	K_q ($= K_t$) (mol^{-1} kg)		
		$h = 0$	$h_0 = 15$	
			(B)[a]	(A)[b]
4.0	72 ± 9	0	0.6	0.8
5.0	102 ± 3	1.2	1.6	1.9
6.0	126 ± 6	1.5	1.8	2.1
7.0	144 ± 8	1.5	1.8	2.1
8.0	159 ± 9	1.4	1.7	2.1
10.0	182 ± 10	1.3	1.5	1.8
12.0	197 ± 10	1.1	1.3	1.6
14.3	210 ± 9	1.0	1.1	1.5

a) $h = h_0[1-\alpha(1+2\beta+2\delta)]$; the assumption for the hydration number of the quadrupole is similar to that described in the paragraph following Case (B) on p. 29.

b) $h = h_0$; a similar assumption to that described in the paragraph following Case (A) on p.28.

Table 3.5

K and Λ_0 Values of Some 2 : 2 Electrolytes Determined by the Reanalysis of the Conductivity Data at 25.0°C with Fuoss-Hsia's Equation[45,46]

	$MgSO_4$[a] (Dunsmore and James[28])		$MgSO_4$[b] (Katayama[29])		$CaSO_4$[c] (Inada *et al.*[30])	
a (Å)	K (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})	K (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})	K (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})
3.0	59 ± 5	132.43	23 ± 12	131.25	62 ± 13	139.39
4.0	83 ± 4	132.63	63 ± 10	132.05	86 ± 12	139.54
5.0	103 ± 3	132.77	92 ± 6	132.50	105 ± 12	139.66
6.0	119 ± 3	132.88	115 ± 4	132.82	121 ± 12	139.75
7.0	133 ± 2	132.96	133 ± 3	133.02	135 ± 12	139.82
8.0	146 ± 2	133.02	148 ± 2	133.15	147 ± 12	139.86
10.0	167 ± 2	133.10	169 ± 2	133.25	167 ± 12	139.93
12.0	183 ± 2	133.11	182 ± 3	133.15	184 ± 12	139.95
14.3	197 ± 2	133.08	188 ± 6	132.86	198 ± 12	139.92

Table 3.5

(Continued)

	$MnSO_4$ [d]		$MnSO_4$ [e]		$[Fe(phen)_3]SO_4$ [f]	
	(Hallada and Atkinson[31])		(Petrucci et al.[32])		(Kubota and Yokoi[33])	
a (Å)	K (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})	K (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})	K (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})
3.0	50 ± 10	131.88	69 ± 10	132.23		
4.0	90 ± 6	132.50	106 ± 6	132.84		
5.0	119 ± 5	132.92	134 ± 4	133.26		
6.0	142 ± 5	133.21	155 ± 2	133.55		
7.0	160 ± 6	133.40	173 ± 2	133.75		
8.0	175 ± 7	133.53	188 ± 2	133.89		
10.0	197 ± 7	133.62	210 ± 2	134.00	19 ± 5	114.40
12.0	210 ± 6	133.54	224 ± 2	133.94	34 ± 5	114.39
14.3	216 ± 6	133.28	232 ± 3	133.70	46 ± 5	114.29

a) The calculations were made by use of eleven data at concentrations from 0.1634 up to 0.8846 x 10^{-3} mol l^{-1}. *b*) 10 data, (0.2 - 3.0) x 10^{-3} mol l^{-1}. *c*) 10 data, (0.1 - 1.0) x 10^{-3} mol l^{-1}. *d*) 9 data, (0.2013 - 3.141) x 10^{-3} mol l^{-1}. *e*) 5 data, (0.2758 - 2.235) x 10^{-3} mol l^{-1}. *f*) 17 data, (0.1745 - 1.662) x 10^{-3} mol l^{-1}.

Table 3.6

The *Best* Values of a and K Obtained with the Help of the Theoretical Expression [Eq.(2.31)] for the Ion-Association Constant (25.0°C)

		from vpo		from conductivity		(recalcd.)
Electrolyte	$r_M + r_A$ (Å)	a (Å)	K (mol^{-1} kg)	a (Å)	K (mol^{-1} l)	data
$MgSO_4$	3.5_3	5.4_6	110	5.4_4	111	28)
				5.5_8	106	29)
$CaSO_4$	3.8_7	4.9_2	134	5.4_2	112	30)
$MnSO_4$	3.6_8	4.6_4	151	5.1_4	123	31)
				4.9_5	132	32)
$[Ru(phen)_3]SO_4$	10.0	11.5_2	40			
$[Fe(phen)_3]SO_4$	10.0			12.3_8	36	33)

Table 4.1

Absorbances of Aqueous Copper Sulfate Solutions Containing 1.01×10^{-4} M H_2SO_4 and of Aqueous Copper Perchlorate Solutions Containing About 2×10^{-3} M $HClO_4$ (250 nm, 1-cm Cells, 25.0°C)

Electrolyte	$10^3 c_M$ (mol l^{-1})	D	D/c_M (mol^{-1} l)
$CuSO_4$	2.000	0.0818 ± 0.0003	40.9
	3.000	0.1426 ± 0.0003	47.5
	4.000	0.2100 ± 0.0004	52.5
	5.000	0.2824 ± 0.0005	56.5
	6.000	0.3595 ± 0.0005	59.9
	7.000	0.4395 ± 0.0006	62.8
	8.000	0.5230 ± 0.0008	65.6
	9.000	0.6083 ± 0.0009	67.6
	10.000	0.6968 ± 0.0011	69.7
$Cu(ClO_4)_2$	5.007	0.0607 ± 0.0003	12.12
	10.01	0.1218 ± 0.0003	12.16

Table 4.2

K_{MA} and ε_{MA} Values of Copper Sulfate Derived from the Spectrophotometric Measurements on the Copper Sulfate Solutions at 25.0°C (with Several *a* Values Assumed)

a (Å)	K_{MA} (mol^{-1} l)	ε_{MA} (cm^{-1} mol^{-1} l)	σ_D (%)
3.0	87 ± 1	403	0.34
4.0	130 ± 1	287	0.15
5.0	161 ± 1	239	0.09
6.0	185 ± 1	213	0.11
7.0	203 ± 1	197	0.14
8.0	219 ± 1	185	0.15
10.0	241 ± 1	170	0.16
12.0	256 ± 1	161	0.16
14.3^a)	269 ± 1	153	0.14

a) The critical distance of ion association at 25°C in Bjerrum's theory.2)

Table 4.3

Absorbances of Mixed Aqueous Solutions of Divalent Metal Sulfate Containing 1.01×10^{-4} M H_2SO_4 (250 nm, 1-cm Cells, 25.0°C)

$10^3 c_M$ (mol l^{-1})	$10^3 c_{M'}$ (mol l^{-1})	$CuSO_4$- $MgSO_4$ *D*	$CuSO_4$- $CaSO_4$ *D*	$CuSO_4$- $MnSO_4$ [a] *D*	$CuSO_4$- $ZnSO_4$ *D*
2.000	4.000	0.1226 ± 0.0003	0.1218 ± 0.0003	0.1224 ± 0.0003	0.1217 ± 0.0003
2.000	6.000	0.1342 ± 0.0003	0.1331 ± 0.0003	0.1341 ± 0.0003	0.1336 ± 0.0003
2.000	8.000	0.1442 ± 0.0003	0.1424 ± 0.0003	0.1432 ± 0.0003	0.1432 ± 0.0003
4.000	2.000	0.2421 ± 0.0004	0.2424 ± 0.0004	0.2428 ± 0.0004	0.2414 ± 0.0004
4.000	4.000	0.2669 ± 0.0004	0.2650 ± 0.0004	0.2656 ± 0.0004	0.2635 ± 0.0004
4.000	6.000	0.2862 ± 0.0004	0.2829 ± 0.0005	0.2840 ± 0.0004	0.2838 ± 0.0004
6.000	2.000	0.3962 ± 0.0006	0.3964 ± 0.0006	0.3964 ± 0.0006	0.3959 ± 0.0006
6.000	4.000	0.4249 ± 0.0008	0.4237 ± 0.0006	0.4241 ± 0.0006	0.4224 ± 0.0006
8.000	2.000	0.5625 ± 0.0008	0.5622 ± 0.0008	0.5630 ± 0.0008	0.5613 ± 0.0008

a) The concentrations of $MnSO_4$ ($c_{M'}$) in the $CuSO_4$- $MnSO_4$ solutions were slightly higher than given in the second column. In this case, read 2.044 for 2.000, 4.088 for 4.000, 6.132 for 6.000, and 8.176 for 8.000.

Table 4.4

$K_{M'A}$ Values of Some 2 : 2 Electrolytes Derived from the Spectrophotometric Measurements on the Mixed Electrolyte Solutions at 25.0°C (with Several a Values Assumed)

a (Å)	$MgSO_4$ $K_{M'A}$ (mol^{-1} l)	$CaSO_4$ $K_{M'A}$ (mol^{-1} l)	$MnSO_4$ $K_{M'A}$ (mol^{-1} l)	$ZnSO_4$ $K_{M'A}$ (mol^{-1} l)
4.0	44 ± 15	60 ± 17	62 ± 16	66 ± 18
5.0	77 ± 10	93 ± 14	95 ± 12	99 ± 14
6.0	101 ± 7	117 ± 14	119 ± 11	123 ± 13
7.0	120 ± 6	136 ± 14	139 ± 11	142 ± 12
8.0	135 ± 5	151 ± 14	154 ± 11	157 ± 12
10.0	157 ± 5	173 ± 14	176 ± 11	180 ± 12
12.0	172 ± 5	188 ± 14	191 ± 11	195 ± 12
14.3	184 ± 6	200 ± 14	203 ± 11	207 ± 13

Table 4.5

Values of the Ion-Association Constant *K* and the limiting Equivalent Conductivity Λ_0 Determined by the Reanalysis of the Conductivity data[71)] at 25.0°C with Fuoss-Hsia's Equation[45,46)] (with Several *a* Values Assumed)

	CuSO$_4$		ZnSO$_4$	
a (Å)	*K* (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})	*K* (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})
3.0	70 ± 12	131.15	44 ± 11	130.46
4.0	119 ± 7	132.40	92 ± 6	131.68
5.0	154 ± 4	133.18	127 ± 3	132.46
6.0	181 ± 2	133.71	153 ± 1	132.98
7.0	202 ± 1	134.04	173 ± 2	133.32
8.0	218 ± 1	134.25	189 ± 2	133.50
10.0	239 ± 1	134.33	210 ± 2	133.58
12.0	249 ± 2	134.10	220 ± 1	133.35
14.3	250 ± 5	133.50	221 ± 5	132.74

Table 4.6

The *Best* Values of *a* and *K* Obtained from Spectrophotometry (sp), Vapor-Pressure Osmometry (vpo), and Conductivity Measurements (con), with the Help of the Theoretical Expression[34)] for the Ion-Association Constant (25.0°C)

Electrolyte	$r_M + r_A$ a) (Å)	from sp *a* (Å)	 *K* (mol^{-1} l)	from vpo *a* (Å)	 *K* (mol^{-1} kg)	from con (recalcd.) *a* (Å)	 *K* (mol^{-1} l)	 data
$MgSO_4$	3.5_3	5.8_5	98	5.4_6	110	5.4_4	111	28)
						5.5_8	106	29)
$CaSO_4$	3.8_7	5.5_5	107	4.9_2	134	5.4_2	112	30)
$MnSO_4$	3.6_8	5.5_1	108	4.6_4	151	5.1_4	123	31)
						4.9_5	132	32)
$CuSO_4$	3.6_0	4.6_5	151			4.7_3	146	71)
$ZnSO_4$	3.6_2	5.4_4	111			5.0_3	128	71)

a) Sum of crystallographic radii of the metal ion (r_M) and the sulfate ion (r_A). (See the footnote in Section 3.3.7.)

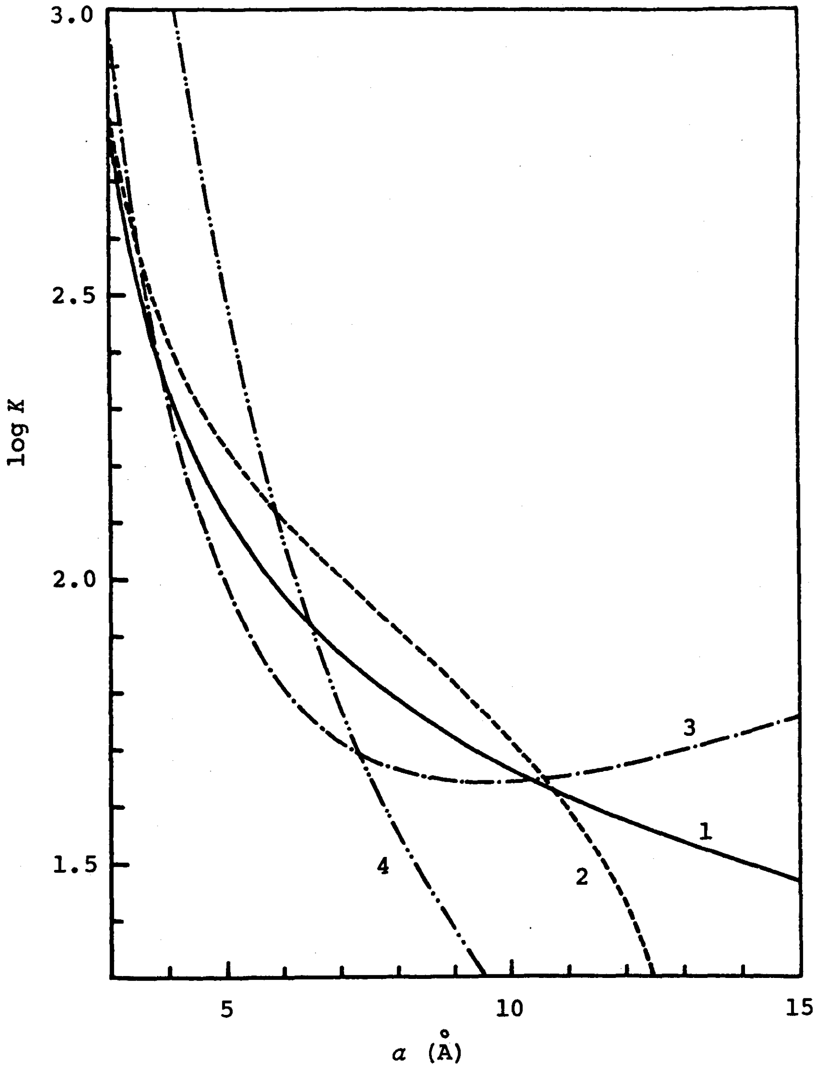

Fig. 2.1. Theoretical log K values for 2 : 2 electrolytes in aqueous solutions at 25.0°C.

1 : Present theory and Ebeling's theory$^{6)}$ (————)

2 : Bjerrum's theory$^{2)}$ (-------)

3 : Fuoss's theory$^{3)}$ (—·——·—)

4 : Denison-Ramsey's theory$^{4)}$ (—··——··—)

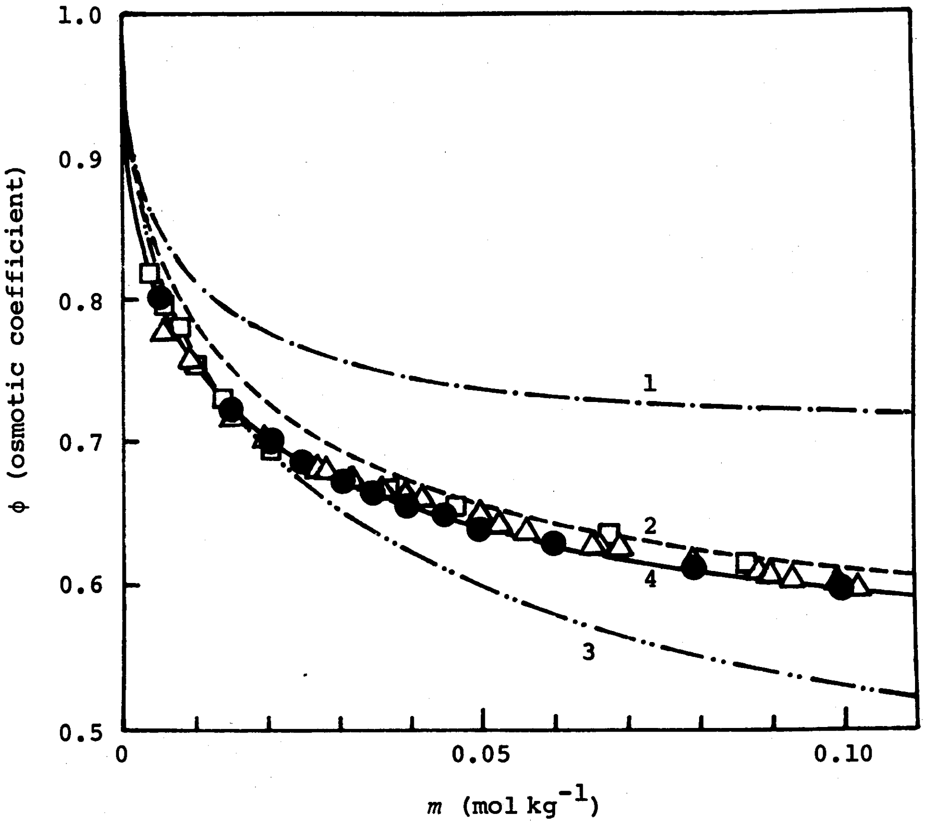

Fig. 3.1. Osmotic coefficients of $MgSO_4$ solutions. ●, present work at 25.0°C (vpo). △, Brown and Prue[24)] at 0°C (cryoscopy). □, Isono[26)] at 0°C (cryoscopy). Curves 1 (—·—), 2 (-----), and 3 (—··—) are theoretical curves due to the Debye-Hückel theory with $a = 6.0$, 4.0, and 3.0 Å, respectively. Curve 4 (——) is calculated with the K and K_t values in Table 3.2 (25.0°C); each set of the K and K_t values gives the essentially same curve.

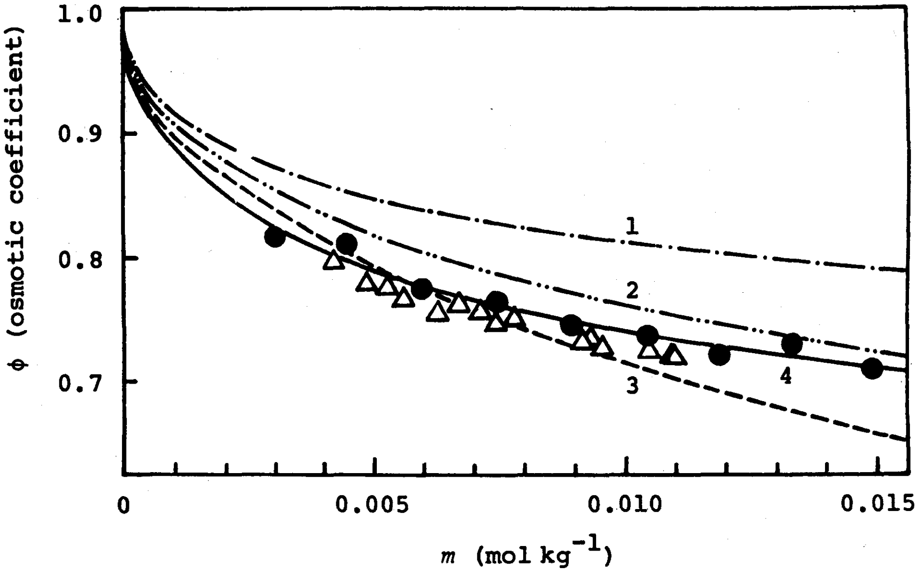

Fig. 3.2. Osmotic coefficients of $CaSO_4$ solutions.

●, present work at 25.0°C (vpo). △, Brown and Prue[24)] at 0°C (cryoscopy). Curves 1 (—·—), 2 (—··—), and 3 (– – – –) are theoretical curves due to the Debye-Hückel theory with $a = 6.0$, 3.0, and 1.0 Å, respectively. Curve 4 (———) is calculated with the K and K_t values in Table 3.2 (25.0°C); each set of the K and K_t values gives the essentially same curve.

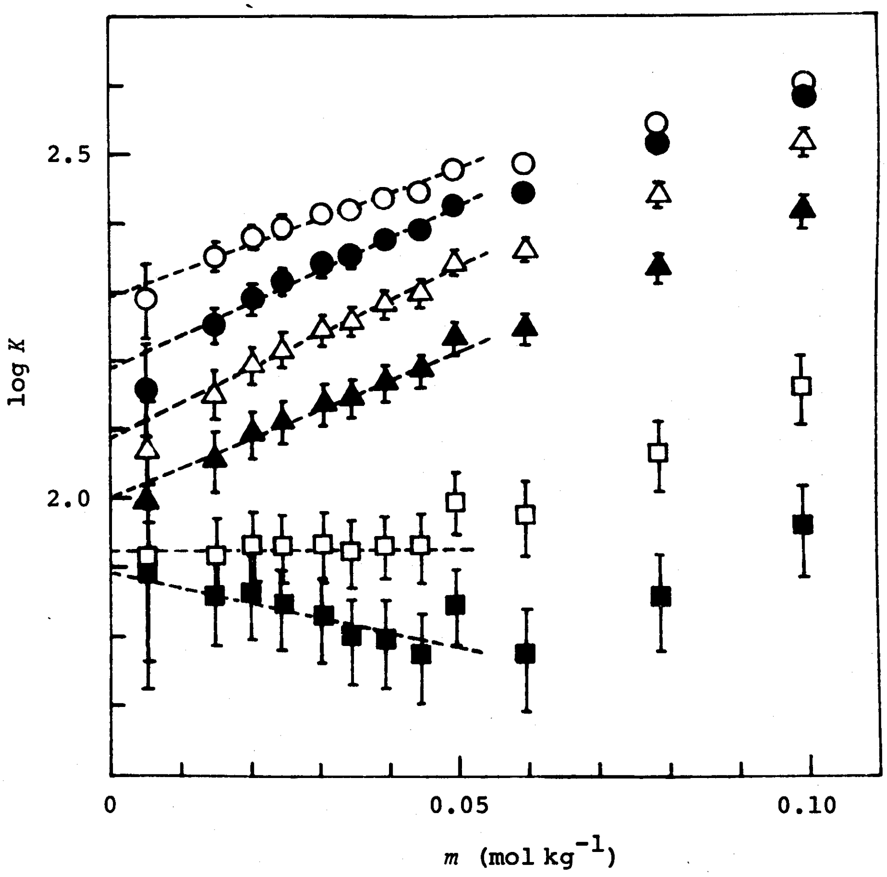

Fig. 3.3. log K values of $MgSO_4$. The assumed a values are 14.3 Å (○), 8.0 Å (●), 6.0 Å (△), 5.0 Å (▲), 4.2 Å (□), and 4.0 Å (■).

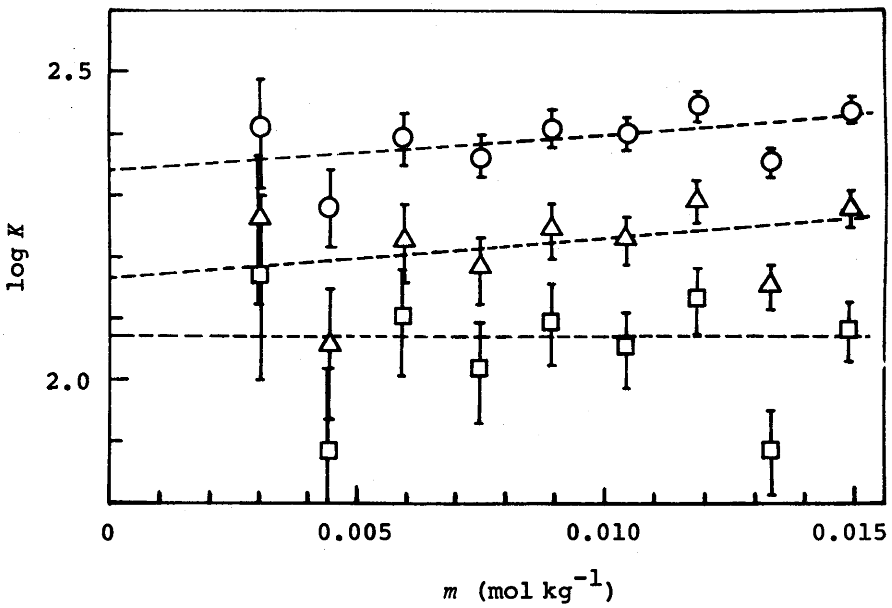

Fig. 3.4. log *K* values of $CaSO_4$. The assumed *a* values are 14.3 Å (○), 6.0 Å (△), and 4.0 Å (□).

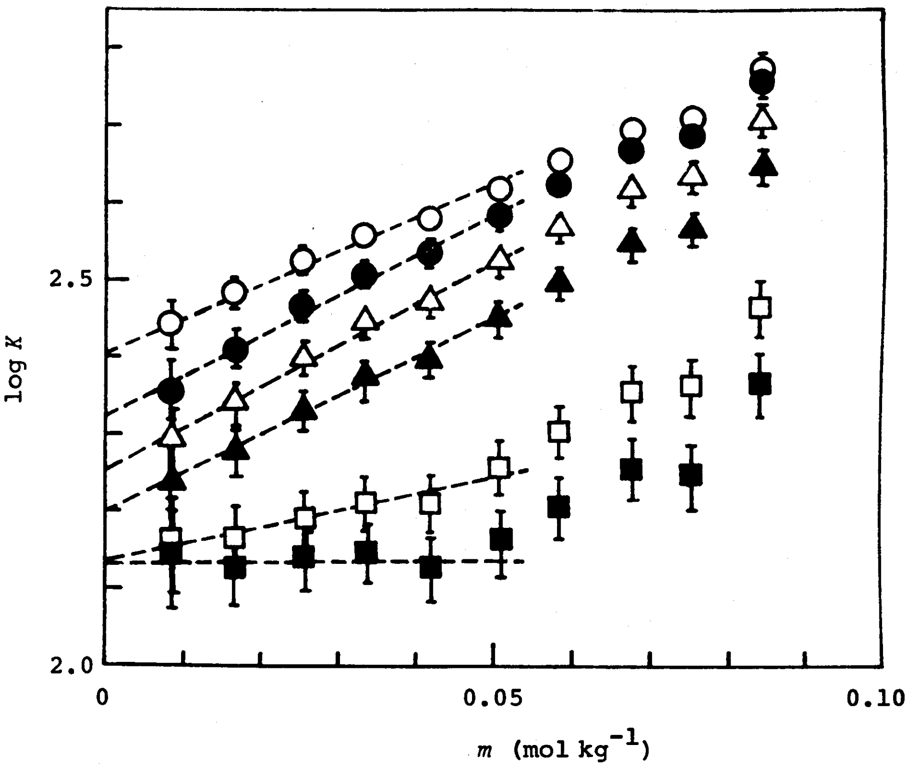

Fig. 3.5. log K values of $MnSO_4$. The assumed a values are 14.3 Å (○), 8.0 Å (●), 6.0 Å (△), 5.0 Å (▲), 4.0 Å (□), and 3.8 Å (■).

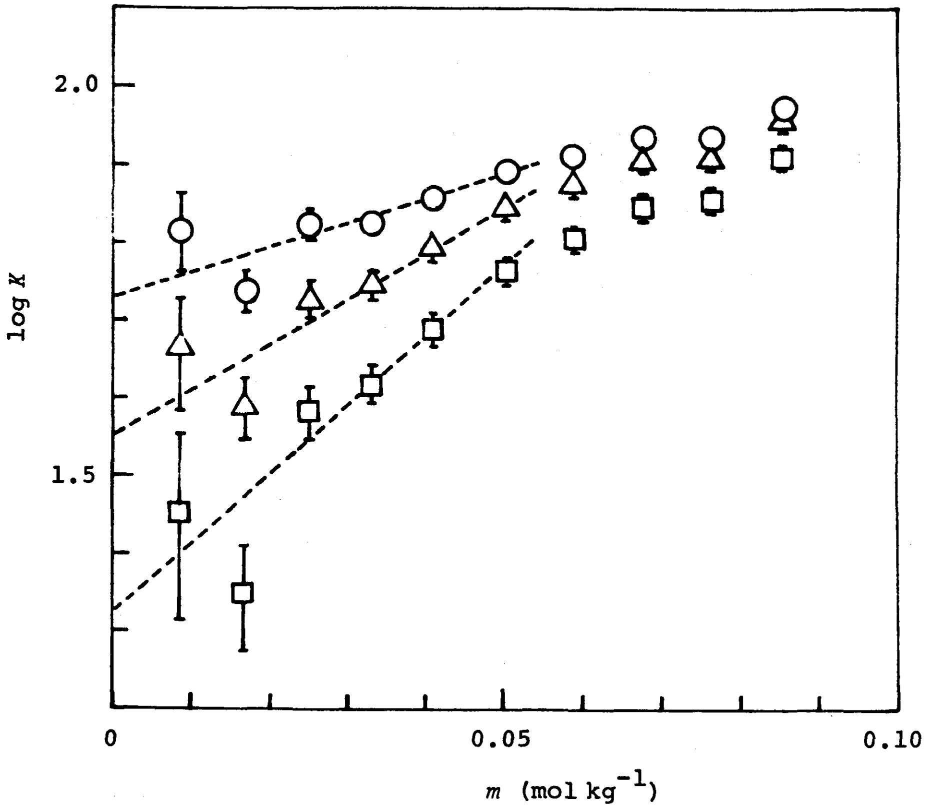

Fig. 3.6. log *K* values of $[Ru(phen)_3]SO_4$. The assumed *a* values are 14.3 Å (○), 11.0 Å (△), and 9.0 Å (□).

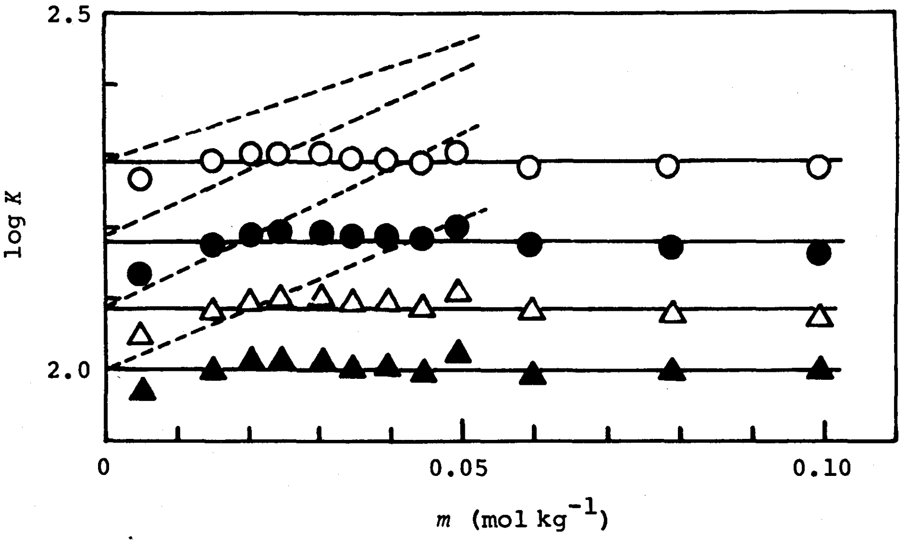

Fig. 3.7. Constant log K values of $MgSO_4$ obtained with the assumption of appropriate K_t values. (See the columm $h = 0$ of Table 3.2.) $a = 14.3$ Å (○), 8.0 Å (●), 6.0 Å (△), and 5.0 Å (▲).

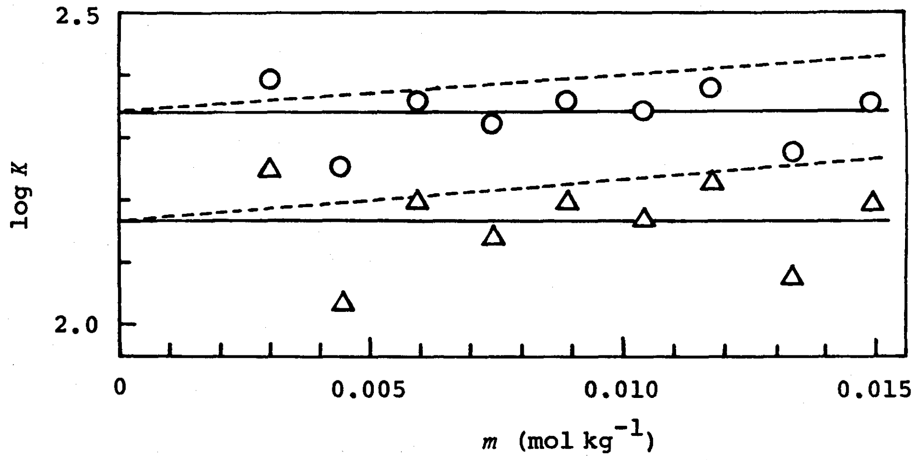

Fig. 3.8. Constant $\log K$ values of $CaSO_4$ with the assumption of appropriate K_t values. (See the columm $h = 0$ of Table 3.2.) $a = 14.3$ Å (○) and 6.0 Å (△).

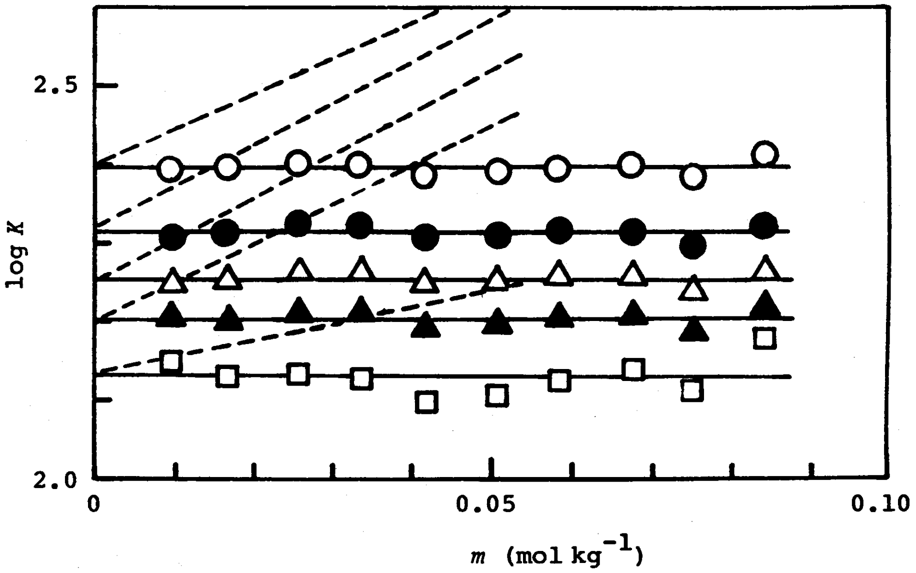

Fig. 3.9. Constant log *K* values of $MnSO_4$ with the assumption of appropriate K_t values. (See the columm $h = 0$ of Table 3.2.) $a = 14.3$ Å (○), 8.0 Å (●), 6.0 Å (△), 5.0 Å (▲), and 4.0 Å (□).

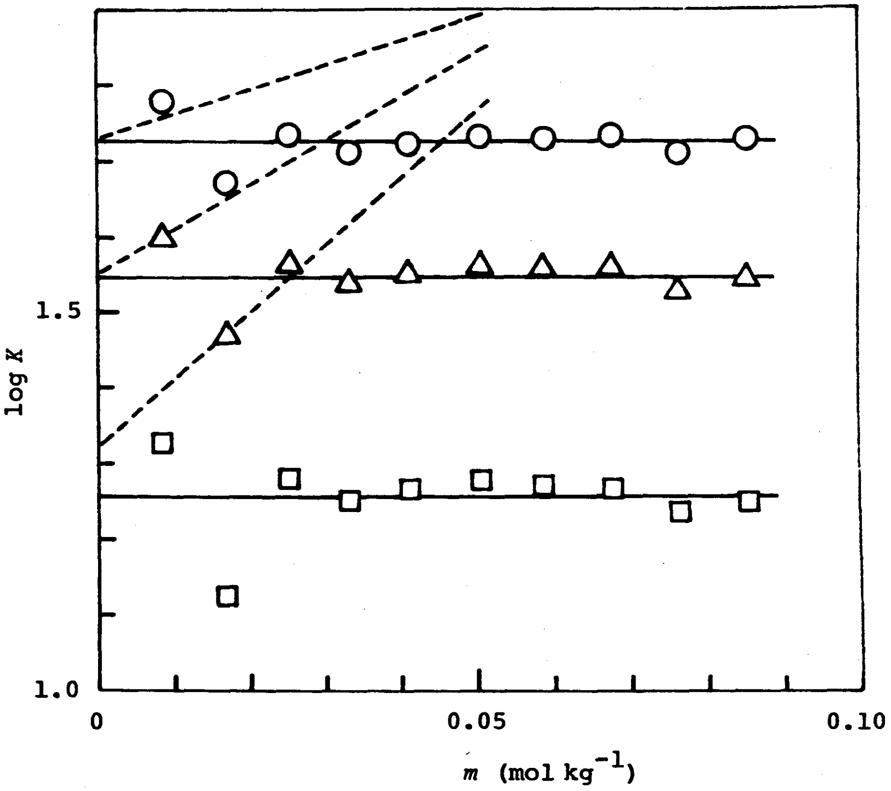

Fig. 3.10. Constant $\log K$ values of $[\mathrm{Ru(phen)_3}]\mathrm{SO_4}$ with the assumption of appropriate K_t values. (See the columm $h = 0$ of Table 3.2.) $a = 14.3$ Å (○), 11.0 Å (△), and 9.0 Å (□).

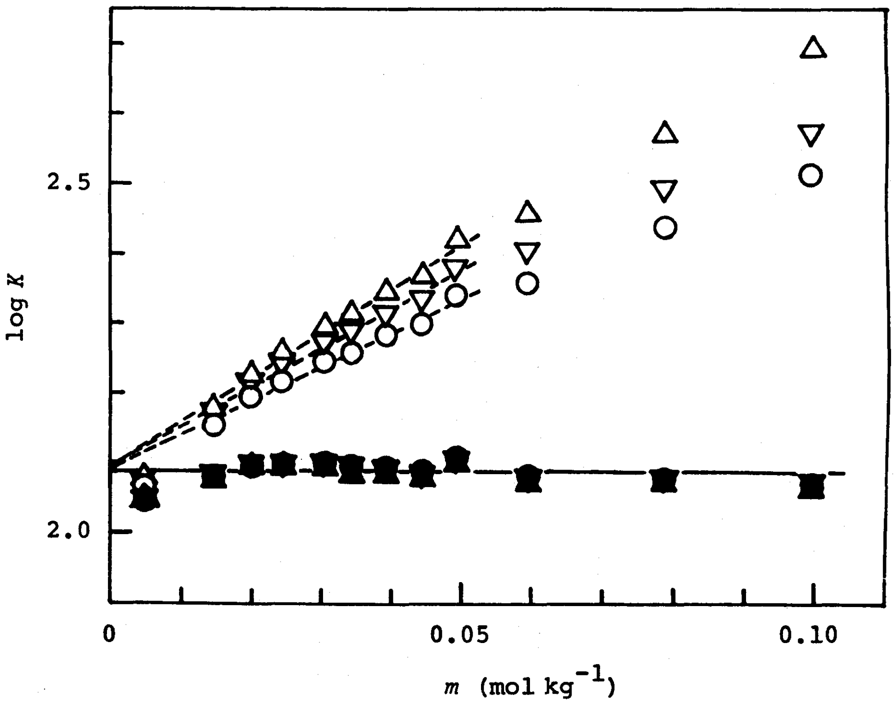

Fig. 3.11. log K values for $MgSO_4$ with $a = 6$ Å allowing for hydration of ions.

○ and ● : $h = 0$, reproduced from Figs. 3.3 and 3.7, respectively. △ and ▲ : $h_0 = 15$, case(A). ▽ and ▼ : $h_0 = 15$, case(B). $K_t = 0$ (○,△,▽), 2.2 (●), 3.1 (▲), and 2.7 (▼) mol^{-1} kg were assumed.

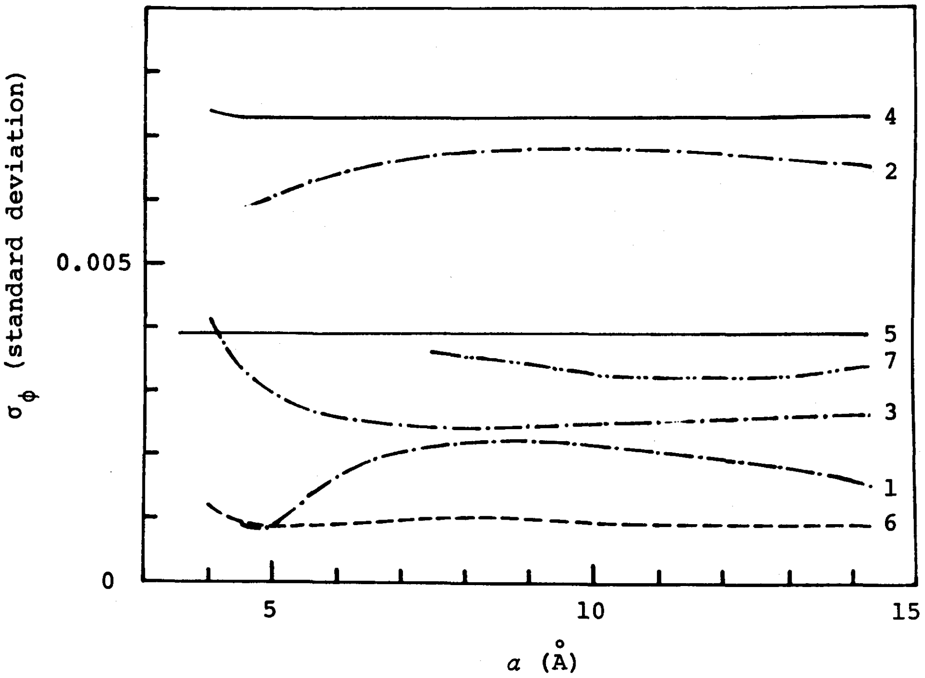

Fig. 3.12. The standard deviation σ_ϕ as a function of a. 1, 2, and 3 : $MgSO_4$. 4 and 5 : $CaSO_4$. 6 : $MnSO_4$. 7 : $[Ru(phen)_3]SO_4$. 1, 4, 6, and 7 are concerned with the vpo data, whereas the others with the cryoscopic data due to Isono[26)] (2) and Brown and Prue[24)] (3 and 5).

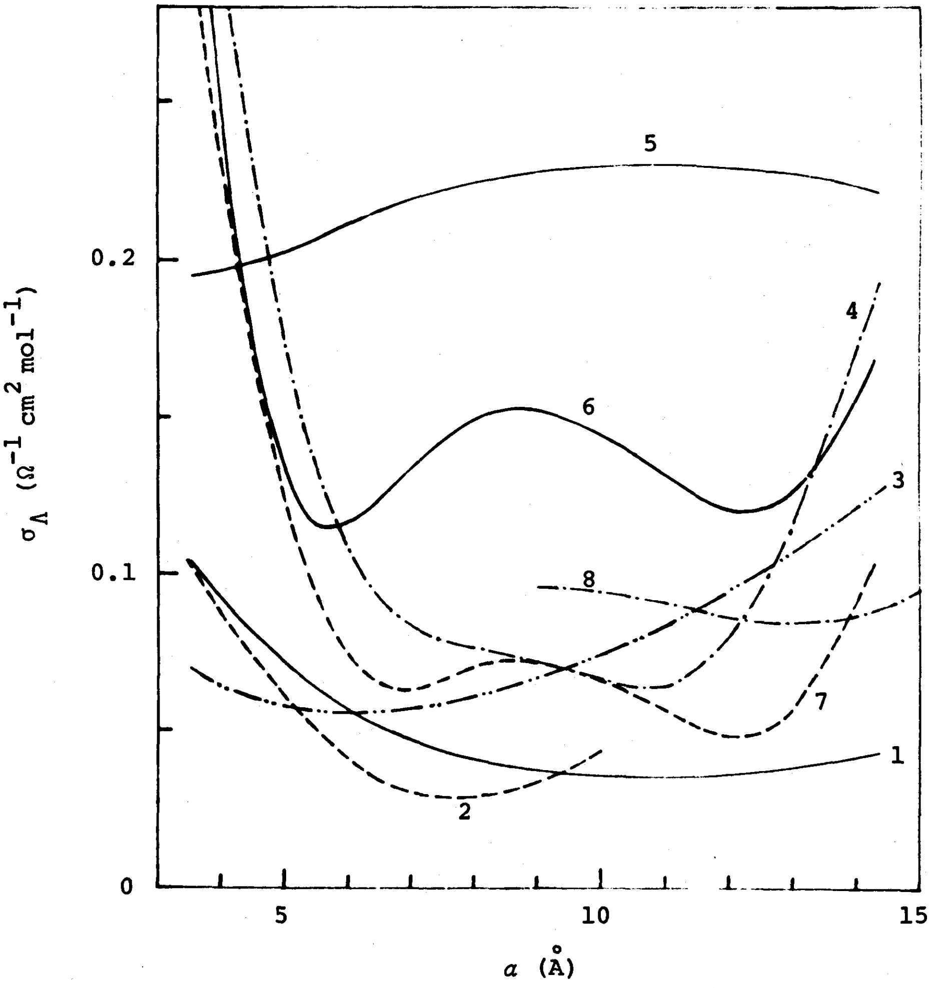

Fig. 3.13. The standard deviation σ_{Λ} as a function of a obtained from reanalysis of conductivity data. 1, 2, and 3 : $MgSO_4$ (Dunsmore and James[28]). 4 : $MgSO_4$ (Katayama[29]). 5 : $CaSO_4$ (Inada *et al.*[30]). 6 : $MnSO_4$ (Hallada and Atkinson[31]). 7 : $MnSO_4$ (Petrucci *et al.*[32]). 8 : $[Fe(phen)_3]SO_4$ (Kubota and Yokoi[33]). Fuoss-Hsia's equation[45,46] was used for the analysis of the data, except for the cases of 2 and 3 where Fuoss-Onsager's[47] and Pitts's equation[48,49] were used, respectively.

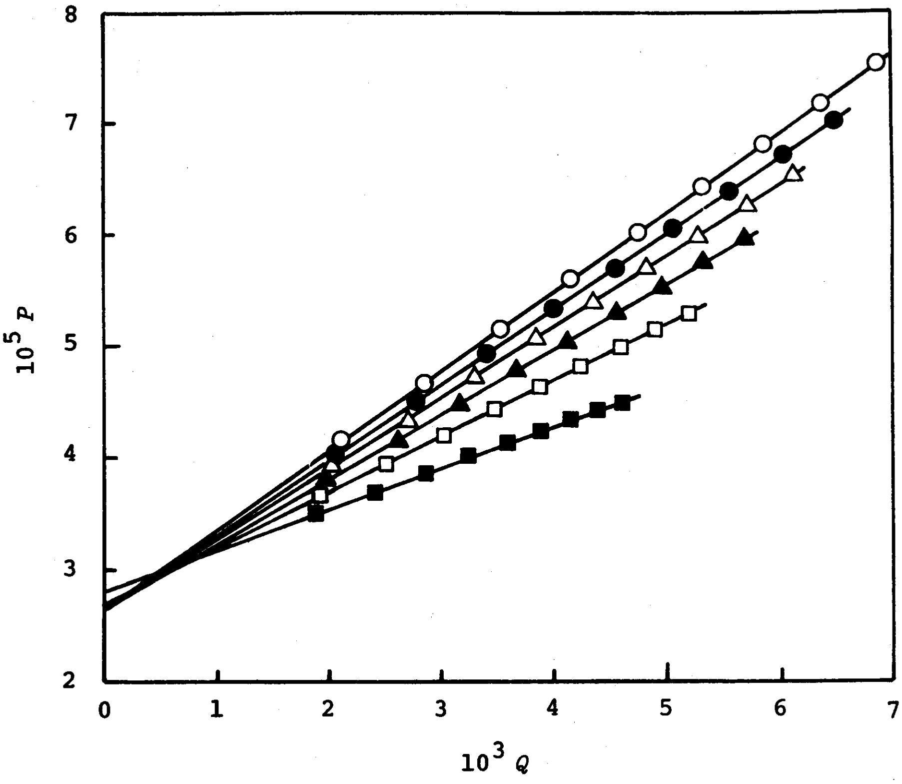

Fig. 4.1. Plots of P against Q. [For the definitions of P and Q, see Eq.(4.8).] The assumed a values are 14.3 Å (○), 12.0 Å (●), 10.0 Å (△), 8.0 Å (▲), 6.0 Å (□), and 4.0 Å (■).

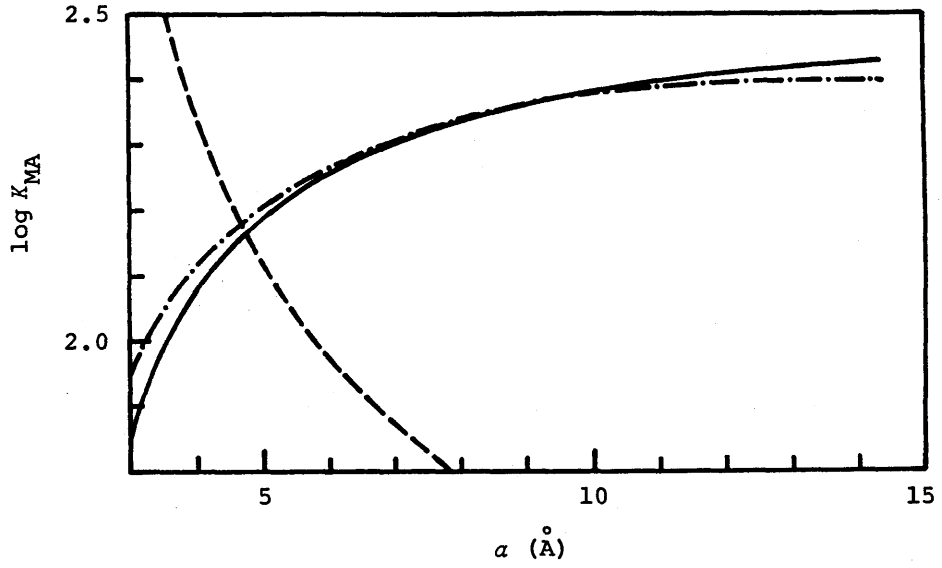

Fig. 4.2. log K_{MA} for $CuSO_4$ as a function of a.
(———): From spectrophotometry. (—·—): From conductivity measurements (recalculation of the data due to Owen and Gurry[71)]). (– – –): Theoretical curve according to Eq.(2.31).

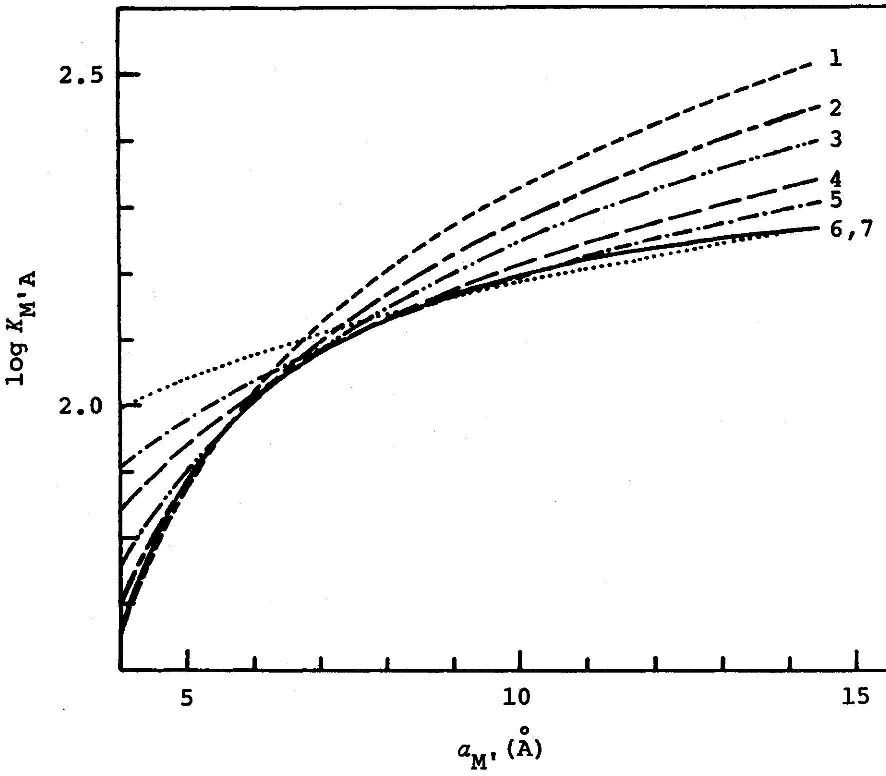

Fig. 4.3. log $K_{M'A}$ for $MgSO_4$ as a function of $a_{M'}$, with the assumption of several a_M values: $a_M = 4.0$ Å [curve 1 (- - - -)], 5.0 Å [curve 2 (—– – —)], 6.0 Å [curve 3 (—··—)], 8.0 Å [curve 4 (— —)], 10.0 Å [curve 5 (—·—)], and 14.3 Å [curve 6 (·········)]. Curve 7 (———) is obtained with the assumption of $a_M = a_{M'}$ [Eq. (4.18)].

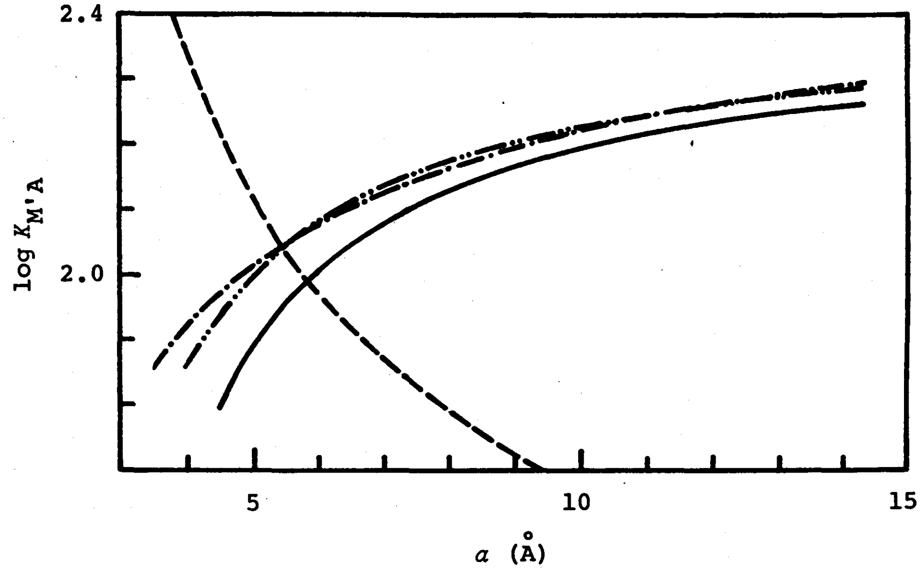

Fig. 4.4. log $K_{M'A}$ for $MgSO_4$ as a function of a. (———): From spectrophotometry. (—·—): From conductivity measurements (recalculation of the data due to Dunsmore and James[28)]). (—··—): From vapor-pressure osmometry.[72)] (— — —): Theoretical curve according to Eq.(2.31).

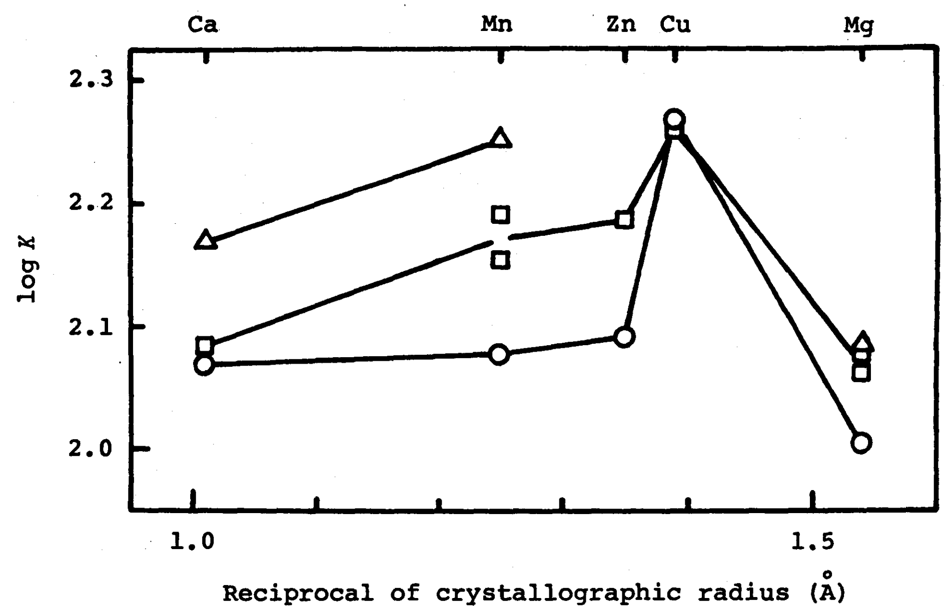

Fig. 4.5. log K values for divalent metal sulfates as a function of the reciprocal of crystallographic radius of the metal ion. ($a = 6$ Å is assumed.) ○ : From spectrophotometry. △ : From vapor-pressure osmometry.$^{72)}$ □ : From conductivity measurements [recalculation of the data due to Dunsmore and James$^{28)}$ ($MgSO_4$, upper), Katayama$^{29)}$ ($MgSO_4$, lower), Inada *et al.*$^{30)}$ ($CaSO_4$), Hallada and Atkinson$^{31)}$ ($MnSO_4$, lower), Petrucci *et al,*$^{32)}$ ($MnSO_4$, upper), and Owen and Gurry$^{71)}$ ($CuSO_4$ and $ZnSO_4$)].

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ACKNOWLEDGEMENT

It is a great pleasure to thank Professor Hideo Yamatera for his encouragement and advice throughout the course of this work.

The author thanks his parents who satisfied his wish to study for a D.Sc. degree at the graduate school of Nagoya University.