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Ionic Association. I. Derivation of Constants from Conductance Data

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By combining the Fuoss–Onsager conductance equation with the law of mass action, a generalized conductance equation is obtained which includes the case of association of free ions to ion pairs. This equation can then be transformed into a linear equation in appropriate variables. It is shown that limiting conductance, ion size and association constant may be obtained by graphical treatment of conductance data at low concentrations ($\kappa a < 0.2$). A viscosity correction is also required if one ionic species is bulky compared to the solvent molecules.

When the classical mass action constant describing the dissociation of ion pairs is less than about 0.01, it can be easily determined to a good approximation from conductance data by application of a suitably modified form of the Ostwald dilution law.[1] But when the fraction of solute present as ion pairs is small, as is the case for ionophores[2] in solvents of high dielectric constant, the constant calculated by this method is necessarily incorrect, because it is forced by the method of calculation to absorb other (now calculable) effects which also lead to terms of the same order in concentration as the one due to association. When the phoreogram lies above the Onsager tangent, the older method cannot give even a poor approximation; from the classical point of view, the only conclusion which can be drawn is that "dissociation is complete," although there may be good reason to suspect that some association nevertheless is occurring.

The origin of the ambiguity lies in the form of the conductance function. If higher terms from long range interactions are ignored, the conductance equation would simply be

$$\Lambda = \Lambda_0 - Sc^{1/2} - c\Lambda_0/K \qquad (1)$$

where S is the Onsager coefficient

$$S = \alpha\Lambda_0 + \beta \qquad (2)$$

and K is the mass action constant. But the square root term is only the leading term of the relaxation and electrophoresis functions, and coefficients of terms of order c and $c \log c$ clearly would be included in the value of K derived from (1). When $K < < 1$, the error is small, but when K approaches unity, the other terms can completely mask association. A recent calculation[3] of the next higher long range terms now provides a means of modifying (1) so that realistic values of K can be obtained, regardless of the magnitude of K.

Before starting the derivation, it seems advisable to introduce a change in nomenclature, which will place proper emphasis on the molecular mechanism under consideration. Traditionally, we speak of "dissociation" constants of electrolytes, following the proposal of Arrhenius that neutral molecules of solute electrolyte partially dissociate into free ions in solution. We now know that in the case of ionophores the ions exist *ab initio;* in a suitable environment, they may cluster to pairs or to higher aggregates under the influence of mutual attraction. Since the primary act therefore is the association of free ions rather than the dissociation of neutral molecules, it appears preferable to introduce the symbol A for the association constant which describes the associative equilibrium

$$A^+ + B' \rightleftarrows A^+ \cdot B' \qquad (3)$$

We therefore write

$$[A^+ \cdot B']/[A^+][B'] = A \qquad (4)$$

where the bracketed quantities refer to activities. As usual, we shall assume that f_{AB} is unity and use the Debye–Hückel equation to calculate the activity coefficient f of the free ions. If γ denotes

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(1) R. M. Fuoss, *Chem. Revs.*, **17**, 27 (1935); R. M. Fuoss and T. Shedlovsky, THIS JOURNAL, **71**, 1496 (1949).

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

(3) R. M. Fuoss and L. Onsager, *Proc. Nat. Acad. Sci.*, **41**, 274, 1010 (1955).

the fraction of solute present as free ions, (4) then becomes

$$(1 - \gamma)/c\gamma^2f^2 = A \quad (5)$$

whence

$$\gamma = 1 - Ac\gamma^2f^2 \quad (6)$$

where

$$-\ln f = \beta' c^{1/2}\gamma^{1/2}/(1 + \kappa a\gamma^{1/2}) \quad (7)$$

and the other symbols have their usual meanings.

At low concentrations ($\kappa a \ngtr 0.2$), the conductance equation for unassociated electrolytes can be approximated closely[4] by

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + J_1c(1 - \alpha c^{1/2})(1 - J_2c^{1/2}/J_1) + O(c^2) \quad (8)$$

where

$$0.4343E = (\kappa^2a^2b^2/24c)\Lambda_0 - \kappa ab\beta/16c^{1/2} \quad (9)$$

$$b = e^2/aDkT \quad (10)$$

$$J_1 = \theta_1\Lambda_0 + \theta_4 \quad (11)$$

$$\theta_1 = (\kappa^2a^2b^2/12c)[g(b) + \ln(\kappa a/c^{1/2}) + 0.9074] \quad (12)$$

$$g(b) = (1 + 2b)/b^2 \quad (13)$$

$$\theta_4 = \alpha\beta + 8\beta\kappa a/9c^{1/2} - \theta_2 \quad (14)$$

$$\theta_2 = (\beta\kappa ab/8c^{1/2})[\ln(\kappa a/c^{1/2}) + 0.8504] \quad (15)$$

$$J_2 = \theta_3\Lambda_0 + 8\beta\kappa^2a^2/9c \quad (16)$$

and

$$\theta_3 = [(ab\kappa/c^{1/2})^3 2^{1/2}/24b][g(b) - 1.0774] \quad (17)$$

(It will be noted that E, the coefficient of the $c \log c$ term, is independent of ion size and concentration, although the symbols a and c appear in (9); the θ's, on the other hand, are functions of a, both explicitly and also implicitly through b, but naturally are independent of c, which only appears in the ratio $\kappa^2/c = \pi e^2N/125DkT$.)

Now let us assume that the conductance Λ_i due to the free ions is given by (8), if c is replaced consistently by $c\gamma$ which gives the actual concentration of free ions (in equivalents per liter). Then

$$\Lambda = \gamma\Lambda_i \quad (18)$$

where Λ is the observed equivalent conductance Combining (18) and (6) immediately gives

$$\Lambda = \Lambda_i - Ac\Lambda\gamma f^2 \quad (19)$$

and substitution of (8) (with $c\gamma$ in place of c) then gives

$$y = J_1 - Ax - J_2c^{1/2}\gamma^{1/2} \quad (20)$$

where

$$y = \Delta\Lambda/c\gamma(1 - \alpha c^{1/2}\gamma^{1/2}) \quad (21)$$

$$\Delta\Lambda = \Lambda + Sc^{1/2}\gamma^{1/2} - Ec\gamma \log c\gamma - \Lambda_0 \quad (22)$$

and

$$x = \Lambda f^2/(1 - \alpha c^{1/2}\gamma^{1/2}) \quad (23)$$

At low concentrations, the J_2 term is small and may be neglected in first approximation, so that

$$y \approx J_1 - Ax \quad (24)$$

Therefore a plot of y against x should be linear: the slope evaluates the association constant A, and

$$J_1 = y(0) + A\Lambda_0 \quad (25)$$

where $y(0)$ is the ordinate at $c = 0$. From the value of J_1, a can then be found by interpolation on a J_1–a plot.

In order to begin the above computation of $\Delta\Lambda$ and f it is, however, necessary to have values for Λ_0 and γ. Extrapolation by Shedlovsky's method[5] gives a suitable starting value for Λ_0; the value found by this method is usually a little too small. At low concentrations, y is approaching 0/0; if the incorrect value of Λ_0 is inserted in (22), y will obviously approach $\pm\infty$ as concentration approaches zero. Hence, if the initial y *vs.* x plot shows a minimum, a larger value of Λ_0 should be used; if it becomes sharply concave downward at low concentrations, a smaller value is needed. For γ, the approximation

$$\gamma_0 = \Lambda/(\Lambda_0 - Sc^{1/2}\Lambda^{1/2}/\Lambda_0^{1/2}) \quad (26)$$

is used; the E and J_1 terms have opposite signs and to a considerable extent the errors so made compensate if both are neglected in (26). Then having determined J_1 by (25) (and hence a) to first approximation, the calculation may be repeated with γ to second approximation, given by

$$\gamma = \Lambda/(\Lambda_0 - Sc^{1/2}\gamma_0^{1/2} + Ec\gamma_0 \log c\gamma_0 + J_1c\gamma_0 - J_2c^{3/2}\gamma_0^{3/2}) \quad (27)$$

Finally

$$y' = y + J_2c^{1/2}\gamma^{1/2} \quad (28)$$

is plotted against x', also computed to second approximation, using (27) in (7) and (23). For $A \leqslant 15$, the values of a and A obtained from the original y–x plot do not differ by more than a few per cent. from those obtained from the y'–x' plot.

When A becomes small, *i.e.*, when the phoreogram lies near (or above) the Onsager tangent, γ may be safely approximated by unity in calculating the various interionic terms which appear in y and x. When A drops to values near unity, the y–x plot becomes practically horizontal within experimental error; in this case, it is necessary to have data for the salt in solvents of lower dielectric constant. These serve to determine a and hence J_1 and J_2 if we may assume that a is independent of composition in mixed solvents. Then one plots Λ''' against $c\Lambda f^2/(1 - \alpha c^{1/2})$; the slope is equal to A. Here Λ''' is defined as

$$\Lambda''' = \Lambda'' - J_1c + J_2c^{3/2} \quad (29)$$

where

$$\Lambda'' = (\Lambda + \beta c^{1/2} - Ec \log c)/(1 - \alpha c^{1/2})$$

and

$$\Lambda''' = \Lambda_0 - A[c\Lambda f^2/(1 - \alpha c^{1/2})] = \Lambda_0 - Az \quad (30)$$

The intercept at $c = 0$ is the final value of Λ_0.

When large ions, such as quaternary ammonium ions (or picrates) are involved, a modification of (8) becomes necessary. These bulky ions interfere with the motion of the balancing counter ions, which in effect are moving in a medium of higher viscosity than that of the pure solvent. We recall that the equivalent conductance is proportional to the mobility which in turn is inversely proportional to the viscosity of the solvent medium to first approximation. In order to estimate this correction, we shall assume that the viscosity η at non-zero concentrations is given by the Einstein equation

$$\eta = \eta_0(1 + 5\phi/2)$$

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[4] R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957).

[5] T. Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

where ϕ is the volume fraction of solute. If we assume that the cations have a hydrodynamic radius R, then

$$\phi = (4\pi R^3/3)(Nc/1000) = \delta c \qquad (31)$$

where N is Avogadro's number. Then the conductance equation becomes

$$\Lambda = [\Lambda_0 - \beta c^{1/2}/(1 + \kappa a)](1 + \Delta X/X)(1 + 5\delta c/2)^{-1} \qquad (32)$$

because viscosity appears in the denominator of both limiting mobility and the electrophoresis term. If $(1 + 5\delta\ c/2)^{-1}$ is approximated by $(1 - 5\delta\ c/2)$ in (31) and the same expansion is made as before, the final result, which replaces (24), is

$$y = J_1 - 5\Lambda_0\delta/2 - Ax \qquad (33)$$

This means that a plot of y against x should still be linear, with slope equal to A, but the ordinate at $c = 0$ ($x = \Lambda_0$) is now

$$y(0) = J_1 - 5\Lambda_0\delta/2 - A\Lambda_0 \qquad (34)$$

Hence if J_1 is known (*i.e.*, if a can be evaluated), δ and hence R are known. Examples of the various cases discussed will be given in the following paper. As will be emphasized there, it would be futile to attempt to apply the equations developed in this paper to data of low precision (± 0.1% or worse).

There are several other corrections due to the actual volume of the ions which should be considered in the next higher approximation. The first is the modification of K which accounts for the fact that an ion and a solvent molecule cannot simultaneously occupy the same site.[6] The second is the change of dielectric constant produced by the ions: a decrease with respect to that of the solvent could be expected as a consequence of dielectric saturation in the close vicinity of ions, or merely due to a dilution effect if one species of ions were essentially paraffin, as is the case with quaternary ammonium ions. Both of these effects would lead to terms of order $c^{3/2}$ in the conductance equation. There may well be, of course, other still unknown terms. Over the range of concentration where we propose to apply the present analysis ($\kappa a < 0.2$), these terms are small. At higher concentrations, where the formally computed values of these terms would become numerically significant compared to the $c^{1/2}$, c and $c \log c$ terms, their inclusion appears to be irrelevant, because the continuum model for the ion atmosphere no longer is a valid physical approximation.[4] Consequently there is no need to contemplate the difficult and tedious task of integrating the equation of continuity to the next higher order of approximation in order to obtain the $c^{3/2}$ and $c^{3/2} \ln \kappa a$ terms.

Finally we consider the association constant A. If association is solely due to electrostatic forces, then a correlation between A and the dielectric constant of the solvent should appear. The relation proposed by Bjerrum[7] has been found to describe

$$A = K^{-1} = (4\pi N/1000)(e^2/DkT)^3Q(b) \qquad (35)$$

scribe ion association satisfactorily in solvents of low dielectric constant,[8] but $Q(b)$ contains a completely arbitrary cut-off limit at $r = e^2/2DkT = ab/2$. This limit is an artifact; convergence of the integral can be attained[9] by a more careful definition of ion pairs than that proposed by Bjerrum. But even so, the statistical approach to the problem still suffers from the esthetic handicap that ions which are not in actual contact still are counted as pairs. The Bjerrum cut-off also leads to another unrealistic situation: beyond a precisely and sharply definable critical limit of dielectric constant, ion association should cease abruptly. Actually, just as soon as the point charge model for the ions is replaced by one in which the ions are assigned a non-zero electrostatic radius a, we are admitting the existence of non-conducting ion pairs at any value (however high) of dielectric constant, because a non-zero size can only manifest itself when ions come into actual contact, and for the duration of the contact the pair can only react as a dipole to the external field. The dilemma can be neatly circumvented by a thermodynamic approach, as proposed by Ramsey,[10] who used a Born cycle to show that

$$K^{-1} \approx e^b \qquad (36)$$

in solvents of low dielectric constant. If the entropy terms[11] are included, (36) becomes

$$A = \exp(b + \Delta S/R) = A_0e^b \qquad (37)$$

Here b is the Bjerrum parameter $e^2/aDkT$ defined by (10). If other interactions in addition to charge-charge forces are involved

$$A = A_0 \exp(b + u/kT) \qquad (38)$$

where u is the potential of the mean force concerned. For example, if one ion carries a dipole

$$u = \mu e/a^2D \qquad (39)$$

provided a continuum model may be used. Arguments presented by Gurney appear to justify the use of the macroscopic dielectric constant in the cases of ion–ion and ion–dipole contacts.[12]

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[6] H. Falkenhagen, M. Leist and G. Kelbg, *Ann. Phys.*, (6) **11**, 51 (1952); M. Eigen and E. Wicke, *Naturwiss.*, **38**, 453 (1951); M. Dutta and S. N. Bagchi, *Ind. J. Phys.*, **24**, 2 (1950); S. N. Bagchi, *J. Ind. Chem. Soc.*, **27**, 4 (1950).

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

[8] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933).

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

[10] J. T. Denison and J. B. Ramsey, THIS JOURNAL, **77**, 2615 (1955).

[11] W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956); J. G. Kirkwood, *ibid.*, **18**, 380 (1950).

[12] R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953, Chap. 2.