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BULLETIN

OF THE

CHEMICAL SOCIETY OF JAPAN

VOL. 48, NO. 11, NOVEMBER 1975

THE CHEMICAL SOCIETY OF JAPAN

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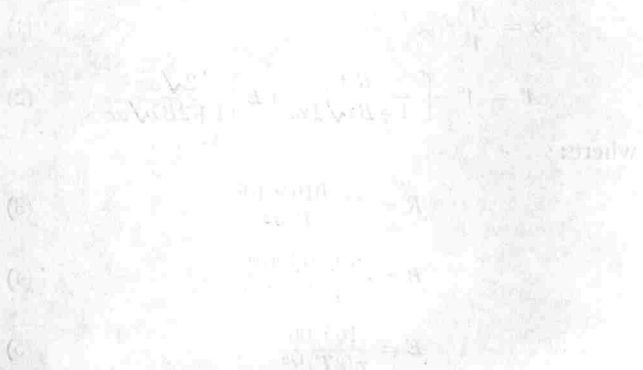
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Results and Discussion

The measured values of conductance (G) are listed in Table I together with the limiting conductance (G_∞) and the calculated values of the dissociation constant (K_d) and the theoretical values (K_t) of the dissociation constant.

Table I: Conductance (G) and limiting conductance (G∞) values for various concentrations of the ion pair. The table lists G values for concentrations from 0.07 to 10.0, and corresponding G∞ values.

From these data the dissociation constant (K_d) of the ion pair was calculated by the method of Hammett and Dyer.¹² The dissociation constant (K_d) of the ion pair was determined by plotting the experimental conductance (G) and the theoretical values (K_t) calculated from eq. (1) and eq. (2). Over the range 0.07 to 10.0 M, the plot of G vs. 1/G_∞ is linear.



The structure of the ion pair of metal sulfates is well established from electrochemical and spectroscopic measurements. It has been found that the structure of the ion pair is more similar to the structure of the ion pair of metal sulfates than that of the ion pair of metal chlorides. Their tendency to form a contact ion pair is in the order of their ionic radii which is in good agreement with the results of the infrared and Raman spectra from the visible absorption spectrum reported by Hamilton and Williams.¹³

The tendency of the ion pair to dissociate from the ion pair of metal sulfates is obtained from the dissociation of the ion pair. The dissociation constant (K_d) and the pressure effect on the dissociation constant of the ion pair¹⁴ are a useful indication of the structure of the ion pair. It is well known that the volume change accompanying the dissociation of the ion pair is negative. The dissociation of the ion pair is accompanied by a volume change which is negative. The dissociation of the ion pair is accompanied by a volume change which is negative. The dissociation of the ion pair is accompanied by a volume change which is negative.

Experimental

Uranyl ion-sensitized isomerization of the stilbenes was carried out in a quartz cell of 1 cm path length. The concentration of the stilbenes was 1.0 x 10⁻⁴ M. The concentration of the uranyl ion was 1.0 x 10⁻³ M. The concentration of the uranyl ion was 1.0 x 10⁻³ M. The concentration of the uranyl ion was 1.0 x 10⁻³ M.

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

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(Received March 22, 1975)

The electrical conductivity of $ZnSO_4$ in water was measured at high pressures up to 3000 kg/cm² 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 (\bar{a}) 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 \bar{a} 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, Larson⁹⁾ 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 Larsson⁷⁾ 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 dilatometry⁹⁾ and the pressure effect on the dissociation constants of ion pairs¹⁰⁻¹⁵⁾ 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 accompanying 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/cm² 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 (A) are listed in Table 1, together with the limiting equivalent con-

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

| Pressure kg/cm ² | Concentration at 1 atm, equiv./l (10^{-4}) | | | | | |
|--------------------------------|--|-------|-------|-------|-------|-------|
| | A° | A | | | | |
| | | 0.0 | 5.0 | 6.0 | 7.5 | 9.0 |
| 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 |

ductances (A°), which were determined by the extrapolation of the Kohlrausch plots,¹⁸⁾ A 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 (A) and the theoretical values (A^i), calculated from Eq. (2) and given by Davies, Otter, and Prue,¹⁹⁾ into Eq. (1):

$$\alpha = \frac{A}{A^i} \quad (1)$$

$$A^i = A^\circ - \left[\frac{RA^\circ}{1 + B\bar{a}\sqrt{2\alpha c}} + E \right] \frac{2\sqrt{\alpha c}}{1 + 2B\bar{a}\sqrt{\alpha c}} \quad (2)$$

where:

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

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

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

$$\bar{a} = \frac{2e^2}{\epsilon kT} \quad (6)$$

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:

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

where A is $7.2984 \times 10^6 / (\epsilon T)^{3/2}$. In applying the above equation to the conditions under a high pressure, the ϵ values calculated by the Owen-Brinkley equation²⁰) and the η data observed by Cappi²¹) were used.

The dissociation constant (K_m) is given by:

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

where m ²²) denotes the molality of ZnSO₄ and where the activity coefficient of ion pairs is assumed to be unity. The K_m values obtained are listed in Table 2. The pres-

TABLE 2. DISSOCIATION CONSTANTS (K_m) AND AVERAGE DISSOCIATION CONSTANTS (K_m)_{av} OF ZnSO₄ AT 25 °C AND AT VARIOUS PRESSURES.

| Pressure kg/cm ² | $(K_m)_{av}$ | 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 |

ent 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 Gury²⁴) and by Patterson and Freitag,²⁵) that of 4.4×10^{-3} equiv./l observed by Denney and Monk²⁶) from their electrical conductivity measurements, and that of 4.17×10^{-3} mol/l observed by Nair and Nancollas¹) 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 calorimetric determinations and from that of 5.4×10^{-3} equiv./l reported by Davies²⁸) 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.

The ΔV° value at 1 atm accompanying the dissociation of the ZnSO₄ ion pair was obtained graphically by the following equation:

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

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 ZnSO₄²⁹) and is close to those of -8.5 ml/mol¹⁰) and

-7.7 ml/mol¹⁴) for MgSO₄ and that of -7.4 ml/mol¹⁴) for MnSO₄, but it is larger than that of -10.2 ml/mol¹⁴) for CaSO₄. The absolute ΔV° values of the above divalent metal sulfate ion pairs are much smaller than those of -20.4 ± 0.5 ml/mol³⁰) and -28.9 ml/mol³¹) accompanying the dissociation of H₂O and NH₄OH 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 \bar{a} by:

$$K_m = \frac{1000}{4\pi N Q(b) \rho} \left(\frac{\epsilon k T}{4e^2} \right)^3 \quad (10)$$

where: $Q(b) = \int_2^b x^{-4} e^{-x} dx$ (11)

$$b = \frac{4e^2}{\bar{a} \epsilon k T} \quad (12)$$

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 Owen³²) was used. Table 3 shows the \bar{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 ZnSO₄ 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 (\bar{a}) OF ZnSO₄ ION PAIR AT 25 °C UNDER VARIOUS PRESSURES.

| Pressure, kg/cm ² | \bar{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 \bar{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 \rightleftharpoons 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 \bar{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 Evans³⁶⁾ 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, Horne³⁷⁾ 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/cm², 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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