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Parametric Analysis of Conductance Data

(ion pairs/association constants/model electrolytes)

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ABSTRACT **It is shown that three and only three parameters are sufficient to generate a function Λ (c; Λ_0, K_A, R) which reproduces observed equivalent conductance Λ as a function of concentration c within experimental error up to concentrations of about $2 \times 10^{-7}D^3$ eq/liter (D = dielectric constant). The three parameters are: Λ_0, the limit of $\Lambda(c)$ at zero concentration; K_A, the association constant; and R, a distance. Realization that conductance data can provide only one distance parameter suggests a model for electrolytic solutions in which R is defined as the radius of the sphere inside of which a unique partner can be found for a paired ion, and outside of which continuum theory may be applied. All system-specific effects (ion–ion and ion–solvent interactions, and the inherent spatial discontinuity of real solutions) appear within the spheres of radius R centered at the cations of the ion pairs. The association constant therefore depends not only on electrostatic attraction but also on the multiplicity of molecular parameters that are needed to describe short range interactions.**

Determination of association constants from conductance data is, strictly speaking, a matter of curve-fitting: given precise data for a given system and a reasonable equation (such as the Ostwald dilution law, or any of the modern improvements on it), the computer will print a number in the output box labeled "ASSOCN CONST = . . .," but that number obviously depends on the mathematical form of the equation used. The equation is a theoretical one, of necessity based on a model because real electrolytic solutions are far too complicated to be amenable to rigorous theoretical treatment. A frequently used model is the so-called primitive model: rigid charged spheres moving in a continuum described by its dielectric constant and viscosity. This model is adequate for prediction of the long range electrostatic interactions. But if the behavior of a given electrolyte paralleled that of the primitive model, it would have the same association constant in isodielectric solvents. Many violations of the isodielectric rule are known: striking examples are the much higher association in acetonitrile–dioxane mixtures than in isodielectric mixtures of p-nitroaniline with dioxane (1), and the contrast between association in ethylidene chloride and the nearly isodielectric 1,2-dichloroethylene (2). In both cases, the association constant in the first-named solvent is over an order of magnitude greater than in the second. A recent systematic study (3) of four quaternary electrolytes in mixtures of i-butyronitrile with five different polar solvents showed poor correlation between association constant and dielectric constant. These examples show that more than simple electrostatic anion–cation attraction must be involved in ion pair formation. The primitive model is too restrictive: it admits only one parameter (the contact distance) characteristics of the electrolyte. The frequently observed variation of this parameter (especially for small ions) for a given electrolyte from solvent to solvent or with solvent composition in mixed solvents demonstrates that the primitive model is oversimplified; we need a model that has more than one degree of freedom that can thereby allow for short range system-specific interactions.

Electrochemists are in general agreement that the concept of ion association is useful, indeed necessary, in the description of electrolytes but no model for pairs so far proposed has achieved general acceptance. Bjerrum's (4) original model [and the statistically improved version of Fuoss (5)], in which ions whose center-to-center distance r lies between $r = a$ (contact) and $r = \epsilon^2/2DkT = \beta/2$ are counted as pairs, calls for abrupt cessation of association when the dielectric constant D is such that $\beta/2$ becomes less than a. This predicts a physically unrealistic situation: for example, in water with $D = 78.35$, $\beta/2 = 3.57$ Å, which is less than the sum of the lattice radii for many salts for which non-zero association constants have been determined. For the contact pair model, the association constant is

$$K_A = (4\pi Na^3/3000) \exp(\epsilon^2/DkT) \qquad [1]$$

as shown thermodynamically by Denison and Ramsey (2), statistically by Fuoss (5), and kinetically by Debye (6) and Eigen (7). According to Eq. [1], a plot of the logarithm of the association constant against reciprocal dielectric constant of the solvent should be linear for a given electrolyte; in general, these plots are concave down.

The purpose of this communication is to make a pragmatic approach to the problem of the determination of association constants from conductance data. It will first be shown that three parameters are necessary and sufficient to construct a function $\Lambda(c)$ that reproduces the observed equivalent conductance Λ as a function of concentration c within experimental error. One of these must be the limiting conductance, $\Lambda_0 = \lim \Lambda(c)$, $c \rightarrow 0$; by hypothesis, the second must be the association constant K_A. A dimensional argument shows that the third must be a distance, R. This observation leads to a model of minimal restraints in which R replaces the $\beta/2$ of the Bjerrum–Fuoss model and the a of the model for Eq. [1]; ions that have no other *unpaired* ions within a distance R are defined as free ions while those that find a *unique* partner at distances $a \leq r \leq R$ are defined as statistically paired or associated ions. This approach brings in ion pairing *ab initio* (instead of grafting the mass action onto a theory for the conductance of "completely dissociated electrolytes") and demands a theory for relaxation and electrophoresis that is based on general boundary conditions that are independent of the molecular parameters that describe short range interactions. The latter development will be summarized in the *Appendix*.

The decrease of equivalent conductance with increasing concentration is the consequence of the retarding relaxation field, the electrophoretic countercurrent and the postulated zero contribution of paired ions to charge transport; symbolically,

$$\Lambda = \gamma\,[\Lambda_0(1 - \Delta X/X) - \Delta\Lambda_e] \qquad [2]$$

where $\Delta X/X$ is the ratio of the relaxation field to the external field and $\Delta\Lambda_e$ is the electrophoretic term. The association constant is defined by the equation

$$(1 - \gamma)/c\gamma^2 f^2 = K_A \qquad [3]$$

where $c\gamma$ is the concentration of unpaired ions and f is their activity coefficient, given by

$$f = \exp[-\beta\kappa/2(1 + \kappa R)] = \exp(-Cc^{1/2}) + O(c) \qquad [4]$$

Substitution of γ from [3] into [2] gives the implicit equation

$$\Lambda = \Lambda_0(1 - \Delta X/X) - \Delta\Lambda_e - K_A c\gamma f^2 \Lambda \qquad [5]$$

The limiting behavior at extreme dilutions can be predicted exactly using point charges to represent the ions. The result is

$$\Lambda_0 \Delta X/X + \Delta\Lambda_e = (\alpha\Lambda_0 + \beta_0)c^{1/2} - (E_1 - 2E_2\Lambda_0)c \ln c \qquad [6]$$

where the coefficients α, β_0, E_1, and E_2 are known. Then an extrapolation function

$$\Lambda' = [\Lambda(\text{obs}) + \beta_0 c^{1/2} - E_1 c \ln c]/(1 - \alpha c^{1/2} + 2E_2 c \ln c) \qquad [7]$$

can be constructed which approaches Λ_0 linearly in concentrations at low concentrations. Assume that Λ_0 has been determined in this way for a given electrolyte; then [2] can be rewritten

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \ln c + \text{HT} \qquad [8]$$

where HT is an abbreviation for terms of order c and higher. Now let us examine these higher terms by plotting

$$Y = [\Lambda(\text{obs}) - \Lambda_0 + Sc^{1/2} - Ec \ln c]/c \qquad [9]$$

against square root of concentration. Several examples are shown in Fig. 1. The plots are all linear, four (8–10) with negative slope and positive intercept, and one, for thallous nitrate (11), with positive slope and negative intercept. We thus establish the empirical result

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \ln c + Ac + Bc^{3/2} \qquad [10]$$

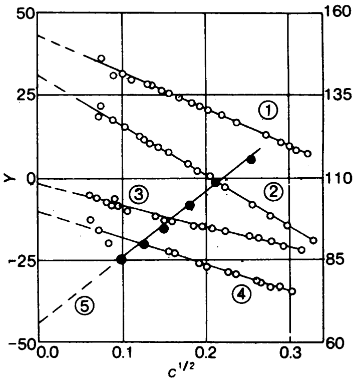

FIG. 1. Function of Eq. [9]. 1, Cesium bromide (8); 2, sodium chloride, $Y - 20$ (9); 3, potassium nitrate (10); 4, silver nitrate (10); 5, (Y-scale left) thallous nitrate (11).

that a 3-parameter equation is both necessary and sufficient to reproduce conductance curves up to concentrations of the order of 0.1 N in water. Comparison of [5] and [10] shows that A and B contain K_A and Λ_0. They also contain theoretically predictable contributions from relaxation and electrophoresis, which must, however, contain a third parameter which originates in the derivation of the higher terms. The independent variable in the differential equations that determine these is r_{ji}, the distance from a given i-ion to a reference j-ion; these equations simplify when the independent variable is changed to the dimensionless κr where $1/\kappa$ is the Debye distance, defined here by the relation

$$\kappa^2 = 8\pi n\gamma\epsilon^2/DkT = \pi Nc\gamma\epsilon^2/125\,DkT \qquad [11]$$

for 1-1 electrolytes. This in turn shows that the origin of the $c \ln c$ terms of [10] must be terms of the form $c \ln \kappa R$ where R is a distance, because only dimensionless numbers may have logarithms.

The conductance function [5] now takes the form

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \ln c + [p(R) - K_A\Lambda_0]c + [-q(R) + 2CK_A\Lambda_0]c^{3/2} + O(c^2) \qquad [12]$$

where $p(R)$ and $q(R)$ are the higher terms from relaxation and electrophoresis. The constants in [10] are seen to be

$$A = p(R) - K_A\Lambda_0 \qquad [13]$$

$$B = -q(R) + 2CK_A\Lambda_0 \qquad [14]$$

The slope and intercept of Fig. 1 are B and A; for small association constants where $p(R) > K_A\Lambda_0$ and $q(R) > 2CK_A\Lambda_0$, the intercept is positive and the slope is negative. As K_A increases, both slope and intercept go through zero and reverse sign. This is the sequence observed in Fig. 1: cesium bromide (8) and sodium chloride (9) have association constants a little less than unity; for potassium and silver nitrates (10), $K_A \simeq 2$; and for thallous nitrate (11), $K_A \simeq 3$.

To summarize, consideration of typical data for a variety of electrolytes shows that the conductance function must be

$$\Lambda = \Lambda(c; \Lambda_0, K_A, R) \qquad [15]$$

The next problem is to find the form of the functions $p(R)$ and $q(R)$; to this end, it is necessary to construct a model characterized by a distance parameter R. In the model to be proposed, R is a distance such that, if $r_{ij} > R$, ions i and j are considered unpaired ("free" ions, atmosphere ions) and paired if $r_{ij} < R$. Unlike the Bjerrum–Fuoss model in which R was fixed at $\epsilon^2/2DkT = \beta/2$, in this model R is a disposable parameter, to be determined along with Λ_0 and K_A from the data.

Represent the ions by charged particles, not necessarily rigid or spherical, that can be enclosed in a sphere of diameter a. Represent the solvent by particles of finite volume such that the sum of the volumes of all the particles is less than the volume of the system; all particles are in Brownian motion, thanks to the free volume available. Surround each cation by a sphere of diameter a, and let all the spheres expand simultaneously at such a rate that their radii increase by distances of the order of a in times of the order of that involved in molecular motion. When

$$4\pi \int_a^r \rho_j(r)\, r^2 dr = -\epsilon_j \qquad [16]$$

for a given cation with a charge ϵ_j, count the cation as paired with that anion that furnished the countercharge. The charge density $\rho_j(r)$ is a discontinuous function for distances from a to perhaps ten times a, depending on concentration. (If uncharged, the average center-to-center distance of ions in a 0.1 N solution would be about 2 nm.) The density ρ_j is zero until $r = r_{ij}$ where r_{ij} locates the center of the nearest *previously uncounted* anion i to the j. If the system had been frozen before starting the count, a *unique* partner could have been assigned to *every* cation. In our model, however, the ions are in thermal motion; therefore, assignment of unique partners becomes blurred as r increases. The integral for some of the ions from a to some larger value R of r is zero, and it is the integral from R to infinity that provides the balancing charge

$$4\pi \int_R^\infty \rho_j(r)\, r^2 \mathrm{d}r = -\epsilon_j \qquad [17]$$

Eq. [17] is simply the statement that the neutralizing charge for the central cation cannot be located on any one particular anion; as a consequence of the thermal motion of the ions and their relatively large mutual distances, the set of discrete charges on all the other ions may be replaced by their time average (the Debye ionic atmosphere), which integrates precisely to $(-\epsilon_j)$. The paired ions in the volume surrounding the reference ion contribute mutually cancelling terms to this average space charge. Now for any cation,

$$4\pi \int_a^\infty \rho_j(r)\, r^2 \mathrm{d}r = -\epsilon_j \qquad [18]$$

Divide the range of integration into two segments: $a \leq r \leq R$ and $R < r < \infty$. Ion pairs are now defined as those for which

$$4\pi \int_a^R \rho_j(r)\, r^2 \mathrm{d}r = -\epsilon_j \qquad [19]$$

and unpaired ions as all others; for the latter

$$\rho_j\,(r) = \Sigma_i n_i \epsilon_i \exp\,(-\epsilon_i \psi_j / kT) \qquad [20]$$

where $\psi_j(r)$ is the potential of average force at a distance r from the reference ion. Since, by the above definition, there are no nearby ions to the unpaired ones, $|\epsilon_i \psi_j / kT| < 1$ and the quadratic expansion of the Boltzmann factor is a completely adequate approximation.

For the unpaired ions, the model reduces to the primitive model; the discrete structure of the solvent and short range interactions play no role; both, however, are determinative for a description of the paired ions. The paired ions include contact pairs, solvent separated pairs, and pairs even farther apart, which are statistically paired by the counting process.

Let us begin by considering a system in which the volume $4\pi a^3/3$ is much larger than the average volume available per solvent molecule and for which $\epsilon^2/aD \gg kT$; here the ionic distribution should closely approximate that for the primitive model. The distribution curve (6) is the solid curve in Fig. 2A, where $G(r)$ is the probability that an anion can be found at a distance r from a given cation, subject to the condition that no other unpaired anion is located inside the sphere of radius r drawn around the cation. The function

$$G(r) = 4\pi n r^2 \exp\left[\beta/r - 4\pi n \int_a^r x^2 \exp(\beta/x)\mathrm{d}x\right] \qquad [21]$$

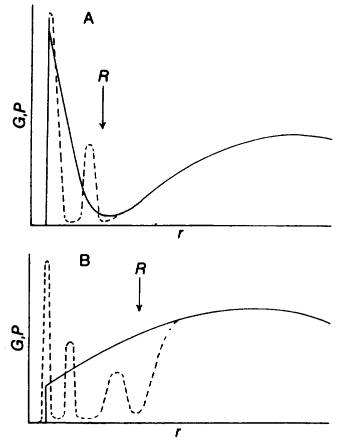

FIG. 2. Pair distribution functions. Solid curves, $G(r)$; broken curves, $P(r)$.

where n is the number of anions per unit volume, has an exponential peak at $r = a$, a minimum near the Bjerrum distance $\beta/2$, and a maximum at a distance of the order $n^{-1/3}$, after which is very rapidly decreases to zero. Based on this distribution function, ion pairs are defined as those for which $a \leq r \leq d$; the corresponding association constant is

$$K_\mathrm{A} = (4\pi N/1000) \int_a^d r^2 \exp(\beta/r)\mathrm{d}r \qquad [22]$$

For $d = \beta/2$, [22] gives the Bjerrum association constant; it quite satisfactorily describes the behavior of salts with large ions in solvents of lower dielectric constant.

Now consider salts with volumes comparable to those of the solvent molecules. Then the continuity implied in [21] is no longer a realistic approximation: the anion and cation of a pair will either be in contact, or will have one or more solvent molecules between them; the distribution becomes something like that shown schematically by the broken curve of Fig. 2A. For $r \gg a$, the distribution approaches continuity, of course, but for distances up to several times a, the probability function must peak for certain distances, which, moreover, must be system-specific. (Here certainly is at least part of the explanation for the violations of the isodielectric rule mentioned in the introduction, and for the variation, for a given electrolyte in different solvents, of a's calculated from association constants by [22] with $d = \beta/2$.) With our model the association constant is given by

$$K_\mathrm{A} = (4\pi N/1000) \int_a^R P(r)\mathrm{d}r \qquad [23]$$

where $P(r)$ is a system-specific distribution function; note that the integrand is proportional to the integrand in [18], where discontinuity is inherent. If a's are calculated by [22] using $d = R$, the result is the contact distance for the *equivalent* primitive model electrolyte; as solvent is changed, and with it free volume and ion-solvent interactions, one should expect a to change.

Next consider a solution of an electrolyte with bulky ions in a solvent of high dielectric constant. Here the distribution curve (Fig. 2B, solid curve) has no minimum; nevertheless, non-zero association constants have been found for such systems. Even for uncharged particles, the probability of finding pairs is not zero, simply as the consequence of chance collision;

the half-life of ion pairs is, of course, increased by short range electrostatic attraction. Furthermore, in real solvents, as contrasted to continua, the dwell time of a pair is increased by the caging effect of the surrounding solvent molecules. The pair distribution function will therefore peak around $r = a$; the corresponding association constant will be given by the integral

$$K_A = (4\pi N/1000) \int_a^R P(r)dr \qquad [\mathbf{24}]$$

where $P(r)$ is the probability of finding a unique pairing anion at a distance $r < R$. If the dimensions of the ions and solvent molecules are comparable, we would expect to find a second peak at $r = a + d_s$, where d_s is the diameter of a solvent molecule, and possibly a third further out. Such a distribution is shown as the broken curve of Fig. 2B. While the primitive model predicts zero association, the stochastic distribution function restores a minimum in probability between paired and unpaired ions and leads to a nonvanishing association constant.

The contrast between the distribution function for the primitive model and that for pairs in real solvents gives physical significance to the distance parameter R: it is the distance beyond which the continuum approximations become valid, and within which short range spatial and energetic interactions (both ion–ion and ion–solvent) must be considered. The following function has the properties required for the distribution in the range $a \leq r \leq R$:

$$P(r)\mathrm{d}r = 4\pi r^2 \mathrm{d}r \exp[\beta/r - \Sigma u(r)/kT] \times \sum_{j=0} w_j \exp[-\alpha_j(r - a - jd_s)^2] \qquad [\mathbf{25}]$$

where the sum of the weighting factors w_j is unity. Here β/r is the Coulomb term and $\Sigma u(r)$ symbolizes all the other interactions which must be considered for a given system. A repulsion term here will give a steep cut-off for $r < a$. The function postulates a Gaussian distribution around the sites of peak probability; the number j of such terms is limited by the condition $jd_s \leq R$. Alternatively, the Gaussians might be replaced by Dirac functions, $\delta(r - a - jd_s)$. Since by definition $u(r)$ sums all the *short range* forces, e^{-u} must quickly approach unity as r increases from $r = a$: therefore, to a good approximation, $u(r)$ may be replaced by $u(a)$ in [**25**]. For rigid spheres, $u(r < a) = \infty$. For $r > R$, $P(r) = G(r)$. The above distribution provides in a natural way places for the insertion of system-specific parameters which experiment tells us must be present in any formulation of the association constant. This virtue is, of course, simultaneously a drawback, in that quantitative comparison with experiment is ambiguous, because K_A must contain *all* the system-specific molecular parameters appearing in $P(r)$. The formula should, however, be useful in qualitative comparisons of the association constants for a family of electrolytes in a given solvent, or for a given electrolyte in a series of solvents or mixtures.

Conductance data of high precision for a large number of systems have been analyzed by the 3-parameter Eq. [**15**], which usually reproduces the observed conductance to about 0.02%. Results for a typical system, potassium nitrate in dioxane-water mixtures in the range $78.35 \leq D \leq 14.56$ (10), are shown in Fig. 3, where R and $\log K_A$ are plotted against $\beta/2$ (proportional to $1/D$). In the water-rich mixtures, R is about 4 Å greater than $\beta/2$; in this range, $G(r)$ has no minimum (compare Fig. 2B), but K_A is not zero. With decreasing dielectric constant, R increases, but less rapidly than $\beta/2$ ($R = \beta/2$ on the 45° line in Fig. 3). At $\beta/2 \simeq 15$, $R \simeq \beta/2$, and then increases very slowly. For $b = \beta/a > 2$, a minimum appears near $\beta/2$ in $G(r)$; $G(a)$ is twice as large as $G(\beta/2)$ for $b = 4.156$. If values of Λ_0 and K_A that minimize $\Sigma[\Lambda(\text{calc.}) - \Lambda(\text{obs.})]^2$ are determined for a sequence of values of R, and the standard deviation is plotted against R, curves with very sharp minima are obtained for the high dielectric constant range. But as dielectric constant decreases, the minima rapidly become shallower; that is, a broad band of paired values of R and K_A will fit the data within about the same tolerance. This simply means that K_A in solvents of lower dielectric constant is primarily determined by the dominating exponential peak near $r = a$, and becomes insensitive to the upper limit R in the integral [**24**]. This pattern of behavior appears to be general, and suggests that for systems for which $b > 4$, the 3-parameter Eq. [**15**] can for all practical purposes be reduced to the 2-parameter equation

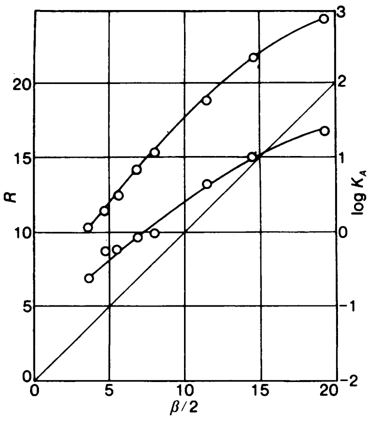

FIG. 3. Parameters for potassium nitrate in dioxane–water mixtures (10). Top curve, $\log K_A$; bottom curve, R; distance scales in Angstrom units.

$$\Lambda = \Lambda(c; \Lambda_0, K_A) \qquad [\mathbf{26}]$$

by setting $R = \beta/2$. If $u(a) = 0$, the equation for the association constant becomes the classical

$$K_A = (4\pi N/1000) \int_a^{\beta/2} r^2 \exp(\beta/r)\, dr \qquad [\mathbf{27}]$$

for solvents of low dielectric constant. More generally,

$$K_A = 4\pi N \exp[u(a)/kT] \int_a^{\beta/2} r^2 \exp(\beta/r)\, dr \qquad [\mathbf{28}]$$

where $u(a)$ includes the ion–solvent energy of interaction proposed by Gilkerson (12), ion–ion attraction due to induced dipoles, short range covalent "forces," and whatever else might be present in any particular case.

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APPENDIX

The relaxation field ΔX is obtained by integrating the Poisson equation

$$\Delta\psi'_j = -(4\pi/D)\Sigma_i f'_{ji}\epsilon_i/n_j \qquad [\mathbf{A1}]$$

where ψ'_j is the asymmetry potential produced by the perturbation f'_{ji} in the pair distribution function [**13**]. The distribution function $f_{ji} = (f^\circ_{ji} + f'_{ji})$ satisfies the equation of continuity

(ref. 13, Eq. 1.2)

$$\mathrm{div}_1\,(f_{ij}\mathbf{v}_{ij}) + \mathrm{div}_2\,(f_{ji}\mathbf{v}_{ji}) = 0 \qquad [\mathbf{A2}]$$

where $\mathbf{v}_{ji}$ is the velocity of an ion of species i at a distance r_{ji} from a reference ion of species j. The equations of motion (ref. 13, Eqs. 1.9 and 1.10) give the velocity in terms of the external field X and the internal forces. Substitution of these in [**A2**], solution of the latter and substitution of the result into [**A1**] gives the fourth order differential equation

$$\Delta\,(\Delta - \kappa^2\psi'_j/2) = \Sigma_k T_k \qquad [\mathbf{A3}]$$

to determine ψ'_j; here

$$\kappa^2 = 8\pi n\gamma\epsilon^2/DkT \qquad [\mathbf{A4}]$$

where γ is the fraction of cations that have no unpaired anionic neighbors at distances $r < R$. The summation on the right represents a group of functions, the first of which is explicit; the others involve ψ'_j and f'_{ji} (ref. 13, Eq. 1.8). Four boundary conditions are needed: the first three are electrostatic, requiring that $\nabla\psi'_j(\infty) = 0$, and that field and potential be continuous at $r = R$ (analogs of Eqs. 3.1–3.3, ref. 13). The fourth boundary condition is the requirement that the ratio (f'_{ji}/n^2) remain finite in the limit of zero concentration. The only system-specific parameters that appear are the charges on the ions (subject to the neutrality condition $\Sigma_i n_i\epsilon_i = 0$) and the macroscopic dielectric constant and viscosity of the solvent for $r > R$. All short range effects are contained in the association constant. The explicit inhomogeneous term of $\Sigma_k T_k$ gives the leading term of the relaxation field

$$\Delta X_1/X = -\beta[\exp(1-q)t - 1]/3R(1+t) \qquad [\mathbf{A5}]$$

where $q^2 = {}^1/_2$ and $t = \kappa R$. For low concentrations, this reduces to the Onsager limit

$$\Delta X^\circ/X = -\tau/3(1+q) \qquad [\mathbf{A6}]$$

with $\tau = \beta\kappa/2$. In the above calculation, the Boltzmann factor $\exp(-\epsilon_i\psi_j/kT) = e^\zeta$ was approximated by the truncated series $(1 + \zeta + \zeta^2/2)$ for $r \geq R$; the terms corresponding to $(\zeta + \zeta^2/2)$ in $\Sigma_k T_k$ give an exponential integral term in ΔX, which has as its leading term

$$\Delta X_L/X = (\tau^2/3\mu^2)\ln t \qquad [\mathbf{A7}]$$

where $1/\mu = e^t/(1+t)$. The other higher terms are obtained by recycling the first approximations to ψ'_j and f'_{ji} in the inhomogeneous terms of [**A3**]. They add up to a long and complicated function, much too long for reproduction here or for practical computations even on the electronic computer. Consequently, they were calculated explicitly as functions of t, summed, and then coefficients of *interpolating* polynomials were derived by the usual methods. The higher electrostatic terms in the relaxation field are

$$\mathrm{DB2} = 4\tau^2\,(\mathrm{FB2}) \qquad [\mathbf{A8}]$$

$$\mathrm{DB3} = (4\beta\tau^2/R)\,(\mathrm{FB3}) \qquad [\mathbf{A9}]$$

where

$$\begin{aligned}\mathrm{FB2} &= 0.0755 - 0.1089t + 0.0705t^2 \\ &\qquad - 0.0569t^3,\ 0 < t < 0.8 \qquad [\mathbf{A10}]\\ \mathrm{FB3} &= -0.08038 + 0.4760t - 1.232t^2 \\ &\qquad + 1.505t^3,\ 0 < t < 0.22 \qquad [\mathbf{A11}]\\ &= -0.07101 + 0.3388t - 0.5533t^2 \\ &\qquad + 0.3752t^3,\ 0.22 < t < 0.4 \qquad [\mathbf{A12}]\\ &= -0.05110 + 0.1940t - 0.1962t^2 \\ &\qquad + 0.0766t^3,\ 0.4 < t < 0.8 \qquad [\mathbf{A13}]\end{aligned}$$

These functions reproduce the explicit functions within 0.01% of Λ; their upper limit of validity ($t \simeq 0.8$) corresponds to concentrations above which the linearization of the basic Poisson–Boltzmann equation is no longer justifiable. This concentration is about $2 \times 10^{-7} D^3$ eq/l. The relaxation field is then

$$\mathrm{RX} = \Delta X_1/X + \Delta X_L/X + \mathrm{DB2} + \mathrm{DB3} \qquad [\mathbf{A14}]$$

The electrophoresis term $\Delta\Lambda_e$ is obtained by substituting the total force $\epsilon(X + \nabla\psi^\circ + \nabla\psi')$ into the Oseen equation (ref. 14, Eq. 7) and integrating. The leading term is

$$\Delta\Lambda_1 = -\beta_0 c^{1/2}\gamma^{1/2}/(1+t) \qquad [\mathbf{A15}]$$

where $\beta_0 = 82.5/\eta(DT)^{1/2}$ is the Onsager coefficient; a logarithmic term also appears, which when combined with the hydrodynamic part of the relaxation field gives

$$\Delta\Lambda_L = -\beta_0 c^{1/2}\gamma^{1/2}[(\tau/2\mu^2)\ln t] \qquad [\mathbf{A16}]$$

Interpolating polynomials were also computed for the algebraic terms of order c and higher; they are

$$\begin{aligned}\mathrm{H1} &= t(0.1248 - 0.10295t + 0.07925t^2 \\ &\qquad - 0.03031t^3),\ 0 < t < 0.8 \qquad [\mathbf{A17}]\\ \mathrm{H2} &= 2\tau(-0.0944 + 0.1174t - 0.2155t^2),\ 0 < t < 0.4 \qquad [\mathbf{A18}]\\ &= 2\tau(-0.08885 + 0.08461t - 0.16796t^2), \\ &\qquad 0.4 < t < 0.8 \qquad [\mathbf{A19}]\end{aligned}$$

giving for the total hydrodynamic terms

$$\begin{aligned}\mathrm{HY} = -\beta_0 c^{1/2}\gamma^{1/2}[1/(1+t) \\ + (\tau/2\mu^2)\ln t + \mathrm{H1} + \mathrm{H2}] \qquad [\mathbf{A20}]\end{aligned}$$

Conductance is then calculable by combining [**A14**] and [**A20**] with γ from the mass action Eq. [**3**] to give

$$\Lambda(c) = \gamma[\Lambda_0(1 + \mathrm{RX}) + \mathrm{HY}] \qquad [\mathbf{A21}]$$

A FORTRAN IV program (15) has been written for the following problem statement: Given, a set of conductance data (c_j, Λ_j, $j = 1, .., N$), Eqs. [**3**], [**4**], and [**A21**]; find the values of the parameters Λ_0, K_A and R which give a least-squares best fit to the data.

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