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The Effect of the Pressure on the Electrical Conductivity of Zinc Sulfate in Water

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The electrical conductivity of $ZnSO_4$ in water was measured at high pressures up to 3000 kg/cm^2 and at 25 °C. The dissociation constant of the ion pair (K_m) increased with an increase in the pressure. The volume change (ΔV°) accompanying the dissociation was -8.0 ± 0.5 ml/mol at 25 °C. The distance of the closest approach (å) of the ion pair, calculated using the observed K_m value and the theoretical equation of Bjerrum, increased with an increase in the pressure. In view of these ΔV° and å values, the ion pair of $ZnSO_4$ was assumed to be of the solvent-separated type. It was also concluded that the number of water molecules separating the ions constituting an ion pair increases with an increase in the pressure.

The structure of the ion pairs of metal sulfates in water has been studied from electrochemical and thermodynamical measurements,[1-3] ultrasonic absorption measurements,[4-6] and spectroscopic measurements.[6-8] As a result, it has been found that there exist two types of ion pairs. One is the contact type, and the other is the separated one with one or more solvent molecules between sandwiched. From the heat of dilution data, Larson[3] has concluded that ion pairs of $MgSO_4$, $NiSO_4$, and $ZnSO_4$ are separated by more water molecules than those of $CaSO_4$, $CuSO_4$, and $CdSO_4$. Their tendency to form a contact ion pair is in the same order as their ionic radii, which is in good agreement with the results from IR reported by Larsson[7] and those from the visible absorption spectrum reported by Smithson and Williams.[8]

The information as to the volume change accompanying the dissociation of the ion pair, ΔV°, obtained from dilatometry[9] and the pressure effect on the dissociation constants of ion pairs[10-15] may be a useful indication of whether a particular ion pair is of the "solvent-separated" or "contact" type. It is well known that the volume change accomapanying the dissociation of electrolytes shows a negative sign upon electrostriction, a negative sign caused by the electrostatic interaction between ions and their surrounding solvent molecules.[16] Therefore, the magnitude of the volume decrease accompanying the dissociation of ion pairs may be expected to be smaller for the solvent-separated type, in which the ions are hydrated in the ion-pair state, than for the contact type.

In the present experiment, we attempted to measure the electrical conductivity of $ZnSO_4$ in water up to 3000 kg/cm^2 at 25 °C and to clarify the structure of the ion pair by considering the ΔV° value together with the value of the ionic distance of the closest approach of the ion pair at high pressures.

Experimental

Materials. Zinc sulfate of a special grade was used without further purification. The conductivity water was prepared by repeatedly distilling the water from a mixed-bed deionizing column. The specific conductivity of this water was 1.320×10^{-6} mho/cm at 25 °C. The solutions of zinc sulfate were prepared in the approximate concentration range from 5.0×10^{-4} to 1.0×10^{-3} M at 25 °C.

Method. The apparatus and the procedure used to obtain the electrical conductivity under high pressures have been described in detail elsewhere.[17]

Results and Discussion

The measured equivalent conductances (Λ) are listed in Table 1, together with the limiting equivalent conductances (Λ°), which were determined by the extrapolation of the Kohlrausch plots,[18] Λ *vs.* $\sqrt{c}$, to an infinite dilution. From these data, the dissociation constants of the ion pair were calculated by the method by Hamann, Pearce, and Strauss.[12] The dissociation degree (α) of the ion pair was determined by inserting the experimental conductances (Λ) and the theoretical values (Λ^i), calculated from Eq. (2) and given by Davies, Otter, and Prue,[19] into Eq. (1):

TABLE 1. EQUIVALENT CONDUCTANCES (Λ) AND LIMITING EQUIVALENT CONDUCTANCES (Λ°) OF $ZnSO_4$ AT 25 °C AND AT VARIOUS PRESSURES.

Pressure kg/cm^2	Concentration at 1 atm, equiv./l (10^{-4})					
	Λ°	Λ				
	0.0	5.0	6.0	7.5	9.0	10.0
1 (atms)	132.8	116.0	114.4	112.1	110.1	108.8
500	135.4	119.8	118.1	116.2	114.2	113.2
1000	135.5	120.0	119.4	117.4	115.8	114.7
1500	134.4	121.0	119.8	118.0	116.4	115.4
2000	132.8	120.4	119.2	117.4	116.0	115.2
2500	131.0	119.3	118.3	116.9	115.4	114.6
3000	129.0	118.2	117.0	115.8	114.5	113.8

$$\alpha = \frac{\Lambda}{\Lambda^i} \tag{1}$$

$$\Lambda^i = \Lambda^\circ - \left[\frac{R\Lambda^\circ}{1+B\mathring{a}\sqrt{2\alpha c}} + E\right]\frac{2\sqrt{\alpha c}}{1+2B\mathring{a}\sqrt{\alpha c}} \tag{2}$$

where:

$$R = \frac{32.816 \times 10^7}{(\varepsilon T)^{3/2}} \tag{3}$$

$$B = \frac{5.029 \times 10^9}{(\varepsilon T)^{1/2}} \tag{4}$$

$$E = \frac{165.00}{\eta(\varepsilon T)^{1/2}} \tag{5}$$

$$\mathring{a} = \frac{2e^2}{\varepsilon kT} \tag{6}$$

Here, ε and η are the dielectric constant and the viscosity of water respectively, k is the Boltzmann constant, T is the absolute temperature, e is the protonic charge, and c is the molarity. The activity coefficient ($f_\pm$) was predicted by the Debye-Hückel limiting law at the c concentration as follows:

$$-\log f_\pm = \frac{2A\sqrt{\alpha c}}{(1+2B\mathring{a}\sqrt{\alpha c})} \tag{7}$$

where A is $7.2984\times 10^6/(\varepsilon T)^{3/2}$. In applying the above equation to the conditions under a high pressure, the ε values calculated by the Owen-Brinkley equation[20] and the η data observed by Cappi[21] were used.

The dissociation constant (K_m) is given by:

$$K_m = \frac{m\alpha^2 f_\pm{}^2}{1-\alpha} \tag{8}$$

where m[22] donates the molality of $ZnSO_4$ and where the activity coefficient of ion pairs is assumed to be unity. The K_m values obtained are listed in Table 2. The present value at atmospheric pressure, 4.55×10^{-3} equiv./l, may be compared with that of 4.90×10^{-3} equiv./l observed by Owen and Gury[24] and by Patterson and Freitag,[25] that of 4.4×10^{-3} equiv./l observed by Denney and Monk[26] from their electrical conductivity measurements, and that of 4.17×10^{-3} mol/l observed by Nair and Nancollas[1] from the electromotive force. These results, ranging from 4.17×10^{-3} to the 4.90×10^{-3} mol/l presented above, rather deviate from the value of 3.24×10^{-3} mol/l reported by Izatt *et al.*[27] on the basis of their calorimetrical determinations and from that of 5.4×10^{-3} equiv./l reported by Davies[28] on the basis of the electrical conductivity. Table 2 shows that K_m increases with an increase in the pressure. Therefore, the formation of the ion pair is depressed by an increase in the pressure.

TABLE 2. DISSOCIATION CONSTANTS (K_m) AND AVERAGE DISSOCIATION CONSTANTS $(K_m)_{av}$ OF $ZnSO_4$ AT 25 °C AND AT VARIOUS PRESSURES.

Pressure kg/cm²	$(K_m)_{av}$	K_m, equiv./l (10^{-3}) Concentration at 1 atm, equiv./l (10^{-4})				
		5.0	6.0	7.5	9.0	10.0
1(atm)	4.554±0.046	4.454	4.541	4.555	4.581	4.640
500	5.461±0.096	5.386	5.295	5.546	5.478	5.599
1000	6.252±0.146	5.916	6.221	6.279	6.447	6.398
1500	7.677±0.096	7.437	7.701	7.726	7.755	7.763
2000	8.865±0.076	8.787	8.888	8.774	8.844	9.030
2500	10.17±0.207	9.722	10.11	10.49	10.20	10.35
3000	11.72±0.266	11.66	11.12	11.98	11.83	12.02

The ΔV° value at 1 atm accompanying the dissociation of the $ZnSO_4$ ion pair was obtained graphically by the following equation:

$$\Delta V^\circ = -RT(\partial \ln K_m/\partial P)_T \tag{9}$$

where R is the gas constant. The obtained ΔV° value of -8.0 ± 0.5 ml/mol agrees with that of -8.2 ml/mol for $ZnSO_4$[29] and is close to those of -8.5 ml/mol[10] and -7.7 ml/mol[14] for $MgSO_4$ and that of -7.4 ml/mol[11] for $MnSO_4$, but it is larger than that of -10.2 ml/mol[14] for $CaSO_4$. The absolute ΔV° values of the above divalent metal sulfate ion pairs are much smaller than those of -20.4 ± 0.5 ml/mol[30] and -28.9 ml/mol[31] accompanying the dissociation of H_2O and NH_4OH respectively. The smallness of the absolute values of ΔV° in comparison with the values for the ionization of weak acid and bases shows that the ions are extensively hydrated in the ion-pair state. The order of the ΔV° values for divalent metal sulfates is independent of their ionic radii. The tendency to form a solvent-separated ion pair shown by the data of the volume change is not in good agreement with the results obtained from the heat of dilution.[3]

Information about the distance of the closest approach of ion pairs derived from both the observed dissociation constant and the theory of the ion association by Bjerrum will contribute to clarifying the structure of ion pairs. The K_m is related theoretically to $\mathring{a}$ by:

$$K_m = \frac{1000}{4\pi N Q(b)\rho}\left(\frac{\varepsilon kT}{4e^2}\right)^3 \tag{10}$$

where:

$$Q(b) = \int_2^b x^{-4}e^x \mathrm{d}x \tag{11}$$

$$b = \frac{4e^2}{\mathring{a}\varepsilon kT} \tag{12}$$

ρ is the density of water at a given temperature and pressure,[23] and the relation between $\log Q(b)$ and b obtained by Harned and Owen[32] was used. Table 3 shows the $\mathring{a}$ values obtained at each pressure up to 3000 kg/cm². The value at 1 atm, 4.3 Å is larger than that of 3.47 Å for the interionic distance of the $ZnSO_4$ crystal.[33] Therefore, the solvent-separated type is assumed for the ion pair. This is the same as the conclusion obtained from the volume change.

TABLE 3. DISTANCE OF THE CLOSEST APPROACH ($\mathring{a}$) OF $ZnSO_4$ ION PAIR AT 25 °C UNDER VARIOUS PRESSURES.

Pressure, kg/cm²	$\mathring{a}$, Å
1 (atm)	4.3
500	4.4
1000	4.5
1500	4.8
2000	5.0
2500	5.3
3000	5.5

The present results, to be found in Table 3, show an increase in the $\mathring{a}$ value with an increase in the pressure; this is in disagreement with the results derived by Nakahara *et al.*,[13] Inada *et al.*,[14] and Ueno *et al.*[15] However, from the study of the pressure effect on the equilibrium of tight ion pairs$\rightleftarrows$loose ion pairs for sodium and lithium fluorenyl in tetrahydrofuran, Claesson *et al.*[34] found that the pressure shifted the equilibrium towards the loose ion pairs. The fact that the structure of the solvated ion pairs strongly depends on the dielectric constant of the solvent has been clarified in a nonaqueous system by Griffiths and Symons.[35] They showed that the tendency to form the solvent-separated ion pair increased with the increase in the dielectric constant of the solvent. The application of pressure causes an increase in the dielectric constant of the solvent. Therefore, the increase in the $\mathring{a}$ value with an increase in the pressure suggests that the ion pair may be expected to become more hydrated as the pressure increases, in spite of the contraction of the water in the hydration sheath of the ion pair by the compression. This consideration was already predicted about small free ions, *i.e.*, sodium and potassium ions, by Kay and Evans[36] from the point of view of the structural change of bulky water as a result of the pressure effect on the Walden product. On the contrary, Horne[37] has suggested that the pressure breaks up the structure of the hydration of small ions. Nakahara *et al.*,[38] have reported that no pressure effect can be found in the hydration number of potassium chloride up to 5000 kg/cm^2, assuming that the average volume of water molecules in the hydration sheath is equal to that of bulky water under pressure. The conclusions about the structure of the solvated ions derived from the pressure effect on the electrical conductivity have thus been conflicting. In order to solve this problem, information about the density of the water in the hydration sheath under pressure will be necessary, along with that about the structure of the bulky water under pressure.

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