EFFECT OF PRESSURE ON DISSOCIATION OF ION PAIRS

—$MnSO_4$, $CuSO_4$ and $ZnSO_4$—

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Conductivity at 15~40°C of aqueous solutions of $MnSO_4$, $CuSO_4$ and $ZnSO_4$ has been measured as a function of pressure up to 1600kg/cm²* for the concentrations from 1×10^{-4} to 4×10^{-4}M**. The effect of pressure on the dissociation constant was calculated and the volume changes in the dissociation process of these ion pairs at 25°C have been estimated to be −8.5 ml/mol for $MnSO_4$, −8.1 ml/mol for $CuSO_4$ and −6.0 ml/mol for $ZnSO_4$, respectively. Since the partial molal volumes at infinite dilution were −3.7 ml/mol for $MnSO_4$, −8.1 ml/mol for $CuSO_4$ and −8.0 ml/mol for $ZnSO_4$, the partial molal volumes of the ion pairs at 25°C would be 4.8 ml/mol for $Mn^{2+}\cdot SO_4^{2-}$, 0.0 ml/mol for $Cu^{2+}\cdot SO_4^{2-}$ and −2.0 ml/mol for $Zn^{2+}\cdot SO_4^{2-}$, respectively. From these results, we have obtained the order of Zn>Cu>Mn for the tendency of metal ion to form outer-sphere ion pair with sulfate ion.

Introduction

The behaviors and the structure of both free ions and ion pairs of the several sulfates in aqueous solution were studied from the measurements of the conductivities of the electrolyte solution under high pressure[1-5]. This report is also concerned with the effect of pressure on the dissociation of the ion pairs of $MnSO_4$, $CuSO_4$ and $ZnSO_4$.

The partial molal volume of ion pairs of $MgSO_4$ was estimated volumetrically by Millero and coworker[6]. With the partial molal volumes of free ions at infinite dilution, $\bar{V}^\circ(M^{2+})+\bar{V}^\circ(SO_4^{2-})$ and the volume change in the dissociation process of ion pairs $\Delta\bar{V}^\circ$, the partial molal volume of the ion pairs $\bar{V}^\circ(M^{2+}\cdot SO_4^{2-})$ can be estimated by the following equation,

$$\Delta\bar{V}^\circ=\bar{V}^\circ(M^{2+})+\bar{V}^\circ(SO_4^{2-})-\bar{V}^\circ(M^{2+}\cdot SO_4^{2-}). \qquad (1)$$

Our knowledge on the volume change of the dissociation of ion pairs at infinite dilution mostly comes from measurements on the effect of pressure on the dissociation constants K°.

$$\left(\frac{\partial \ln K^\circ}{\partial P}\right)_T=-\frac{\Delta\bar{V}^\circ}{RT}. \qquad (2)$$

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* 1kg/cm² = 9.80665×10^4 Pa ** 1M = 10^3mol/m³

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Fisher and Davis[7] measured the effect of pressure on the dissociation of $MnSO_4$ ion pairs in water at 25°C, and from a two-state dissociation model, they found $\Delta\bar{V}^\circ$ to be -7.4 m*l*/mol. Taniguchi and coworkers[8] measured the effect of the pressure on the electrical conductivity of $ZnSO_4$ in water at 25°C. They found $\Delta\bar{V}^\circ$ to be -8.0 m*l*/mol and concluded by the electrostriction theory that the ion pair of $ZnSO_4$ was assumed to be of outer-sphere type. Hamann and coworkers[9] pointed out that the small value of $-\Delta\bar{V}^\circ$ (less than half the volume of a water molecule) suggested that the ions were almost fully hydrated in the ion pair state and that an ion pair contained at least one water molecule sandwiched between the two ions.

Spiro and coworkers[10] found that the amounts of the volume changes for the formation of both inner- and outer-sphere complexes were much the same order and there could be no general criterion for distinguishing between them based on volume changes.

And also Hemmes[11] concluded that the volume changes were of little use in distinguishing between the inner- and outer-spheres.

On the other hand, from the heat of dilution data for several divalent metal sulfates, Larson[12] concluded that there was good agreement between the extent of hydration of the ion pairs assumed in order to account for the $\Delta\bar{S}^\circ$ values in the dissociation process of ion pairs and the extent of hydration estimated by spectroscopic techniques[13]: the tendency to form the inner-sphere complex of two-valent metals increases in the order of Ni<Mn<Co<Zn<Cu<Cd.

In comparison with these results, it is interesting to examine the $\Delta\bar{V}^\circ$ and $\bar{V}^\circ(M^{2+}\cdot SO_4^{2-})$ for the ion pairs of $MnSO_4$, $CuSO_4$ and $ZnSO_4$ and to provide a basis for the judgement of the structure type of ion pairs.

Experimentals

The conductivity measurements under high pressure (~1,600kg/cm^2) were carried out at 15, 25 and 40°C. The conductivity cell, the high pressure apparatus and the method of measurements were already described in the previous papers[2, 4].

The stock solutions (5×10^{-3}M) of sulfates were prepared with $MnSO_4\cdot4H_2O$, $CuSO_4\cdot5H_2O$ and $ZnSO_4\cdot7H_2O$ of guaranteed reagent grade. The concentration of solution was determined by the gravimetry of $BaSO_4$. The solutions for measurement were prepared in the concentration range of $1\times10^{-4}\sim4\times10^{-4}$M by dilution of the stock solution with conductivity water. The concentrations of these dilute solutions at high pressure were corrected with the molar volume of water at corre-

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sponding pressure calculated by Tait equation[14]. For the evaluation of the partial molal volumes of ions at infinite dilution, the density of solution at 25°C was measured in the concentration range of $1\times10^{-2}\sim1\times10^{-1}$M with the Weld type pycnometer of 50m*l*.

Results and Considerations

The molar conductances $\Lambda(MSO_4)$ at 15, 25 and 40°C are shown in Table 1. The Kohlrausch relationship was so satisfied that the molar conductances at infinite dilution $\Lambda^\circ(MSO_4)$ were determined by the extrapolation of $\Lambda(MSO_4)\sim$ square root of molar concentration plot to zero concentration.

Table 1 $\Lambda(MSO_4)/\Omega^{-1}cm^2mol^{-1}$ at 15, 25 and 40°C

$MnSO_4$

—15°C—

$C\times10^4$/M P/kg cm^{-2}	1.0	1.5	2.0	2.5	3.0	4.0	Λ°
1 atm	192.8	190.2	188.0	186.0	184.2	181.0	204.6
400	197.0	194.6	192.6	190.8	189.2	186.6	207.8
800	199.8	197.6	195.8	194.0	192.6	190.0	209.6
1200	201.0	198.8	197.2	195.6	194.4	192.0	210.2
1600	200.8	199.0	197.4	196.0	194.8	192.4	209.4

—25°C—

$C\times10^4$/M P/kg cm^{-2}	1.0	1.5	2.0	2.5	3.0	4.0	Λ°
1 atm	249.0	245.2	242.0	239.0	236.4	231.8	266.4
400	253.2	249.6	246.4	243.8	241.4	237.0	269.2
800	255.4	252.0	249.2	246.8	244.6	240.6	270.2
1200	255.8	252.8	250.0	247.8	245.8	242.0	269.6
1600	255.2	252.4	250.0	248.0	246.0	242.6	268.0

—40°C—

$C\times10^4$/M P/kg cm^{-2}	1.0	1.5	2.0	2.5	3.0	4.0	Λ°
1 atm	331.2	325.8	321.2	317.0	313.4	306.8	355.8
400	333.2	328.0	323.6	319.8	316.2	310.0	356.2
800	332.8	328.0	324.0	320.4	317.2	311.6	354.2
1200	331.6	327.2	323.4	320.2	317.2	312.0	351.4
1600	329.2	325.0	321.6	318.6	315.8	310.8	347.4

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14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solution" p. 379, Reinhold, (1959)

$CuSO_4$

—15°C—

$C\times10^4$/M P/kg cm^{-2}	1.0	1.5	2.0	2.5	3.0	4.0	Λ°
1 atm	195.8	192.8	190.4	188.2	186.2	182.8	208.8
400	200.8	198.0	195.7	193.6	191.8	188.5	213.0
800	203.6	201.0	198.8	196.9	195.2	192.1	215.0
1200	204.7	202.3	200.2	198.4	196.8	193.8	215.5
1600	204.3	202.1	200.2	198.5	196.9	194.2	214.4

—25°C—

$C\times10^4$/M P/kg cm^{-2}	1.0	1.5	2.0	2.5	3.0	4.0	Λ°
1 atm	250.8	246.8	243.4	240.2	237.6	232.8	268.6
400	255.0	251.2	248.0	245.2	242.6	238.2	271.8
800	256.6	253.0	250.0	247.4	244.9	240.6	272.6
1200	256.6	253.2	250.4	247.9	245.6	241.6	271.6
1600	255.3	252.2	249.6	247.3	245.2	241.5	269.2

—40°C—

$C\times10^4$/M P/kg cm^{-2}	1.0	1.5	2.0	2.5	3.0	4.0	Λ°
1 atm	338.8	332.4	327.0	322.6	318.2	310.6	367.0
400	340.8	335.0	330.0	325.6	321.6	314.6	367.2
800	340.4	335.2	330.4	326.4	322.8	316.2	365.0
1200	338.4	333.2	329.0	325.2	321.8	315.8	361.0
1600	335.4	330.8	326.8	323.2	320.0	314.4	356.4

$ZnSO_4$

—15°C—

$C\times10^4$/M P/kg cm^{-2}	1.0	1.5	2.0	2.5	3.0	4.0	Λ°
1 atm	195.6	192.8	190.2	188.2	186.4	183.0	207.8
400	200.2	197.6	195.4	193.2	191.6	188.4	212.0
800	202.8	200.2	198.2	196.2	194.6	191.6	214.0
1200	203.6	201.4	199.2	197.4	195.8	193.0	214.4
1600	203.6	201.2	199.2	197.4	195.8	193.0	213.8

—25°C—

$C\times10^4$/M P/kg cm^{-2}	1.0	1.5	2.0	2.5	3.0	4.0	Λ°
1 atm	250.2	246.2	243.2	240.4	237.8	233.4	266.8
400	255.0	251.2	248.0	245.2	242.8	238.4	271.0
800	257.0	253.6	250.6	248.0	245.6	241.2	272.6
1200	257.6	254.4	251.6	249.0	246.8	243.0	272.2
1600	256.8	253.8	251.2	248.8	246.8	243.2	270.4

—40°C—

$C\times10^4$/M P/kg cm^{-2}	1.0	1.5	2.0	2.5	3.0	4.0	Λ°
1 atm	332.8	327.2	322.6	318.6	315.0	308.4	357.2
400	334.6	329.6	325.2	321.4	318.0	311.8	357.8
800	334.4	329.6	325.4	322.0	318.6	313.0	356.0
1200	333.0	328.2	324.8	321.4	318.2	313.0	353.2
1600	330.4	326.2	322.6	319.6	316.6	311.8	349.2

The values of $\Lambda^\circ(\mathrm{MSO_4})$ at 25°C under atmospheric pressure were in agreement with that of Hallada and Atkinson[15] in $\mathrm{MnSO_4}$ and those of Owen and Gurry[16] in $\mathrm{CuSO_4}$ and $\mathrm{ZnSO_4}$, respectively. The hydration number based on the Robinson-Stokes method[17] was estimated to be 11~12 for these metal ions and 4 for sulfate ion and these values are almost constant under the experimental conditions.

For the degree of dissociation, α, the limiting law leads to the following equation :

$$\alpha=\frac{\Lambda\left(\frac{1}{2}\mathrm{MSO_4}\right)}{\Lambda^\circ\left(\frac{1}{2}\mathrm{MSO_4}\right)-\left[B_1\Lambda^\circ\left(\frac{1}{2}\mathrm{MSO_4}\right)+B_2\right]\sqrt{4\alpha C}} \tag{3}$$

where $\Lambda\left(\frac{1}{2}\mathrm{MSO_4}\right)$ is the equivalent conductance at molar concentration $C(\mathrm{MSO_4})$, $\Lambda^\circ\left(\frac{1}{2}\mathrm{MSO_4}\right)$ is the equivalent conductance at infinite dilution, B_1 and B_2 are the constants of the Onsager limiting equation. The values of α in the equation can be solved with the observed values of $\Lambda(\mathrm{MSO_4})$ and $\Lambda^\circ(\mathrm{MSO_4})$ by successive approximation. The dielectric constant of water at pressure is determined from the Owen-Brinkley equation[18] and the viscosity data of water are obtained by the graphical interpolation of the data of Cappi[19].

The equilibrium constant K_c° is given by Eq. (4) :

$$K_c^\circ=\frac{C\alpha^2 f_+f_-}{(1-\alpha)f}=K_c\frac{f_+f_-}{f} \tag{4}$$

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where f_+, f_- and f are the activity coefficients of metal ion, sulfate ion and ion pairs and K_c the concentration quotient, respectively. As shown in the previous papers[4,5], K_c° would be empirically represented by Eq. (5):

$$\ln K_c = \ln K_c^\circ - S\sqrt{\alpha C} \qquad (5)$$

where S is the constant. According to this equation, the equilibrium constant K_c° is obtained by the extrapolation of log $K_c \sim \sqrt{\alpha C}$ curve to infinite dilution[5]. K_c° are shown in Table 2. The equilibrium constant expressed in the mole ratio, K°, in Table 3 was determined from K_c° by correction of the molar volume of water. The dissociation constants, K_c°, in Table 2 are in the same order but

Table 2 The dissociation constants of $M^{2+} \cdot SO_4^{2-}$ ion pairs on the molar scale ($K_c^\circ \times 10^3$/mol l^{-1})

$Mn^{2+} \cdot SO_4^{2-}$

P/kg cm^{-2} \ t/°C	1 atm	400	800	1200	1600
15	2.00	2.41	3.05	3.41	4.15
25	1.58	1.86	2.17	2.56	2.90
40	1.44	1.57	1.82	2.00	2.26

$Cu^{2+} \cdot SO_4^{2-}$

P/kg cm^{-2} \ t/°C	1 atm	400	800	1200	1600
15	1.88	2.24	2.70	3.11	3.67
25	1.59	1.86	2.15	2.49	2.88
40	1.26	1.43	1.63	1.83	2.10

$Zn^{2+} \cdot SO_4^{2-}$

P/kg cm^{-2} \ t/°C	1 atm	400	800	1200	1600
15	2.09	2.39	2.72	3.07	3.45
25	1.87	2.12	2.37	2.61	2.97
40	1.57	1.72	1.91	2.09	2.28

Table 3 The dissociation constants of $M^{2+} \cdot SO_4^{2-}$ ion pairs on the mole fraction scale ($K^\circ \times 10^5$)

$Mn^{2+} \cdot SO_4^{2-}$

P/kg cm^{-2} \ t/°C	1 atm	400	800	1200	1600
15	3.60	4.27	5.31	5.86	7.03
25	2.85	3.30	3.79	4.42	4.93
40	2.60	2.80	3.19	3.46	3.85

$Cu^{2+}\cdot SO_4^{2-}$

t/°C \ P/kg cm^{-2}	1 atm	400	800	1200	1600
15	3.38	3.97	4.71	5.35	6.22
25	2.90	3.30	3.76	4.31	4.91
40	2.28	2.54	2.85	3.16	3.58

$Zn^{2+}\cdot SO_4^{2-}$

t/°C \ P/kg cm^{-2}	1 atm	400	800	1200	1600
15	3.77	4.24	4.74	5.27	5.85
25	3.39	3.77	4.15	4.56	5.05
40	2.83	3.05	3.34	3.61	3.89

apparently somewhat smaller than those in the literatures already reported[7,8,15,16]. But this may be ascribed to the difference of the methods of estimation of K_c°. Analyzing the present conductance data with the Shedlovsky conductance equation[20], we could obtain 4.7×10^{-3} mol/l as K_c° in $CuSO_4$ at 25°C and 1 atm, and this value is in good agreement with those of Owen and Gurry[16] and others[21]. It is unreasonable for K_c° values to vary with the concentrations of solution[2,7,8] and this may be due to the inadequacy in the calculation of the activity coefficients of components so that in this paper we have obtained K_c° graphically according to Eq. (5). Table 2 shows that K_c° increases with increasing pressure and decreasing temperature.

Plotting $\log K_c^\circ$ against the reciprocal of dielectric constant of solvent corresponding to the applied pressure at a constant temperature, the straight lines were obtained and K_c° could be represented by the following equation[22,23],

$$\ln K_c^\circ = -\frac{4e^2}{a\varepsilon kT} + \text{constant}, \qquad (6)$$

where a, e, ε and k are the closest approach distance of the ions in ion pair, the absolute electronic charge, the dielectric constant of solvent and Boltzmann's constant. So the values of a were calculated with the slope of $\log K_c^\circ \sim 1/\varepsilon$ plots. These values are shown in Table 4. The closest approach distances of ion pairs, a, increase with increasing temperature and are not changed by pressure. In the ion pairs of $ZnSO_4$, a at 25°C is larger than the sum of ionic radii in the crystal as well as in the ion pairs of $CoSO_4$[4]. In $CuSO_4$, a is comparable with the sum of ionic radii in the crystal. In $MnSO_4$, a is smaller than the sum of ionic radii in the crystal. As the dielectric constant in the vicinity of the ion would be smaller than that of bulk water, the closest approach distance would be larger than the estimated value. But, the variation of the difference between the value of a and the

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22) J. T. Denison and J. B. Ramsey, *J. Amer. Chem. Soc.*, **77**, 2615 (1955)
23) R. M. Fuoss, *ibid.*, **80**, 5059 (1958)

Table 4 The closest approach distance, a and crystal ionic radii, $r_+ + r_-$

ion pairs	t/°C	a/Å	$(r_+^{a)}+r_-^{b)})$/Å
$\mathrm{Mn^{2+}\cdot SO_4^{2-}}$	15	3.1	3.53
	25	3.4	
	40	4.2	
$\mathrm{Cu^{2+}\cdot SO_4^{2-}}$	15	3.3	3.45
	25	3.5	
	40	3.7	
$\mathrm{Zn^{2+}\cdot SO_4^{2-}}$	15	4.2	3.47
	25	4.4	
	40	5.1	
$\mathrm{Co^{2+}\cdot SO_4^{2-}}$	15	3.2	3.45
	25	4.1	
	40	4.8	
$\mathrm{Mg^{2+}\cdot SO_4^{2-}}$*	25	4.2	3.38
$\mathrm{Ca^{2+}\cdot SO_4^{2-}}$*	25	4.0	3.72
$\mathrm{Ni^{2+}\cdot SO_4^{2-}}$**	25	3.4	3.43

* Ref. 2)
** Ref. 5)
a) L. Pauling, "Nature of Chemical Bond." Cornell Univ. Press 2nd. ed. (1948)
b) O. K. Rice, "Electronic Structure and Chemical Binding", McGraw-Hill Book Company, New York (1940)

crystal ionic radii in these ion pairs may be due to the structure types of hydration of ion pairs, inner- or outer-sphere.

According to Eq. (2), the volume change accompanying the dissociation of the ion pairs, $\Delta\bar{V}^{\circ}$, is obtained from the slope of the curve of $\log K^{\circ}$ versus pressure. In the present cases, $\log K^{\circ}$ changes lineally with increasing pressure at constant temperature. We can calculate $\bar{V}^{\circ}(\mathrm{M^{2+}\cdot SO_4^{2-}})$ with $\Delta\bar{V}^{\circ}$ and $\bar{V}^{\circ}(\mathrm{M^{2+}})+\bar{V}^{\circ}(\mathrm{SO_4^{2-}})$ by Eq. (1). These values are shown in Table 5. $\Delta\bar{V}^{\circ}$ is always negative as expected from the electrostriction due to the ion-dipole interaction between free ions and hydrated water molecules and increases with increasing temperature. $\Delta\bar{V}^{\circ}$ in $\mathrm{MnSO_4}$ at 25°C, -8.5 ml/mol is somewhat more negative than that by Fisher[7], but in good agreement with the theoretical value by Fuoss equation[11,23]. On the other hand, $\Delta\bar{V}^{\circ}$ in $\mathrm{ZnSO_4}$, -6.0 ml/mol is somewhat less negative than that by Taniguchi[8]. As shown in Table 5, the volume changes accompanying the dissociation of $\mathrm{NiSO_4}$[5], $\mathrm{MnSO_4}$ and $\mathrm{CuSO_4}$ ion pairs are more negative than those in $\mathrm{CoSO_4}$[4] and $\mathrm{ZnSO_4}$ ion pairs. From these values, the partial molal volumes of ion pairs at 25°C resulted to be 4.8 ml/mol in $\mathrm{MnSO_4}$, 0.0 ml/mol in $\mathrm{CuSO_4}$ and -2.0 ml/mol in $\mathrm{ZnSO_4}$. Moreover, the partial molal volume would be the sum of two major components.

Table 5 The volumetric data of sulfates in aqueous solution

sulfate	t/°C	$\Delta\bar{V}^\circ$/ml mol^{-1}	$\bar{V}^\circ(M^{2+})+\bar{V}^\circ(SO_4^{2-})$/ m$l$ mol^{-1}	$\bar{V}^\circ(M^{2+}\cdot SO_4^{2-})$/ m$l$ mol^{-1}	$\bar{V}^\circ$(elect)/ml mol^{-1}
$MnSO_4$	15	−9.9	−3.7	4.8	−47.8
	25	−8.5			
	40	−6.1			
$CuSO_4$	15	−9.2	−8.1	0.0	−52.2
	25	−8.1			
	40	−6.9			
$ZnSO_4$	15	−6.6	−8.0	−2.0	−54.3
	25	−6.0			
	40	−5.1			
$CoSO_4$*	25	−7.0	−9.5	−2.5	−54.7
$MgSO_4$**	25	−6.6	−7.2‡	−0.6	−52.6
$CaSO_4$**	25	−9.1	−3.9‡	5.2	−48.5
$NiSO_4$***	25	−8.6	−10.0‡	−1.4	−53.6

* Ref. 4)

** Ref. 2) and 3)

*** Ref. 5)

‡ F. J. Millero, *Chem. Rev.*, 71, 147 (1971)

$$\bar{V}^\circ(M^{2+}\cdot SO_4^{2-})=\bar{V}^\circ(\mathrm{int})+\bar{V}^\circ(\mathrm{elect}) \qquad (7)$$

where $\bar{V}^\circ$(int) is the intrinsic partial molal volume and $\bar{V}^\circ$(elect) is the electrostriction partial molal volume. The intrinsic partial molal volume of ion pairs could be tentatively represented by the equation of

$$\bar{V}^\circ(\mathrm{int})=\frac{4}{3}\pi L(r_+^3+r_-^3) \qquad (8)$$

where L is Avogadro's number and r_+ and r_- are the crystal radii of free ions, respectively. Then the $\bar{V}^\circ$(int) are calculated to be 52.6 ml/mol in $MnSO_4$, 52.2 ml/mol in $NiSO_4$, $CuSO_4$ and $CoSO_4$ and 52.3 ml/mol in $ZnSO_4$. So, we have −47.8 ml/mol in $MnSO_4$, −52.2 ml/mol in $CuSO_4$, −53.6 ml/mol in $NiSO_4$, −54.7 ml/mol in $CoSO_4$ and −54.3 ml/mol in $ZnSO_4$ as the electrostriction partial molal volume of ion pairs, $\bar{V}^\circ$(elect).

It has been considered that the less negative values of $\Delta\bar{V}^\circ$ would be due to the more extensive hydration of ions in the ion pair state and these ion pairs have been classified in the outer-sphere type[9]. The more extensive hydration of ion pair may be also directly supported by the more negative value of $\bar{V}^\circ$(elect). In Table 5, the differences in $\Delta\bar{V}^\circ$ or in $\bar{V}^\circ$(elect) can be found with one another in these ion pairs. These differences may be caused by the difference of the extent of hydration of ion pair and/or the difference of the structural type, inner- and outer-spheres.

From the heat of dilution data, Larson[12] concluded that ion pairs $ZnSO_4$ and $MgSO_4$ are predominantly solvent-separated ones and ion pairs of $CaSO_4$ and $CdSO_4$ are predominantly contact ion pairs[24]. As shown in Table 5, $\Delta\bar{V}^{\circ}$, $\bar{V}^{\circ}(M^{2+}\cdot SO_4^{2-})$ and $\bar{V}^{\circ}$(elect) in $MgSO_4$ are -6.6, -0.6 and -52.6 m*l*/mol, respectively. And these values in $CaSO_4$ are -9.1, 5.2 and -48.5 m*l*/mol, respectively. Comparing these values in $MgSO_4$ and $CaSO_4$ with each other, we can conclude, at least in qualitative agreement with the conclusion drawn from other works[6,12,25], that ions in ion pair state of $MgSO_4$ are separated by more water molecules than those of $CaSO_4$. This volumetric judgement for the structure type of ion pairs may be applied to the present cases of $MnSO_4$, $CuSO_4$ and $ZnSO_4$ and to $NiSO_4$, $CoSO_4$. Moreover, taking into consideration the closest approach distance compared with the crystal ionic radii (Table 4), we arrived at the order of $Zn \simeq Co > Ni > Mg \simeq Cu > Ca \simeq Mn$ for the tendency of the divalent metal ion to form outer-sphere ion pair with the sulfate ion.

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[24] Solvent-separated ion pairs and contact ion pairs are often referred to as outer-sphere complexes and inner-sphere complexes.

[25] E. J. Millero, F. Gombar and J. Oster, *J. Solution Chem.*, 6, 269 (1977)