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THE ELECTRICAL CONDUCTIVITY OF $[Co(NH_3)_5NO_2]SO_4$ IN AQUEOUS SOLUTION UNDER HIGH PRESSURE

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The electrical conductivity of aqueous $[Co(NH_3)_5NO_2]SO_4$ solution has been measured as a function of pressure up to 3,000 kg/cm^2 for concentrations from 2.0×10^{-4} to 1.0×10^{-3} N at the temperatures of 15, 25 and 40°C. The equivalent conductance at infinite dilution, Λ°, has a maximum against pressure. The pressure of this maximum conductance has been found to be higher than that of the minimum viscosity of water at each temperature. These phenomena may be attributed to the decrease in the effective radii of the hydrated ions with increasing pressure.

The hydration numbers of the ions estimated by the Robinson-Stokes method are little changed by pressure and temperature.

Both the closest approach distance of the ion-pair, a, calculated by using the theoretical equation of Fuoss and the thermodynamic parameter, $\Delta\bar{V}^\circ$, calculated from the pressure coefficient of the dissociation constant suggest that this ion-pair, $[Co(NH_3)_5NO_2]^{2+}\cdot SO_4^{2-}$, would be very near to the contact one.

Introduction

To study the ion-solvent interaction under high pressure, the conductivity measurement is very useful. From the results of the measurement of the electrical conductivity, the hydration number can be estimated as one of the important numerical measures for the ion-solvent interaction. There are various view points concerning the pressure[1~4] and temperature[5~8] dependence of the hydration number of the ion, which we examined by the Robinson-Stokes[9] method.

In aqueous solutions at high pressure, the dissociation constants of the ion-pairs have been determined for $Mg^{2+}\cdot SO_4^{2-}$ [3,10], $Co(NH_3)_6^{3+}\cdot Cl^-$ [11], $Fe^{3+}\cdot NO_3^-$ [12], $Fe^{3+}\cdot Cl^-$ [12], $La^{3+}\cdot Fe(CN)_6^{3-}$ [13],

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$Mn^{2+}\cdot SO_4^{2-}$ 14), $Co(NH_3)_6^{3+}\cdot SO_4^{2-}$ 2,15), $La^{3+}\cdot SO_4^{2-}$ 16) and $Ca^{2+}\cdot SO_4^{2-}$ 3). Concerning 2-2 electrolytes of $CaSO_4$ and $MgSO_4$ 3), the structure of the ion-pair was investigated by both the closest approach distance, a, and the volume change for the dissociation, $\Delta\bar{V}^\circ$, and it was concluded that these ion-pairs are solvent-separated ones because the value of $|\Delta\bar{V}^\circ|$ is small and that of a is larger than the sum of the crystal radii of the ions. We have extended these studies to the electrolyte, $[Co(NH_3)_5NO_2]SO_4$, which has a common anion but a large complex cation, for the purpose of elucidating whether or not the ion-pair of the complex cation is the same type as that of the simple cation.

Experimental

Apparatus

The diagram of the apparatus is shown in Fig. 1. The high pressure vessel is a cylinder made of SNCM 8, 20 mm in inner diameter and 80 mm in outer diameter. As shown in Fig. 2, the high pressure conductivity cell made of teflon has a capacity of 3.5 m*l* and a membrane thin enough to transmit the pressure generated in the high pressure vessel to the sample solution. The platinum electrodes supported by teflon and adhesive Araldite, were lightly coated with platinum black. The cell constant at normal pressure was determined using 10^{-2} N aqueous solution of KCl 17) and the cell constant at high pressure was corrected with the compression data of teflon 18) as described elsewhere 2).

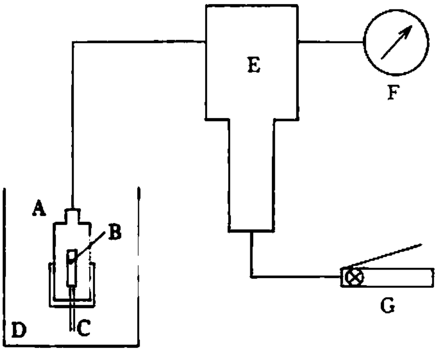

Fig. 1 Apparatus
A: High pressure vessel
B: Conductivity cell
C: Leading wire
D: Oil-bath
E: Intensifier
F: Bourdon gauge
G: Hand pump

The high pressure was developed in the pressure vessel with the hand pump and the intensifier, and measured with an accuracy of ±1.0% by the Bourdon gauge calibrated to a free piston gauge.

The pressure vessel was immersed in the liquid paraffin bath kept constant within ±0.03°C. About 1.5 hr were required for the apparatus to reach an initial thermal equilibrium and 30 min were

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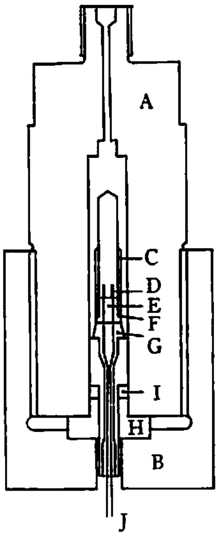

Fig. 2 High pressure vessel and conductivity cell
A: Cylinder B: Nut
C: Teflon capsule D: Platinum electrode
E: Teflon plug F: Rubber packing
G: Araldite H: Modified Bridgman seal
I: Packing J: Leading wire

also required after a change of the pressure of 500 kg/cm^2.

The resistances were measured by the conductivity equipment (Model MY-7) supplied by Yanagimoto Seisakusho.

Materials

The conductivity water was distilled and passed through ion-exchange resin prior to use (specific conductivity at 25°C and 1 atm. $\kappa^\circ \fallingdotseq 1.3\times10^{-6}\Omega^{-1}\cdot cm^{-1}$).

The compound $[Co(NH_3)_5NO_2]Cl_2$ was first synthesized and then converted to the sulfate salt by the method of Jörgensen[19]. The final product was recrystallized three times from water by adding methanol as described by Masterton and Bierly[20] and dried at 80–100°C in an electric oven to a constant weight. The conductivity of aqueous solution of $[Co(NH_3)_5NO_2]SO_4$ increased slowly when exposed to light, so that the solution was always manipulated in the dark.

The concentrations of dilute solutions at high pressure were corrected with the density of water at high pressure calculated by the Tait equation[21].

Results and Consideration

Pressure dependence of the limiting equivalent conductance

The equivalent conductance of the electrolyte is defined as

$$\Lambda=\frac{10^3(\kappa-\kappa^\circ)}{C}, \qquad (1)$$

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[19] S. M. Jörgensen, *Z. Anorg. Chem.*, 5, 172 (1894)

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[21] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold New York (1958)

where κ and κ° are the specific conductivities of the solution and solvent, respectively, and C is the corrected concentration in equiv/l. Fig. 3 shows the plots of Λ against the square root of the equivalent concentration, $C^{1/2}$, which are linear as found at normal pressure by Kohlrausch. The limiting equivalent conductance, Λ°, was determined by extrapolating the Kohlrausch plot. The values of Λ and Λ° are shown in Table 1. Fig. 4 shows the curve of Λ° *vs* pressure at 15, 25 and 40°C, respectively. Each curve has a maximum and it is noted that the pressure at this maximum point is higher than that of the minimum viscosity of water[22] at each temperature as shown in Fig. 5. At 15 and 25°C, the pressure of the minimum viscosity of water ($P_{m,\,vis}$) is about 950 and 600 kg/cm², respectively, though the pressure of the maximum limiting equivalent conductance ($P_{m,\,con}$) were found at about 1,150 and 900 kg/cm², respectively. Moreover, the curve of Λ° *vs* pressure has a maximum even at 40°C where the viscosity of water increases monotonously as pressure increases.

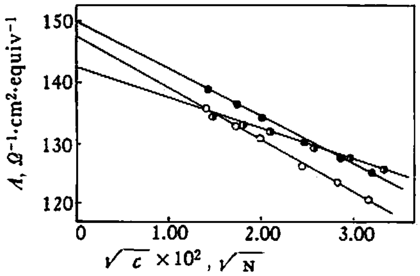

Fig. 3 Λ *vs.* $\sqrt{C}$

○: 1 atm, ●: 500 kg/cm²,
◑: 3,000 kg/cm²

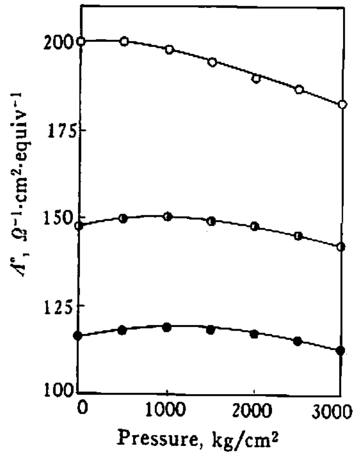

Fig. 4 Λ° *vs.* pressure

●: 15°C, ◑: 25°C,
○: 40°C

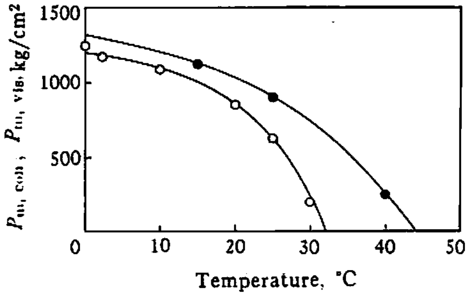

Fig. 5 The variation of $P_{m,\,con}$ and $P_{m,\,vis}$ with temperature

●: $P_{m,\,con}$, ○: $P_{m,\,vis}$[22]

If the ion satisfies the wet condition, its equivalent conductance can be expressed by the Stokes equation as follows:

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22) J. B. Cappi, Ph. D. Thesis, London University (1964)

Table 1 Λ and Λ° ($\Omega^{-1}\cdot$cm$^2\cdot$equiv^{-1})

(a) 15°C

$C\times10^4$, N / P, kg/cm^2	2.000	3.000	4.000	6.000	8.000	10.00	Λ°
1	107.3	104.9	103.3	100.3	98.0	95.5	116.4
500	110.0	107.5	106.2	103.4	101.3	99.0	118.1
1,000	111.8	109.5	108.1	105.7	103.8	101.7	119.0
1,500	112.2	110.0	108.5	106.2	104.5	102.5	118.7
2,000	111.3	109.2	107.9	106.0	104.1	102.4	117.7
2,500	109.8	107.9	106.7	104.8	103.0	101.3	115.7
3,000	107.5	105.9	104.8	102.9	101.5	99.6	113.0

(b) 25°C

$C\times10^4$, N / P, kg/cm^2	2.000	3.000	4.000	6.000	8.000	10.00	Λ°
1	135.8	133.0	130.9	126.5	123.9	121.1	147.4
500	138.7	136.6	134.3	130.2	127.7	125.2	149.9
1,000	140.4	138.5	136.5	132.8	130.6	128.1	150.6
1,500	140.2	138.6	136.8	133.5	131.3	129.2	149.6
2,000	139.0	137.6	136.0	133.0	131.0	128.8	147.8
2,500	137.1	135.8	134.4	131.6	129.7	127.6	145.7
3,000	134.6	133.3	132.1	129.5	127.8	125.9	142.7

(c) 40°C

$C\times10^4$, N / P, kg/cm^2	2.000	3.000	4.000	6.000	8.000	10.00	Λ°
1	184.6	180.5	178.3	172.9	169.2	165.1	200.2
500	185.0	181.7	179.2	174.7	170.9	167.2	200.2
1,000	184.0	182.3	178.5	174.7	171.4	168.1	197.8
1,500	182.1	179.2	176.9	173.4	170.8	167.3	194.6
2,000	179.7	177.3	174.8	171.8	169.1	165.9	191.2
2,500	176.6	174.3	171.6	169.1	166.8	164.0	186.8
3,000	172.9	171.2	168.3	165.8	163.7	160.7	183.1

$$\lambda_i^\circ=\frac{|z_i|eF}{6\pi\cdot\eta^\circ\cdot r_{s,i}}, \qquad (2)$$

where λ_i°, z_i, $r_{s,i}$, e, F and η° are the limiting equivalent conductance of the i-ion, the ionic valence, the Stokes radius, the proton charge, the Faraday constant and the viscosity of water, respectively. As $|z_+|=|z_-|=2$ for this electrolyte, we have from Eq. (2)

$$\Lambda^\circ=\lambda_+^\circ+\lambda_-^\circ=\frac{eF}{3\pi\cdot\eta^\circ}\left(\frac{1}{r_{s,+}}+\frac{1}{r_{s,-}}\right). \qquad (3)$$

If the Stokes radii of the cation and the anion would not change with pressure, it would be concluded that

$$P_{m,con}=P_{m,vis}. \tag{4}$$

However, when the sizes of the ions are comparable with that of the solvent molecule, the Stokes law, Eq. (2), should be modified as follows:

$$\lambda_i^\circ=\frac{|z_i|eF}{C(r_{e,i})\cdot\eta^\circ\cdot r_{e,i}}, \tag{5}$$

where $r_{e,i}$ is the effective radius of the i-ion and $C(r_{e,i})$ is a function of $r_{e,i}$ instead of being a constant, 6π, as in Eq. (2). Then,

$$\begin{aligned}\Lambda^\circ&=\frac{eF}{\eta^\circ}\left(\frac{|z_+|}{C(r_{e,+})\cdot r_{e,+}}+\frac{|z_-|}{C(r_{e,-})\cdot r_{e,-}}\right)\\&=\frac{2eF}{\eta^\circ}(A_++A_-),\end{aligned} \tag{6}$$

where

$$A_i=\frac{1}{C(r_{e,i})\cdot r_{e,i}}. \tag{7}$$

By differentiating the logarithmic form of Eq. (6) with pressure at constant temperature, we have

$$\frac{1}{\Lambda^\circ}\left(\frac{\partial\Lambda^\circ}{\partial P}\right)_T=-\frac{1}{\eta^\circ}\left(\frac{\partial\eta^\circ}{\partial P}\right)_T+\left(\frac{1}{A_++A_-}\right)\left[\left(\frac{\partial A_+}{\partial P}\right)_T+\left(\frac{\partial A_-}{\partial P}\right)_T\right]. \tag{8}$$

When pressure is applied to the hydrated ion, the effective radius of the ion in Eq. (7) decreases due to the compression as shown in Table 2 and $C(r_{e,i})$ in Eq. (7) also decreases with the decrease in $r_{e,i}$ as shown elsewhere[2]. Therefore,

$$\left(\frac{\partial A_i}{\partial P}\right)_T>0. \tag{9}$$

At the pressure where the viscosity of water has a minimum against pressure,

$$\left(\frac{\partial\eta^\circ}{\partial P}\right)_T=0. \tag{10}$$

From Eqs. (8), (9) and (10) we have at $P=P_{m,vis}$

$$\left(\frac{\partial\Lambda^\circ}{\partial P}\right)_T>0, \tag{11}$$

which means that Λ° is still increasing at the pressure of the minimum viscosity. Thus the compression effect could explain qualitatively $P_{m,con}>P_{m,vis}$ and that the limiting equivalent conductance of this electrolyte has a small maximum against pressure even at 40°C where the viscosity of water has no minimum against pressure.

The hydration numbers of the free ions

The hydration numbers of the ions were estimated from the method of the Robinson-Stokes[9]. The justification of applying this method to high pressure was discussed by Nakahara *et al.*[2]. $\Lambda^{\circ(P)}$ can be splitted into the ionic limiting conductance, $\lambda_i^{\circ(P)}$, by the limiting transference number, $t_i^{\circ(P)}$,

$$\lambda_i^{\circ(P)} = \Lambda^{\circ(P)} \cdot t_i^{\circ(P)}. \tag{12}$$

Table 2 r_e, h and V_w
$r_c([Co(NH_3)_5NO_2]^{2+}) \fallingdotseq r_c(Co(NH_3)_6^{3+}) = 2.55\,Å$[6],
$r_c(SO_4^{2-}) = 2.73\,Å$[23]

(a) 15°C

P, kg/cm^2	$[Co(NH_3)_5No_2]^{2+}$		SO_4^{2-}		V_w (Å^3)
	r_e (Å)	h	r_e (Å)	h	
1	3.91	6.0	3.62	3.8	30.0
500	3.91	6.2	3.63	3.9	29.4
1,000	3.91	6.3	3.63	4.0	28.8
1,500	3.91	6.4	3.64	4.1	28.3
2,000	3.89	6.4	3.61	4.0	27.9
2,500	3.89	6.4	3.60	4.0	27.5
3,000	3.87	6.4	3.61	4.1	27.1

(B) 25°C

P, kg/cm^2	$[Co(NH_3)_5NO_2]^{2+}$		SO_4^{2-}		V_w (Å^3)
	r_e (Å)	h	r_e (Å)	h	
1	3.94	6.2	3.66	4.0	30.0
500	3.94	6.4	3.63	3.9	29.4
1,000	3.91	6.3	3.62	3.9	28.8
1,500	3.90	6.3	3.63	4.1	28.4
2,000	3.89	6.4	3.60	4.0	27.9
2,500	3.87	6.3	3.59	3.9	27.5
3,000	3.86	6.3	3.56	3.8	27.2

(c) 40°C

P, kg/cm^2	$[Co(NH_3)_5NO]^{2+}$		SO_4^{2-}		V_w (Å^3)
	r_e (Å)	h	r_e (Å)	h	
1	3.96	6.4	3.67	4.1	30.0
500	3.91	6.2	3.66	4.1	29.4
1,000	3.90	6.2	3.65	4.1	28.9
1,500	3.88	6.2	3.62	4.0	28.4
2,000	3.88	6.3	3.63	4.1	28.0
2,500	3.87	6.3	3.62	4.1	27.6
3,000	3.86	6.3	3.61	4.1	27.3

But no such data are available for $[Co(NH_3)_5NO_2]SO_4$ solutions under high pressure and thus the anionic transference number under high pressure were assumed to be equal to that at atmospheric pressure. The values of $t_-^{\circ(P)}$ are as follows:

$$t_-^{\circ(P)}=t_-^{\circ(1)}=\frac{\lambda_-^{\circ(1)}}{\Lambda^{\circ(1)}}, \qquad \begin{cases} 0.541 & \text{at} \quad 15^\circ\text{C} \\ 0.543 & \text{at} \quad 25^\circ\text{C} \\ 0.540 & \text{at} \quad 40^\circ\text{C} \end{cases} \tag{13}$$

where the values of $\lambda_-^{\circ(1)}$ were cited from the literature[9]. The Stokes radius, $r_{s,i}$, calculated from Eq. (2) was corrected into the effective radius of the hydrated ion, $r_{e,i}$, as follows:

$$r_{e,i}=r_{s,i}\cdot f_{\text{R-S}}, \tag{14}$$

where $f_{\text{R-S}}$ is the Robinson-Stokes correction factor. The hydration number, h_i, is estimated as follows:

$$h_i=\frac{1}{V_w}\frac{4}{3}\pi(r_{e,i}^3-r_{c,i}^3), \tag{15}$$

where $r_{c,i}$ is the crystal radius of the i-ion and V_w is the average volume of one water molecule in the hydration sheath and was assumed to be equal to that of the bulk water at each pressure. These results are given in Table 2. Considering the approximations of this method[24], the accuracy of the hydration number is within ±0.5. The hydration numbers given in Table 2 hardly change with pressure and temperature within the experimental error as in the cases of $Co(NH_3)_6^{3+}$[2], Ca^{2+}[3], Mg^{2+}[3], SO_4^{2+}[2,3], K^+[4] and Cl^-[4], though Horne[1] proposed an idea of pressure-induced dehydration on the basis of his own multizone hydration atmosphere model several years ago.

The hydration number of $[Co(NH_3)_5NO_2]^{2+}$ is about 6.3 which is much smaller than those of Ca^{2+} and Mg^{2+}[3], 10 and 11, respectively. It may be reasonable to consider that the ligands in $[Co(NH_3)_5NO_2]^{2+}$ have already occupied the nearest neighbouring positions around Co^{3+} ion.

Effect of pressure on the dissociation of the ion-pair

The ion-pair of $[Co(NH_3)_5NO_2]^{2+}\cdot SO_4^{2-}$ would be in equilibrium with $[Co(NH_3)_5NO_2]^{2+}$ and SO_4^{2-} ions,

$$\underset{m(1-\alpha)}{[Co(NH_3)_5NO_2]^{2+}\cdot SO_4^{2-}} \rightleftarrows \underset{m\alpha}{[Co(NH_3)_5NO_2]^{2+}}+\underset{m\alpha}{SO_4^{2-}}, \tag{16}$$

where m is the molar concentration $(=C/2)$ and α is the degree of dissociation. Corresponding to Eq. (16), the dissociation constant, K, is defined as

$$K=\frac{m\alpha^2 f_\pm^2}{1-\alpha}, \tag{17}$$

where the activity coefficient of the ion-pair was assumed to be unity and $f_\pm$ is the mean activity co-

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23) O. K. Rice, "Electronic Structure and Chemical Binding", McGraw-Hill Book Company, New York (1940)

24) M. Nakahara, K. Shimizu and J. Osugi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), 92, 785 (1971)

efficient of the ions which was calculated from the Debye-Hückel equation,

$$-\log f_{\pm}=|z_+\cdot z_-|\frac{1.291\times 10^6}{(DT)^{3/2}}\Gamma^{1/2}, \tag{18}$$

$$(\Gamma=\Sigma m_i\cdot z_i^2=8m\alpha=4C\alpha). \tag{19}$$

Once α has been determined, the dissociation constant, K, can be calculated from Eqs. (17), (18) and (19). The parameter α can be determined by the use of the conductance data obtained and the Onsager conductance equation which was verified[4] to be valid for dilute solutions at high pressure. For this electrolyte, we have

$$\Lambda=\alpha\{\Lambda^{\circ}-S\cdot(\alpha C)^{1/2}\}, \tag{20}$$

where S is the constant which is determined by the dielectric constant of water, D[21], the viscosity of water, η°[22], the absolute temperature, T, and the limiting equivalent conductance, Λ°. Eq. (20) is an irrational equation with respect to α but can be solved approximately. The calculated results of the dissociation constant, K, are shown in Table 3. The values of K of this ion-pair are smaller than those of $Ca^{2+}\cdot SO_4^{2-}$ and $Mg^{2+}\cdot SO_4^{2-}$[3] which have the same valence type as this ion-pair.

Table 3 Dissociation constants of the ion-pair, K

P, kg/cm^2 \ T, °C	15	25	40
1	1.97×10^{-3}	2.05×10^{-3}	2.12×10^{-3}
500	2.56×10^{-3}	2.36×10^{-3}	2.43×10^{-3}
1,000	3.29×10^{-3}	3.05×10^{-3}	2.96×10^{-3}
1,500	3.78×10^{-3}	3.73×10^{-3}	3.50×10^{-3}
2,000	4.21×10^{-3}	4.37×10^{-3}	4.14×10^{-3}
2,500	4.81×10^{-3}	4.75×10^{-3}	5.02×10^{-3}
3,000	5.63×10^{-3}	5.28×10^{-3}	5.03×10^{-3}

To investigate the hydration of the ion-pair, the closest approach distance of the ion-pair, a, was calculated from the Fuoss equation[25],

$$K=\frac{3000}{4\pi Na^3}\exp\left(-\frac{|z_+\cdot z_-|e^2}{aDkT}\right) \tag{21}$$

where N and k are Avogadro's number and the Boltzmann constant, respectively. The result is shown in Table 4. The value of a of this ion-pair is much smaller at each temperature and pressure than those of $Ca^{2+}\cdot SO_4^{2-}$ and $Mg^{2+}\cdot SO_4^{2-}$[3] which are 4.02 and 4.17 Å at 25°C and 1 atm, respectively, though the sum of the crystal radii of the cation and anion for this salt is much larger than for $CaSO_4$ and $MgSO_4$. In addition, the systematic changes by pressure are not observed. These suggest that there exist statistically many contact ion-pairs among them contrary to the cases of $Ca^{2+}\cdot SO_4^{2-}$ and $Mg^{2+}\cdot SO_4^{2-}$. It can be thought that the paradox, *i. e.*, a is smaller than the sum of the crystal radii, would occur be-

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[25] R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958)

cause of using the bulk dielectric constant in Eq. (21). The value of a would become larger if the effective dielectric constant in the vicinity of the ion would be used; the effective dielectric constant would be smaller than that of bulk water.

Table 4 Changes in the closest approach distances of the ion-pair by pressure, a (Å)

P, kg/cm² \ T, °C	15	25	40
1	3.25	3.35	3.46
500	3.27	3.29	3.40
1,000	3.29	3.33	3.41
1,500	3.27	3.34	3.40
2,000	3.23	3.35	3.41
2,500	3.22	3.30	3.45
3,000	3.24	3.29	3.36

Sum of the crystal radii is 5.28 (Å).

Moreover, the pressure coefficient of $\ln K$ gives the volume change for the dissociation of the ion-pair, $\Delta\bar{V}^\circ$, according to the thermodynamic relation[26].

$$\Delta\bar{V}^\circ = -RT\left(\frac{\partial \ln K}{\partial P}\right)_T + RT\beta^\circ. \tag{22}$$

where β° is the compressibility of water and was calculated by the Tait equation[21]. The values of $\Delta\bar{V}^\circ$ summarized in Table 5 are always negative as expected from the electrostriction theory and become less negative with increasing pressure and temperature. The values of $\Delta\bar{V}^\circ$ of this ion-pair are comparable at each pressure and temperature with those of $Ca^{2+}\cdot SO_4^{2-}$ and $Mg^{2+}\cdot SO_4^{2-}$[3] which are −9.1 and −6.6 cm³/mol** at 25°C and 1 atm, respectively. The left side of Eq. (22) can be expressed as follows:

Table 5 Volume changes for the dissociation of the ion-pair, $\Delta\bar{V}^\circ$ (cm³/mole)

P, kg/cm² \ T, °C	15	25	40
1~1,000	−12.5	−9.5	−8.2
1,000~2,000	−6.0	−8.5	−8.4
2,000~3,000	−6.1	−4.5	−4.2

$$\Delta\bar{V}^\circ = \bar{V}^\circ(\mathrm{c}) + \bar{V}^\circ(\mathrm{a}) - \bar{V}^\circ(\mathrm{i-p}), \tag{23}$$

where $\bar{V}^\circ(\mathrm{c})$, $\bar{V}^\circ(\mathrm{a})$ and $\bar{V}^\circ(\mathrm{i-p})$ are the partial molal volumes of the cation, anion and ion-pair at infinite dilution, respectively. Applying Eq. (23) to such ion-pairs as $Ca^{2+}\cdot SO_4^{2-}$ and $Mg^{2+}\cdot SO_4^{2-}$ and using the literature values[3,27] of the partial molal volumes of the ions at infinite dilution, we have at

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** The literature values were corrected by compressibility.

26) S. D. Hamann, "Physico-Chemical Effects of Pressure", Chap. 8, Butterworths Scientific Pub., London (1957)

27) F. J. Millero, "Water and Aqueous Solutions", Chap. 13, ed. by R. A. Horne, Wiley-Interscience, New York (1972)

25°C and 1 atm,

$$\bar{V}^\circ(Ca^{2+}\cdot SO_4^{2-})=5.2 \quad \text{and} \quad \bar{V}^\circ(Mg^{2+}\cdot SO_4^{2-})=-0.6\,\text{cm}^3/\text{mol}.$$

Generally, the partial molal volume at infinite dilution, $\bar{V}^\circ$, can be expressed as follws:

$$\bar{V}^\circ=\bar{V}^\circ_{\text{crys}}+\bar{V}^\circ_{\text{elect}}+\cdots\cdots, \tag{24}$$

where $\bar{V}^\circ_{\text{crys}}$ is the crystal partial molal volume and $\bar{V}^\circ_{\text{elect}}$ is the electrostriction partial molal volume. When the partial molal volume of the ion-pair is subtracted by its crystal partial molal volume which is assumed to be expressed by

$$\bar{V}^\circ_{\text{crys}}(\text{i}-\text{p})=\frac{4}{3}\pi N(r_{c,+}{}^3+r_{c,-}{}^3)^{***}, \tag{25}$$

we have $-48.5\,\text{cm}^3/\text{mol}$ for $Ca^{2+}\cdot SO_4^{2-}$ and $-51.5\,\text{cm}^3/\text{mol}$ for $Mg^{2+}\cdot SO_4^{2-}$ at 25°C and 1 atm, respectively. When we see these large negative values, we may say at least that electrostriction considerably contributes to the partial molal volumes of these ion-pairs and possibly that these ion-pairs are solvent-separated ones. As for the ion-pair, $[Co(NH_3)_5NO_2]^{2+}\cdot SO_4^{2-}$, its partial molal volume can't be calculated accurately since we don't know exactly the value of $\bar{V}^\circ([Co(NH_3)_5NO_2]^{2+})$ neither from experiment nor from calculation. But the difference between the partial molal volume of this ion-pair and those of $Ca^{2+}\cdot SO_4^{2-}$ and $Mg^{2+}\cdot SO_4^{2-}$ can be attributed to the difference between the partial molal volumes of the cations, since the value of $\Delta\bar{V}^\circ$ of this ion-pair is the same order as those of $Ca^{2+}\cdot SO_4^{2-}$ and $Mg^{2+}\cdot SO_4^{2-}$. This suggests that it is not unreasonable to consider that the contribution of electrostriction to the partial molal volume of this ion-pair is fairly large judging from the magnitude of electrostriction in the cases of $Ca^{2+}\cdot SO_4^{2-}$ and $Mg^{2+}\cdot SO_4^{2-}$, though less than in the latter cases.

From the discussion above, it would be concluded that this ion-pair would be classified as the contact one rather than the solvent-separated one compared with $Ca^{2+}\cdot SO_4^{2-}$ and $Mg^{2+}\cdot SO_4^{2-}$; even if the cation and anion approach each other, the charges of the ions of this ion-pair could not be electrically neutralized completely on account of the large ionic radii and then electrostriction due to the effective charge could still strongly act upon the water molecules surrounding the ion-pair.

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*** Pauling's[28] values are used for the crystal radii of Ca^{2+} and Mg^{2+}, and Rice's[23] value for that of SO_4^{2-}.

28) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press (1960)