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Ion Association of Some 2 : 2 Electrolytes in Water at 25 °C. I. Studies of Magnesium, Calcium, Manganese, and Tris(1,10-phenanthroline)-ruthenium(II) Sulfate Solutions with a Vapor-Pressure Osmometer*

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The osmotic coefficients of aqueous solutions of magnesium, calcium, manganese, and tris(1,10-phenanthroline)ruthenium(II) sulfates were measured at 25 °C by means of a vapor-pressure osmometer. Then the ion-association constants of these electrolytes were obtained as a function of the closest distance of approach of ions from the measured osmotic coefficients as well as from the available conductivity and cryoscopy data. The *best* values of the closest distance of approach and the ion-association constant (given in Table 6) were estimated with the help of theories of ion association. The formation of triple-ions and quadrupoles and the hydration of ions are also discussed in connection with the ion-association constant.

In a previous paper,1) we re-examined the Debye-Hückel theory2) 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.1) Except in a few cases,3–7) 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.3–7) 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.3,6,8–13) These results will be shown and discussed in connection with the theories of ion association.1,14,15)

Experimental

The osmotic coefficients of the electrolyte solutions were measured by vapor-pressure osmometry (vpo). This method has been described by many authors.16) 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:

$$\Delta R = s_1(\nu m\phi) + s_2(\nu m\phi)^2 + s_3(\nu m\phi)^3 + s_4(\nu m\phi)^4 \qquad (1)$$

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 $s_1=4925$, $s_2=-998.7$, $s_3=13050$, and $s_4=-47920$ by the method of least-squares. The observed values of ΔR for various solutions were put into Eq. (1), and the osmotic coefficients (ϕ) were evaluated. We measured the osmotic coefficients (ϕ) of sodium chloride and obtained the approximate expression:

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

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. measurements17) within the range of experimental error. This shows that the assumption of $\phi=1$ for glucose solutions is adequate.

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

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Table 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						

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.[18] 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,[19] and indirectly by the gravimetric analysis of sulfate.

Results and Discussion

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. (1) and are shown in Table 1.*** The measured ϕ values are plotted against the molal concentration of the solute, m, in Fig. 1 for $MgSO_4$ and in Fig. 2 for $CaSO_4$, together with the results from cryosocopic measurements.[3,6] These figures also give the ϕ *vs.* m curves predicted by the Debye-Hückel theory[2] 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 experimental 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.[3-6] 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.

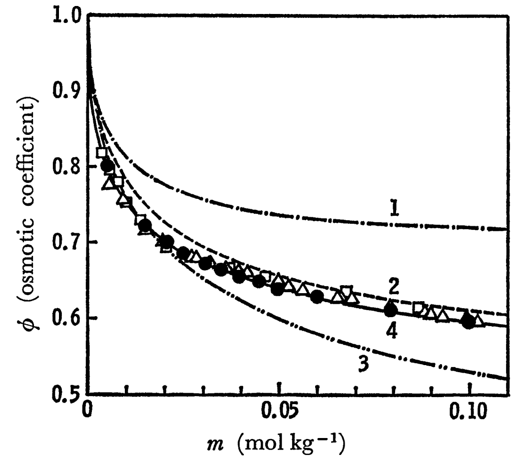

Fig. 1. Osmotic coefficients of $MgSO_4$ solutions. ●, present work at 25.0°C (vpo). △, Brown and Prue[3] at 0 °C (cryoscopy). □, Isono[6] at 0 °C (cryoscopy). Curves 1 (—·—), 2 (----), and 3 (—··—) are theoretical curves due to the Debye-Hückel theory with a=6.0, 4.0, and 3.0 Å, respectively. Curve 4 (——) is calculated with the K and K_t values in Table 2 (25.0 °C); each set of the K and K_t values gives the essentially same curve.

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

$$\begin{array}{lcccccc} & M & + & A & \rightleftharpoons & MA & \\ \text{concentration} & m(1-\alpha) & & m(1-\alpha) & & m\alpha & \quad (2) \end{array}$$

*** 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,[20] who made isopiestic vapor-pressure measurements.

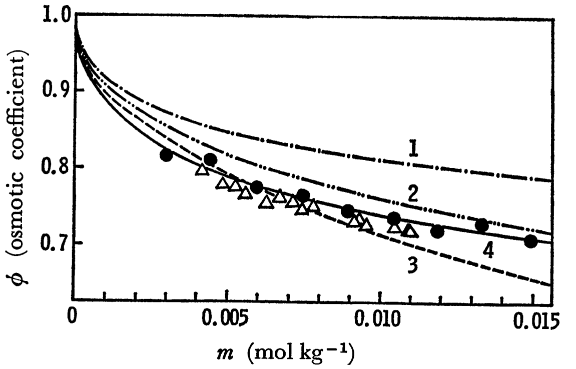

Fig. 2. Osmotic coefficients of $CaSO_4$ solutions. ●, present work at 25.0 °C (vpo). △, Brown and Prue[3] at 0 °C (cryoscopy). Curves 1 (—·—), 2 (—··—), and 3 (----) are theoretical curves due to the Debye-Hückel theory with $a=6.0$, 3.0, and 1.0 Å, respectively. Curve 4 (——) is calculated with the K and K_t values in Table 2 (25.0 °C); each set of the K and K_t values gives the essentially same curve.

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

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

The brackets indicate the concentration of a given species. The ions, M and A, having the z_1e and z_2e charges respectively ($z_1=-z_2=z>0$), 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)

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

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

$$\phi_{DH} = 1 - \frac{z^2\kappa s}{6}\sigma(\kappa a) \tag{4}$$

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

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

In Eq. (4), a is the closest distance of approach of ions, and s is a parameter equal to $e^2/\varepsilon kT$, whose value is 7.157 Å[†] in water at 25.0 °C with the dielectric constant (ε) of 78.30_3. The parameter κ is the so-called "reciprocal thickness of the ionic atomsphere" and is defined by:

$$\kappa^2 = \frac{8\pi N}{1000}z^2sm(1-\alpha) \tag{5}$$

where N is the Avogadro number and 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. (5), with $\alpha=0$ provisionally. The value of ϕ_{DH} was evaluated with Eq. (4), and then the value of α, with Eq. (3). This value of α was in turn put into Eq. (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:

$$\ln\gamma_M = \ln\gamma_A = -\frac{z^2\kappa s}{2(1+\kappa a)} \tag{6}$$

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 to 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 de-

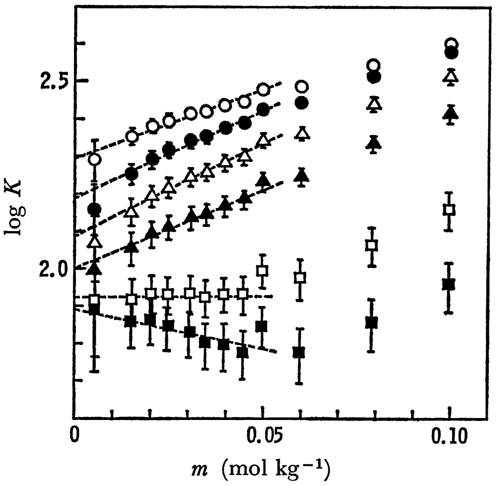

Fig. 3. log K values of $MgSO_4$. The assumed a values are 14.3 Å (○), 8.0 Å (●), 6.0 Å (△), 5.0 Å (▲), 4.2 Å (□), and 4.0 Å (■).

[†] 1 Å$=10^{-10}$ m

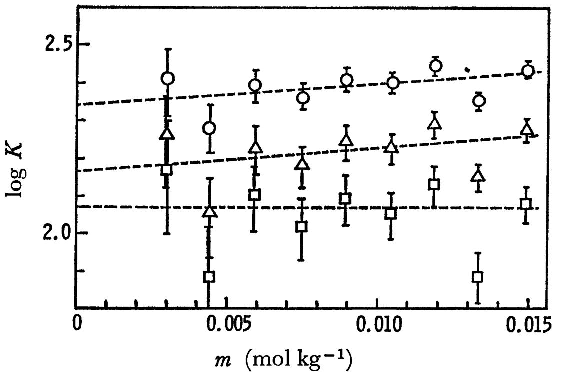

Fig. 4. log K values of $CaSO_4$. The assumed a values are 14.3 Å (○), 6.0 Å (△), and 4.0 Å (□).

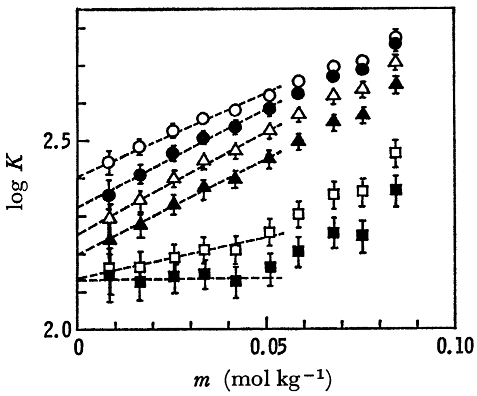

Fig. 5. log K values of $MnSO_4$. The assumed a values are 14.3 Å (○), 8.0 Å (●), 6.0 Å (△), 5.0 Å (▲), 4.0 Å (□), and 3.8 Å (■).

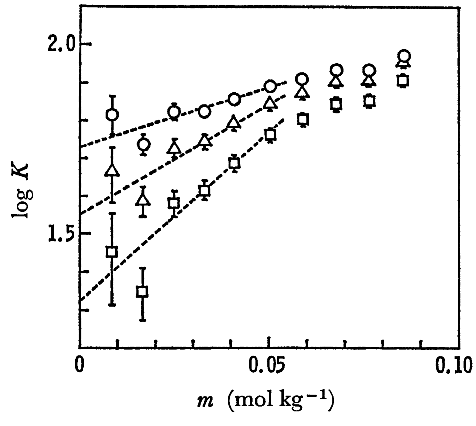

Fig. 6. log K values of $[Ru(phen)_3]SO_4$. The assumed a values are 14.3 Å (○), 11.0 Å (△), and 9.0 Å (□).

pendence 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.

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:

$$K_t = \frac{[M_2A]\gamma_{M_2A}}{[MA][M]\gamma_M} = \frac{[MA_2]\gamma_{MA_2}}{[MA][A]\gamma_A} = \frac{\beta}{[1-\alpha(1+3\beta)]m} \quad (7)$$

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:

$$\phi = [1-\alpha(1+2\beta)]\phi_{DH} + \frac{\alpha}{2} \quad (8)$$

where

$$\phi_{DH} = 1 - \frac{z^2\kappa s}{6}\sigma(\kappa a) \quad (9)$$

Eq. (9) is apparently the same as Eq. (4), but here the parameter κ is given by:

$$\kappa^2 = \frac{8\pi N}{1000}z^2 sm[1-\alpha(1+2\beta)] \quad (10)$$

Assuming the value of K_t for a given a value and using Eqs. (7) to (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:

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

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. Fig. 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

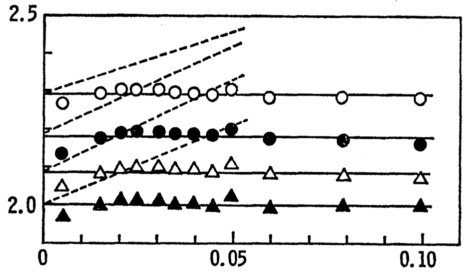

Fig. 7 Constant log K values of $MgSO_4$ obtained with the assumption of appropriate K_t values. (See the columm $h=0$ of Table 2.) $a=14.3$ Å (○), 8.0 Å (●), 6.0 Å (△), and 5.0 Å (▲).

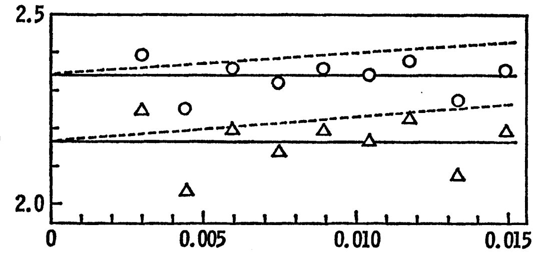

Fig. 8. Constant log K values of $CaSO_4$ with the assumption of appropriate K_t values. (See the column $h=0$ of Table 2.) $a=14.3$ Å (○) and 6.0 Å (△).

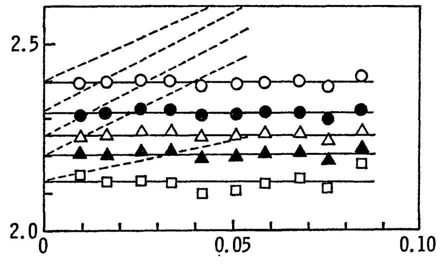

Fig. 9. Constant log K values of $MnSO_4$ with the assumption of appropriate K_t values. (See the columm $h=0$ of Table 2.) $a=14.3$ Å (○), 8.0 Å (●), 6.0 Å (△), 5.0 Å (▲), and 4.0 Å (□).

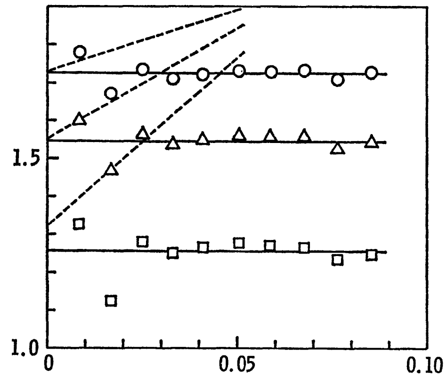

Fig. 10. Constant log K values of $[Ru(phen)_3]SO_4$ with the assumption of appropriate K_t values. (See the column $h=0$ of Table 2.) $a=14.3$ Å (○), 11.0 Å (△), and 9.0 Å (□).

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. 8 to 10 for the other electrolytes.

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:

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

$$= (h_M+h_A)[1-\alpha(1+3\beta)]+h_{MA}\alpha+(h_{M_2A}+h_{MA_2})\alpha\beta \qquad (11)$$

where h_M, h_A, h_{MA}, h_{M_2A}, and h_{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:

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

and the expression for the osmotic coefficient ϕ becomes:

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

where ϕ_{DH} is given by Eq. (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. (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.

$$\begin{aligned} h_{MA} &= h_M + h_A = h_0 \\ h_{M_2A} &= 2h_M + h_A \\ h_{MA_2} &= h_M + 2h_A \end{aligned} \qquad (12)$$

where the parameter h_0 can be determined by the measurement of the hydration number in very dilute solutions. By using Eq. (12), the parameter h in Eq. (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. 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. 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.

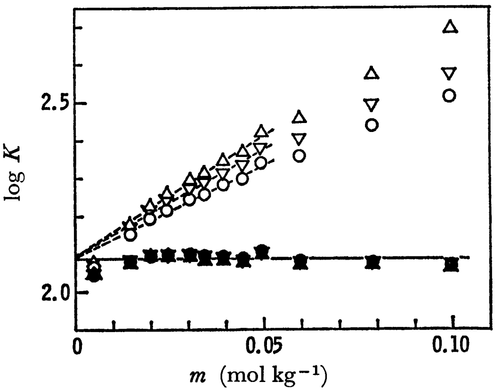

Fig. 11. log K values for $MgSO_4$ with $a=6$ Å allowing for hydration of ions.
○ and ●: $h=0$, reproduced from Figs. 3 and 7, respectively. △ and ▲: $h_0=15$, case (A). ▽ and ▼: $h_0=15$, case (B). $K_t=0$ (○, △, ▽), 2.2 (●), 3.1 (▲), and 2.7 (▼) mol^{-1} kg were assumed.

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 Figs. 3 to 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 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. 1 and 2. In each of the figures, the best-fitting curves for different a values coalesce into a curve (the solid line).

Fuoss and Kraus[22)] 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 2).

Gardner and Glueckauf[5)] have obtained K and K_t values for some 2 : 2 electrolytes by a reanalysis of the cryoscopic data given by Brown an Prue.[3)] The manner of the analysis of the data was different from that described in the present paper. We also reanalyzed the same and other cryoscopic data[3,6)] for $MgSO_4$ and $CaSO_4$ in the manner followed in the analysis of the vpo data. The results are shown in Table 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, whereas for $MgSO_4$ the results are close to each other and also to the result of our vpo experiment (25 °C).

TABLE 2. K AND K_t VALUES OF SOME 2 : 2 ELECTROLYTES DETERMINED BY THE VAPOR-PRESSURE OSMOMETRIC MEASUREMENTS AT 25.0 °C

a (Å)	$MgSO_4$				$CaSO_4$				$MnSO_4$				$[Ru(phen)_3]SO_4$			
	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)			K (mol^{-1} kg)	K_t (mol^{-1} kg)		
		$h=0$	$h_0=15$ (B)[a)]	(A)[a)]		$h=0$	$h_0=15$ (B)	(A)		$h=0$	$h_0=15$ (B)	(A)		$h=0$	$h_0=15$ (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. 2712). b) The critical distance of ion association at 25 °C in Bjerrum's theory.[14)]

[††] The literature gives various values of the hydration number of the electrolyte.[21)] The average value of h_0 for $MgSO_4$ is probably about 15.

TABLE 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 and Prue[3])				MgSO$_4$ (Isono[6])				CaSO$_4$ (Brown and Prue[3])			
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. 2712). b) The critical distance of ion association at 0 °C in Bjerrum's theory.[14]

Quadrupole Formation. In the preceding sections, 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:

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

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 4. The ion-association constants (K) given here are slightly greater than the corresponding values shown in Table 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 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 2, but would affect the K values very little.

TABLE 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. 2712. b) $h=h_0$; a similar assumption to that described in the paragraph following case (A) on p. 2712.

Comparison with the Ion-Association Constants Obtained from Conductivity Experiments. The electric conductivity was mesaured for MgSO$_4$ solutions by Dunsmore and James[8] and Katayama,[9] for CaSO$_4$ solutions by Inada *et al.*,[10] and for MnSO$_4$ solutions by Hallada and Atkinson[11] and Petrucci *et al.*[12] 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.[13] 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 equation[23] expanded by Fernândez-

Prini.[24] This equation gives the equivalent conductivity, Λ, for an association system as follows:

$$\frac{\Lambda}{1-\alpha} = \Lambda_0 - S[c(1-\alpha)]^{1/2} + Ec(1-\alpha)\log[c(1-\alpha)] + J_1 c(1-\alpha) - J_2[c(1-\alpha)]^{3/2} \tag{13}$$

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:

$$K = \frac{\alpha}{(1-\alpha)^2 c y_M y_A} \tag{14}$$

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. (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. (13) and (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:

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

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 5 as a function of a for each of the electrolytes. The log K values given in Table 5 show a tendency similar to that observed in Table 2 (results from vpo), and each of the K values has a magnitude similar to the corresponding one in Table 2.

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

TABLE 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[23,24]

a (Å)	$MgSO_4$[a] (Dunsmore and James[8]) K (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})	$MgSO_4$[b] (Katayama[9]) K (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})	$CaSO_4$[c] (Inada *et al.*[10]) 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

a (Å)	$MnSO_4$[d] (Hallada and Atkinson[11]) K (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})	$MnSO_4$[e] (Petrucci *et al.*[12]) K (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})	$[Fe(phen)_3]SO_4$[f] (Kubota and Yokoi[13]) 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 the use of eleven data at the concentrations from 0.1634×10^{-3} up to 0.8846 ×10^{-3} mol l^{-1}. b) 10 data, (0.2—3.0)×10^{-3} mol l^{-1}. c) 10 data, (0.1—1.0)×10^{-3} mol l^{-1}. d) 9 data, (0.2013—3.141)×10^{-3} mol l^{-1}. e) 5 data, (0.2758—2.235)×10^{-3} mol l^{-1}. f) 17 data, (0.1745—1.662)×10^{-3} mol l^{-1}.

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. 12 and 13 respectively. In the latter, the results obtained for $MgSO_4$ by the use of Fuoss-Onsager's equation[25] and Pitt's equation[26] are also shown for comparison. In Fig. 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 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.*[7,27] Thus, we shall try to estimate the *best* a and K values with the help of theories of ion association.[1,14,15]

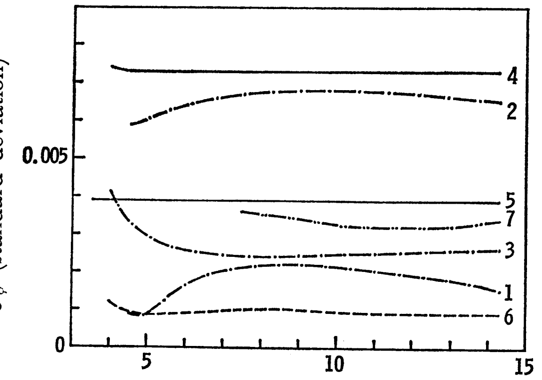

Fig. 12. The standard deviation σ_ϕ as a function of a. 1, 2, and 3: $MgSO_4$. 4 and 5: $CaSO_4$. 6: $MnSO_4$. 7: $[Ru(phen)_3]SO_4$. 1, 4, 6, and 7 are concerned with the vpo data, whereas the others with the cryoscopic data due to Isono[6] (2) and Brown and Prue[3] (3 and 5).

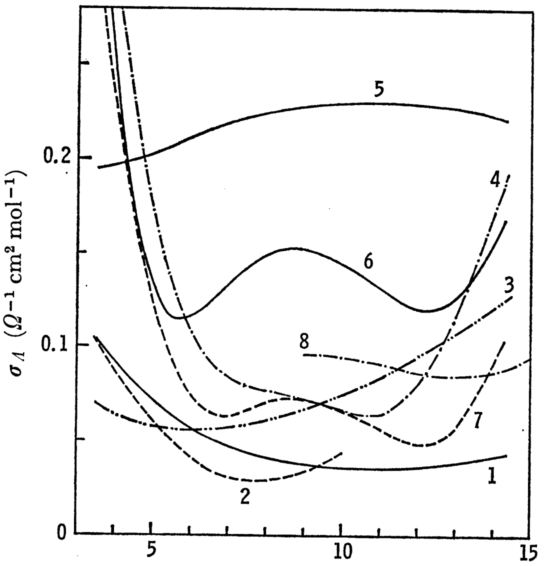

Fig. 13. The standard deviation σ_Λ as a function of a obtained from reanalysis of conductivity data. 1, 2, and 3: $MgSO_4$ (Dunsmore and James[8]). 4: $MgSO_4$ (Katayama[9]). 5: $CaSO_4$ (Inada *et al.*[10]). 6: $MnSO_4$ (Hallada and Atkinson[11]). 7: $MnSO_4$ (Petrucci *et al.*[12]). 8: $[Fe(phen)_3]SO_4$ (Kubota and Yokoi[13]). Fuoss-Hsia's equation[23,24] was used for the analysis of data, except for the cases of 2 and 3 where Fuoss-Onsager's[25] and Pitts's equation[26] were used, respectively.

Estimation of the Best *Values with the Help of Theories of Ion Association.* In a previous paper,[1] we made a refinement of the Debye-Hückel theory[2] 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 following expression for the ion-association constant:

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

where b is Bjerrum's parameter as defined by $b = z^2e^2/\varepsilon kTa$. This equation 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 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.

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††† The values of $r_M + r_A$ given in Table 6 were estimated as follows. The crystallographic data of $CaSO_4 \cdot 2H_2O$ and K_2SO_4[28] were used for the estimation of the radius, r_A, of the sulfate ion. Pauling's radius[29] 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,[28,30] to obtain 2.8_8 Å as the value of r_A for the sulfate ion. Pauling's radii[29] were used as the r_M values for magnesium, calcium, and manganese ions. For $[Fe(phen)_3]^{2+}$, the data of X-ray diffraction[31] 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.[31] The r_M value for $[Ru(phen)_3]^{2+}$ was assumed to be equal to that for the iron-complex ion.

Table 6. The *best* values of a and K obtained with the help of the theoretical expression[1] for the ion-association constant (25 °C)

Electrolyte	$r_M + r_A$ (Å)	From vpo		From conductivity (recalcd)		
		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	8)
				5.5_8	106	9)
$CaSO_4$	3.8_7	$4{\cdot}9_2$	134	5.4_2	112	10)
$MnSO_4$	3.6_8	4.6_4	151	5.1_4	123	11)
				4.9_5	132	12)
$[Ru(phen)_3]SO_4$	10.0	11.5_2	40			
$[Fe(phen)_3]SO_4$	10.0			12.3_8	36	13)

Fuoss's theory[15] 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 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[1] of Fuoss's theory of ion association.

Bjerrum's theory[14] 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. (4) and (9)] should give a K value consistent with Bjerrum's theory. Such K values are given at the bottoms of Tables 2 to 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 electrolyte 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 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.

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