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Ion Association of Some 2 : 2 Electrolytes in Water at 25 °C. III. A New Interpretation of Experimental Results and the Determination of Formation Constants of Inner-sphere Ion-pairs

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The results of previous studies on ion association were re-examined. The formation constants of inner-sphere ion-pairs were obtained for several bivalent-metal sulfates by estimating the formation constants of outer-sphere ion-pairs with the help of the ion-association theory. The interactions between metal and sulfate ions were discussed by comparing these results.

Ion association usually refers to the formation of pairs of ions existing in the close vicinity of each other. In this concept, ion-pairs may be considered to be a chemical species, which is in equilibrium with the free ions in solution:

$$\mathrm{M}^{n+} + \mathrm{A}^{n-} \rightleftharpoons \mathrm{M}^{n+}\mathrm{A}^{n-}. \qquad (1)$$

Sometimes they are classified into more than one chemical species, *e.g.* outer-sphere ion-pairs and inner-sphere ion-pairs, according to whether or not the ions of a pair are separated by at least one solvent molecule:

$$\mathrm{M}^{n+} + \mathrm{A}^{n-} \rightleftharpoons \mathrm{M}^{n+}\mathrm{A}^{n-}(\mathrm{os}) \rightleftharpoons \mathrm{M}^{n+}\mathrm{A}^{n-}(\mathrm{is}). \qquad (2)$$

Another concept of ion-pairs has been shown in a previous paper.[1] There we have extended the Debye-Hückel theory[2] of strong electrolyte solutions, making approximation to the next higher order beyond that considered in the Debye-Hückel treatment. An expression was obtained for the chemical potential of an arbitrary central ion. This was compared with the corresponding Debye-Hückel expression. An extra term appearing in our equation arises from the excess interaction of the central ion with a counter-ion, since the probability of finding the latter in the vicinity of the central ion is greater than that assumed in the Debye-Hückel approximation. Although the counter-ion has probabilities of being found at various distances from the central ion and therefore of making different extents of contribution to the chemical potential of the latter, the total effect of the excess interactions can be regarded as equivalent to the effect of the conventional ion-pair formation. Accordingly, our concept of ion association complements the Debye-Hückel theory, which is not a good approximation for solutions of multivalent electrolytes and of solvents having a low dielectric constant.

The ion association expressed by Eq. 1 or 2 also complements the Debye-Hückel theory, since the free ions are regarded in these equations as hypothetical ions behaving in accordance with the Debye-Hückel theory. Therefore the above two concepts of ion association may be related to each other. From this point of view, we have derived the following expression for the ion-association constant at infinite dilution of a symmetrical electrolyte:

$$K = \frac{8\pi N a^3}{1000} \sum_{n=1}^{\infty} \frac{b^{2n+2}}{(2n+2)\,!\,(2n-1)}, \qquad (3)$$ [†]

where N represents the Avogadro number, a the closest distance of approach between ions, and b the Bjerrum parameter given by $b = z^2e^2/\varepsilon kTa$.

It should be noted that Eq. 3 resulted from the consideration of the chemical potentials of the free and paired species, not from the counting of their numbers; however, the limiting expression ($b \rightarrow \infty$) of Eq. 3:

$$K(b \rightarrow \infty) = \frac{4\pi N a^3}{1000} \cdot \frac{\exp{(b)}}{b},$$

is the same as the corresponding limiting expression derived from the Bjerrum equation for ion-association constant,[1] which was obtained by counting the number of ions within the critical distance of a central ion.

Equation 3 has been utilized in the vapor-pressure osmometric, spectrophotometric, and conductivity investigations of several electrolytes for determining the *best* values of K and a.[3,4] Thus, when an appropriate value was chosen for a, the ion-association constant derived from the experimental results agreed with that predicted by the theoretical expression. Such a value of a was larger than the sum of the crystallographic radii of cation and anion ($r_\mathrm{M}+r_\mathrm{A}$) of each electrolyte, but smaller than the sum plus the diameter of a water molecule ($r_\mathrm{M}+r_\mathrm{A}+2r_{\mathrm{H_2O}}$, $r_{\mathrm{H_2O}}=1.4$ Å). From the viewpoint that the solvent is a continuous medium, the result can reasonably be taken as implying that the ions are hydrated to some extent. However, if a structual or microscopic view is taken of ions dissolved in water, the result can be interpreted as indicating that hydrated cations and anions may sometimes come so near to each other as to displace water molecules in the coordination spheres of ions to form inner-sphere ion-pairs. The latter view is preferred, since the water molecules in the first sphere of a bivalent-metal ion are strongly oriented or coordinated to the metal ion and consequently may have a different dielectric constant from that of the water in bulk. Then the solvent may not be regarded as a continuous medium of a certain dielectric constant, nor the ions as rigid spheres. Moreover, the interaction between ions may not be solely electrostatic in the first sphere of the ion. Thus, the conditions assumed in

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[†] There are some misprints in our 1975 paper.[1] Equation 31 of the 1975 paper should be the same as Eq. 3 of the present paper ("when $b \rightarrow \infty$" should be deleted). For other misprints, refer to "Corrections" of the journal [*Bull. Chem. Soc. Jpn.*, **48**, 3002 (1975)].

deriving the Debye-Hückel theory[2] and our ion-association theory[1] may not be satisfied. Therefore, the value of a obtained in previous investigations[3,4] may not have a definite physical meaning, but may be only a measure of the closest distance of approach between ions. In this paper, another interpretation of the experimental results will be made by using the ion-association theory in a different way.

Basic Viewpoint

In this paper, we shall classify ion-pairs into inner-sphere ion-pairs and outer-sphere ion-pairs, and define an inner-sphere ion-pair as a pair of positive and negative ions with an inter-ionic distance less than the distance, $r_M+r_A+2r_{H_2O}$, which will be denoted by a_{os} in the following discussion. Then, for ions not forming an inner-sphere ion-pair, the so-called closest distance of approach can be taken to be equal to a_{os}. With this greater distance than usually assumed, the solvent may be reasonably approximated by a medium of a certain dielectric constant, and non-electrostatic interactions of the hydrated ions with further water molecules may be justifiably disregarded. Thus the theory is expected to give a satisfactory prediction for the formation of such outer-sphere ion-pairs.

The inner-sphere ion-pair can be regarded as a kind of neutral molecule, the presence of which has only a negligible effect on the theoretical treatment of very dilute solutions. Therefore, the theoretical ion-association constant can be derived in essentially the same way as that for Eq. 3[1] by employing the parameter a_{os} instead of a. The *theoretical* ion-association constant obtained here refers to the formation of all the ion-pair species[††] except the inner-sphere ion-pair, namely to the formation of outer-sphere ion-pairs, for which the constant K_{os} becomes:

$$K_{os}=\frac{8\pi N a_{os}{}^3}{1000}\sum_{n=1}^{\infty}\frac{b^{2n+2}}{(2n+2)!\,(2n-1)} \tag{4}$$

On the other hand, analysis of the *experimental* data by taking a_{os} as "the closest distance of approach of ions" gives us the overall constants for the ion-pair formation, K_Σ. When the value of K_Σ is larger than K_{os}, it is reasonable to assume the formation of inner-sphere ion-pairs in solutions. With such an assumption, we can estimate the formation constant of the inner-sphere ion-pair, K_{is}, from the difference of K_Σ and K_{os}.

Recently, Fuoss has proposed a new method of analysis of conductivity data for a purpose similar to ours but from a viewpoint different from ours.[5] He introduced the critical distance R as the closest distance of approach of unpaired ions (free ions), which is assumed to be equal to the sum of the radii of the Gurney cospheres of cation and anion. Ion-pairs are classified into solvent-separated pairs (diffusion pairs) and contact pairs (nearest-neighbor pairs). The solvent-separated pair is defined as a pair of a cation and an anion separated by at least one solvent molecule. His concept for the contact pair is similar to ours for the "inner-sphere ion-pair" as defined above, whereas that for the solvent-separated pair is very different from ours for the "outer-sphere ion-pair." That is, the solvent-separated pair is restricted to the pair of ions existing within the critical distance R of each other, and its formation constant is assumed to be given by the Fuoss 1958 equation[6] for the ion-pair formation, $K_R=4\pi NR^3\exp(b)/3000$.[5] His concept is specific in the respect that the solvent-separated pairs contribute to the transport current to the same extent as do the unpaired ions.

Fuoss's new method is of interest from the viewpoint that it precludes various problems at the vicinity of ions. However, some questions may be raised about his method: how his concept of ion-association can be thermodynamically connected with the Debye-Hückel theory; how the discontinuity at the distance of R can be justified; and what is the reasoning for the solvent-separated pair being equivalent to unpaired ions in the ionic conductance. On the other hand, our method of analysis of experimental data, which is simpler than Fuoss's method, has no adjustable parameter except for the distance a_{os} with a definite physical meaning, and is connected complementarily with the Debye-Hückel theory by Eq. 3.

Analysis of Experimental Data

The osmotic coefficient was measured on $MgSO_4$, $CaSO_4$, and $MnSO_4$ solutions with a vapor-pressure osmometer. The absorption at 250 nm was measured for copper sulfate solutions and mixed electrolyte solutions of copper sulfate and another bivalent-metal sulfate such as $MgSO_4$, $CaSO_4$, $MnSO_4$, and $ZnSO_4$. The experimental procedures and results have been described in previous papers.[3,4] In the present study, use was made of these experimental data as well as conductivity data given in the literature,[7–14] which are available for $CoSO_4$, $NiSO_4$, and $CdSO_4$ in addition to those mentioned above.

The analysis was made from the viewpoint described above: that is, with a a_{os} value characteristic of each electrolyte, the value of K_Σ was obtained from experimental data. In estimating a_{os}, r_M was assumed to be equal to Pauling's radius[15] and r_A to be 2.8_8 Å.[3] The former assumption seems to be reasonable, because the ionic radii of bivalent transition-metal ions from manganese(II) to zinc(II) obtained from X-ray scattering measurements in aqueous solutions[16] are in agreement with Pauling's radii within 0.1 Å.

The procedure used for deriving K_Σ values from experimental data of each kind is essentially the same as described in the previous papers,[3,4] except for the following modifications: (1) the parameter a_{os} was substituted for a; (2) the conventional expression for the concentration of the ion-pair, [MA], was (formally) replaced by the sum of the concentrations of outer-sphere ion-pairs and inner-sphere ion-pairs; (3) in the analysis of spectrophotometric data, in particular, the

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[††] A pair of cation and anion may not necessarily be divided strictly into two categories: a pair of the pure free ions and the pure ion-pair. There may be pairs which do not fully exhibit the characteristics of ion-pairs. These partial ion-pairs may be counted as fractions of an ion-pair.

conventional molar extinction coefficient, ε_{MA}, was (formally) replaced by $(\varepsilon_{MA(os)}K_{os}+\varepsilon_{MA(is)}K_{is})/K_{\Sigma}$, where $\varepsilon_{MA(os)}$ and $\varepsilon_{MA(is)}$ are the extinction coefficients of the respective ion-pair species. The last two formal substitutions have arisen from the use of Eq. 2 instead of Eq. 1, and do not affect the K_{Σ} value to be obtained.

Results and Discussion

The experimental K_{Σ} values are given in Table 1, together with the values of K_{os} calculated by the use of Eq. 4. In each case, the value of K_{Σ} is larger than that of K_{os}, showing that the inner-sphere ion-pairs exist in the solution. Table 1 also lists the values of $K_{is}(=K_{\Sigma}-K_{os})$ and K_{is}/K_{Σ} for each electrolyte. We also calculated the values for K_{is}/K_{Σ} based on a similar (but not exactly the same) definition, using the results of ultrasonic absorption studies;[17-19] the values are 0.10 for $MgSO_4$,[17] 0.48 for $MnSO_4$,[18] and 0.50 for $CuSO_4$,[19] which are close to those obtained in the present study. This implies that the above assumptions are reasonable.

The K_{is} values for the first-row transition-metal ions (Table 1) appears to follow the order of the Irving-Williams series.[20] In order to discuss the formation of inner-sphere ion-pairs in more detail, we re-analyzed the conductivity data at various temperatures between 0 °C and 45 °C presented by Katayama.[8,11] The values of K_{Σ} and K_{is} at each temperature were obtained in the same way as described above and their logarithmic values were plotted against T^{-1}. However, the plots showed curvatures like those found with the transition-metal dicarboxylates.[21,22] Therefore, according to the previously outlined procedure,[21,22] we evaluated the standard enthalpy and entropy of the ion-pair formation. The results are shown in Table 2. An approximately

TABLE 1. ION-PAIR FORMATION CONSTANTS, K_{Σ}, K_{os}, AND K_{is},[a)] FOR BIVALENT-METAL SULFATES IN AQUEOUS SOLUTIONS OBTAINED FROM VARIOUS METHODS AT 25 °C

Salt	From vapor-pressure osmometry[3)]					From spectrophotometry[4)]			From conductivity (re-calculated)			
	a_{os}/Å	K_{os}	K_{Σ}	K_{is}	K_{is}/K_{Σ}	K_{Σ}	K_{is}	K_{is}/K_{Σ}	K_{Σ}	K_{is}	K_{is}/K_{Σ}	Ref.
$MgSO_4$	6.3	86.7	127±6	40±6	0.31±0.04	107±7	20±7	0.19±0.06	124±3	37±3	0.30±0.02	7
									121±4	34±4	0.28±0.03	8
									118±2[b)]	31±2	0.26±0.02	9
$CaSO_4$	6.7	79.0	155±24	76±24	0.49±0.10	131±14	52±14	0.40±0.08	131±12	52±12	0.40±0.06	10
									170±2	91±2	0.54±0.01	11
$MnSO_4$	6.5	82.7	185±4	102±4	0.55±0.01	130±11	47±11	0.36±0.06	152±6	69±6	0.45±0.03	12
									165±2	82±2	0.50±0.01	13
$CoSO_4$	6.4	84.7							163±4	78±4	0.48±0.02	11
$NiSO_4$	6.3	86.7							169±4	82±4	0.49±0.02	8
$CuSO_4$	6.4[c)]	84.7				193±1	108±1	0.56±0.01	190±2	105±2	0.55±0.01	14
$ZnSO_4$	6.4	84.7				132±13	47±13	0.36±0.07	162±1	77±1	0.48±0.01	14
									175±3	91±3	0.52±0.01	11
$CdSO_4$	6.6	80.8							202±4	121±4	0.60±0.01	11

a) The values of the formation constants are expressed in $dm^3\ mol^{-1}$ except for the values obtained from vapor-pressure osmometry; in the latter case, the K_{Σ} and K_{is} values are expressed in $kg\ mol^{-1}$. b) The K_{Σ} value has been re-calculated on the basis of a part of the reported conductivity data (at concentrations below $4.0\times10^{-3}\ mol\ dm^{-3}$). c) Since the hexa-aquacopper(II) ion is tetragonally distorted due to the Jahn-Teller effect, its average radius was used in the estimation of the a_{os} value for $CuSO_4$.

TABLE 2. STANDARD ENTHALPY AND ENTROPY OF ION-PAIR FORMATION OF BIVALENT-METAL SULFATES IN AQUEOUS SOLUTIONS AT 25 °C OBTAINED BY THE RE-ANALYSIS OF THE CONDUCTIVITY DATA[8,11)]

Salt	For overall ion-pair formation		For outer-sphere ion-pair formation		For inner-sphere ion-pair formation	
	$\Delta H^{\circ}_{\Sigma}$[a)] / kJ mol^{-1}	$\Delta S^{\circ}_{\Sigma}$[a)] / J K^{-1} mol^{-1}	ΔH°_{os} / kJ mol^{-1}	ΔS°_{os} / J K^{-1} mol^{-1}	ΔH°_{is} / kJ mol^{-1}	ΔS°_{is} / J K^{-1} mol^{-1}
$MgSO_4$	6.78±0.08	62.7±0.3	4.01	50.5	12.96±0.26	73.1±0.9
$CaSO_4$	5.92±0.09	62.6±0.3	3.94	49.5	7.60±0.16	63.1±0.6
$CoSO_4$	5.33±0.11	60.2±0.4	3.99	50.3	6.74±0.22	58.9±0.8
$NiSO_4$	5.24±0.04	60.2±0.2	4.01	50.5	6.49±0.07	58.4±0.3
$ZnSO_4$	6.64±0.11	65.1±0.4	3.99	50.3	9.13±0.19	67.8±0.7
$CdSO_4$	8.07±0.06	71.2±0.2	3.95	49.8	10.75±0.10	75.9±0.4

a) Ten experimental data points between 0 °C and 45 °C were used for the evaluation of ΔH° and ΔS° values. The variation of log K with temperature was expressed by the equation $\log K=A+BT+CT^2$ (K represents K_{Σ} or K_{is}) and the parameters A, B, and C were determined by the least-squares method. The values of the enthalpy and entropy changes were calculated from the equations $\Delta H^{\circ}=2.303\ RT^2\ (B+2CT)$ and $\Delta S^{\circ}=(\Delta H^{\circ}-\Delta G^{\circ})/T$. Uncertainties were estimated by using different combinations of experimental results at nine temperatures for the calculation of A, B, and C.

linear relationship exists between $\Delta H^\circ_{\mathrm{is}}$ and $\Delta S^\circ_{\mathrm{is}}$ and between ΔH°_{Σ} and ΔS°_{Σ} except for the case of magnesium sulfate. In each electrolyte, the values of $\Delta H^\circ_{\mathrm{is}}$ and $\Delta S^\circ_{\mathrm{is}}$, are positive and larger than those of $\Delta H^\circ_{\mathrm{os}}$ and $\Delta S^\circ_{\mathrm{os}}$, respectively; the difference is relatively small in the ΔS° values, however. The entropy changes favor the formation of both inner-sphere and outer-sphere ion-pairs, while the enthalpy changes oppose the reactions. Although the $T\Delta S^\circ$ terms predominate over the ΔH° terms, the differences between the ΔH° terms are significant for relative magnitudes of the formation constants given in Table 1.

The largest $\Delta H^\circ_{\mathrm{is}}$ value is shown by $MgSO_4$, reflecting the facts that the magnesium ion has the smallest ionic radius and accordingly the strongest hydration. The $\Delta H^\circ_{\mathrm{is}}$ value is considerably smaller for $NiSO_4$, in spite of the fact that the nickel ion has a radius close to that of the magnesium ion. This suggests that some interaction may exist between nickel and sulfate ions in addition to the electrostatic one. A similar argument seems to hold for the other transition-metal sulfates.

The enthalpy change is less unfavorable for cobalt and nickel sulfates than for zinc sulfate. On the contrary, the entropy change is more favorable for zinc sulfate. Such tendencies have also been observed with the malonates, succinates, and phthalates of these metals.[22,23] As regards the coordination of the acetate ion to the zinc ion, the comparatively large and positive enthalpy and entropy changes for the formation of ZnL_2 from ZnL^+ (where L=acetate ion) are considered to be consistent with the tendency of Zn(II) to form tetrahedral complexes.[23] If we take into account the above information and the ability of the dicarboxylate and sulfate ions to act as bidentate ligands, the formation of inner-sphere ion-pairs with the zinc ion would cause at least in part the change of the coordination number of the zinc ion from six to four. This will lead to increased positive ΔH° and ΔS° values, because a greater number of coordinated water molecules are released.

The speculation described above might seem to be opposed by the X-ray diffraction study[16] on aqueous zinc sulfate and zinc perchlorate solutions, which shows that the zinc ion is surrounded by six oxygen atoms in the solution. However, this does not seem to exclude the possibility that part of the zinc ions in inner-sphere ion-pairs are surrounded by four oxygen atoms; a majority of the zinc ions in the solutions exist as free ions and outer-sphere ion-pairs, and thus the decrease in the coordination number occurring in part on the formation of inner-sphere ion-pairs may have escaped detection.

The relatively large values of K_{is}, $\Delta H^\circ_{\mathrm{is}}$, and $\Delta S^\circ_{\mathrm{is}}$ for $CdSO_4$ appear to show that more than one water molecule are released by the entrance of one sulfate ion into the inner-sphere of a cadmium ion; this may be supported by the fact that a cadmium ion in the $CdSO_4 \cdot 8/3\,H_2O$ is surrounded by sulfate ions (4 O of $2SO_4{}^{2-}$) and water molecules ($2H_2O$) in an entirely different way from that observed in the other metal sulfates.[24]

Conclusion

The theoretical formation constant for the outer-sphere ion-pairs was estimated by assuming a parameter a_{os} for the closest distance of approach for outer-sphere ion-pairs. Although some arbitrariness may be involved in the estimation of the a_{os} values, the present treatment has the merit of removing the theoretical difficulties encountered at the close vicinity of the ions in the application of the Debye-Hückel and ion-association theories.[1,2] Then from the re-analysis of various experimental data, the thermodynamic parameters were obtained for the formation of inner-sphere ion-pairs. The trends shown by the obtained parameters are consistent with other experimental findings and give useful information regarding the formation of inner-sphere ion-pairs.

References

1) H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 1770, 3002 (1975).

2) P. Debye and E. Hückel, *Phys. Z.*, **24**, 185 (1923).

3) H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 2708 (1975).

4) H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 2719 (1975).

5) R. M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 16 (1978); *J. Solution Chem.*, **7**, 771 (1978); *J. Phys. Chem.*, **82**, 2427 (1978).

6) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

7) H. S. Dunsmore and J. C. James, *J. Chem. Soc.*, **1951**, 2925.

8) S. Katayama, *Bull. Chem. Soc. Jpn.*, **46**, 106 (1973).

9) A. D. Pethybridge and S. S. Taba, *Faraday Discuss. Chem. Soc.*, **64**, 274 (1977).

10) E. Inada, K. Shimizu, and J. Osugi, *Nippon Kagaku Zasshi*, **92**, 1096 (1971); *Rev. Phys. Chem. Jpn.*, **42**, 1 (1972).

11) S. Katayama, *J. Solution Chem.*, **5**, 241 (1976).

12) C. J. Hallada and G. Atkinson, *J. Am. Chem. Soc.*, **83**, 3759 (1961).

13) S. Petrucci, P. Hemmes, and M. Battistini, *J. Am. Chem. Soc.*, **89**, 5552 (1967).

14) B. B. Owen and R. W. Gurry, *J. Am. Chem. Soc.*, **60**, 3074 (1938).

15) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell Univ. Press (1960), p. 514.

16) H. Ohtaki, T. Yamaguchi, and M. Maeda, *Bull. Chem. Soc. Jpn.*, **49**, 701 (1976).

17) G. Atkinson and S. Petrucci, *J. Phys. Chem.*, **70**, 3122 (1966).

18) G. Atkinson and S. K. Kor, *J. Phys. Chem.*, **71**, 673 (1967).

19) P. Hemmes and S. Petrucci, *J. Phys. Chem.*, **74**, 467 (1970).

20) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, **1953**, 3192.

21) A. McAuley and G. H. Nancollas, *J. Chem. Soc.*, **1961**, 2215, 4458.

22) V. S. K. Nair, *J. Chem. Soc.*, **1965**, 1450.

23) G. H. Nancollas, "Interactions in Electrolyte Solutions," Elsevier Publishing Company (1966), p. 185; *Coodr. Chem. Rev.*, **5**, 379 (1970).

24) H. Lipson, *Proc. R. Soc., London, Ser. A*, **156**, 462 (1936).