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Ion Association of Some 2 : 2 Electrolytes in Water at 25° C. II. Spectrophotometric Studies of the Ion Association of Magnesium, Calcium, Manganese, Copper, and Zinc Sulfates*

Haruhiko YOKOYAMA** and Hideo YAMATERA

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

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Simple and mixed aqueous solutions of copper, magnesium, calcium, manganese, and zinc sulfates were spectrophotometrically studied in order to obtain the ion-association constants of the divalent metal ions with the sulfate ion. The ion-association constant of copper sulfate was obtained from the measured absorbances of copper sulfate solutions at 250 nm as a function of the closest distance of approach of ions. For the other metal sulfates which show a negligible absorption at 250 nm, absorbances were measured on the mixed solutions with copper sulfate, and the results were analyzed by the use of the results on copper sulfate in order to obtain the ion-association constants. The *best* values of the ion-association constant and the closest distance of approach were determined for each metal sulfate with the help of the theory of ion association. The results were compared with those obtained from the measurements of osmotic coefficients and electric conductivities. The numerical results are summarized in Table 6 of the text.

In previous papers,[1,2] 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.[3-6] The ion association of divalent ions has been observed between the Cu^{2+}, Hg^{2+}, $[CoCl(NH_3)_5]^{2+}$, and $UO_2{}^{2+}$ cations and the $SO_4{}^{2-}$ ion,[7-13] and between some metal cations such as Mg^{2+} and the $S_2O_3{}^{2-}$ ion.[14] 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.[15] 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.*[16] 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 the present study, 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,[7-11] 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,[7-11] 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.

Experimental

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 the preceding paper.[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.[17] 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.

Measurements. The absorption measurements were made at 250 nm with a Carl Zeiss PMQ II spectrophotometer equipped with a M4Q III monochromator, using 1-cm quartz

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** Present address: Department of Chemistry, Yokohama City University, 4646 Mutsuura-cho, Kanazawa-ku, Yokohama, 236.

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 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%.

Results and Discussion

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 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.[7-11] In the following, the absorption data will be analyzed in order to obtain the ion-association constant.

TABLE 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

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

$$M + A \rightleftharpoons MA \qquad (1)$$

$$H + A \rightleftharpoons HA \qquad (2)$$

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 a previous work,[2] 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:

$$K_{MA} = \frac{[MA]}{[M][A]y_M y_A} \qquad (3)$$

$$K_{HA} = \frac{[HA]y_{HA}}{[H][A]y_H y_A} \qquad (4)$$

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:

$$\left.\begin{aligned} c_M &= [M] + [MA] \\ c_A &= [A] + [MA] + [HA] \\ c_H &= [H] + [HA] \end{aligned}\right\} \qquad (5)$$

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:

$$\begin{aligned} D &= \varepsilon_M[M] + \varepsilon_{MA}[MA] \\ &= \varepsilon_M c_M + (\varepsilon_{MA} - \varepsilon_M)[MA] \end{aligned} \qquad (6)$$

where ε_M and ε_{MA} are the molar extinction coefficients of Cu^{2+} and $Cu^{2+}SO_4{}^{2-}$ respectively. Using Eqs. (3), (5), and (6), one can derive the relation:

$$P = \frac{1}{\varepsilon_{MA} - \varepsilon_M} Q + \frac{1}{K_{MA}(\varepsilon_{MA} - \varepsilon_M)} \qquad (7)$$

where P and Q are variables defined by:

$$\left.\begin{aligned} P &= \frac{(c_A - [HA])y_M y_A}{(D/c_M) - \varepsilon_M} \\ Q &= (c_M + c_A - [MA] - [HA])y_M y_A \end{aligned}\right\} \qquad (8)$$

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. (7). The parameters appearing in Eq. (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 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:

$$[\mathrm{HA}] = \frac{R_1 - \sqrt{R_1^2 - 4c_H(c_A - [\mathrm{MA}])}}{2} \tag{9}$$

where R_1 is a variable defined by:

$$R_1 = c_H + c_A - [\mathrm{MA}] + \frac{1}{K_{HA}y_A}$$

These equations were derived from Eqs. (4) and (5) on the assumption that $y_{HA} = y_H$. This assumption is acceptable for the calculation of the P and Q values with Eq. (8), since, at the low acid concentration of $c_H = 2.02 \times 10^{-4}$ M, [HA] is very low compared with c_A. The value of K_{HA} was taken from the literature.18) The $\log K_{HA}$ 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:19)

$$\log y_M = \log y_A = -\frac{4A\sqrt{I}}{1+Ba\sqrt{I}} \tag{10}$$

where a is a parameter representing the closest distance of approach of ions (in Å[†]), where A and B are constants involving the absolute temperature and the dielectric constant of the solvent ($A = 0.5115$ and $B = 0.3291$ in aqueous solutions at 25.0 °C), and where I is the ionic strength given by:

$$I = 2(c_M + c_A - 2[\mathrm{MA}] - [\mathrm{HA}]) + \frac{1}{2}c_H \tag{11}$$

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. (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, $1/(\varepsilon_{MA} - \varepsilon_M)$, and the second term, $1/K_{MA}(\varepsilon_{MA} - \varepsilon_M)$, of the right-hand side of Eq. (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. (3)—(5) and (9)—(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 $1/(\varepsilon_{MA} - \varepsilon_M)$ and $1/K_{MA}(\varepsilon_{MA} - \varepsilon_M)$ in Eq. (7) became constant within 0.05% of their respective values.

The resulting plot of P *vs.* Q is shown in Fig. 1 for each value of the parameter a. In Table 2, the values of K_{MA} and ε_{MA} are shown for the several a values assumed. Figure 2 gives the plot of $\log K_{MA}$ *vs.* a. For $a = 10$ Å, the result in the present work, $K_{MA} = 241$ mol^{-1} l, is in essential agreement with that obtained by Davies *et al.*9) at 240 nm, $K_{MA} = 250$ mol^{-1} l.

Table 2 also gives the standard deviation of D in percentage, σ_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 i-th copper sul-

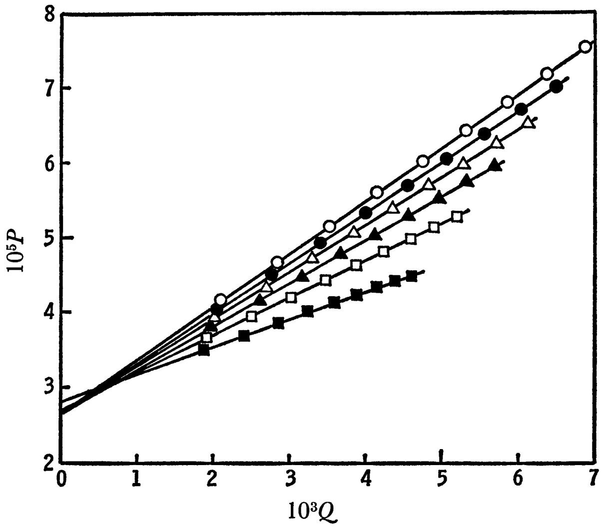

Fig. 1. Plots of P against Q. [For the definitions of P and Q, see Eq. (8).] The assumed a values are 14.3 Å (○), 12.0 Å (●), 10.0 Å (△), 8.0 Å (▲), 6.0 Å (□), and 4.0 Å (■).

TABLE 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.20)

[†] 1 Å = 10^{-10} m.

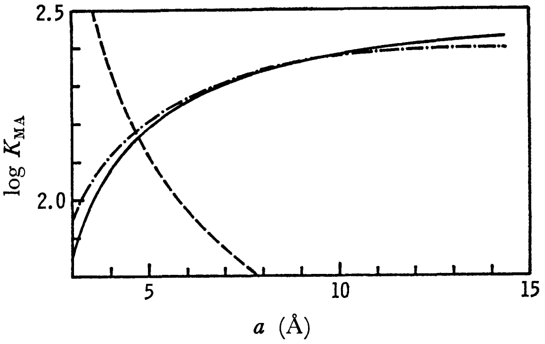

Fig. 2. log K_{MA} for $CuSO_4$ as a function of a.
(——): From spectrophotometry. (—·—): From conductivity measurements (recalculation of the data due to Owen and Gurry[29]). (----): Theoretical curve according to Eq. (20).

fate solution. The value of $D_{calcd,i}$ was calculated by means of Eq. (6), where the ε_{MA} value given in Table 2 was used together with the connected K_{MA} value from which the [MA] value was derived. As is shown in Table 2, the $\sigma_D(\%)$ values for the a values between 4 and 14.3 Å (Bjerrum's critical distance of ion association[20]) 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 ε_{MA} values. The value of a which gives the minimum $\sigma_D(\%)$ 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.

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 3. A comparison of Table 3 with Table 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. (12), must be considered in addition to Eqs. (1) and (2) for copper sulfate solutions:

$$M' + A \rightleftharpoons M'A \qquad (12)$$

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, $K_{M'A}$, is expressed by:

$$K_{M'A} = \frac{[M'A]}{[M'][A]y_{M'}y_A} \qquad (13)$$

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

$$\left.\begin{aligned} c_M &= [M] + [MA] \\ c_H &= [H] + [HA] \\ c_{M'} &= [M'] + [M'A] \\ c_A &= [A] + [MA] + [M'A] + [HA] \end{aligned}\right\} \qquad (14)$$

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

$$[MA] = \frac{D - \varepsilon_M c_M}{\varepsilon_{MA} - \varepsilon_M} \qquad (15)$$

which was obtained by rewriting Eq. (6). Equation (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 $c_{M'}=10^{-2}$ M; the small absorbance has been allowed for in obtaining each D value given in Table 3. By combining Eqs. (3) and (14), one obtains:

$$[M'A] = c_A - [MA] - [HA] - \frac{[MA]}{(c_M - [MA])K_{MA}y_M y_A} \qquad (16)$$

The concentration [HA] is given by:

TABLE 3. ABSORBANCES OF MIXED AQUEOUS SOLUTIONS OF DIVALENT METAL SULFATES 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±0.00$_0$5	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.

$$[\mathrm{HA}] = \frac{R_2 - \sqrt{R_2{}^2 - 4c_\mathrm{H}(c_\mathrm{A} - [\mathrm{MA}] - [\mathrm{M'A}])}}{2} \qquad (17)$$

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 (17) was derived from Eqs. (4) and (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. (13)—(17), $K_\mathrm{M'A}$ can be calculated if the values of K_HA, K_MA, ε_M, ε_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[18] and the value of ε_M has been experimentally determined to be 12.14 (Table 1). The values of K_MA and ε_MA have already been obtained as a function of a; they are listed in Table 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[19] as follows:

$$\log y_\mathrm{M} = \log y_\mathrm{M'} = \log y_\mathrm{A} = -\frac{4A\sqrt{I}}{1 + Ba\sqrt{I}} \qquad (18)$$

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 $[\mathrm{M'A}] = [\mathrm{HA}] = 0$ 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. (15) with the corresponding ε_MA value for the given a value. By putting these values into the right-hand side of Eq. (16), the value of [M'A] was obtained, and then the value of [HA] was calculated by the use of Eq. (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. (13), (14), and (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, the averaged $K_\mathrm{M'A}$ value of $\mathrm{MgSO_4}$ as well as those of the other sulfates are shown for the several a values assumed.

TABLE 4. $K_\mathrm{M'A}$ 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)	$\mathrm{MgSO_4}$ $K_\mathrm{M'A}$ (mol^{-1} l)	$\mathrm{CaSO_4}$ $K_\mathrm{M'A}$ (mol^{-1} l)	$\mathrm{MnSO_4}$ $K_\mathrm{M'A}$ (mol^{-1} l)	$\mathrm{ZnSO_4}$ $K_\mathrm{M'A}$ (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

A comparison of Table 4 with Table 2 shows that the ion-association constants ($K_\mathrm{M'A}$) of $\mathrm{MgSO_4}$, $\mathrm{CaSO_4}$, $\mathrm{MnSO_4}$, and $\mathrm{ZnSO_4}$ are considerably smaller than that of $\mathrm{CuSO_4}$ (K_MA) at the same a value, and that, as the assumed a value increases, $K_\mathrm{M'A}$ increases in parallel with K_MA, with the difference kept almost constant; *i.e.*, $K_\mathrm{MA} - K_\mathrm{M'A} = 84$—86 for $\mathrm{MgSO_4}$, 68—70 for $\mathrm{CaSO_4}$, 65—68 for $\mathrm{MnSO_4}$, and 61—64 for $\mathrm{ZnSO_4}$.

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) 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:

$$\log y_i = -\frac{4A\sqrt{I}}{1 + Ba_i\sqrt{I}} \qquad (19)$$

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. (19) and a similar equation for j-ions to satisfy the thermodynamical relation:[21]

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

As an approximation, however, Eq. (19) will be used without the condition that $a_i = a_j$.

The main ionic species existing in the mixed $\mathrm{CuSO_4}$–$\mathrm{MgSO_4}$ solutions are $\mathrm{Cu^{2+}}$, $\mathrm{Mg^{2+}}$, and $\mathrm{SO_4{}^{2-}}$. 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 $a_\mathrm{M'}$ for the magnesium ion. Considering the probability of a sulfate ion colliding with each of the metal cations, we assumed the equation:

$$a_\mathrm{A} = \frac{a_\mathrm{M} c_\mathrm{M} + a_\mathrm{M'} c_\mathrm{M'}}{c_\mathrm{M} + c_\mathrm{M'}}$$

Then the activity coefficient of each ion was calculated by the use of Eq. (19). The K_MA and ε_MA values were so chosen from Table 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 $K_\mathrm{M'A}$ were thus obtained for various combinations of the values of a_M and $a_\mathrm{M'}$.

In Fig. 3, the values of $K_\mathrm{M'A}$ obtained for $\mathrm{MgSO_4}$ are plotted against the values of $a_\mathrm{M'}$, with several fixed a_M values. This figure also shows, for comparison, the plot of the results given in Table 4, which was

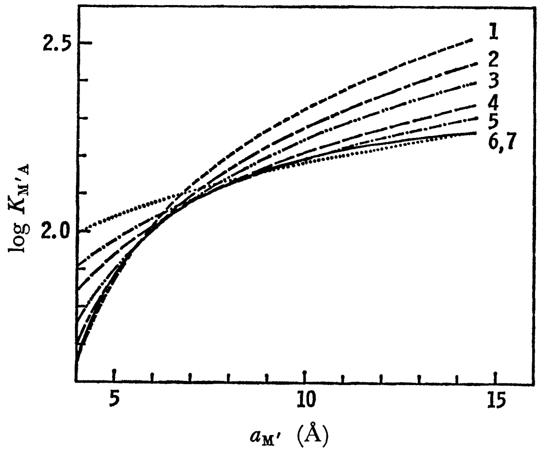

Fig. 3. log $K_{M'A}$ for $MgSO_4$ as a function of $a_{M'}$ with the assumption of several a_M values: $a_M=4.0$ Å [curve 1 (----)], 5.0 Å [curve 2 (———)], 6.0 Å [curve 3 (—··—)], 8.0 Å [curve 4 (— —)], 10.0 Å [curve 5 (—·—)], and 14.3 Å [curve 6 (·········)]. Curve 7 (——) is obtained with the assumption of $a_M=a_{M'}$ [Eq. (18)].

obtained above with the assumption that $a_M=a_{M'}$ $(=a_A)$ [Eq. (18)]. The values of $K_{M'A}$ obtained with and without this assumption [Eq. (18)] are close to each other when the value of $a_{M'}$ is not very different from the value of a_M; for example, $a_{M'}=3$—7 Å for $a_M=5$ Å and $a_{M'}=6.5$—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 6). Thus, the $K_{M'A}$ values given in Table 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.

Comparison with the Vapor-Pressure Osmometry and the Conductivity Method. In the preceding paper,[2] 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[22–26] by means of Fuoss-Hsia's equation[27] expanded by Fernändez-Prini.[28] In connection with the present spectrophotometric studies, the conductivity data on aqueous $CuSO_4$ and $ZnSO_4$ solutions measured by Owen and Gurry[29] were reanalyzed in the same manner as in the previous work, and the ion-association constants were evaluated with various a values assumed. The results are shown in Table 5; the log K_{MA} for $CuSO_4$ is plotted against a in Fig. 2. In the range of $a=3.0$—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 2).

TABLE 5. VALUES OF THE ION-ASSOCIATION CONSTANT K AND THE LIMITING EQUIVALENT CONDUCTIVITY Λ_0 DETERMINED BY THE REANALYSIS OF THE CONDUCTIVITY DATA[29] AT 25.0 °C WITH FUOSS-HSIA'S EQUATION[27,28] (with several a values assumed)

a (Å)	$CuSO_4$ K (mol^{-1} l)	Λ_0 (Ω^{-1} cm^2 mol^{-1})	$ZnSO_4$ 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

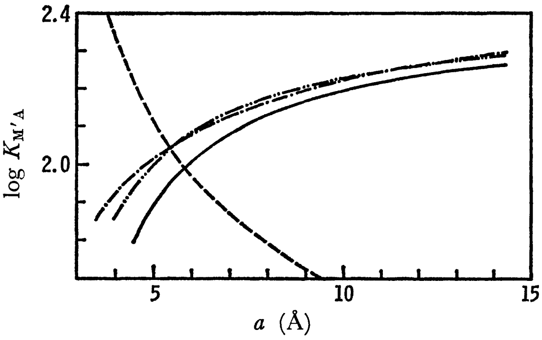

Fig. 4. log $K_{M'A}$ for $MgSO_4$ as a function of a. (——): From spectrophotometry. (—·—): From conductivity measurements (recalculation of the data due to Dunsmore and James[22]). (—··—): From vapor-pressure osmometry.[2] (———): Theoretical curve according to Eq. (20).

Figure 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 previously obtained from the vapor-pressure osmometric and conductivity studies of the single electrolyte solutions.[2] The spectrophotometric method gives slightly smaller ion-association constants than those given by the other methods.

In Fig. 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.

Estimation of the Best *Value of a with the Help of the Theory of Ion Association.* In a previous work,[1]

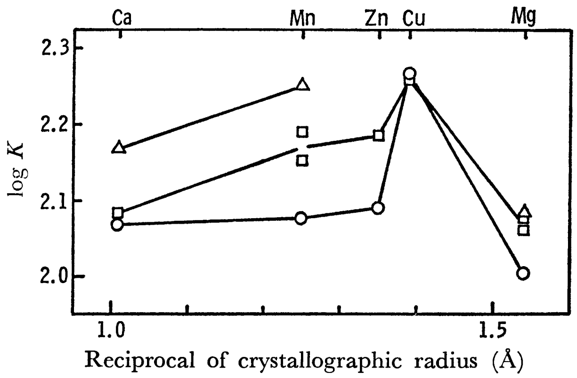

Fig. 5. log K values for divalent metal sulfates as a function of the reciprocal of crystallographic radius of the metal ion. (a=6 Å is assumed.) ○: From spectrophotometry. △: From vapor-pressure osmometry.[2] □: From conductivity measurements [recalculation of the data due to Dunsmore and James[22] ($MgSO_4$, upper), Katayama[23] ($MgSO_4$, lower), Inada *et al.*[24] ($CaSO_4$), Hallada and Atkinson[25] ($MnSO_4$, lower), Petrucci *et al.*[26] ($MnSO_4$, upper), and Owen and Gurry[29] ($CuSO_4$ and $ZnSO_4$)].

we derived an expression for the excess chemical potential of a symmetrical electrolyte in very dilute solutions. This expression has, in addition to the Debye-Hückel term, a supplementary term resulting from a more proper account of the energy of the interactions of ions existing near each other. Assuming that the contribution of ion association to the chemical potential of the electrolyte corresponds to this supplementary term, we obtained the expression for the ion-association constant:

$$K = \frac{8\pi N a^3}{1000} \sum_{n=1}^{\infty} \frac{b^{2n+2}}{(2n+2)!(2n-1)} \tag{20}$$

where b is Bjerrum's parameter defined by $b = z^2e^2/\varepsilon kTa$. ε is the dielectric constant of the solvent, and ze is the absolute value of the charge of the ions. The log K *vs.* a curves obtained with the theoretical equation (20) are shown in Figs. 2 and 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.[1]

The values of a and K for each electrolyte were obtained in this way; they are shown in Table 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 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.

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TABLE 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[1] FOR THE ION-ASSOCIATION CONSTANT (25.0 °C)

Electrolyte	$r_M + r_A$[a] (Å)	From sp		From vpo		From con (recalcd)		
		a (Å)	K (mol^{-1} l)	a (Å)	K (mol^{-1} kg)	a (Å)	K (mol^{-1} l)	data
$MgSO_4$	3.5_3	5.8_5	98	5.4_6	110	5.4_4	111	22)
						5.5_8	106	23)
$CaSO_4$	3.8_7	5.5_5	107	4.9_2	134	5.4_2	112	24)
$MnSO_4$	3.6_8	5.5_1	108	4.6_4	151	5.1_4	123	25)
						4.9_5	132	26)
$CuSO_4$	3.6_0	4.6_5	151			4.7_3	146	29)
$ZnSO_4$	3.6_2	5.4_4	111			5.0_3	128	29)

a) Sum of crystallographic radii of the metal ion (r_M) and the sulfate ion (r_A). (The values have been given in the preceding paper.[2])

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