150. *Some Factors Affecting Ion-pair Formation in Water.*

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Calculations are presented of the effect of dielectric saturation on derived distances of closest approach in bi-bivalent sulphates. The displacement of hydration molecules in ion-pair formation is discussed. It is suggested that screening by the other ions in solution introduces an activity coefficient for the ion pair.

DIELECTRIC SATURATION

EQUALITY of distances of closest approach in ion-pairs (denoted by *a*) and interionic distances in crystals is frequently quoted [1,2] as supporting theories of electrolyte solutions. However, dielectric saturation in the vicinity of multiply charged aqueous ions complicates the interpretation of ion-pair formation.[3,4,5] This factor, which will generally

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[1] Guggenheim, *Discuss. Faraday Soc.*, 1957, **24**, 53.
[2] Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 3163; 1959, **81**, 2659.
[3] Davies, *Discuss. Faraday Soc.*, 1957, **24**, 83.
[4] Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publns., London, 2nd edn., p. 422.
[5] Williams, *Discuss. Faraday Soc.*, 1957, **24**, 81; Nancollas, *Quart. Rev.*, 1960, **14**, 402.

be effective only over the interionic range within which oppositely charged ions are considered paired, will appear as an increase in derived a values. An approximate calculation of the extent of the effect appears worthwhile.

A method due to Laidler[6] is applied here to the Bjerrum derivation[7] of the association constant K. The solvent permittivity which occurs in the Boltzmann factor is assumed to diminish continuously in a high potential gradient, the molecular nature of the solvent being ignored. The field causing dielectric saturation is taken to arise from one ion only, on the grounds that in the examples chosen the orientation of water molecules between the two close oppositely charged ions is more likely to be determined by the smaller cation than by the anion. The modified expression for K can then be used to afford a values from experimental association constants. The latter depend partly on the distance (d) of closest approach of *free* ions. We therefore used Brown and Prue's[8] K values for a series of bi-bivalent sulphates, which were evaluated from cryoscopic measurements for several choices of d.

Laidler's method was originally used[9] in calculating the electrostatic free energies and entropies of hydration of single ions, and particularly good agreement with experiment was obtained for bivalent cations. The modified derivation of K for bi-bivalent electrolytes, while approximate, should therefore by more realistic than that involving use of the low-field dielectric constant ε_0 throughout.

Electrostatic Attraction with Dielectric Saturation.—For water the variation of the differential dielectric constant ε with field strength E is given by:[6]

$$\varepsilon = \mathrm{d}D/\mathrm{d}E = n^2 + (\varepsilon_0 - n^2)/(1 + bE^2), \tag{1}$$

where D is the electric displacement, ε_0 is the dielectric constant at zero field strength (88·2 at 0°), n is the refractive index of water ($n^2 = 1{\cdot}78$), and b is constant. The electric displacement at a distance x from a cation of valency z is ze/x^2. This may be used in the integrated form of equation (1):

$$D = n^2E + [(\varepsilon_0 - n^2)/\sqrt{b}]\tan^{-1}(E\sqrt{b}) = ze/x^2. \tag{2}$$

Equation (2) can now be used in drawing curves of the variation of E with x for $z = 2$, the case of interest.

It is assumed that the force acting on an anion at a distance x is equal to the field E multiplied by the charge on the anion. The work done in bringing up a unit charge from infinity to a distance r from the cation is obtained by graphical integration of the plot of E against x from infinity up to r. Multiplication by the charge on the anion then gives a value for the work $u(r)$ required to bring the anion from infinity to a distance r from the cation.

Since the experimental K values[8] were measured at 0° a value of b at 0° is required. Laidler and Pegis[9] give the expression for b as

$$b = 9\pi Nh/10VkT^3(\varepsilon_0 - n^2), \tag{3}$$

where h is a function of the dipole moment of an individual water molecule and the total resultant moment of a given cluster of water molecules, and V is the molar volume of water at a temperature T (°K). For h at 0°C, $\mathrm{d}h/\mathrm{d}T$ is assumed constant at the value indicated by calculations[9] of h from 35° to 15°C. The assumption that the structural change in water below 5°C does not affect $\mathrm{d}h/\mathrm{d}T$ should not be much in error since the

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[6] Laidler, *Canad. J. Chem.*, 1959, **37**, 138.

[7] Bjerrum, *Kgl. danske Videnskab. Selskab*, 1926, **7**, No. 9.

[8] Brown and Prue, *Proc. Roy. Soc.*, 1955, *A*, **232**, 320.

[9] Laidler and Pegis, *Proc. Roy. Soc.*, 1957, *A*, **241**, 80.

variation of ε_0 with T shows no anomaly in this range.[10] The extrapolated value of h, $6{\cdot}595 \times 10^{-70}$ at 0°c, leads to $b = 1{\cdot}345 \times 10^{-8}$ [(e.s.u.)$^{-2}$] at that temperature.

Values of $u(r)$ calculated by the method outlined above are summarised in Table 1.

TABLE 1.

Electrostatic attractive energy with distance apart for bi-bivalent ions at 0°c.

r (Å)	5·0	4·6	4·2	3·8	3·6	3·4	3·3
$10^{13}u(r)$ (erg/mol.)	2·10	2·28	2·54	2·87	3·09	3·37	3·54

The variation of ε with r for $z = 2$ is similar to that obtained by Laidler[6] at 25°c, except that ε_0 is 88·2 in this case. At 7 Å ε starts dropping steeply, reaching 1·78 at about 3 Å.

Dielectric Saturation in the Calculation of a *Values.*—The expression for K may be written

$$K = \frac{4\pi N}{1000}\int_a^d \exp\left[\frac{u(r)}{kT}\right] r^2 \mathrm{d}r, \tag{4}$$

in which Bjerrum[7] put $u(r)$ equal to $z^2e^2/\varepsilon_0 r$ for all values of r. However, dielectric saturation is found to interfere at $r < 5$ Å. It is therefore an improvement, when $d > 5$ Å, to split the integral and write

$$K = \frac{4\pi N}{1000}\left\{\int_a^{5\text{Å}} \exp\left[\frac{u(r)}{kT}\right] r^2 \mathrm{d}r + \int_{5\text{Å}}^d \exp\left[\frac{z^2e^2}{\varepsilon_0 rkT}\right] r^2 \mathrm{d}r\right\}, \tag{5}$$

with $u(r)$ calculated as for Table 1. With the usual substitution[7] in the second term, the expression finally obtained is

$$K = \frac{4\pi N}{1000}\left\{\int_a^{5\text{Å}} \exp\left[\frac{u(r)}{kT}\right] r^2 \mathrm{d}r + \tfrac{1}{6} q^3\left[\mathrm{Ei}(y) - e^y\left(\frac{y^2+y+2}{y^3}\right)\right]_{q/d}^{q/5\text{Å}}\right\} \tag{6}$$

where $q = z^2e^2/\varepsilon_0 kT$. The first term is obtained by graphical integration of the plot of $\{r^2 \exp[u(r)/kT]\}$ against r between chosen values of a and $r = 5$ Å. The second term can be calculated from tabulated values[11] of $\mathrm{Ei}(y)$ or obtained directly from Tables[10,1] for $d = q/2$. For choices of d equal to 5 Å and 4 Å expression (4) can be used as written.

TABLE 2.

Distances of closest approach of paired ions, from experimental association constants.

Electro-lyte	K (kg./mole)	a (Å)	a (BP) (Å)	K (kg./mole)	a (Å)	a (BP) (Å)	K (kg./mole)	a (Å)	a (BP) (Å)	K (kg./mole)	a (Å)	a (BP) (Å)
	$d = 13{\cdot}87$ Å			$d = 6{\cdot}94$ Å			$d = 5{\cdot}0$ Å			$d = 4{\cdot}0$ Å		
$CuSO_4$	303	3·68	3·56	244	3·58	3·42	200	3·53	3·40	152	3·48	3·32
$ZnSO_4$	238	3·96	3·91	182	3·78	3·70	137	3·71	3·67	100	3·58	3·49
$MgSO_4$	244	3·92	3·88	190	3.75	3·66	143	3·69	3·63	95	3·60	3·50
$CaSO_4$	303	3·68	3·56	233	3·61	3·48	200	3·53	3·40	185	3·43	3·26
$CoSO_4$	227	4·03	4·01	182	3·78	3·70	137	3·71	3·67	100	3·58	3·49
$NiSO_4$	244	3·92	3·88	190	3·75	3·66	143	3·69	3·63	114	3·55	3·43

To obtain a, one of the values of d used by Brown and Prue[8] was first chosen, say $d = 13{\cdot}87$ Å. Then K was calculated from equation (6) for an arbitrary series of a values

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[10] Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 3rd edn., p. 161.

[11] Jahnke and Emde, " Tables of Functions," Dover Publns., New York, 4th edn., p. 6.

over the range $a = 3{\cdot}3$—$4{\cdot}1$ Å. From the plot of calculated K values against a, experimental association constants for $d = 13{\cdot}87$ Å were used in reading off the corresponding distances a. The procedure was then repeated for $d = 6{\cdot}94$, $5{\cdot}0$, and $4{\cdot}0$ Å. The results are recorded in Table 2. The a values obtained by Brown and Prue [8] (BP), using ε_0 for all values of r, are tabulated for comparison.

Discussion.—The differences Δa between values calculated with ε_0 and ε are small but not negligible; they lie between 0·02 and 0·17 Å, being largest for smallest d and smallest a, as would be expected. Neglect of the influence of the anion in dielectric saturation gives Δa too small, while omission of the screening effect discussed in the third section gives Δa too large. The magnitude of these two errors is not known.

The continuous decrease of ε with r at small r should approximate to the process occurring when a charge is brought from infinity to the cation. The actual values of ε may be somewhat doubtful, since with real ions the process may involve, besides the orientation of the water molecules by the high field of the cation, the actual removal of an H_2O molecule from a site adjacent to the cation. In this case the operative dielectric constant would finally become unity. Over the range of r in which the displacement of the H_2O molecule would occur [about (a plus diameter of H_2O) to a, say $r = 6{\cdot}4$ Å to $r = 3{\cdot}6$ Å] the present calculation shows ε to drop from about 80 to 15. Scatchard [12] has pointed out that, although rigid orientation of an H_2O molecule by ionic hydration lowers the dielectric constant, the molecule itself is correspondingly more difficult to shift while being replaced by an anion. The value of ε at a greater than unity, obtained in this paper, crudely eliminates part of the difficulty. A more complete discussion of the role played by water displacement in ion association follows in the next section.

The present calculation gives results contradictory to those obtained by Levine and Wrigley [13] for oppositely charged ions with rigidly oriented hydration molecules. They found a repulsive term in addition to the Coulomb energy. The cause of the discrepancy is not known, but the results of the present calculation agree more closely with expectation.

CATIONIC RADII AND ASSOCIATION CONSTANTS

Equilibrium constants for association in water of particular anions each with a series of cations have been listed by Davies.[3] Contrary to widespread belief,[14] association increases with increasing crystallographic radius r_+ of the cation for sulphates (Li^+, Na^+, K^+), nitrates (Ca^{2+}, Sr^{2+}, Ba^{2+}), and thiosulphates (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}). The cations involved in each case may be considered truly spherical, and there will be no anomalous effects arising from asphericity (in which we may include crystal-field effects in the interaction of the cation with water, if not with the anion). The spherical cations in the series of sulphates studied by Brown and Prue [8] also show increasing association with increasing r_+, this order being followed for all the d values chosen. Further, association of most alkali halides would be required [15] to follow the order of increasing cationic radii in order to explain conductance behaviour.

Duncan [16] has expressed scepticism concerning explanations of relations involving only a restricted series of ions. Nevertheless it seems necessary to explain why a theory such as Bjerrum's,[7] with a values in the sequence of the crystalline radii, does not predict the right order of association for the spherical cations, since a simple electrostatic model would be expected to hold best for these ions.

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[12] Scatchard, " The Structure of Electrolytic Solutions," ed. W. J. Hamer, John Wiley and Sons, Inc., New York, 1959, p. 16.

[13] Levine and Wrigley, *Discuss. Faraday Soc.*, 1957, **24**, 43.

[14] Ref. 4, p. 552.

[15] Kay, *J. Amer. Chem. Soc.*, 1960, **82**, 2099.

[16] Duncan, *Discuss. Faraday Soc.*, 1957, **24**, 129; for further discussion by Duncan, see ref. 12, p. 380; *Austral. J. Chem.*, 1959, **12**, 356.

One explanation is that the anion can penetrate only part of the way into the primary hydration sheath of the cation. The stronger the cation–water interaction, the less deep the penetration by the anion. Diamond's[17] explanation of the order of the distances of closest approach, required in order that the Debye–Hückel expression should fit experimental activity coefficients of alkali chlorides, bromides, and iodides, is of this kind. This picture implies kinetically inert (non-exchanging) water molecules in the primary hydration sheath of the more strongly hydrated ions. Such behaviour occurs[18] only with $Cr(OH_2)_6^{3+}$, and if the hydration water of other cations is able to exchange rapidly it seems likely that an energetically favourable site adjacent to the cation can become available to an anion.

Closer examination of how this happens requires rejection of the model with a continuous dielectric. If hydration of the anion, and any quantum mechanical interaction of anion with cation, are ignored, the molecular processes involved in ion association may be written:[19]

$$A^+OH_2 + B^- \overset{K_1}{\rightleftharpoons} A^+OH_2B^- \overset{K_2}{\rightleftharpoons} A^+B^- + OH_2$$

It is assumed that the water molecules in the primary hydration shell of A^+ are held by an attraction somewhat greater than that given by the $ze\mu/r^2$ plus $ze\alpha/r^4$ interactions,[20] this attraction decreasing with increase of r_+. (μ and α are the dipole moment and polarisability of water, and r is the distance between centres of the cation and the water molecule.) Only the water undergoing displacement by the anion is shown. For simplicity those oppositely charged ions separated by a few water molecules are omitted. The ions may be singly, doubly, or triply charged. The configuration $A^+OH_2B^-$ corresponds to localised hydrolysis[17,21] which, it has been suggested, arises from the attachment of B^- to a highly polarised water molecule. Two favoured positions for pairs are postulated in the equilibria: oppositely charged ions either in contact or separated by one solvent molecule. The existence of distinct species in a molecular solvent, as opposed to a series of associated species, at distances apart varying continuously between a and d according to a distribution function governed by Coulomb's law, is indicated by sound-absorption measurements.[22]

From considerations presented by Guggenheim[1] and others, experimentally determined association constants K (for bi-bivalent electrolytes as least) generally include both $A^+OH_2B^-$ and A^+B^- as associated species. Thus $K = K_1\ (1 + K_2)$.

The influence of r_+ on K_1 and K_2 may now be considered with the aid of simple ideas on the forces of attraction operating in $A^+OH_2B^-$ and A^+B^-. For a series of similarly charged cations with r_+ increasing, the following will apply: (i) A decrease in anion–cation attraction will occur with increasing distance apart. This effect will lead to a decrease in both K_1 and K_2. (ii) A decrease of localised hydrolysis will occur owing to diminishing polarisation of the intervening water. This effect will lead to a decrease in K_1. (iii) (*a*) Progressive diminution of the intimate $A^+–OH_2$ interaction in the case of the water that is being displaced will allow easier access to B^-. (*b*) Progressively weaker interaction between A^+ and the remaining water in its primary hydration sphere will allow the latter to become more easily adjusted to configurations favourable to the entry of B^-. Effects (iii) (*a*) and (*b*) will lead to an increase in K_2. (iv) The Born stabilisation energy of the free cation[20] arising from polarisation of the solvent outside the first hydration sphere will be progressively less diminished by close approach of B^-. Effect (iv) will lead to an increase in both K_1 and K_2. [If A^+B^- is considered to resemble, approximately, a dipolar molecule, the increase in K_2 in (iii) and (iv) may alternatively be taken to arise from the

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[17] Diamond, *J. Amer. Chem. Soc.*, 1958, **80**, 4808.

[18] Plane and Hunt, *J. Amer. Chem. Soc.*, 1957, **79**, 3343.

[19] Prue, *Ann. Reports*, 1958, **55**, 14.

[20] Buckingham, *Discuss. Faraday Soc.*, 1957, **24**, 151.

[21] Ref. 4, p. 423.

[22] Eigen, *Discuss. Faraday Soc.*, 1957, **24**, 25.

increasing interaction of A^+B^- and the solvent with increasing dipole moment of the former. This view, however, is not completely consistent with the original model.]

The variation of K with r_+ will then depend on which of (i), (ii), (iii), and (iv) dominate in a series. It is suggested that the factors in (iii) and (iv) are predominant in the series of ion pairs cited earlier; K would then increase with r_+ as found.

The definition of association in which it is stipulated[23] that only ions in contact be considered as pairs requires, if K is small, that $K_2 \gg 1$ and $K = K_1K_2$. Effects (i)—(iv) will still determine the order. The above considerations should also apply to a charged ion-pair in an unsymmetrical electrolyte.

The emphasis on localised hydrolysis[17,21] in explaining the sequence of activity coefficients of univalent ions seems unnecessary. Calculations by Fuoss[24] and Guggenheim[1] for univalent ions in water, in which a model of spheres in a continuous dielectric ε_0 is used, show that there is a high probability of finding an anion in contact with the cation at about 0·1M-concentrations. While localised hydrolysis may occur, there appears to be little reason for excluding the occurrence of the A^+B^- species; the number of these may well be far greater than that of $A^+OH_2B^-$. Those anions (OH^-, F^-, formate, and acetate) associating in order of decreasing radius of univalent cation, probably do so because both effects (i) and (ii) predominate over (iii) and (iv). Their strong proton-accepting properties need not necessarily indicate that localised hydrolysis alone is the determining factor.

Conductance measurements should be particularly suitable for distinguishing between the effects of association and hydration, since in the conductance of free ions hydration has the same influence at infinite dilution as it has at higher concentrations, whereas the effect of hydration on activity coefficients increases with concentration. If Fuoss's[2] and Kay's[15] interpretation of the conductance of alkali halides in terms of association is correct (K increasing with r_+), both association and hydration would cause the activity coefficients to decrease with r_+. However, the choice of d for the alkali halides, on which the assumed extent of association depends, is still controversial.[25]

The MnO_4^-–MnO_4^{2-} electron exchange[26] is accelerated by cations in the order of rates, Cs > K > Na > Li. This order may again be interpreted as arising from the predominance of the effects (iii) and (iv) over (i) and (ii) in the incorporation of the cation into the activated complex. The alternative explanation in terms of hydration has also been offered.[27]

SCREENING IN THE ATTRACTION BETWEEN PAIRED IONS

The need to define an ion pair[1] arises from the breakdown of the Debye–Hückel approximation for the interaction of two oppositely charged ions separated by less than a certain distance (d). For bi-bivalent ions d is 9—10 Å, which leads to the expression, with $B = 2{\cdot}0$, for the mean ionic activity coefficient $f_\pm$ of the free ions,

$$\ln f_\pm = -Az^2\{[\sqrt{I}/(1 + \sqrt{I})] - BI\}. \qquad (7)$$

Davies, Nancollas, and others[28] have used this expression with $B = 0{\cdot}20$, which has been criticised[1] on the grounds that it gives d as about 4·3 Å for bi-bivalent electrolytes. Brown and Prue[8] found that activity coefficient expressions with $B \approx 2{\cdot}4$ and $B \approx 1{\cdot}0$ (*i.e.*, their expressions with q_1 and q_2) led to systematic deviations between calculated and

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[23] Fuoss, *J. Amer. Chem. Soc.*, 1957, **79**, 3301.
[24] Fuoss, *J. Amer. Chem. Soc.*, 1935, **57**, 2604.
[25] Guggenheim, *Trans. Faraday Soc.*, 1960, **56**, 1159.
[26] Sheppard and Wahl, *J. Amer. Chem. Soc.*, 1957, **79**, 1020.
[27] Marcus, *Discuss. Faraday Soc.*, 1960, **29**, 120, and refs. therein.
[28] Davies, *J.*, 1938, 2093; Nair and Nancollas, *J.*, 1958, 3706.

experimental values of freezing-point depressions. Nair and Nancollas[28] similarly found that use of the larger values of B was unsatisfactory.

The association constant K is usually defined as

$$K = (1 - \alpha)/\alpha^2 m f_{\pm}^2. \qquad (8)$$

This expression implies that the oppositely charged ions within the distance d are uninfluenced by the other ions in solution, which is obviously an oversimplification. The association constant should, more completely, be written:

$$K = (1 - \alpha) f_p / \alpha^2 m f_{\pm}^2, \qquad (9)$$

where f_p is the activity coefficient of the ion pair arising from the free energy of interaction (ΔG_p) of the paired ions with the remaining ions in solution.

Bjerrum's derivation[7] of an association constant takes as a model two isolated oppositely charged ions. The expression obtained is therefore applicable to a value of K at infinite dilution, *i.e.*,

$$m \longrightarrow 0, \; K \longrightarrow (1 - \alpha)/m. \qquad (10)$$

The presence of ions other than the pair, in solutions of finite concentration, will affect the pair as follows. While a free cation, say, has for electroneutrality an ionic atmosphere of equal and opposite charge made up of fractions of charges of several anions, in an ion pair most, but not all, of the opposite charge is contributed by the single anionic partner. The relative contribution of the remaining ions will increase with increasing concentration of the latter, and increased screening of the attraction between the pair will result. The condition $m \longrightarrow 0$ in expression (10) justifies omission of the screening effect in Bjerrum's derivation (4) of K. Fuoss[29] noted this effect, but the concentrations considered in his paper were so low that it could be neglected. At concentrations used in measurements of association the neglect is almost certainly no longer justified. In making allowance for the screening effect ΔG_p must thus be taken as positive.

The magnitude of the effect is not clearly calculable. Whatever it is, if f_p is included with $f_{\pm}$ the resultant value of B will be less than that calculated with the assumption that B is determined by the value of d alone. Therefore use of small values of B does not necessarily imply that d has also been assumed small. The empirical success of the value $B = 0{\cdot}20$ would indicate that the screening effect is large.

In the two methods of calculating a described in the first section (*i.e.*, with ε or ε_0) inclusion of the screening effect would result in larger values of a and consequently decreased values of Δa, as noted there.

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[29] Fuoss, *Trans. Faraday Soc.*, 1934, **30**, 967.