Statistical Mechanical Theory of the Effect of Added Nonelectrolytes on the Conductances of Electrolytes

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When a neutral nonelectrolyte is added to an electrolytic solution, the electrical conductance of the electrolytic solution is usually reduced. Attempts to correlate this effect with changes in the bulk properties of the solvent have been unsuccessful. The purpose of this paper is to account for this effect (for dilute solutions) in terms of a statistical mechanical theory which takes into account the specific interactions between molecules of the nonelectrolyte and ions of the electrolyte. A simple continuum model is used to represent the solution containing nonelectrolyte molecules and electrolyte ions placed in a constant, homogeneous electric field. With an approximate theory valid at infinite dilution, an equation describing the variation of the limiting equivalent conductance of the electrolyte with the concentration of an ideal dipolar nonelectrolyte is obtained. Comparisons with experiments are made.

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1. INTRODUCTION

When a neutral nonelectrolyte is added to an electrolytic solution, the electrical conductance of the electrolytic solution is usually reduced. Attempts to correlate this effect with changes in the bulk properties (for example, the increase in viscosity) of the solvent have been unsuccessful.[1-3] The purpose of this paper is to account for this effect (for dilute solutions) in terms of a statistical mechanical theory which takes into account the specific interactions between molecules of the nonelectrolyte and ions of the electrolyte. A simple continuum model is used to represent the solution containing nonelectrolyte molecules and electrolyte ions placed in a constant, homogeneous electric field. With an approximate theory valid at infinite dilution, an equation describing the variation of the *limiting equivalent conductance* of the electrolyte with the concentration of an ideal dipolar nonelectrolyte is obtained. The calculations are similar to those given by Onsager and Fuoss (see Ref. 4) in their theory of the conductance of electrolytes, and to those in the theory of the electrolytic transport of nonelectrolytes presented in a previous paper,[5] hereafter referred to as I. For the most part, the notations and previous results used here are those of I.

   In addition to the force due to the external electric field, three origins of translatory force acting on a reference ion are considered. The first, called the *relaxation force* (see Ref. 4, p. 123, and Ref. 5, pp. 4, 38, and 39), is due to the asymmetry which the external electric field produces in the distribution of nonelectrolyte molecules about the reference ion. Because of this asymmetry, the forces between the nonelectrolyte molecules and the reference ion are no longer in balance, and there is an average resultant translatory force on the ion. The second, called the *kinetic force* (see Ref. 6 and Ref. 5, pp. 86–91), is also due to the asymmetry in the distribution of nonelectrolyte molecules about the reference ion. However, this effect arises through an imbalance of collisions between the nonelectrolyte molecules and the ion; or, alternately, through an imbalance of the osmotic pressure on the reference ion. In order to obtain explicit expressions for these forces the *(nonelectrolyte molecule, electrolyte ion) pair configuration correlation function* is needed. This is assumed to consist of an equilibrium term of order zero in the external electric field (that is, of the canonical ensemble pair correlation function applicable to the system when not subjected to the external electric field) plus a first-order perturbation term proportional to the external electric field. This perturbation term is obtained by solving the equation of continuity in the (nonelectrolyte molecule, electrolyte ion) pair configuration space. The third and final force gives rise to the *electrophoretic velocity* (see Ref. 4, p. 156, and Ref. 5, pp. 92–94) of the reference ion. This velocity results from fluid motion in the neighborhood of the reference ion—it arises when

the solute particles being transported through the solution cause the fluid in the neighborhood of the reference ion to move with a velocity differing from that of the fluid as a whole. In determining this velocity, we assume that our model obeys Stokes' law.

As mentioned before, the calculations carried out in this paper are valid only at infinite dilution. In the equation for the limiting equivalent conductance of the electrolyte, terms linear in the nonelectrolyte concentration, but independent of the electrolyte concentration, appear. Indeed, we express the limiting equivalent conductance of the electrolyte (extrapolated to zero electrolyte concentration) at the fixed nonelectrolyte concentration $\mathscr{C}_0$ (in moles/liter) in the form

$$\Lambda_0^{(0)} = \Lambda^{(0)} + J\mathscr{C}_0$$

where $\Lambda^{(0)}$ is the limiting equivalent conductance of the electrolyte (extrapolated to zero electrolyte concentration) in the absence of added nonelectrolyte; and

$$J = \lim_{\mathscr{C}_0 \to 0} \frac{d\Lambda_0^{(0)}}{d\mathscr{C}_0} = \lim_{\substack{\mathscr{C} \to 0 \\ \mathscr{C}_0 \to 0}} \frac{d\Lambda}{d\mathscr{C}_0}$$

Here Λ is the equivalent conductance of the electrolyte and $\mathscr{C}$ is the concentration of the electrolyte (in moles/liter). The purpose of this paper, then, is to obtain a theoretical expression for the coefficient J.

Finally, comparisons with experiments are made.

2. A MODEL REPRESENTING THE SOLUTION

As stated in the introduction, a simple *continuum model* is used to represent the dilute solution containing nonelectrolyte molecules and electrolyte ions (see Ref. 5, pp. 96–100). Our classical fluid system is a dilute solution containing N solute molecules or ions dissolved in a solvent so that the total volume of the system is V. There are N_0 nonelectrolyte molecules (species o) and N_α electrolyte ions of species α, where α runs from 1 to σ.

The *solvent* is a structureless, viscous, incompressible dielectric continuum with dielectric constant ϵ and viscosity η.

The *nonelectrolyte molecules* are rigid spheres, large in comparison to the solvent molecules, each having radius b_0 and dielectric constant ϵ_0. Each such sphere has a zero net charge, and a possibly nonzero dipole moment (of magnitude μ_0) which we represent as a point or ideal dipole of moment μ_0 located at its center. The center of mass of each sphere is located at its center. The kinetic entity moving in the solvent is not necessarily the bare nonelectrolyte molecule of radius b_0; usually it is the nonelectrolyte molecule plus a number of adjacent solvent molecules. This entity is assumed to be a

sphere of radius $\mathscr{R}_o$, with $\mathscr{R}_o$ being called the hydrodynamic radius of the nonelectrolyte molecule (at infinite dilution). Finally, we let D_o be the translational diffusion coefficient of the nonelectrolyte molecule (at infinite dilution); and we let $D_o^{(rot)}$ be its rotational diffusion coefficient (also at infinite dilution).

The *electrolyte ions* are rigid spheres having nonzero net charges, having dielectric constants the same as that of the solvent, and having spherically symmetric charge and mass distributions. We let e_α be the charge of an ion of species α; we let b_α be its radius; we let $\mathscr{R}_\alpha$ be its hydrodynamic radius (at infinite dilution); and we let D_α be its translational diffusion coefficient (also at infinite dilution).

The very existence of a solution of nonelectrolyte molecules and electrolyte ions depends on their having finite closest distances of approach. Thus we let $a_{\alpha o}$ represent the *center-to-center distance of closest approach* of an ion of species α and a nonelectrolyte molecule of species o.

According to our picture of the solution, the various solute particles are rigid, charged spheres which interact with one another according to the laws of classicial electrostatics and classical mechanics. The nonelectrolyte molecules are assumed to be present at extremely low concentrations so that their mutual interactions can be neglected. The *forces operative between the nonelectrolyte molecules and the electrolyte ions* are the long-range ion–dipole electrostatic forces, the short-range ion–cavity electrostatic forces, which are respusive in nature, and possibly other (unspecified) short-range forces. In particular, the electrostatic contribution to the mutual potential energy of a nonelectrolyte molecule of species o in configuration $\mathbf{q}_o = (\mathbf{r}_o, \mathbf{R}_o)$ and of an electrolyte ion of species α in configuration $\mathbf{q}_\alpha = (\mathbf{r}_\alpha, \mathbf{R}_\alpha)$, as given by Eqs. (D10), (D15), (D12), and (D13) of I, is

$$V_{o\alpha}(\mathbf{q}_o, \mathbf{q}_\alpha) = V_{o\alpha}^{\mathrm{LR}}(\mathbf{q}_o, \mathbf{q}_\alpha) + V_{o\alpha}^{\mathrm{SR}}(\mathbf{q}_o, \mathbf{q}_\alpha) \tag{1}$$

where

$$V_{o\alpha}^{\mathrm{LR}}(\mathbf{q}_o, \mathbf{q}_\alpha) = \frac{3e_\alpha}{2\epsilon + \epsilon_o} \frac{1}{r_{\alpha o}^2} \boldsymbol{\mu}_o \cdot \mathbf{1}_{r_{\alpha o}}, \qquad r_{\alpha o} \geqslant a_{\alpha o} \tag{2}$$

is the potential of the long-range ion–dipole electrostatic force, and where

$$V_{o\alpha}^{\mathrm{SR}}(\mathbf{q}_o, \mathbf{q}_\alpha) = - \sum_{n=4}^{+\infty} d_{o\alpha,n} \left(\frac{a_{\alpha o}}{r_{\alpha o}}\right)^n, \qquad r_{\alpha o} \geqslant a_{\alpha o} \tag{3}$$

with

$$d_{o\alpha,n} = -e_\alpha^2 \frac{(n-2)(\epsilon - \epsilon_o)}{2\epsilon[n\epsilon + (n-2)\epsilon_o]} \frac{b_o^{n-1}}{a_{\alpha o}^n}, \qquad n \text{ even}$$

$$d_{o\alpha,n} = 0 \qquad\qquad\qquad\qquad\qquad\qquad\quad n \text{ odd} \tag{4}$$

represents a short-range ion–cavity repulsive force between the electrolyte ion and an image distribution in the spherical cavity of low dielectric

constant created by the nonelectrolyte molecule in the solvent. Of course, $\mathbf{r}_{\alpha o} = \mathbf{r}_\alpha - \mathbf{r}_o$ is the vector from the center of the nonelectrolyte molecule of species o to the center of the electrolyte ion of species α; the number $r_{\alpha o}$ is the length of the vector $\mathbf{r}_{\alpha o}$; and $\mathbf{1}_{r_{\alpha o}} = (1/r_{\alpha o})\mathbf{r}_{\alpha o}$ is the unit vector with the same direction as $\mathbf{r}_{\alpha o}$.

To account for the fact that the nonelectrolyte molecules and electrolyte ions are rigid spheres which do not interpenetrate one another, we define

$$V_{\alpha o}^{\mathrm{SR}}(\mathbf{q}_o, \mathbf{q}_\alpha) = +\infty, \qquad r_{\alpha o} < a_{\alpha o} \tag{5}$$

Finally, we recognize that other short-range forces may exist. In order to account for these, we can allow the constant coefficients $d_{o\alpha,n}$ in Eq. (3) to be parameters which may be determined by various experimental or theoretical methods.

3. EQUIVALENT IONIC CONDUCTANCES

When a solution containing an electrolyte is placed in a constant homogeneous electric field (a dc electric field with the constant homogeneous electric field intensity $\mathbf{E} = E\mathbf{k}$) and maintained at a constant uniform temperature T, the ions of the electrolyte undergo transport. Steady state motion is set up. The mean velocity of the ions of species α is denoted by $\mathbf{u}_\alpha$, and the macroscopic stream velocity of the whole fluid is denoted by $\mathbf{u}$. The relative mean velocity of the ions of species α, denoted by $\mathbf{u}_\alpha - \mathbf{u}$, is ordinarily assumed to be proportional to the electric field strength. The corresponding quantity (see Ref. 2, p. 43) which depends only on molecular and ionic parameters is the *equivalent ionic conductance* λ_α given (in units of cm² equiv⁻¹ ohm⁻¹) by

$$\lambda_\alpha = \frac{1}{299.79} \frac{e_\alpha}{|e_\alpha|} F \frac{\mathbf{u}_\alpha - \mathbf{u}}{\mathbf{E}} \tag{6}$$

where F is the Faraday (in units of C/equiv); e_α is the charge of an ion of species α (in electrostatic units); $\mathbf{E}$ is the electric field intensity (in electrostatic units); and $\mathbf{u}_\alpha - \mathbf{u}$ is the relative mean velocity of the ions of species α (in units of cm/sec).

It is the *equivalent conductance* Λ of the electrolyte, given by

$$\Lambda = \sum_{\alpha=1}^{\sigma} \lambda_\alpha \tag{7}$$

which is ordinarily determined from experimental data. With a fixed nonelectrolyte concentration, Λ is measured at a number of differing low electrolyte concentrations. Extrapolation to zero electrolyte concentration [hence the superscript (0)] gives the *limiting equivalent conductance* $\Lambda_o^{(0)}$ of the

electrolyte at the fixed nonelectrolyte concentration (the subscript o specifies the nonelectrolyte).

We must obtain a theoretical equation describing the variation of $\Lambda_o^{(0)}$ with the concentration of the nonelectrolyte for extremely small nonelectrolyte concentrations. Our task then is to obtain a theoretical expression for $\mathbf{u}_\alpha - \mathbf{u}$, and hence for λ_α, which shows explicitly its dependence on the nature of the electrolyte and on the nature and concentration of the added non-electrolyte.

The *relative mean velocity* of the ions of species α, as given by Eq. (114) of I, is

$$\mathbf{u}_\alpha(\mathbf{r}_\alpha) - \mathbf{u}(\mathbf{r}_\alpha) = \mathbf{v}_{|\alpha}(\mathbf{r}_\alpha|\mathbf{r}_\alpha) + \frac{D_\alpha}{kT}\left[\mathbf{F}_\alpha^{(1)}(\mathbf{r}_\alpha) + \mathbf{K}_\alpha^{(1)}(\mathbf{r}_\alpha)\right] \qquad (8)$$

Here $\mathbf{F}_\alpha^{(1)}(\mathbf{r}_\alpha)$ represents the force on a reference ion of species α at position $\mathbf{r}_\alpha$ due to the external field as well as the relaxation force on the ion [see Eq. (29) of I]; $\mathbf{K}_\alpha^{(1)}(\mathbf{r}_\alpha)$ represents the kinetic force on the reference ion [see Eq. (103) of I]; and, $\mathbf{v}_{|\alpha}(\mathbf{r}_\alpha|\mathbf{r}_\alpha) = \mathbf{u}_{|\alpha}(\mathbf{r}_\alpha|\mathbf{r}_\alpha) - \mathbf{u}(\mathbf{r}_\alpha)$ represents the electrophoretic velocity of the reference ion [see Eq. (107) of I]. Since the electric field is homogeneous, $\mathbf{u}_\alpha(\mathbf{r}_\alpha) - \mathbf{u}(\mathbf{r}_\alpha)$ and the various quantities in Eq. (8) do not depend on position, i.e., they are independent of absolute locations in the fluid.

4. AN APPROXIMATE THEORY VALID AT INFINITE DILUTION

Using the model described in Section 2, we now turn to the task of obtaining an approximate theoretical expression for the equivalent ionic conductance λ_α as given by Eqs. (6) and (8). The theory presented here will be valid only at infinite dilution, i.e., as the macroscopic number densities of the nonelectrolyte molecules and of the electrolyte ions approach zero. In particular, we shall restrict our attention to solutions in which: (1) the macroscopic number density of the nonelectrolyte molecules C_o is so low that we can neglect higher order terms in C_o relative to terms of order C_o, *and* intermolecular forces between nonelectrolyte molecules can be neglected; and (2) the macroscopic number densities of the electrolyte ions C_α, where $\alpha = 1,...,\sigma$, are so small that they can be neglected relative to unity (or relative to any nonzero term).

4.1. Pair Correlation Functions

In order to proceed further, we need an approximate expression for the *nonequilibrium oα-pair configuration correlation function* $g_{o\alpha}^{(2)}(\mathbf{q}_o; \mathbf{q}_\alpha)$, as defined by Eq. (43) of I. Using Eq. (44) of I, we write

$$g_{o\alpha}^{(2)}(\mathbf{q}_o; \mathbf{q}_\alpha) = g_{o\alpha}^{(2,0)}(\mathbf{q}_o; \mathbf{q}_\alpha) + g_{o\alpha}^{(2,1)}(\mathbf{q}_o; \mathbf{q}_\alpha) \qquad (9)$$

expressing $g_{o\alpha}^{(2)}(\mathbf{q}_o ; \mathbf{q}_\alpha)$ as the sum of an equilibrium term $g_{o\alpha}^{(2,0)}(\mathbf{q}_o ; \mathbf{q}_\alpha)$ of order zero in the external electric field E plus a first-order perturbation $g_{o\alpha}^{(2,1)}(\mathbf{q}_o ; \mathbf{q}_\alpha)$ proportional to E. As usual, we are neglecting terms of order E^2 relative to terms of order E. Here we shall *also* neglect terms of order C_o relative to unity—this being allowed so that we later retain only terms of order C_o and omit higher order terms in C_o.

When terms of order $1/N_o$ and $1/N_\alpha$, where $\alpha = 1,...,\sigma$, and terms of order C_o and C_α, where $\alpha = 1,...,\sigma$, are neglected relative to unity, the *equilibrium oα-pair configuration correlation function*, as given by Eq. (39) of I, is

$$g_{o\alpha}^{(2,0)}(\mathbf{q}_o ; \mathbf{q}_\alpha) = \exp[-(1/kT)V_{o\alpha}(\mathbf{q}_o, \mathbf{q}_\alpha)] \tag{10}$$

In other words, an expression for the potential of mean force which is valid at "infinite dilution" is $V_{o\alpha}(\mathbf{q}_o, \mathbf{q}_\alpha)$. In solvents of relatively high dielectric constant at ordinary temperatures, a satisfactory approximation [7] to $g_{o\alpha}^{(2,0)}(\mathbf{q}_o ; \mathbf{q}_\alpha)$ may be obtained by expanding the exponential expression of Eq. (10) and retaining terms up to order $(1/kT)^2$ only. In order to simplify our notation, we shall (often) omit the subscripts $o\alpha$ and αo and thus replace $a_{\alpha o}$, $r_{\alpha o}$, and $d_{o\alpha,n}$ by a, r, and d_n, respectively. From Equations (1)–(3) and (10) we thus have

$$g_{o\alpha}^{(2,0)}(\mathbf{q}_o ; \mathbf{q}_\alpha) = 1 + \sum_{n=4}^{+\infty} \frac{d_n}{kT} \left(\frac{a}{r}\right)^n + \frac{1}{2} \sum_{n,l=4}^{+\infty} \frac{d_n}{kT} \frac{d_l}{kT} \left(\frac{a}{r}\right)^{n+l} \tag{11}$$

$$- \frac{3e_\alpha}{(2\epsilon + \epsilon_o)kT} \frac{1}{r^2} \boldsymbol{\mu}_o \cdot \mathbf{1}_r$$

$$- \frac{3e_\alpha}{(2\epsilon + \epsilon_o)kT} \boldsymbol{\mu}_o \cdot \mathbf{1}_r \sum_{n=4}^{+\infty} \frac{d_n}{kT} \frac{a^n}{r^{n+2}}$$

$$+ \frac{9e_\alpha^2}{2(2\epsilon + \epsilon_o)^2(kT)^2} \frac{1}{r^4} \boldsymbol{\mu}_o \cdot \mathbf{1}_r \boldsymbol{\mu}_o \cdot \mathbf{1}_r$$

provided $r \geqslant a$.

Using the model which we described in Section 2 and the approximate equilibrium oα-pair configuration correlation function given by Eq. (11), Kirkwood [7] studied the influence of electrolytes on the activity coefficients of nonelectrolytes (salting out, Setchenow coefficients). This theory, which may be employed to test the applicability of our model and the validity of our approximations, is discussed in the appendix.

An approximate expression for the *nonequilibrium perturbation* to the *oα-pair configuration correlation function* $g_{o\alpha}^{(2,1)}(\mathbf{q}_o ; \mathbf{q}_\alpha)$ can be obtained by solving the approximate steady-state equation of continuity in oα-pair configuration space [see Eqs. (91), (123), and (131) of I] subject to the appropriate boundary conditions. These boundary conditions are: (1) no

interpenetration of the rigid spherical molecules or ions [see Eqs. (26), (48), (92), (124), and (134) of I]; and (2) no correlation at infinite separation of molecules or ions in the fluid [see Eqs. (46), (125), and (136) of I]. As in the equilibrium case, we neglect terms of order C_0 and C_α and terms of order $1/N_0$ and $1/N_\alpha$, where $\alpha = 1,..., \sigma$, relative to unity. Also, we retain only quadratic terms in $(1/kT)$. The resulting expression for $g_{0\alpha}^{(2,1)}(\mathbf{q}_0 ; \mathbf{q}_\alpha)$ as given by Eq. (152) of I is (see pp. 114–129 of I for all the details of these calculations)

$$g_{0\alpha}^{(2,1)}(\mathbf{q}_0 ; \mathbf{q}_\alpha)$$

$$= \left[-N^{(1)} \frac{1}{r^2} + \frac{D_\alpha e_\alpha}{(D_0 + D_\alpha)kT} \sum_{n=4}^{+\infty} \frac{d_n}{kT} \left(-\frac{1}{n-3} \frac{a^n}{r^{n-1}} \right. \right.$$

$$\left. \left. - \frac{n+1}{2(n+3)} \frac{a^{n+3}}{r^{n+2}} + \frac{1}{2} B_0^3 \frac{a^n}{r^{n+2}} \right) \right] \mathbf{E} \cdot \mathbf{1}_r$$

$$+ \left\{ Q^{(1)} \frac{1}{\omega r} e^{-\omega r} + \frac{3\epsilon}{(2\epsilon + \epsilon_0)kT} \left[1 + \sum_{n=4}^{+\infty} \frac{d_n}{kT} \left(\frac{a}{r} \right)^n \right] \right.$$

$$+ \frac{D_\alpha e_\alpha^2}{4(D_0 + D_\alpha)(2\epsilon + \epsilon_0)(kT)^2} \left[\frac{1}{r^4} (a^3 - 2B_0^3) + \frac{\omega^3 a^3}{4r} F(\omega r) \right] \right\} \mathbf{E} \cdot \boldsymbol{\mu}_0$$

$$+ \left\{ N^{(2)} \left(\frac{3}{\omega^3 r^3} + \frac{3}{\omega^2 r^2} + \frac{1}{\omega r} \right) e^{-\omega r} \right.$$

$$+ \frac{3D_\alpha e_\alpha^2}{(D_0 + D_\alpha)(2\epsilon + \epsilon_0)(kT)^2} \left[-\frac{3}{\omega^2 r^3} \right.$$

$$+ \frac{1}{r^4} \left(\frac{7}{16} a^3 - \frac{1}{2} B_0^3 \right) + \frac{1}{64} (3 + \omega^2 r^2) \frac{\omega a^3}{r^3} F(\omega r)$$

$$\left. \left. - \frac{3}{64} \frac{\omega^2 a^3}{r^2} F'(\omega r) \right] \right\} (\mathbf{E} \cdot \mathbf{1}_r \boldsymbol{\mu}_0 \cdot \mathbf{1}_r - \frac{1}{3} \mathbf{E} \cdot \boldsymbol{\mu}_0)$$

$$- \frac{9\epsilon e_\alpha}{(2\epsilon + \epsilon_0)^2 (kT)^2} \frac{1}{r^2} (\mathbf{E} \cdot \boldsymbol{\mu}_0 \boldsymbol{\mu}_0 \cdot \mathbf{1}_r - \frac{1}{3} \boldsymbol{\mu}_0^2 \mathbf{E} \cdot \mathbf{1}_r) \tag{12}$$

provided $r \geqslant a$. By definition,

$$\omega = \omega_{\alpha 0} = \left(\frac{2D_0^{(\text{rot})}}{D_0 + D_\alpha} \right)^{1/2} \tag{13}$$

(we will write $\omega_{\alpha 0}$ when we want to emphasize that ω depends on properties of the nonelectrolyte molecules of species o and the electrolyte ions of species α, in solution) and

$$B_0^3 = \frac{2(\epsilon - \epsilon_0)}{2\epsilon + \epsilon_0} b_0^3 \tag{14}$$

The constants of integration $N^{(1)}$, $N^{(2)}$, and $Q^{(1)}$ are given by

$$N^{(1)} = \frac{D_\alpha e_\alpha a^3}{2(D_o + D_\alpha)kT} \left[1 - \left(\frac{B_o}{a}\right)^3 - 3 \sum_{n=4}^{+\infty} \frac{d_n}{kT} \frac{n+1}{(n-3)(n+3)} \right] \tag{15}$$

$$+ \frac{3\epsilon e_\alpha \mu_o^2}{(2\epsilon + \epsilon_o)^2 (kT)^2}$$

$$Q^{(1)} = \frac{D_\alpha e_\alpha^2 \omega \exp(\omega a)}{(D_o + D_\alpha)(2\epsilon + \epsilon_o)(kT)^2 (1 + \omega a)}$$

$$\times [1 - \tfrac{1}{16}\omega^3 a^3 F(\omega a) + \tfrac{1}{16}\omega^4 a^4 F'(\omega a)]$$

$$N^{(2)} = \frac{3 D_\alpha e_\alpha^2 \omega \exp(\omega a)}{(D_o + D_\alpha)(2\epsilon + \epsilon_o)(kT)^2}$$

$$\times \frac{1 + \tfrac{7}{144}\omega^2 a^2 - \tfrac{1}{64}\omega^3 a^3 (1 + \tfrac{4}{9}\omega^2 a^2) F(\omega a) + \tfrac{1}{64}\omega^4 a^4 (1 + \tfrac{1}{9}\omega^2 a^2) F'(\omega a)}{1 + \omega a + \tfrac{4}{9}\omega^2 a^2 + \tfrac{1}{9}\omega^3 a^3}$$

Finally, the function $F(x)$ and its derivative $F'(x)$ are defined by

$$F(x) = -(2/x) + e^x \mathrm{Ei}(x) - e^{-x}\mathrm{Ei}(-x)$$
$$F'(x) = (2/x^2) + e^x \mathrm{Ei}(x) + e^{-x}\mathrm{Ei}(-x) \tag{16}$$

in terms of the exponential integrals

$$\mathrm{Ei}(x) = \int_x^{+\infty} \frac{1}{u} e^{-u}\, du, \qquad -\mathrm{Ei}(-x) = \int_{-\infty}^x \frac{1}{u} e^u\, du \tag{17}$$

By simply averaging over orientations of the nonelectrolyte molecule and of the electrolyte ion [see Eqs. (32), (49), (44), (130), and (153) of I], we obtain an approximate expression for the *nonequilibrium $o\alpha$-pair position correlation function*, namely

$$g_{o\alpha}^{(2)}(\mathbf{r}_o ; \mathbf{r}_\alpha) = g_{o\alpha}^{(2,0)}(r) + g_{o\alpha}^{(2,1)}(\mathbf{r}_o ; \mathbf{r}_\alpha) \tag{18}$$

where

$$g_{o\alpha}^{(2,0)}(r) = 1 + \sum_{n=4}^{+\infty} \frac{d_n}{kT} \left(\frac{a}{r}\right)^n + \frac{1}{2} \sum_{n,l=4}^{+\infty} \frac{d_n}{kT}\frac{d_l}{kT} \left(\frac{a}{r}\right)^{n+l}$$

$$+ \frac{3 e_\alpha^2 \mu_o^2}{2(2\epsilon + \epsilon_o)^2 (kT)^2} \frac{1}{r^4} \tag{19}$$

and

$$g_{o\alpha}^{(2,1)}(\mathbf{r}_o ; \mathbf{r}_\alpha) = \left[-N^{(1)}\frac{1}{r^2} + \frac{D_\alpha e_\alpha}{(D_o + D_\alpha)kT} \sum_{n=4}^{+\infty} \frac{d_n}{kT}\left(-\frac{1}{n-3}\frac{a^n}{r^{n-1}} \right. \right.$$

$$\left. \left. - \frac{n+1}{2(n+3)}\frac{a^{n+3}}{r^{n+2}} + \frac{1}{2}B_o^3 \frac{a^n}{r^{n+2}} \right) \right] \mathbf{E} \cdot \mathbf{1}_r \tag{20}$$

when $r \geqslant a$.

4.2. Relaxation Force

With intermolecular interactions assumed to be pair-additive, $F_\alpha^{(1)}(r_\alpha)$, which includes the force on the reference ion of species α at position r_α due to the external field as well as the *relaxation force* on that ion, is given by [see Eqs. (29), (44), (50), (51), and (53) of I]

$$F_\alpha^{(1)}(r_\alpha) = e_\alpha E + \frac{1}{64\pi^4} \sum_{\beta=1}^{\sigma} C_\beta \iint F_{\beta\alpha}(q_\beta, q_\alpha) g_{\alpha\beta}^{(2)}(q_\alpha; q_\beta) \, d^3R_\alpha \, d^6q_\beta$$

$$+ \frac{1}{64\pi^4} C_o \iint F_{o\alpha}(q_o, q_\alpha) g_{o\alpha}^{(2)}(q_\alpha; q_o) \, d^3R_\alpha \, d^6q_o \tag{21}$$

Since we are neglecting terms of order C_β, where $\beta = 1,..., \sigma$, relative to unity, only the first and last terms on the right-hand side of this equation will be retained.

The approximate αo-pair configuration correlation function $g_{\alpha o}^{(2)}(q_\alpha; q_o) = g_{o\alpha}^{(2)}(q_o; q_\alpha)$ is given by Eqs. (9), (11), and (12). The force $F_{o\alpha}(q_o, q_\alpha)$ on the reference ion of species α at position r_α due to the nonelectrolyte molecule of species o in configuration $q_o = (r_o, R_o)$ as given by Eqs. (D16) and (D30) of I is

$$F_{o\alpha}(q_o, q_\alpha) = -\nabla_r V_{o\alpha}(q_o, q_\alpha) + e_\alpha \frac{\epsilon - \epsilon_o}{2\epsilon + \epsilon_o} \frac{b_o^3}{r^3} (E - 3E \cdot 1_r 1_r)$$

$$= \left[\frac{9e_\alpha}{2\epsilon + \epsilon_o} \frac{1}{r^3} \mu_o \cdot 1_r - \sum_{n=4}^{+\infty} n d_n \frac{a^n}{r^{n+1}} \right] 1_r$$

$$- \left[\frac{3e_\alpha}{2\epsilon + \epsilon_o} \frac{1}{r^3} \right] \mu_o + e_\alpha \frac{\epsilon - \epsilon_o}{2\epsilon + \epsilon_o} \frac{b_o^3}{r^3} (E - 3E \cdot 1_r 1_r) \tag{22}$$

The last term is a force on the electrolyte ion of species α due to the external electric field E. It arises as a result of having a spherical cavity of low dielectric constant created by the nonelectrolyte molecule in the solvent. Here it is considered as being due to a dipole of moment $\mu_o^{(ind)} = [(\epsilon_o - \epsilon)/3] b_o^3 E$ induced in the nonelectrolyte molecule—hence it is included in $F_{o\alpha}(q_o, q_\alpha)$. Integration of Eq. (21), with terms of order E^2 neglected relative to terms of order E, yields the result

$$F_\alpha^{(1)}(r_\alpha) = e_\alpha E - \frac{\pi D_\alpha e_\alpha^3 \mu_o^2}{(D_o + D_\alpha)(2\epsilon + \epsilon_o)^2 (kT)^2 a} C_o E \left[\frac{B_o^3}{a^3} + G(\omega a) \right]$$

$$+ \frac{2\pi D_\alpha e_\alpha}{3(D_o + D_\alpha)} C_o E (a^3 - B_o^3) \sum_{n=4}^{+\infty} \frac{d_n}{kT}$$

$$+ \frac{4\pi\epsilon e_\alpha \mu_o^2}{(2\epsilon + \epsilon_o)^2 (kT)} C_o E \sum_{n=4}^{+\infty} \frac{d_n}{kT}$$

$$
-\frac{2\pi D_\alpha e_\alpha}{3(D_o + D_\alpha)}\, C_o \mathbf{E} a^3 \sum_{n=4}^{+\infty} \sum_{l=4}^{+\infty} \frac{d_n}{kT}\frac{d_l}{kT}\left[\frac{l}{(n+l)}\frac{B_o{}^3}{a^3}\right.
$$

$$
\left. -\frac{n^2(l-3) + n(l^2 - 6l - 3) - 6l}{(n+3)(n+l)(n+l-3)}\right] \tag{23}
$$

The function $G(x)$ is defined by

$$
G(x) = \frac{13 - 3x - \frac{13}{6}x^2 - \frac{7}{6}x^3 + \frac{1}{2}x^4 e^x \mathrm{Ei}(x)}{6 + 6x + \frac{8}{3}x^2 + \frac{2}{3}x^3} \tag{24}
$$

4.3. Kinetic Force

The *kinetic force* on the reference ion of species α at position $\mathbf{r}_\alpha$ is given by [see Eq. (103) of I]

$$
\mathbf{K}_\alpha^{(1)}(\mathbf{r}_\alpha) = -kT \sum_{\beta=1}^{\sigma} C_\beta \iint g_{\alpha\beta}^{(2)}(\mathbf{r}_\alpha ; \mathbf{r}_\alpha + \mathscr{R}_\alpha \mathbf{1}_{r_{\beta\alpha}}) \mathbf{1}_{r_{\beta\alpha}} \mathscr{R}_\alpha{}^2 \sin\theta_{\beta\alpha}\, d\theta_{\beta\alpha}\, d\phi_{\beta\alpha}
$$

$$
-kTC_o \iint g_{\alpha o}^{(2)}(\mathbf{r}_\alpha ; \mathbf{r}_\alpha + \mathscr{R}_\alpha \mathbf{1}_{r_{o\alpha}}) \mathbf{1}_{r_{o\alpha}} \mathscr{R}_\alpha{}^2 \sin\theta_{o\alpha}\, d\theta_{o\alpha}\, d\phi_{o\alpha} \tag{25}
$$

Since we are neglecting terms of order C_β, where $\beta = 1,..., \sigma$, relative to unity, only the last term on the right-hand side of this equation will be retained. The function

$$
g_{\alpha o}^{(2)}(\mathbf{r}_\alpha ; \mathbf{r}_\alpha + \mathscr{R}_\alpha \mathbf{1}_{r_{o\alpha}}) = g_{o\alpha}^{(2)}(\mathbf{r}_\alpha + \mathscr{R}_\alpha \mathbf{1}_{r_{o\alpha}} ; \mathbf{r}_\alpha)
$$

is given by Eqs. (18)–(20) when $\mathscr{R}_\alpha \geq a_{\alpha o}$; it vanishes when $\mathscr{R}_\alpha < a_{\alpha o}$. As in I (p. 132), we refine our model by identifying $\mathscr{R}_\alpha$ with $a_{\alpha o}$. Integration of Eq. (25) yields the result

$$
\mathbf{K}_\alpha^{(1)}(\mathbf{r}_\alpha) = -\frac{2\pi D_\alpha e_\alpha}{3(D_o + D_\alpha)}\, C_o \mathbf{E}(a^3 - B_o{}^3) - \frac{4\pi\epsilon e_\alpha \mu_o{}^2}{(2\epsilon + \epsilon_o)^2 kT}\, C_o \mathbf{E}
$$

$$
-\frac{2\pi D_\alpha e_\alpha}{3(D_o + D_\alpha)}\, C_o \mathbf{E} a^3 \sum_{n=4}^{+\infty} \frac{d_n}{kT}\left(\frac{n}{n+3} - \frac{B_o{}^3}{a^3}\right) \tag{26}
$$

4.4. Electrophoretic Velocity

The *electrophoretic velocity* of the reference ion of species α at position $\mathbf{r}_\alpha$ is given by [see Eq. (107) of I]

$$
\mathbf{v}_{l\alpha}(\mathbf{r}_\alpha | \mathbf{r}_\alpha) = \frac{1}{6\pi\eta}\, \mathbf{E} \sum_{\beta=1}^{\sigma} C_\beta e_\beta \int_{r_{\beta\alpha} = \mathscr{R}_\alpha}^{r_{\beta\alpha} = +\infty} \frac{1}{r_{\beta\alpha}}\, [g_{\alpha\beta}^{(2,0)}(r_{\beta\alpha}) - 1]\, d^3\mathbf{r}_{\beta\alpha}
$$

$$
+\frac{1}{6\pi\eta}\, \mathbf{E} C_o e_o \int_{r_{o\alpha} = \mathscr{R}_\alpha}^{r_{o\alpha} = +\infty} \frac{1}{r_{o\alpha}}\, [g_{\alpha o}^{(2,0)}(r_{o\alpha}) - 1]\, d^3\mathbf{r}_{o\alpha} \tag{27}
$$

Since the nonelectrolyte molecules have zero net charges ($e_o = 0$) and since we are neglecting the macroscopic number densities of the electrolyte ions C_β, where $\beta = 1,..., \sigma$, relative to unity, for the solutions considered here, motion of the electrolyte ions resulting from electrophoresis does not exist [see Eqs. (8), (23), and (26)]; i.e.,

$$\mathbf{v}_{|\alpha}(\mathbf{r}_\alpha|\mathbf{r}_\alpha) = 0 \tag{28}$$

4.5. Limiting Equivalent Ionic Conductances

From Eqs. (6), (8), (23), (26), and (28), the *limiting equivalent ionic conductance* of ionic species α in a dilute solution containing nonelectrolyte molecules of species o (hence the subscript o) extrapolated to zero electrolyte concentration [hence the superscript (0)] is (with the subscripts oα and αo now retained):

$$\lambda_{\alpha,\text{o}}^{(0)} = \lambda_\alpha^{(0)} + \lambda_{\alpha,\text{o}1}^{(0)} + \lambda_{\alpha,\text{o}2}^{(0)} + \lambda_{\alpha,\text{o}3}^{(0)} + \lambda_{\alpha,\text{o}4}^{(0)} \tag{29}$$

where

$$\lambda_\alpha^{(0)} = \frac{F}{299.79} |e_\alpha| \frac{D_\alpha}{kT}$$

$$\lambda_{\alpha,\text{o}1}^{(0)} = \frac{-2\pi D_\alpha}{3(D_\text{o} + D_\alpha)} (a_{\alpha\text{o}}^3 - B_\text{o}{}^3)\lambda_\alpha^{(0)}C_\text{o}$$

$$\lambda_{\alpha,\text{o}2}^{(0)} = \frac{-4\pi\epsilon\mu_\text{o}{}^2}{(2\epsilon + \epsilon_\text{o})^2 kT} \lambda_\alpha^{(0)}C_\text{o}$$

$$- \frac{\pi D_\alpha e_\alpha{}^2 \mu_\text{o}{}^2}{(D_\text{o} + D_\alpha)(2\epsilon + \epsilon_\text{o})^2(kT)^2 a_{\alpha\text{o}}} \left[\frac{B_\text{o}{}^3}{a_{\alpha\text{o}}^3} + G(\omega_{\alpha\text{o}}a_{\alpha\text{o}})\right]\lambda_\alpha^{(0)}C_\text{o}$$

$$\lambda_{\alpha,\text{o}3}^{(0)} = \frac{2\pi D_\alpha}{(D_\text{o}+D_\alpha)} a_{\alpha\text{o}}^3\lambda_\alpha^{(0)}C_\text{o} \sum_{n=4}^{+\infty} \frac{1}{n+3} \frac{d_{\text{o}\alpha,n}}{kT}$$

$$- \frac{2\pi D_\alpha}{3(D_\text{o}+D_\alpha)} a_{\alpha\text{o}}^3\lambda_\alpha^{(0)}C_\text{o} \sum_{n=4}^{+\infty}\sum_{l=4}^{+\infty} \frac{d_{\text{o}\alpha,n}}{kT}\frac{d_{\text{o}\alpha,l}}{kT}$$

$$\times \left\{\frac{l}{n+l}\frac{B_\text{o}{}^3}{a_{\alpha\text{o}}^3} - \frac{n^2(l-3) + n(l^2-6l-3) - 6l}{(n+l-3)(n+l)(n+3)}\right\}$$

$$\lambda_{\alpha,\text{o}4}^{(0)} = \frac{4\pi\epsilon\mu_\text{o}{}^2}{(2\epsilon + \epsilon_\text{o})^2 kT} \lambda_\alpha^{(0)}C_\text{o} \sum_{n=4}^{+\infty} \frac{d_{\text{o}\alpha,n}}{kT}$$

The first term, $\lambda_\alpha^{(0)}$, is the limiting equivalent conductance of ionic species α extrapolated to zero nonelectrolyte concentration as well as to zero electrolyte concentration. The remaining terms describe the variation of $\lambda_{\alpha,\text{o}}^{(0)}$ with the concentration of the nonelectrolyte in extremely dilute solutions. The second term, $\lambda_{\alpha,\text{o}1}^{(0)}$, is a kinetic or pressure term, and results from collisions of the

reference ion of species α with the nonelectrolyte molecules considered to be uncharged, rigid, dielectric spheres. This is perhaps the "obstruction-effect" discussed by Robinson and Stokes (see Ref. 2). The third term, $\lambda^{(0)}_{\alpha,02}$, results from the long-range electrostatic ion–dipole interactions between the reference ion and the nonelectrolyte molecules in its atmosphere. It consists of two parts: The first arises from the kinetic force, and the second arises from the relaxation force. The fourth term, $\lambda^{(0)}_{\alpha,03}$, results from the short-range forces between the reference ion and the nonelectrolyte molecules. It also consists of two parts: The first arises from both the relaxation force and the kinetic force, and the second arises from the relaxation force alone. Finally, the fifth term, $\lambda^{(0)}_{\alpha,04}$, is a cross term resulting from both the short-range forces and the long-range ion–dipole forces. It arises from the relaxation force.

When the only important short-range forces are the electrostatic ion–cavity repulsive (or attractive) forces between the electrolyte ions and their image distributions in the spherical cavities of low (or high) dielectric constant created by the nonelectrolyte molecules in the solvent, we can use for the coefficient $d_{o\alpha,n}$ the value given by Eq. (4). This yields the results

$$\lambda^{(0)}_{\alpha,03} = -\frac{\pi D_\alpha e_\alpha{}^2}{14(D_0 + D_\alpha)\epsilon kT}\frac{b_0{}^3}{a_{\alpha o}} K\left(\frac{b_0}{a_{\alpha o}}\right)\lambda^{(0)}_\alpha C_0$$

$$\lambda^{(0)}_{\alpha,04} = -\frac{\pi e_\alpha{}^2\mu_0{}^2}{(2\epsilon + \epsilon_0)^2(kT)^2}\frac{b_0{}^3}{a_{\alpha o}^4} L\left(\frac{b_0}{a_{\alpha o}}\right)\lambda^{(0)}_\alpha C_0 \tag{30}$$

Terms of order $(kT)^{-2}$ in $\lambda^{(0)}_{\alpha,03}$ resulting from the short-range forces have been neglected. The functions $K(x)$ and $L(x)$ are defined by the series

$$K(x) = \sum_{n=0}^{+\infty} \frac{14(n + 1)(\epsilon - \epsilon_0)}{(2n + 7)[(n + 2)\epsilon + (n + 1)\epsilon_0]} x^{2n}$$

$$L(x) = \sum_{n=0}^{+\infty} \frac{2(n + 1)(\epsilon - \epsilon_0)}{[(n + 2)\epsilon + (n + 1)\epsilon_0]} x^{2n} \tag{31}$$

Each of these series is absolutely convergent for $0 \leqslant x < 1$.

Upon neglecting the dielectric constant in the interior of the nonelectrolyte cavity ϵ_0 in relation to the much larger macroscopic dielectric constant of the solvent ϵ, we may write the above series in closed form, namely

$$K(x) = \sum_{n=0}^{+\infty} \frac{14(n + 1)}{(2n + 7)(n + 2)} x^{2n} \tag{32}$$

$$= \frac{14}{3x^4}\left[\left(1 + \frac{5}{2x^3}\right)\ln(1 + x) + \left(1 - \frac{5}{2x^3}\right)\ln(1 - x) - \frac{5}{x^2} - \frac{5}{3}\right]$$

$$L(x) = \sum_{n=0}^{+\infty} \frac{2(n + 1)}{n + 2} x^{2n} = \frac{2}{1 - x^2} + \frac{2}{x^2} + \frac{2}{x^4}\ln(1 + x)(1 - x)$$

This approximation was used by Kirkwood (see Ref. 7, p. 238). It is "generally believed" that the dielectric constant in the interior of organic molecules is about 2 (if it is even defined there?), whereas the dielectric constant of water is about 80.

Upon introducing $\mathscr{C}_0$, the concentration of the nonelectrolyte in (moles/liter), with μ_0 expressed in Debye units, b_0, $a_{\alpha 0}$, and B_0 in Angström units, D_0 and D_α in units of 10^{-6} cm^2/sec, and $D_0^{(\text{rot})}$ in units of 10^{10} sec^{-1}, Eq. (29) with $\lambda_{\alpha,03}^{(0)}$ and $\lambda_{\alpha,04}^{(0)}$ given by Eq. (30) reduces to

$$\lambda_{\alpha,0}^{(0)} = \lambda_\alpha^{(0)} + \lambda_{\alpha,01}^{(0)} + \lambda_{\alpha,02}^{(0)} + \lambda_{\alpha,03}^{(0)} + \lambda_{\alpha,04}^{(0)} \tag{33}$$

where

$$\lambda_{\alpha,01}^{(0)} = -\frac{(1.26159 \times 10^{-3})D_\alpha}{D_0 + D_\alpha}(a_{\alpha 0}^3 - B_0^3)\lambda_\alpha^{(0)}\mathscr{C}_0$$

$$\lambda_{\alpha,02}^{(0)} = -\frac{54.8414\epsilon\mu_0^2}{(2\epsilon + \epsilon_0)^2 T}\lambda_\alpha^{(0)}\mathscr{C}_0$$

$$-\frac{(2.29073 \times 10^6)D_\alpha z_\alpha^2 \mu_0^2}{(D_0 + D_\alpha)(2\epsilon + \epsilon_0)^2 T^2}\frac{1}{a_{\alpha 0}}\left[\frac{B_0^3}{a_{\alpha 0}^3} + G(\omega_{\alpha 0}a_{\alpha 0})\right]\lambda_\alpha^{(0)}\mathscr{C}_0$$

$$\lambda_{\alpha,03}^{(0)} = -\frac{22.5843 D_\alpha z_\alpha^2}{(D_0 + D_\alpha)\epsilon T}\frac{b_0^3}{a_{\alpha 0}}K\left(\frac{b_0}{a_{\alpha 0}}\right)\lambda_\alpha^{(0)}\mathscr{C}_0$$

$$\lambda_{\alpha,04}^{(0)} = -\frac{(2.29073 \times 10^6)z_\alpha^2 \mu_0^2}{(2\epsilon + \epsilon_0)^2 T^2}\frac{b_0^3}{a_{\alpha 0}^4}L\left(\frac{b_0}{a_{\alpha 0}}\right)\lambda_\alpha^{(0)}\mathscr{C}_0$$

Here, z_α is the valence of an ion of species α. When comparing this "theoretical result" with experiments we shall use for $K(x)$ and $L(x)$ the closed forms given by Eq. (32) in which ϵ_0 is neglected relative to ϵ.

4.6. Limiting Equivalent Conductances

From Eqs. (7) and (33), the limiting equivalent conductance of a strong electrolyte of two ionic species, called species α and species β, as a function of the nonelectrolyte concentration is

$$\Lambda_0^{(0)} = \lambda_{\alpha,0}^{(0)} + \lambda_{\beta,0}^{(0)} = \Lambda^{(0)} + J\mathscr{C}_0 \tag{34}$$

where $\Lambda^{(0)} = \lambda_\alpha^{(0)} + \lambda_\beta^{(0)}$ is the limiting equivalent conductance of the strong electrolyte in the pure solvent (0% nonelectrolyte by weight) and

$$J = (\lambda_{\alpha,0}^{(0)} - \lambda_\alpha^{(0)})/\mathscr{C}_0 + (\lambda_{\beta,0}^{(0)} - \lambda_\beta^{(0)})/\mathscr{C}_0 \tag{35}$$

is a constant whose theoretical value can be obtained from Eq. (33). Equation (34) is our "law" describing the variation of $\Lambda_0^{(0)}$ with the concentration of the nonelectrolyte.

5. COMPARISON OF THEORY WITH EXPERIMENTS

There have been a large number of experimental papers concerned with the conductances of electrolytes in mixed solvents.[8] Incidentally, for mixed solvents with two solvent species, we shall call the species present at the lower concentration the added nonelectrolyte and we shall call the other species the solvent. Unfortunately, in these experiments, the nonelectrolyte concentrations have been relatively high (0.2 mole/liter or higher). Nevertheless, we include here a comparison of our theory with some typical experimental results.

To facilitate comparisons with experiments, a program was written for a computer (IBM System/360 Model 75) using as input data T, ϵ, D_o, D_α, $D_o^{(rot)}$, μ_o, z_α, b_o, and b_α, and giving as output the values of the coefficients of $\lambda_\alpha^{(0)}\mathscr{C}_o$ in Eq. (33). It was assumed that $\epsilon_o = 2$, and also that $a_{\alpha o} = b_o + b_\alpha$. For the functions $K(x)$ and $L(x)$ the closed forms given by Eq. (32) were used. Finally, the exponential integral $Ei(x)$ appearing in the function $G(x)$ [see Eq. (24)] was approximated by the Laguerre–Gauss quadrature using the zeros and weight factors of the Laguerre polynomial of degree 15.[9]

5.1. Equivalent Conductances of Electrolytes in Mixtures of Acetonitrile and Triisopropanolamine Borate

Fuoss and Fabry[10] have measured the equivalent conductances of solutions of triisoamylbutylammonium tetraphenylboride, picrate, and iodide in mixtures of acetonitrile (MeCN) and triisopropanolamine borate

Table I. Experimental Limiting Equivalent Conductances of Electrolytes in Solutions of TPAB in MeCN at 25°C[a]

Electrolyte	$\mathscr{C}_o$	$\Lambda_o^{(0)}$
i-Am$_3$BuN$^+$ I$^-$	0	160.68
	0.4455	135.04
	1.159	98.81
	1.657	76.18
i-Am$_3$BuN$^+$ Pi$^-$	0	135.70
	0.433	115.00
	0.862	96.06
	1.467	72.33
i-Am$_3$BuN$^+$	0	116.26
BPh$_4$$^-$	0.4455	97.10
	1.159	69.90
	1.657	53.08

[a] $\mathscr{C}_o$ is the concentration of TPAB in moles/liter.

Table II. Properties of Electrolyte Ions in Acetonitrile at 25.00°C

Ion (α)	$\lambda_\alpha^{(0)}$	$D_\alpha \times 10^6$	b_α
$i\text{-Am}_3\text{BuN}^+$	58.0	15.44	5.20
I^-	102.1	27.18	2.17
Pi^-	77.0	20.50	3.48
BPh_4^-	58.1	15.47	4.20

(TPAB) at 25°C. They found that "initial addition of the highly polar borate decreases conductance due to ion–dipole interaction." Their results are summarized in Table I. We shall now test our theory against their experimental data. Of course MeCN is the solvent, and TPAB is the added non-electrolyte, henceforth called species o.

At 25.00°C the dielectric constant ϵ of acetonitrile[10] is 36.01. The dipole moment μ_o of TPAB is 8.00 Debye units.[10] The radius b_o of the TPAB molecule—as estimated by summing atomic increments and also from viscosity measurements—is 4.00 Å units. Using Stokes' laws [see Eqs. (73) and
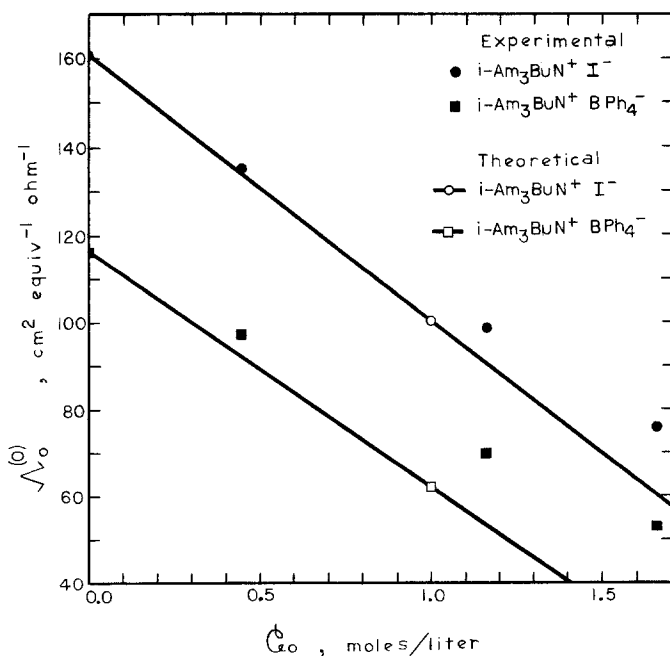

Fig. 1. The variations of the limiting equivalent conductances of electrolytes in acetonitrile solutions of TPAB at 25°C with the concentration of the TPAB. (Results for the picrate are not included so as to keep the figure uncluttered.)

Table III. Theoretical Limiting Equivalent Ionic Conductances in Acetonitrile Solutions of TPAB at 25°C

Ion (α)	$\dfrac{\lambda_{\alpha,01}^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$	$\lambda_{\alpha,02}^{(0)}/\lambda_\alpha^{(0)}\mathscr{C}_0$		$\dfrac{\lambda_{\alpha,03}^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$	$\dfrac{\lambda_{\alpha,04}^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$	$\dfrac{\lambda_{\alpha,0}^{(0)}-\lambda_\alpha^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$	$\dfrac{\lambda_{\alpha,0}^{(0)}-\lambda_\alpha^{(0)}}{\mathscr{C}_0}$
		Term 1	Term 2				
i-Am$_3$BuN$^+$	-0.44857	-0.077368	+0.00266613	-0.0089415	-0.0035470	-0.53576	-31.07
I$^-$	-0.14041	-0.077368	-0.017346	-0.023553	-0.027055	-0.28573	-29.17
Pi$^-$	-0.25613	-0.077368	-0.0038138	-0.014240	-0.0095821	-0.36114	-27.81
BPh$_4^-$	-0.30723	-0.077368	+0.00050869	-0.010679	-0.0060964	-0.40086	-23.29

Table IV. Theoretical Limiting Equivalent Conductances in Acetonitrile Solutions of TPAB at 25°C

Electrolyte	$\Lambda^{(0)}$	J	$\Lambda_0^{(0)} = \Lambda^{(0)} + J\mathscr{C}_0$
i-Am$_3$BuN$^+$ I$^-$	160.68	-60.24	$\Lambda_0^{(0)} = 160.68 - 60.24\mathscr{C}_0$
i-Am$_3$BuN$^+$ Pi$^-$	135.70	-58.88	$\Lambda_0^{(0)} = 135.70 - 58.88\mathscr{C}_0$
i-Am$_3$BuN$^+$ BPh$_4$$^-$	116.26	-54.36	$\Lambda_0^{(0)} = 116.26 - 54.36\mathscr{C}_0$

(81) of I] and noting that the viscosity η of acetonitrile at 25.00°C is 3.449 $\times$ 10^{-3} P,[11] the translational diffusion constant of TPAB is estimated to be $D_0 = 15.82 \times 10^{-6}$ cm^2/sec and its rotational diffusion coefficient is estimated to be $D_0^{(\mathrm{rot})} = 0.742 \times 10^{10}$ sec^{-1}.

Table II contains limiting equivalent conductances[12] and limiting translational diffusion constants for the ions i-Am$_3$BuN$^+$, I$^-$, Pi$^-$, and BPh$_4$$^-$ in acetonitrile at 25.00°C as well as ionic radii—either crystallographic radii or estimates based on molecular models. The diffusion constants were computed from the limiting ionic conductances with Eq. (29).

Tables III and IV summarize the computation of theoretical limiting equivalent conductances using Eqs. (33)–(35). Finally, in Fig. 1, the theoretical results from Table IV are compared with the experimental results of Table I.

5.2. Equivalent Conductances of Electrolytes in Mixtures of Glycine and Water

Justice and Fuoss[13] and Treiner and Justice (see Ref. 8, p. 838) have measured the conductances of solutions of potassium chloride and of

Table V. Experimental Limiting Equivalent Conductances of Electrolytes in Solutions of Glycine in Water at 25°C^a

Electrolyte	$\mathscr{C}_0$	$\Lambda_0^{(0)}$
K$^+$ Cl$^-$	0	149.85
	0.258	144.7
	0.475	140.8
	0.731	136.3
	0.918	133.0
	1.223	127.8
	1.477	123.4
(C$_4$H$_9$)$_4$N$^+$ Br$^-$	0	97.23
	0.3296	93.18
	0.7003	88.70
	1.2816	82.10

^{a} $\mathscr{C}_0$ is the concentration of glycine in moles/liter.

Table VI. Properties of Electrolyte Ions in Water at 25.00°C

Ion (α)	$\lambda_\alpha^{(0)}$	$D_\alpha \times 10^6$	b_α
K$^+$	73.50	19.568	1.331
Cl$^-$	76.35	20.327	1.806
(C$_4$H$_9$)$_4$N$^+$	19.47	5.183	4.94
Br$^-$	78.14	20.803	1.951

tetrabutylammonium bromide, respectively, in mixtures of glycine and water at 25°C. Their results are summarized in Table V.

At 25.00°C the dielectric constant ϵ of water is 78.303. The dipole moment μ_o of glycine is 15.5 Debye units (see Appendix J of I for this and other properties of glycine). The radius b_o of the glycine molecule—as estimated by summing atomic increments—is 2.40 Å units. The translational diffusion constant of glycine at 25°C is $D_o = 10.635 \times 10^{-6}$ cm^2/sec and its rotational diffusion coefficient at 25°C is $D_0^{(\text{rot})} = 1.02 \times 10^{10}$ sec^{-1}.

Table VI (see Appendix I of I) contains limiting equivalent conductances and limiting translational diffusion constants for the ions K$^+$, Cl$^-$, (C$_4$H$_9$)$_4$N$^+$, and Br$^-$ in water at 25.00°C, and also ionic radii.
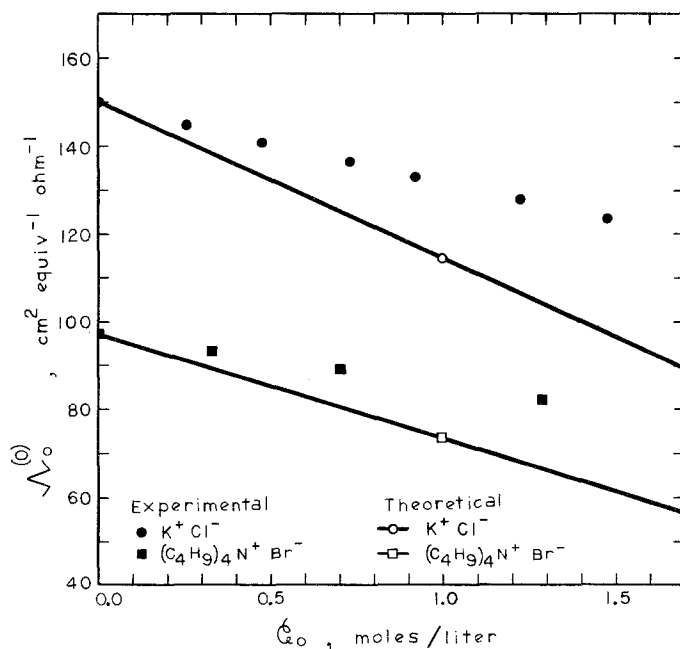

Fig. 2. The variations of the limiting equivalent conductances of electrolytes in solutions of glycine in water at 25°C with the concentration of the glycine.

Table VII. Theoretical Limiting Equivalent Ionic Conductances in Solutions of Glycine in Water at 25°C

Ion (α)	$\dfrac{\lambda_{\alpha,01}^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$	$\dfrac{\lambda_{\alpha,02}^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$		$\dfrac{\lambda_{\alpha,03}^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$	$\dfrac{\lambda_{\alpha,04}^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$	$\dfrac{\lambda_{\alpha,0}^{(0)}-\lambda_\alpha^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$	$\dfrac{\lambda_{\alpha,0}^{(0)}-\lambda_\alpha^{(0)}}{\mathscr{C}_0}$
		Term 1	Term 2				
K$^+$	-0.03158	-0.13755	-0.031718	-0.0039248	-0.035230	-0.24000	-17.64
Cl$^-$	-0.05061	-0.13755	-0.021255	-0.0030913	-0.018225	-0.23073	-17.62
(C$_4$H$_9$)$_4$N$^+$	-0.15797	-0.13755	$+0.00471138$	-0.0006704	-0.001362	-0.29284	-5.70
Br$^-$	-0.05766	-0.13755	-0.019037	-0.0029232	-0.015286	-0.23246	-18.16

Table VIII. Theoretical Limiting Equivalent Conductances in Solutions of Glycine in Water at 25°C

Electrolyte	$\Lambda^{(0)}$	J	$\Lambda_0^{(0)} = \Lambda^{(0)} + J\mathscr{C}_0$
$K^+ Cl^-$	149.85	-35.26	$\Lambda_0^{(0)} = 149.85 - 35.26\mathscr{C}_0$
$(C_4H_9)_4N^+ Br^-$	97.23	-23.86	$\Lambda_0^{(0)} = 97.23 - 23.86\mathscr{C}_0$

Tables VII and VIII summarize the computation of the theoretical limiting equivalent conductances. Finally, in Fig. 2, the theoretical results from Table VIII are compared with the experimental results of Table V.

5.3. Equivalent Ionic Conductances in Mixtures of Sucrose and Water

Stokes *et al.*[1,2] have determined the limiting equivalent conductances and the limiting transference numbers for a number of electrolytes in 10% (by weight) and 20% solutions of sucrose in water at 25°C. Their results are summarized in Table IX. In order to save space, this table also includes limiting equivalent ionic conductances in water at 25°C, limiting translational diffusion constants for ions in water at 25°C, and ionic radii. Incidentally, a 10% aqueous sucrose solution at 25°C has a sucrose concentration of 0.302 mole/liter; and a 20% solution has a sucrose concentration of 0.631 mole/liter.

Table IX. Experimental Limiting Equivalent Ionic Conductances in Solutions of Sucrose in Water at 25°C and Properties of Ions in Water at 25°C

Ion (α)	$\lambda_\alpha^{(0)}$ (0% Sucrose)	$\lambda_{\alpha,0}^{(0)}$ (10% Sucrose)	$\lambda_{\alpha,0}^{(0)}$ (20% Sucrose)	$D_\alpha \times 10^6$	b_α
Li^+	38.68	31.0	23.6	10.298	0.607
Na^+	50.10	40.6	31.1	13.338	0.958
K^+	73.50	59.7	46.1	19.568	1.331
Ag^+	61.90	49.5	37.6	16.480	1.26
Mg^{2+}	53.05	41.8	30.9	7.062	0.65
Ca^{2+}	59.50	46.8	34.8	7.920	0.99
La^{3+}	69.75	54.2	39.5	6.185	1.15
$(n\text{-}Am)_4N^+$	17.47	13.3	9.6	4.651	5.29
Cl^-	76.35	62.2	48.2	20.327	1.806
Br^-	78.14	63.1	48.4	20.803	1.951
I^-	76.84	61.2	46.4	20.457	2.168

Table X. Theoretical Limiting Equivalent Ionic Conductances in Solutions of Sucrose in Water at 25°C

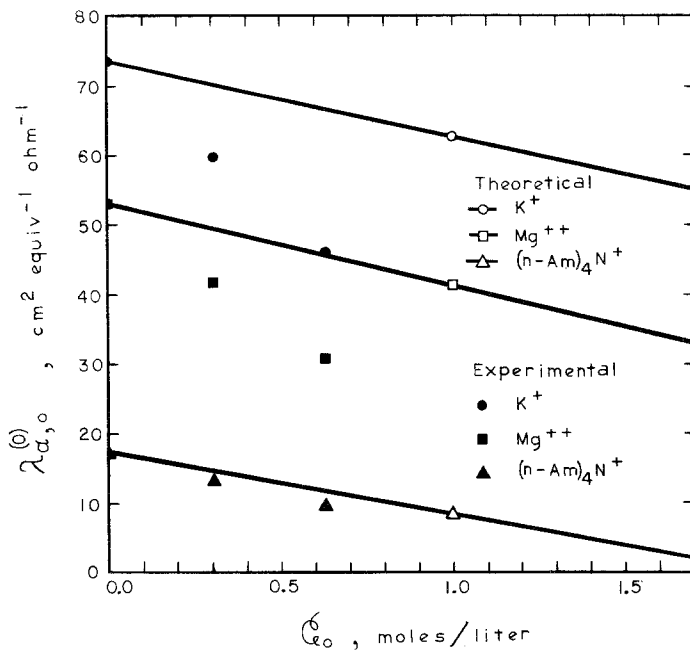| Ion (α)	$\dfrac{\lambda_{\alpha,01}^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$	$\lambda_{\alpha,02}^{(0)}/\lambda_\alpha^{(0)}\mathscr{C}_0$		$\dfrac{\lambda_{\alpha,03}^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$	$\dfrac{\lambda_{\alpha,04}^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$	$\dfrac{\lambda_{\alpha,0}^{(0)}-\lambda_\alpha^{(0)}}{\lambda_\alpha^{(0)}\mathscr{C}_0}$	$\dfrac{\lambda_{\alpha,0}^{(0)}-\lambda_\alpha^{(0)}}{\mathscr{C}_0}$
		Term 1	Term 2				
Li^+	-0.03810	-0.0051528	-0.0016436	-0.043217	-0.008090	-0.096199	-3.72
Na^+	-0.06790	-0.0051528	-0.0015487	-0.033154	-0.004032	-0.11179	-5.60
K^+	-0.11010	-0.0051528	-0.0015661	-0.028074	-0.002325	-0.14722	-10.82
Ag^+	-0.09906	-0.0051528	-0.0014818	-0.028220	-0.002556	-0.13648	-8.45
Mg^{2+}	-0.03546	-0.0051528	-0.0050643	-0.14242	-0.029280	-0.21738	-11.53
Ca^{2+}	-0.05913	-0.0051528	-0.0044022	-0.10839	-0.015294	-0.19236	-11.44
La^{3+}	-0.06338	-0.0051528	-0.0074947	-0.19500	-0.026874	-0.29790	-20.78
$(n\text{-}Am)_4N^+$	-0.50534	-0.0051528	+0.0000352	-0.005392	-0.000125	-0.51597	-9.01
Cl^-	-0.16367	-0.0051528	-0.0012810	-0.022096	-0.001335	-0.19353	-14.78
Br^-	-0.18228	-0.0051528	-0.0012167	-0.020840	-0.001152	-0.21064	-16.46
I^-	-0.20982	-0.0051528	-0.0010960	-0.019047	-0.000937	-0.23605	-18.14

Fig. 3. The variations of the limiting equivalent ionic conductances in solutions of sucrose in water at 25°C with the concentration of the sucrose. (Only the results for the ions K^+, Mg^{2+}, and $(n\text{-}Am)_4N^+$ are shown.)

The dipole moment μ_0 of sucrose is 3 Debye units, and the radius b_0 of the sucrose molecule is 4.5 Å units (see Appendix J of I). Its translational diffusion coefficient in water at 25°C is[14] $D_0 = 5.226 \times 10^{-6}\,cm^2/sec$; and from Stokes' law we estimate that its rotational diffusion coefficient in water at 25°C is $D_0^{(\text{rot})} = 0.1783 \times 10^{10}\,sec^{-1}$.

Table X summarizes the computation of the theoretical limiting equivalent ionic conductances. Finally, in Fig. 3, the theoretical results from Table X are compared with the experimental results of Table IX.

5.4. Concluding Remark

Agreement between theory and experiments is not impressive (this is clear from the graphs). In those cases for which agreement is good, this may be fortuitous. Nevertheless, the work done here is one which needed to be done so as to push forward the study of the conductances of electrolytes in mixed solvents.[15] Final judgment on the applicability of our simple model and on the validity of our approximate theory must await further measurements, at higher dilutions (lower nonelectrolyte concentrations), on

systems which one would expect to be most amenable to representation by our model.

APPENDIX. INFLUENCE OF ELECTROLYTES ON THE ACTIVITY COEFFICIENTS OF NONELECTROLYTES

Using the model which we have described in Section 2, Kirkwood[7] obtained a "limiting law"—valid at infinite dilution—relating the activity coefficient of the nonelectrolyte to the concentrations of the solute species. We shall summarize his results. On the one hand, this theory may be employed to test the applicability of our model and the validity of (some of) our approximations, and on the other, to determine structural parameters and information about the forces between ions and neutral molecules in solution.

The activity coefficient γ_0 of the nonelectrolyte component of the solution is defined by the equations

$$\mu_0 = \mu_0^*(T, p) + RT \ln (\gamma_0 \mathscr{C}_0) \tag{A.1}$$

$$\mu_0^*(T, p) = \lim_{\substack{\mathscr{C}_\alpha \to 0 \\ \alpha = 1, \ldots, \sigma}} (\mu_0 - RT \ln \mathscr{C}_0) \tag{A.2}$$

where μ_0 is the chemical potential of the nonelectrolyte species, $\mathscr{C}_0$ is its molar concentration, and $\mathscr{C}_\alpha$ is the molar concentration of the ionic species α.

Kirkwood has shown that with the solvent idealized as a structureless dielectric continuum a "limiting law" for the logarithm of the activity coefficient is

$$\ln \gamma_0 = \sum_{\alpha=1}^{\sigma} B_{0\alpha} \mathscr{C}_\alpha \tag{A.3}$$

with

$$B_{0\alpha} = \frac{N_A}{1000} \int_{r_{\alpha o} = a_{\alpha o}}^{r_{\alpha o} = +\infty} [1 - g_{0\alpha}^{(2,0)}(\mathbf{q}_0 ; \mathbf{q}_\alpha)] \, d^3 \mathbf{r}_{\alpha o}$$

where N_A is the Avogadro number.

For an ideal dipolar nonelectrolyte $g_{0\alpha}^{(2,0)}(\mathbf{q}_0 ; \mathbf{q}_\alpha)$ is given (approximately) by Eq. (11) so $B_{0\alpha}$ becomes (with the subscripts αo and $o\alpha$ retained):

$$B_{0\alpha} = -\frac{4\pi N_A}{1000} \left[a_{\alpha o}^3 \sum_{n=4}^{+\infty} \frac{1}{n-3} \frac{d_{0\alpha,n}}{kT} \right.$$
$$+ \frac{1}{2} a_{\alpha o}^3 \sum_{n=4}^{+\infty} \sum_{l=4}^{+\infty} \frac{1}{(n+l-3)} \frac{d_{0\alpha,n}}{kT} \frac{d_{0\alpha,l}}{kT}$$
$$\left. + \frac{3 e_\alpha^2 \mu_0^2}{2(2\epsilon + \epsilon_0)^2 (kT)^2} \frac{1}{a_{\alpha o}} \right] \tag{A.4}$$

where μ_0 is the dipole moment (magnitude) of the nonelectrolyte molecule.

When the only important short-range forces are the electrostatic ion–cavity repulsive forces between the electrolyte ions and their image distributions in the spherical cavities of low dielectric constant created by the nonelectrolyte molecules in the solvent, we can use for $d_{o\alpha,n}$ the value given in Eq. (4) and obtain the result

$$B_{o\alpha} = -\frac{2\pi N_A e_\alpha^2}{1000\epsilon kT} \left[\frac{3\epsilon\mu_0^2}{(2\epsilon + \epsilon_0)^2 kT} \frac{1}{a_{\alpha o}} - \frac{1}{2} \frac{b_0^3}{a_{\alpha o}} M\left(\frac{b_0}{a_{\alpha o}}\right) \right] \qquad \text{(A.5)}$$

where $M(x)$ is defined by the series

$$M(x) = \sum_{n=0}^{+\infty} \frac{2(n+1)}{2n+1} \frac{\epsilon - \epsilon_0}{(n+2)\epsilon + (n+1)\epsilon_0} x^{2n} \qquad \text{(A.6)}$$

In Eq. (A.5) we have neglected terms of order $(kT)^{-2}$ resulting from short-range forces. If we now neglect terms of order ϵ_0 relative to terms of order ϵ, we have
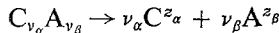
$$M(x) = \sum_{n=0}^{+\infty} \frac{2(n+1)}{(2n+1)(n+2)} x^{2n}$$

$$= \frac{1}{3x^4} [(x^3 - 2)\ln(1 + x) - (x^3 + 2)\ln(1 - x) - 2x^2] \qquad \text{(A.7)}$$

From Eqs. (A.5) and (A.3), the logarithm of the activity coefficient is

$$\log_{10} \gamma_0 = -\frac{2\pi N_A e^2}{2303\epsilon kT} \left[\frac{3\mu_0^2}{4\epsilon kT} \sum_{\alpha=1}^{\sigma} \frac{\mathscr{C}_\alpha z_\alpha^2}{a_{\alpha o}} - \frac{1}{2} b_0^3 \sum_{\alpha=1}^{\sigma} \frac{\mathscr{C}_\alpha z_\alpha^2}{a_{\alpha o}} M\left(\frac{b_0}{a_{\alpha o}}\right) \right]$$

$$\qquad \text{(A.8)}$$

where e is the protonic charge.

For a strong electrolyte $C_{\nu_\alpha} A_{\nu_\beta}$ of two ionic species C^{z_α} and A^{z_β} which is completely dissociated,

$$C_{\nu_\alpha} A_{\nu_\beta} \rightarrow \nu_\alpha C^{z_\alpha} + \nu_\beta A^{z_\beta}$$

we can write $\mathscr{C}_\alpha = \nu_\alpha \mathscr{C}$ and $\mathscr{C}_\beta = \nu_\beta \mathscr{C}$, where $\mathscr{C}$ is the molar concentration of the electrolyte. Consequently,

$$\lim_{\substack{\mathscr{C} \to 0 \\ \mathscr{C}_0 \to 0}} \frac{\partial(\log_{10} \gamma_0)}{\partial \mathscr{C}} = -\frac{3\pi N_A e^2 \mu_0^2}{4606(\epsilon kT)^2} \left(\frac{\nu_\alpha z_\alpha^2}{a_{\alpha o}} + \frac{\nu_\beta z_\beta^2}{a_{\beta o}} \right)$$

$$+ \frac{\pi N_A e^2 b_0^3}{2303\epsilon kT} \left[\frac{\nu_\alpha z_\alpha^2}{a_{\alpha o}} M\left(\frac{b_0}{a_{\alpha o}}\right) + \frac{\nu_\beta z_\beta^2}{a_{\beta o}} M\left(\frac{b_0}{a_{\beta o}}\right) \right] \qquad \text{(A.9)}$$

Finally, for water as the solvent at 25°C, this becomes

$$\lim_{\substack{\mathscr{C}\to 0 \\ \mathscr{C}_0\to 0}} \frac{\partial(\log_{10}\gamma_0)}{\partial\mathscr{C}} = -2.74 \times 10^{-3}\mu_0{}^2\left(\frac{\nu_\alpha z_\alpha{}^2}{a_{\alpha o}} + \frac{\nu_\beta z_\beta{}^2}{a_{\beta o}}\right)$$

$$+ 5.88 \times 10^{-3}b_0{}^3\left[\frac{\nu_\alpha z_\alpha{}^2}{a_{\alpha o}}M\left(\frac{b_0}{a_{\alpha o}}\right)\right.$$

$$\left.+ \frac{\nu_\beta z_\beta{}^2}{a_{\beta o}}M\left(\frac{b_0}{a_{\beta o}}\right)\right] \tag{A.10}$$

with μ_0 expressed in Debye units, and b_0, $a_{\alpha o}$, and $a_{\beta o}$ in Angström units.

System: Glycine–KCl–Water

For glycine and KCl in water at 25°C, Roberts and Kirkwood[16] found that

$$\lim_{\substack{\mathscr{C}\to 0 \\ \mathscr{C}_0\to 0}} \frac{\partial(\log_{10}\gamma_0)}{\partial\mathscr{C}} = -0.1794$$

Using α for the ionic species K^+ and β for Cl^- and letting $b_0 = 2.40$, $a_{\alpha o} = b_0 + b_\alpha = 2.40 + 1.331 = 3.731$, and $a_{\beta o} = b_0 + b_\beta = 2.40 + 1.806 = 4.206$, we find from Eq. (A.10) $\mu_0 = 12.9$ for glycine. This is close to the value 14.4 based on structural considerations.[17] Our model seems to be adequate in this case.

System: Mannitol–NaCl–Water

For mannitol and NaCl in water at 25°C Kelly et al.[18] found that

$$\lim_{\substack{\mathscr{C}\to 0 \\ \mathscr{C}_0\to 0}} \frac{\partial(\log_{10}\gamma_0)}{\partial\mathscr{C}} = -0.00632$$

Using α for the ionic species Na^+ and β for Cl^- and letting $b_0 = 4.0$, $a_{\alpha o} = b_0 + b_\alpha = 4.0 + 0.958 = 4.958$, and $a_{\beta o} = b_0 + b_\beta = 4.0 + 1.806 = 5.806$, we find from Eq. (A.10) $\mu_0 = 14.3$ for mannitol. This is far too large. The dipole moment of mannitol is about 4 (see I, p. 201). Doubt is cast on the use of our model to represent mannitol. Since the sucrose molecule is about the same size as the mannitol molecule (see I, p. 204) and has about the same dipole moment (see I, p. 201) and since conductance measurements for electrolytes in mannitol solutions are similar to those for electrolytes in sucrose solutions,[19] doubt is also cast on the use of our model to represent sucrose.

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