EFFECT OF PRESSURE ON DISSOCIATION OF NICKEL SULFATE ION PAIR

IN WATER

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The ionic conductivities of aqueous solutions of nickel sulfate have been measured as a function of pressure up to $1600 \, kg/cm^2$* for the concentrations from $1 \times 10^{-4} M$ to $3 \times 10^{-4} M$** at 15, 25, and 40°C. The Kohlrausch relationship between Λ and $\sqrt{C}$ was satisfied at each pressure and temperature.

The molar conductivity, Λ ($NiSO_4$) is affected by the variations of mobility of free ions and of the degree of dissociation of ion pair by pressure. The mobility of Ni^{2+} ion and SO_4^{2-} ion increases with increasing pressure up to definite pressure in this temperature range. The initial increase in the mobility of free ions at infinite dilution with pressure would be due to the destruction of the water structure and the decrease of the effective radii of hydrated ion by pressure. Analyzed with the Robinson-Stokes method, the hydration number of Ni^{2+} ion was 12 and that of SO_4^{2-} ion was 4.

The dissociation of $Ni^{2+} \cdot SO_4^{2-}$ ion pair proceeded with increasing pressure and decreasing temperature. The volume changes in the dissociation process of $Ni^{2+} \cdot SO_4^{2-}$ ion pair, $\Delta \bar{V}°$ were $-10.1 \, cc/mol$ at 15°C, $-8.6 \, cc/mol$ at 25°C and $-7.4 \, cc/mol$ at 40°C, and the entropy change was $-26 \, cal/deg. \, mol$***. These volume contraction and the decrease of entropy may be ascribed to the electrostriction due to the ion-dipole interaction and the free ions would be hydrated much more (by 4 molecules of water) than ion pair. The partial molal volume of $Ni^{2+} \cdot SO_4^{2-}$ ion pair and the entropy of hydration of this ion pair were found to be $-1.4 \, cc/mol$ and $-69.6 \, cal/deg. \, mol$ at 25°C.

Introduction

The behaviors and the structure of both free ions and ion pair of the several sulfates in aqueous solution were studied from the measurements of the conductivities of the electrolyte solution under high pressure[1-4].

The molar conductivity Λ is the function of the mobility of free ions and their concentrations. The pressure effect on the mobility of free ions is revealed by the variation of the molar conductivity at infinite dilution with pressure. On the other hand, the degree of dissociation and the dissociation constant are estimated by the Onsager equation with the data of molar conductivities. The pressure and temperature dependences of the dissociation constant give the information on the volume change $\Delta \bar{V}°$ and the entropy change $\Delta \bar{S}°$ in the dissociation process of the ion pair, respectively. For such

1) M. Nakahara, K. Shimizu and J. Osugi, This Journal, 40, 1, 12 (1970)
2) E. Inada, K. Shimizu and J. Osugi, ibid., 42, 1 (1972)
3) M. Ueno, K. Shimizu and J. Osugi, ibid., 43, 33 (1973)
4) K. Shimizu and T. Okamoto, Sci. Eng. Rev. Doshisha Univ., 16, 120 (1975)

thermodynamical information, we have need to have the accurate data of the dissociation constant. But, in the aqueous solutions of $MgSO_4$[5], $MnSO_4$[6], $CaSO_4$[2], $LaFe(CN)_6$[7] and $ZnSO_4$[8], the dissociation constants were dependent on the concentrations of the solutions. Some of these values were given as the reasonable dissociation constants and the discussion about the structure of the species in the solutions were based on these values. So, there may be something yet to learn for estimation of the dissociation constants.

Now, the molar conductivity of nickel sulfate in aqueous solution have been measured at 15, 25 and 40°C under high pressure up to $1600 \, kg/cm^2$. In this paper, the equilibrium constants $K_c°$ have been determined by extrapolation of $\log K_c \sim \sqrt{2\alpha C}$ curve to zero concentration as described later. The thermodynamic data have been calculated with these values for the clarification of the hydrated structure of free ions and ion pair of nickel sulfate.

Experimentals

The stock solution (5×10^{-3} M) of nickel sulfate was prepared with $NiSO_4 \cdot 6H_2O$ of guaranteed reagant grade. The concentration of the solution was determined by the gravimetry of $BaSO_4$. The solutions for measurement in the concentration range of $1 \times 10^{-4} \sim 3 \times 10^{-4}$ M were prepared by diluting the stock solution with conductivity water. The concentrations of these dilute solutions at high pressure were corrected with the compressibility of water at corresponding pressure calculated by the Tait equation[9],

$$\frac{V(1) - V(P)}{V(1)} = C \log \frac{B+P}{B+1} \qquad (1)$$

where $V(1)$ and $V(P)$ are the molar volumes of water at 1 atm and $P \, kg/cm^2$, respectively. B and C are the empirical constants.

The conductivity cell, the high pressure apparatus and the method of measurements were already described in the previous papers[2,4].

Results and Considerations

Λ and $\Lambda°$

The electrolytic conductivity of the solution κ is defined by Eq. (2),

5) F. H. Fisher, *J. Phys. Chem.*, **66**, 1607 (1962)
6) F. H. Fisher and D. F. Davis, *ibid.*, **69** 2595 (1965)
7) S. D. Hamann, P. J. Pearce and W. Strauss, *ibid.*, **68**, 375 (1964)
8) Y. Taniguchi, T. Watanabe and K. Suzuki, *Bull. Chem. Soc. Japan*, **48**, 3032 (1975)
9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions", p. 379, Reinhold, (1959)

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$$\kappa = \frac{K_{cell}}{R} \qquad\qquad (2)$$

where K_{cell} is the cell constant and R is the resistance of solution. By subtracting from κ the electrolytic conductivity of water $\kappa(H_2O)$, the molar conductivity is obtained by

$$\varLambda = \frac{10^3[\kappa - \kappa(H_2O)]}{C} \qquad\qquad (3)$$

where C is the corrected molar concentration of salt solution.

The molar conductivity $\varLambda$ (NiSO$_4$) at 15, 25 and 40°C are shown in Table 1. As shown in Fig. 1, these values changed linearly against $\sqrt{2C}$ at constant pressure and the Kohlrausch relationship between $\varLambda$ and $\sqrt{2C}$ was satisfied. Then, the molar conductivities at infinite dilution $\varLambda°$ (NiSO$_4$) were determined by the extrapolation of $\varLambda \sim \sqrt{2C}$ curves to zero concentration. The values of $\varLambda°$ (NiSO$_4$) at each temperature and pressure are also shown in Table 1.
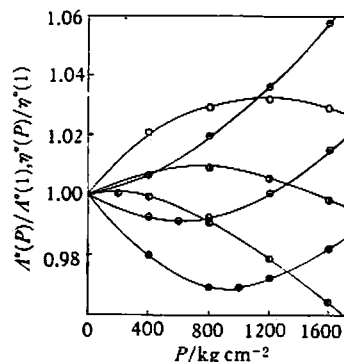
Now, in the case of the dissociation of the symmetrical electrolyte of 2–2, such as nickel sulfate, into the free ions, the electrolytic conductivity is given by Eq. (4),

Table 1　　$\varLambda$ (NiSO$_4$)/Ω^{-1}cm^{2}mol^{-1} at 15, 25 and 40°C

— 15°C —

P/kg cm^{-2} ╲ $C \times 10^4$/M	1	1.5	2	2.5	3	$\varLambda°$
1 atm	196.4	193.4	191.0	188.8	186.8	209.0
400	201.4	198.6	196.4	194.2	192.4	213.4
800	204.2	201.6	199.6	197.6	195.8	215.2
1200	205.4	203.0	201.0	199.2	197.6	215.8
1600	205.4	203.2	201.4	199.8	198.2	215.2

— 25°C —

P/kg cm^{-2} ╲ $C \times 10^4$/M	1	1.5	2	2.5	3	$\varLambda°$
1 atm	251.8	248.0	244.8	241.8	239.4	268.8
400	255.0	251.4	248.6	245.8	243.6	270.6
800	256.6	253.2	250.4	248.0	245.8	271.2
1200	256.6	253.6	251.0	248.6	246.6	270.4
1600	255.8	252.8	250.4	248.0	246.2	268.6

— 40°C —

P/kg cm^{-2} ╲ $C \times 10^4$/M	1	1.5	2	2.5	3	$\varLambda°$
1 atm	338.0	332.4	327.6	323.6	320.0	362.0
400	338.8	333.6	329.2	325.4	322.2	361.6
800	337.6	332.8	328.6	325.0	321.8	358.8
1200	334.6	330.2	326.4	323.0	320.2	354.4
1600	331.4	327.2	324.0	321.0	318.2	349.2
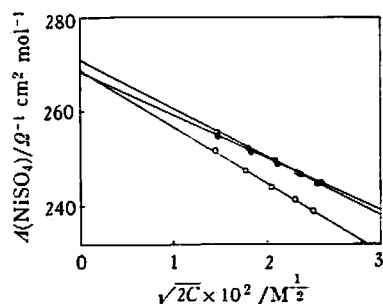
Fig. 1 $\Lambda(\text{NiSO}_4)$ vs. $\sqrt{2C}$ at 25°C

    ○:   1 atm
    ◗:   800 kg/cm²
    ●:   1600 kg/cm²

Fig. 2 $\Lambda^\circ(P)/\Lambda^\circ(1)$, $\eta^\circ(P)/\eta^\circ(1)$ vs. pressure

$\Lambda^\circ(P)/\Lambda^\circ(1)$ $\begin{cases} \bigcirc: 15°C \\ \circleddash: 25°C \\ \circ: 40°C \end{cases}$ $\eta^\circ(P)/\eta^\circ(1)$ $\begin{cases} \bullet: 15°C \\ \circleddash: 25°C \\ \circleddash: 40°C \end{cases}$

$$10^3[\kappa - \kappa(\text{H}_2\text{O})] = \Sigma C_i \lambda_i = C\alpha \ \Sigma \ \lambda_i \qquad (4)$$

where, C_i and λ_i are the molar concentration and molar ionic conductivity of i-ion and α the degree of dissociation, respectively. From Eqs. (3) and (4),

$$\Lambda = \alpha \ \Sigma \ \lambda_i = \alpha(\lambda_+ + \lambda_-) \qquad (5)$$

That is, the molar conductivity is varied with the degree of dissociation and the sum of the molar ionic conductivity. The molar ionic conductivity is proportional to the mobility of free ions. So, the pressure effects on Λ° and Λ reveals the pressure dependences of the mobility of free ions at infinite dilution and the dissociation of ion pair, respectively.

Pressure effect on the mobility

At the infinite dilution, the salt in aqueous solution completely dissociates into the free ions, so that the pressure effect on the mobility is reflected by the variation of the molar conductivity at infinite dilution Λ° (NiSO₄) with pressure. Fig. 2 shows the pressure dependence of Λ° and the viscosity of water η° at each temperature. Λ° increases with increasing pressure and then decreases through the maximum point located at 1200 kg/cm² at 15°C, 800 kg/cm² at 25°C and 200 kg/cm² at 40°C, respectively. As compared with the pressure dependence of η°, the pressure at the maximum point of Λ° is higher than that at the minimum point of η° at each temperature; the maximum point of Λ° is found even at 40°C, where the viscosity of water increases monotonously with increasing pressure. These phenomena of Λ° suggest the increase of the mobility of free ions with increasing pressure up to corresponding pressure. This would be due to the destruction of the structure of water and the decrease of radii of hydrated free ions by pressure.

According to the Robinson-Stokes method[2,10], the hydration number was estimated to be 11~12 for Ni^{2+} ion and 4 for SO_4^{2-} ion as well as in the previous data[4]. These values are almost constant

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10) R. A. Robinson and R. H. Stokes, "Electrolyte Solution", p. 124 Butterworths, London, (1965)

under the experimental condition. This means that the hydrated ions would be compressed by pressure without dehydration.

Dissociation of the ion pair

The equilibrium of the dissociation of $Ni^{2+} \cdot SO_4^{2-}$ ion pair is shown in the following equation,

$$\underset{(1-\alpha)C}{Ni^{2+} \cdot SO_4^{2-}} \underset{}{\rightleftharpoons} \underset{\alpha C}{Ni^{2+}} + \underset{\alpha C}{SO_4^{2-}} \qquad (6)$$
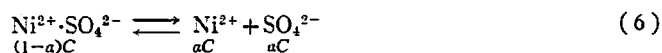
where C is the molar concentration of salt and α the degree of dissociation. Then, the equilibrium constant K_c° is given in Eq. (7),

$$K_c^\circ = \frac{C\alpha^2 f_+ \cdot f_-}{(1-\alpha)f} = K_c \frac{f_+ f_-}{f} \qquad (7)$$

where f_+, f_- and f are the activity coefficients of Ni^{2+} ion, SO_4^{2-} ion and ion pair and K_c the concentration quotient, respectively. The values of all the activity coefficients must approach unity as molarity approaches zero. Then Eq. (7) becomes Eq. (8) at infinite dilution as follows,

$$K_c^\circ = \lim_{C \to 0} K_c \qquad (8)$$

Moreover, as shown in Fig. 3, $\log K_c$ varied linearly against $\sqrt{2\alpha C}$ so that the relation between K_c and K_c° would be reasonably represented by Eq. (9),

$$\ln K_c = \ln K_c^\circ + S\sqrt{\alpha C} \qquad (9)$$

where S is the empirical constant. Now, using the Onsager theoretical equation for the equivalent conductivity, we obtain

$$A\left(\frac{1}{2}NiSO_4\right) = \alpha\left[A^\circ\left(\frac{1}{2}NiSO_4\right) - \left(B_1 A^\circ\left(\frac{1}{2}NiSO_4\right) + B_2\right)\sqrt{4\alpha C}\right] \qquad (10)$$

where B_1 is the function of dielectric constant ε and temperature T and B_2 the function of ε, η° and T.

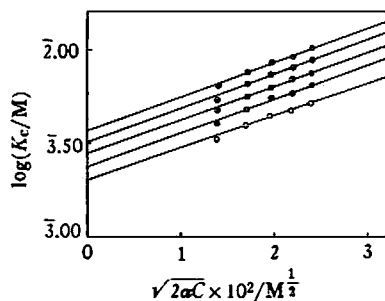

Fig. 3 $\log K_c$ vs. $\sqrt{2\alpha C}$ at 25°C
O: 1 atm
◑:   400 kg/cm²
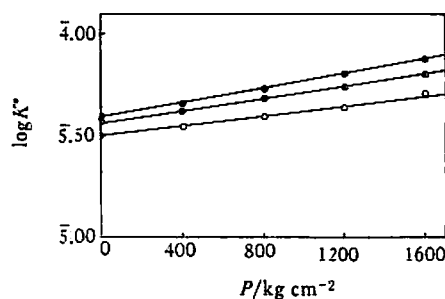◑:   800 kg/cm²
◒:   1200 kg/cm²
◓:   1600 kg/cm²

Fig. 4 $\log K^*$ vs. pressure
●:   15°C
◑:   25°C
O: 40°C

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Table 2   The concentration quotient at equilibrium in $Ni^{2+} \cdot SO_4^{2-}$ ion pair dissociation ($K_c \times 10^3$/mol)

— 15°C —

$C \times 10^4$/M P/kg cm^{-2}	1	1.5	2	2.5	3
1 atm	3.66	4.25	4.82	5.21	5.56
400	4.25	4.99	5.72	6.11	6.62
800	5.42	6.31	7.30	7.84	8.23
1200	6.30	7.40	8.38	9.12	9.83
1600	7.26	8.74	10.08	11.19	11.80

— 25°C —

$C \times 10^4$/M P/kg cm^{-2}	1	1.5	2	2.5	3
1 atm	3.33	3.97	4.48	4.83	5.27
400	4.09	4.84	5.59	5.99	6.57
800	4.80	5.63	6.39	7.06	7.63
1200	5.42	6.65	7.54	8.16	8.90
1600	6.51	7.64	8.70	9.20	10.20

— 40°C —

$C \times 10^4$/M P/kg cm^{-2}	1	1.5	2	2.5	3
1 atm	3.04	3.56	3.95	4.33	4.67
400	3.35	3.97	4.44	4.88	5.33
800	3.83	4.56	5.09	5.55	5.99
1200	4.35	5.22	5.88	6.40	7.30
1600	5.52	6.43	7.48	8.22	8.76

Table 3   The dissociation constant of $Ni^{2+} \cdot SO_4^{2-}$ ion pair on the molar scale ($K_c^\circ \times 10^3$/mol)

P/kg cm^{-2} t/°C	1 atm	400	800	1200	1600
15	2.19	2.60	3.12	3.71	4.41
25	2.04	2.40	2.82	3.24	3.72
40	1.74	1.95	2.24	2.54	3.20

Table 4   The dissociation constant of $Ni^{2+} \cdot SO_4^{2-}$ ion pair on the mole fraction scale ($K^\circ \times 10^5$)

| P/kg cm^{-2} t/°C	1 atm	400	800	1200	1600
15	3.94	4.60	5.45	6.38	7.48
25	3.69	4.26	4.95	5.57	6.32
40	3.16	3.48	3.94	4.41	5.18

The values of α in Eq. (10) are solved by means of successive approximation. The dielectric constant of water at pressure is determined from the Owen-Brinkley equation[11] and the viscosity data of water are obtained graphically by the interpolation of the data of Cappi[12]. K_c thus obtained from Eqs. (7) and (10) at each temperature and pressure are listed in Table 2. According to Eq. (9), log K_c were plotted against $\sqrt{2\alpha C}$ in Fig. 3 and the equilibrium constants K_c° were obtained by the extrapolation of log $K_c \sim \sqrt{2\alpha C}$ curve to zero concentration. K_c° are listed in Table 3. The equilibrium constant expressed in the mole ratio, K° in Table 4 was determined from K_c° by correction of the molar volume of water. As shown in these tables, the dissociation of $Ni^{2+} \cdot SO_4^{2-}$ ion pair proceeded with increasing pressure and decreasing temperature. The pressure coefficient of ln K° gives the volume change for the dissociation of ion pair $\Delta \bar{V}^\circ$ (Fig. 4) and the temperature coefficient of ln K° gives the enthalpy change $\Delta \bar{H}^\circ$ (Fig. 5). These values are summarized in Table 5 together with other thermodynamic data for this process. As shown in Table 5, $\Delta \bar{V}^\circ$ and $\Delta \bar{S}^\circ$ for the dissociation of $Ni^{2+} \cdot SO_4^{2-}$ ion pair are always negative as expected from the electrostriction due to the ion-dipole interaction between free ions and hydrated water molecules.

Table 5   Thermodynamic parameters for the dissociation of $Ni^{2+} \cdot SO_4^{2-}$ ion pair in aqueous solution

P/kg cm^{-2}	$-\Delta \bar{H}^\circ$/ kcal mol^{-1}	15°C		25°C		40°C	
		$-\Delta \bar{V}^\circ$/ cc mol^{-1}	$-\Delta \bar{S}^\circ$/cal deg^{-1} mol^{-1}	$-\Delta \bar{V}^\circ$/ cc mol^{-1}	$-\Delta \bar{S}^\circ$/cal deg^{-1} mol^{-1}	$-\Delta \bar{V}^\circ$/ cc mol^{-1}	$-\Delta \bar{S}^\circ$/cal deg^{-1} mol^{-1}
1 atm	1.65		26		26		26
400	2.01		27		27		27
800	2.47	10.1	28	8.6	28	7.4	28
1200	2.84		29		29		29
1600	3.20		30		30		30

The volume change for the dissociation $\Delta \bar{V}^\circ$ can be expressed as follows,
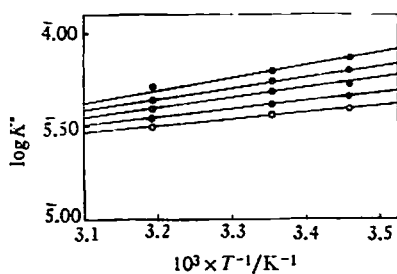
Fig. 5   log K° vs. reciprocal absolute temperature

○:   1 atm
◐:   400 kg/cm^2
◑:   800 kg/cm^2
◕: 1200 kg/cm^2
◒: 1600 kg/cm^2
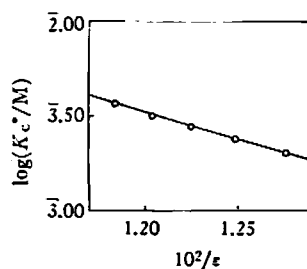
Fig. 6   log K_c° vs. reciprocal dielectric constant at 25°C

11) H. S. Harned and B. B. Owen, *op. cit.*, p. 162
12) J. B. Cappi, Thesis for Ph. D. of London University (1964)

$$\Delta \bar{V}^\circ = \bar{V}^\circ(Ni^{2+}) + \bar{V}^\circ(SO_4^{2-}) - \bar{V}^\circ(Ni^{2+} \cdot SO_4^{2-}) \tag{11}$$

where $\bar{V}^\circ(Ni^{2+})$, $\bar{V}^\circ(SO_4^{2-})$ and $\bar{V}^\circ(Ni^{2+} \cdot SO_4^{2-})$ are the partial molal volumes of the free ions and the ion pair at infinite dilution, respectively. According to Millero[13], the conventional $\bar{V}^\circ(Ni^{2+})$ and $\bar{V}^\circ$ (SO_4^{2-}) are $-24\,cc/mol$ and $13.98\,cc/mol$ at 25°C, respectively. As shown in Table 5, $\Delta \bar{V}^\circ$ is $-8.6\,cc/mol$ at 25°C so that the partial molal volume of $Ni^{2+} \cdot SO_4^{2-}$ ion pair would be $-1.4\,cc/mol$.

Moreover, the partial molal volume would be the result of two major components.

$$\bar{V}^\circ = \bar{V}^\circ(int) + \bar{V}^\circ(elect) \tag{12}$$

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 $Ni^{2+} \cdot SO_4^{2-}$ ion pair could be tentatively represented by Eq. (13).

$$\bar{V}^\circ(int) = \frac{4}{3}\pi L(r_{c+}^3 + r_{c-}^3)$$
$$= 52.2\,cc/mol \tag{13}$$

where L is Avogadro's number and r_{c+} and r_{c-} are the crystal radii of the free ions, respectively. Then, we have $-53.6\,cc/mol$ as $\bar{V}^\circ(elect)$ so that the electrostriction would considerably contribute to the partial molal volume of $Ni^{2+} \cdot SO_4^{2-}$ ion pair and the ion pair would be also hydrated.

From the viewpoint of entropy, the entropy of Ni^{2+} ion in the aqueous solution at 25°C is -29.5 cal/deg.mol[14] and that of SO_4^{2-} ion is 4.1 cal/deg.mol[15]. With these values and the entropy change for the dissociation process $\Delta \bar{S}^\circ = -26\,cal/deg.mol$, the entropy of $Ni^{2+} \cdot SO_4^{2-}$ ion pair in aqueous solution can be calculated to be 0.6 cal/deg.mol. The entropy of $Ni^{2+} \cdot SO_4^{2-}$ ion pair in gaseous state at 25°C is 70.2 cal/deg.mol[16] and that of Ni^{2+} ion is 42.3 cal/deg.mol by the Sackur-Tetrode equation. Thus, the entropy change for the hydration of $Ni^{2+} \cdot SO_4^{2-}$ ion pair and that of Ni^{2+} ion are $-69.6\,cal/$ deg.mol and $-71.8\,cal/deg.mol$, respectively. These facts show that $Ni^{2+} \cdot SO_4^{2-}$ ion pair would be considerably hydrated and contracted dy electrostriction as well as the free ions.

Now, the volume contraction of water molecule by hydration is $-2.1\,cc/mol$ at 25°C by Padova[17] and the entropy change of water molecule by hydration is $-6.0\,cal/deg.mol$ by Ulich[18]. From the $\Delta \bar{V}^\circ$ and $\Delta \bar{S}^\circ$ for this dissociation process, the number of water molecules newly hydrated for the free ion was calculated to be 4. And also, from the entropy changes of hydration, both the hydration numbers of Ni^{2+} ion and $Ni^{2+} \cdot SO_4^{2-}$ ion pair are calculated to be 12. This hydration number of Ni^{2+} ion is in agreement with that calculated by the Robinson-Stokes method as already described. The hydration number of SO_4^{2-} ion is 4 as mentioned above and the number of coordinated water molecules for Ni^{2+} ion is 6[19] so that, in the ion pair, the hydrated Ni^{2+} ion and SO_4^{2-} ion would contact with

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17) J. Padova, *J. Chem. Phys.*, **39**, 1552 (1963)
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two more water molecules.

The closest approach distance at 25°C was estimated to be 3.4Å by the slope of the curve of log $K_c°\sim 1/\varepsilon$ according to the theories[20] as shown in Fig. 6. This value is constant under high pressure and is comparable with the sum of the crystal radii of the cation and anion for this salt, 3.43Å. 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.

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