[CONTRIBUTION FROM THE ARTHUR D. LITTLE, INC.]

Entropies of Association of Ions in Aqueous Solution[1]

BY J. H. B. GEORGE

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Experimental evidence shows that entropies of association (ΔS_a^0) of certain series of ion pairs having one ion in common are related to the entropies of hydration (ΔS_h^0) of the variable ion by the equation $\Delta S_a^0 = -\Delta S_h^0 + \text{constant}$. The implications of this empirical equation are discussed and it is concluded that in systems to which it is applicable, water of hydration is lost in the association process. Coulombic treatments of ion association in solution predict that ΔS_a^0 for a series of ion pairs in the same solvent should be determined by charge type alone. It is shown that the experimental data for the entropies of association of sulfates with bivalent cations are consistent with such treatments, implying that in these systems no water of hydration is lost in the association process. Two classes of behavior are thus indicated by the experimental data; in some systems there is conformance to the empirical equation, loss of water of hydration and possible complex formation; in others ΔS_a^0 is independent of ΔS_h^0 and ion association leads to the formation of true ion pairs.

Experimental values for the entropies of association of ions in aqueous solution are rather sparse and the significance of the existing data is sometimes obscured by (i) the lack of agreement between values obtained by different methods and (ii) the somewhat arbitrary choice of standards of ideal behavior for completely dissociated electrolytes in situations where there can be no independent experimental test of the assumptions. Certain interesting regularities, however, have emerged from a comparison of entropy changes in series of related systems. The purpose of this paper is to call attention to these regularities and to discuss their possible implications.

It was pointed out by Evans and Uri[2] that the entropies of association ΔS_a^0, of the ferric ion Fe^{+3} with various monovalent anions, are related to the entropies of hydration ΔS_h^0 of the anion by the equation

$$\Delta S_a^0 = -\Delta S_h^0 + \text{constant} \qquad (1)$$

The entropies of hydration were derived by subtracting the calculated Sackur–Tetrode standard entropy of the anion in the gas phase from the Latimer standard entropy of the ion in aqueous solution.[3] In cases where the anion was not monatomic, a correction was made for the loss of rotational entropy of the ion upon association.

This relationship has now been found to apply to a number of other series of ion pairs and a collection of selected data for such systems is presented in Table I. In Fig. 1 the entropies of association are plotted against the entropies of hydration of the variable ion to which has been added the most appropriate value of the constant for the particular series. The entropy changes were calculated from measurements made by a variety of techniques including conductimetric, potentiometric, solubility and spectrophotometric methods. There appears to be good evidence of the validity of equation 1 in these particular cases.

Some idea of the significance of equation 1 can be gained by considering a cycle in which the association process is broken down into a number of steps. It is assumed that because of its smaller electrical charge the associated species, complex or "ion pair," has less "water of hydration" than the sum of the waters of hydration of the free ions. There is, of course, no satisfactory definition of water of hydration, and it is here assumed arbitrarily to mean the oriented water molecules in immediate contact with the ions. Since ion-

TABLE I

ENTROPIES OF ASSOCIATION AND OF HYDRATION OF SYSTEMS CONFORMING TO EQUATION 1

System	ΔS_a^0 (cal./deg. mole)	$-\Delta S_h^0$ (cal./deg. mole)	Ref.
$Fe^{+3}OH^-$	50[a]	44	2
$Fe^{+3}F^-$	49	39.5	2
$Fe^{+3}Cl^-$	35	22.9	2
$Fe^{+3}Br^-$	23	19.4	2
$Co(NH_3)_6^{+3}Cl^-$	26	22.9	4
$Co(NH_3)_6^{+3}Br^-$	20	19.4	4
$Co(NH_3)_6^{+3}I^-$	16	14.4	4
$Cd^{+2}Cl^-$	13.2	22.9	5a
$Cd^{+2}Br^-$	7.0	19.4	5b
$Cd^{+2}I^-$	2.8	14.4	5c
$Pb^{+2}Cl^-$	22	22.9	6
$Pb^{+2}Br^-$	16.4	19.4	6
$Sn^{+2}OH^-$	23[a]	44	7
$Sn^{+2}Cl^-$	14	22.9	7
$Sn^{+2}Br^-$	8	19.4	7
$Ca^{+2}(HCO_2^-)$	10	48.1	8
$Sr^{+2}(HCO_2^-)$	8.3	47	8
$Ba^{+2}(HCO_2^-)$	−0.3	40	8
$Ca^{+2}(CH_3CO_2^-)$	8.7	48.1	8
$Sr^{+2}(CH_3CO_2^-)$	7.8	47	8
$Ba^{+2}(CH_3CO_2^-)$	−2.5	40	8
Tl^+OH^-	5.1[a]	44	9
Tl^+Cl^-	−1.7	22.9	9
Tl^+Br^-	−4.2	19.4	10
Tl^+Cl^-	−1.7	13.0	9
Ag^+Cl^-	6	22.4	11

[a] To compare these values for hydroxide with those involving monatomic ions, 8 cal./deg. mole is added to ΔS_a^0 to allow for the loss of rotational entropy on association.

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(1) Presented in part at the 135th ACS National Meeting, Boston, Mass., April, 1959.

(2) M. G. Evans and N. Uri, S.E.B. Symposium No. 5, Cambridge (1951).

(3) D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).

(4) M. G. Evans and G. H. Nancollas, *ibid.*, **49**, 363 (1953).

(5) J. H. B. George, D. Phil. Thesis, Oxford, 1952, calculated from data of (a) H. S. Harned and M. E. Fitzgerald, THIS JOURNAL, **58**, 2624 (1936); (b) R. G. Bates, *ibid.*, **61**, 308 (1939); (c) *ibid.*, **63**, 399 (1941).

(6) G. H. Nancollas, *J. Chem. Soc.*, 1458 (1955).

(7) C. E. Vanderzee, THIS JOURNAL, **74**, 3552, 4806 (1952).

(8) G. H. Nancollas, *J. Chem. Soc.*, 744 (1956).

(9) R. P. Bell and J. H. B. George, *Trans. Faraday Soc.*, **49**, 619 (1953).

(10) V. S. K. Nair and G. H. Nancollas, *J. Chem. Soc.*, 318 (1957).

(11) J. H. Jonte and D. S. Martin, THIS JOURNAL, **74**, 2053 (1952).

solvent interaction falls off rapidly with increasing distance from the ion, this definition has reasonable physical significance.

$$\begin{tikzcd} M^+(g) & + & A^-(g) \arrow[r, "\Delta S_g^0"] & M^+A^-(g) \arrow[d, "\Delta S_{hMA}^0"] \\ M^+(s) \arrow[u, phantom] & + & A^-(s) \arrow[r, "\Delta S_a^0"] & M^+A^-(s) + \kappa H_2O \\ \arrow[from=1-1, to=2-1, "\Delta S_{hM^+}^0"] \arrow[from=1-3, to=2-3, "\Delta S_{hA^-}^0"] \end{tikzcd}$$

In this cycle the ΔS_h^0 terms refer to the standard entropies of the ions and ΔS_g^0 is the entropy change for the association in the gas phase. It can be seen that

$$\Delta S_a^0 = \Delta S_g^0 + \Delta S_{hMA}^0 + \kappa S_{H_2O}^0 - \Delta S_{hM^+}^0 - \Delta S_{hA^-}^0 \quad (2)$$

This takes the form of equation 1 if the sum of ΔS_g^0, $\kappa S_{H_2O}^0$ and ΔS_{hMA}^0 is constant in a series in which there is a common M^+ and variable A^- or *vice versa*. In such a series the term ΔS_g^0 can be calculated from the appropriate partition functions and will not vary by more than one or two entropy units from system to system. Conformance to the equation therefore (i) indicates that the sum of ΔS_{hMA}^0 and $\kappa S_{H_2O}^0$ does not vary appreciably in the series and (ii) supports the assumption that there is a change in the degree of hydration as the ions come together to form the associated species. For otherwise, ΔS_{hMA}^0 would to a first approximation be equal to the sum of $\Delta S_{hM^+}^0$ and $\Delta S_{hA^-}^0$ and vary markedly over the series. The equation may therefore be used to distinguish systems in which water of hydration is lost in the association process. In some of these systems, such as the ferric and cadmium halides, the resulting contact of the ions results in complex formation which can be demonstrated spectroscopically.

The interaction of ions in solution to form associated species can, of course, be treated as a problem in electrostatics. The ions are considered as rigid spheres contained in a fluid medium of uniform dielectric constant. The original theories were those of Bjerrum[12] and Fuoss[13] and more recently treatments have been presented by Denison and Ramsey,[14] Gilkerson[15] and Fuoss.[16] In all of these treatments an expression for the association constant, K_a, is obtained in terms of the charges on the ions, the dielectric constant of the solvent, the temperature and a length parameter a, usually interpreted as the contact distance in the ion pair. Values of this parameter a can be calculated from experimentally determined association constants and comparisons made with the sum of the crystallographic radii of the component ions. Discrepancies are variously attributed to effects such as solvation of the ions if a is large and complex formation or dielectric saturation if a is small.

The point to be made here is that in all these treatments in which specific solvent–ion interactions are neglected, the entropy of association, related to the association constant by the equation

$$\Delta S_a^0 = \frac{d}{dT}(RT \ln K_a) \quad (3)$$

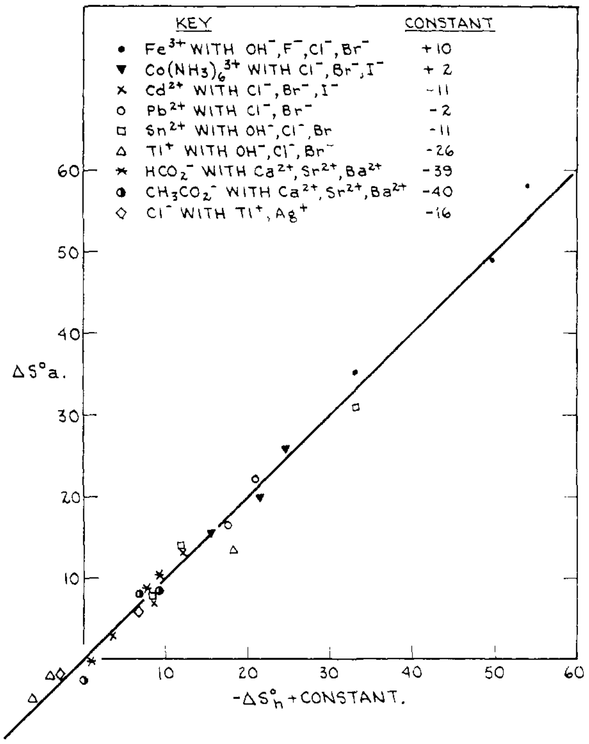

Fig. 1.—The relationship between entropy of association and entropy of hydration for systems following equation 1.

is a function of just the same variables. The validity of the coulombic treatments thus can be tested indirectly by comparing the experimental entropies of association of ion pairs of the same charge type having very similar association constants in the same solvent and, therefore, similar values of the ion size parameter a. Since all other quantities have the same values, such systems would be expected to have almost equal values of ΔS_a^0. The sulfates of bivalent cations in water form such a group and experimental values for ΔS_a^0 have been quoted by Singh[17] and by Nancollas.[18] These data are presented in Table II where it can be seen that although the entropies of hydration of the variable cation range from −39 for Pb^{+2} to −71 for Mg^{+2}, the entropies of association are practically constant. The implication is that in these ion pairs, water of hydration is not lost and a treatment based on coulombic forces accounts satisfactorily for the entropy change.

Table II

Entropies of Association and of Hydration of Some Bivalent Sulfates

System	ΔS_a^0 (cal./deg. mole)	ΔS_h^0 (cal./deg. mole)	Ref.
$Mg^{+2}SO_4^{-2}$	26.1	71	18
$Ca^{+2}SO_4^{-2}$	26.3	48	17
$Sr^{+2}SO_4^{-2}$	28.8	47	17
$Ba^{+2}SO_4^{-2}$	25.1	40	17
$Pb^{+2}SO_4^{-2}$	28.0	39	17

The experimental entropy data discussed here therefore indicate two distinct types of behavior. Those listed in Table I apparently lose water of

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[12] N. Bjerrum, *Kgl. Danske Videnskab. Selskab*, **7**, No. 9 (1926).

[13] R. M. Fuoss, *Trans. Faraday Soc.*, **30**, 967 (1934).

[14] J. T. Denison and J. B. Ramsey, This Journal, **77**, 2615 (1955).

[15] W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).

[16] R. M. Fuoss, This Journal, **80**, 5059 (1958).

[17] D. Singh, *J. Sci. Research Benares Hindu Univ.*, **6**, 131 (1955).

[18] G. H. Nancollas, *Disc. Faraday Soc.*, **24**, 108 (1957).

hydration in the association process while the sulfates listed in Table II do not. The first group should be particularly susceptible to the formation of covalent complexes in solution.

Not all the available data in aqueous solution can be assigned satisfactorily to one or other of these types of behavior. Particularly surprising are the hydroxides of the alkaline earth metals[19] which do not conform to equation 1 in spite of other evidence[20] that they exhibit the same type of "localized hydrolysis" as other salts of weak acids. The assumptions made in the consideration of the hydration cycle are no doubt an over-simplification in such systems.

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(19) F. G. R. Gimblett and C. B. Monk, *Trans. Faraday Soc.*, **50**, 965 (1954).

(20) R. M. Diamond, THIS JOURNAL, **80**, 4808 (1958).

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[CONTRIBUTION NO. 891 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Conductance Measurements of the Halides, Nitrates and Nitrites of the Alkali Metals in Anhydrous Ethanolamine

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Conductances of a number of salts of the alkali metals have been measured in anhydrous ethanolamine at 25°. Linear plots of Λ *vs.* $c^{1/2}$, approach the Onsager tangent from below (catabatic phoreograms in Fuoss Nomenclature[2]) are obtained up to about $c = 0.005$ M. Owing to the magnitude of the solvent correction, the data do not allow extrapolation by the Fuoss x–y plot. The data, however, give good extrapolations by the Fuoss–Shedlovsky procedure and Λ_0 and $1/K_D$ values determined by this method are reported. The results reported here also do not confirm the behavior obtained by Briscoe and Dirske for the salts in this solvent. A reason for this discrepancy is suggested. Also, these results are not in agreement with results recently published by Muniyapan and Anjaneyalu on the conductances of solutions of alkali metal and silver nitrites. The limiting conductance data afford numerous confirmations of the Kohlrausch Law of independent ion migration in anhydrous ethanolamine solutions. The usual trend is observed in the limiting equivalent conductances of the salts of a given anion type, *i.e.*, Li < Na < K. However, for a given cation, the conductance increases in the order I < Br < Cl. This is exactly opposite to the effect observed in anhydrous N-methylformamide and in the substituted acetamides.

Introduction

Briscoe and Dirkse[3] have reported conductances at various concentrations of a number of quaternary picrates and halides. These authors conclude from the slope of the Λ *vs.* $c^{1/2}$ plots (phoreograms), typical of those obtained in solvents of low dielectric constant, that all salts are weakly ionized in ethanolamine, or in terms of Fuoss nomenclature[2] these salts behave as weak ionogens. Extrapolation of the very catabatic phoreograms by the method of Fuoss led in some cases to limiting equivalent conductances in excess of 2000. No explanation was given for this apparently remarkable behavior which would certainly seem to involve an entirely new conductance mechanism, since the viscosity of ethanolamine is about eight times that of water. The weakly ionized character of the salts was attributed to the high viscosity of the solvent. The possibility that the viscosity of the solvent could affect the dissociation of a species in solution seemed unlikely to the present authors. Therefore, it was of interest to re-investigate the properties of ethanolamine as a conducting solvent, using initially the simple alkali metal salts instead of the high molecular weight quaternary ammonium salts.

Experimental

Preparation of the Solvent.—Eastman "White Label" ethanolamine was used throughout this investigation. The slight decomposition of the solvent and the resulting formation of conducting impurities when distilled at atmospheric pressure rendered imperative a purification by vacuum distillation. A suitable desiccant was not found for the solvent, so that a straight vacuum distillation at about 5 mm. pressure was used to purify all solvent used in the measurements. One distillation of the purchased ethanolamine gave a specific conductance of about 10^{-5}. It seemed impossible to obtain a solvent of lower conductance. Thus it was concluded that this relatively high conductance was due to remarkably high self-ionization (autoprotolysis) of the solvent. The distillations were carried out on three-liter batches, the first 200 ml. and the last 300 ml. being rejected as precaution. However, failure to reject forerun portions of this size causes only a slight increase in the solvent correction. It would seem that the main impurities in the crude amine are non-volatile salt-like substances which remain in the stillpot.

The following data for ethanolamine were used in the calculations: density, 1.0117; viscosity, 0.19346 poise; dielectric constant, 37.72.[3] Values of constants used in the evaluation of the Onsager slopes were taken from those of Fuoss and Shedlovsky.

Chemicals.—The salts, Baker's Reagent Grade, were powdered and dried at 150–200° and finally over phosphorus(V) oxide *in vacuo*. The samples of NaCl and KCl were Johnson–Matthey "*Spec pure*" reagents. These were similarly powdered and dried. It was found that recrystallization of the Baker salts produced no detectable change in conductance. The silver nitrite was C.P. material and was twice recrystallized from conductivity water in the dark. This salt was dried in the dark *in vacuo*. The pale yellow-needle-like crystals of silver nitrite dissolved in ethanolamine to give colorless solutions.

Conductance Cells.—The cells used were of two types and were made of Pyrex glass in this Laboratory. Platinum electrodes were sealed into the cell with uranium glass, giving a seal which did not leak.

Cells of the first type were similar in design to those used by Hibbard and Schmidt.[4] These cells had a capacity of about 120 ml. The solute was added portionwise to the cell

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[1] Address all correspondence to F. C. Schmidt. This investigation was carried out under contract No. AT(11-1)256 and was presented at the 134th meeting of the American Chemical Society in Chicago, September, 1958.

(2) R. M. Fuoss, *J. Chem. Ed.*, **32**, 527 (1955).

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