PROPERTIES OF ELECTROLYTIC SOLUTIONS[1]

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I. INTRODUCTION

The most general problem in the theory of solutions may be formulated as follows: Given a homogeneous mixture of several substances of known chemical composition, what are the properties of the solution as functions of temperature, pressure, concentration, and parameters describing external forces? The phrase "of known composition" implies, of course, that parameters characteristic of the various components will appear in the final result. In principle, these should be reducible to atomic and molecular constants. It is, in general, possible to express any property as a function of any variable by means of empirical equations based on accurate experimental data, but, while such a result serves to correlate measurements on various phenomena, it may not be considered as a solution of the problem. A satisfactory solution of the problem will be one in which all constants have an assignable physical significance (which may perhaps be fictitious; we must, however, require at least a one to one correspondence between model and fact), and in which the mathematical form of the functions is predicted on the basis of reasonable theoretical arguments.

It is the purpose of the present paper to consider a very restricted phase of the general problem,—the properties of dilute solutions of binary electrolytes. Unsymmetrical electrolytes are excluded for the sake of mathematical simplicity. Furthermore, those electrolytes which form true neutral molecules by electron rearrangement of the constituent ions after contact are excluded from discussion, because so little is known of their properties. (It is true that weak acids, for example, have been extensively investigated in aqueous solution, but these represent too special a case to permit generalization.)

Among the various measurable properties of electrolytic solutions, the conductance is probably the one which can be measured with the highest precision over the widest range of all of the physical variables. For

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[1] This paper was read at the Ninetieth Meeting of the American Chemical Society, at San Francisco, August 20, 1935, on the occasion of the presentation of the American Chemical Society Award in Pure Chemistry for 1935.

practical purposes, therefore, we shall base most of our examples and arguments on conductance data. One fundamental difference between conductance and thermodynamic properties should perhaps be emphasized; the former represents an irreversible process, while the latter are (or at least, should be) measured by means of reversible processes. A satisfactory theory of electrolytes must be able to account for both types; unfortunately, very few data on thermodynamic properties of electrolytes in non-aqueous solvents are available at present for comparison with theory, and again the abundance of data on aqueous solutions has served primarily to obscure the general problem, inasmuch as conclusions based on a special limiting case (solvent of high dielectric constant) cannot be extrapolated into regions where entirely different microscopic phenomena appear.

On the basis of well-known general principles, it is possible to derive all of the properties of a solution from its free energy and this, in turn, by means of the phase integral, from the total energy which is the sum of the individual energies of the solute particles. These energies depend, finally, on the relative positions of the solute particles, so that the problem resolves itself fundamentally into the question of the relative location of the ions, assuming, of course, that we know the laws of force as a function of distance. The actual solution of the problem directly through the phase integral[2] involves a number of mathematical difficulties, most of which are yet to be overcome. It is possible, however, to obtain an approximate solution of the problem by considering the distribution of the ions in an electrolytic solution, and then treating various ions in different ways, according to the relative magnitudes of the terms in the total energy of each ion. This approximate treatment will be the subject of the present paper; the distribution of ions in solution will be investigated and it will be shown that it is possible to split interionic effects into long and short range interactions. The former may be treated by the time average method of Debye and Hückel (5) and the latter by the formal methods of dissociation theory. Based on these results, equations will be derived which quantitatively reproduce experimental data on conductance for dilute solutions of ordinary electrolytes in all solvents so far investigated. Various limitations to the treatment will be pointed out.

II. IONIC DISTRIBUTION

Any theoretical calculation of physical properties meets at the very beginning the necessity for a series of arbitrary assumptions, because an

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[2] Kirkwood (19) has presented a very careful analysis of the problem for the case of strong electrolytes and has suggested, in section IV of his paper, an alternative to the method presented here for handling association.

idealized and simplified model must be chosen to represent the actual physical system under consideration. Inevitably, parameters with the dimensions of distance appear; within certain limits, we may ascribe to them the nature of molecular dimensions, but as a matter of fact, they represent the dimensions of a fictitious particle in a hypothetical medium, the two so chosen that the idealized system will duplicate the properties of the real system when a given variable is changed. For the present discussion, we shall use the conventional model: the ions are assumed to be uniformly charged spheres (charges $\pm\epsilon$) of diameter a in a homogeneous medium which is completely described electrically by its macroscopic dielectric constant and hydrodynamically by its macroscopic viscosity. Interaction between solvent and solute is excluded; solvation, which may mean actual complex ion formation, or simply electrostatic dipole saturation, is absorbed in the assumption that the size of the ion in solution may be larger than that of the lattice ion. The dielectric constant is assumed to be a true constant, although the effective dielectric constant between two real ions at short distances is presumably much smaller than D, the macroscopic dielectric constant.[3] Furthermore, the ion is assumed to be rigid mechanically and also unpolarizable, so that all forces of repulsion are approximated by a potential which becomes positively infinite at $r = a$. Electron rearrangement is completely neglected in this model, and quantized bonds are, of course, entirely excluded from discussion. The assumption of spherical symmetry of charge distribution in the model is also a special restriction.[4]

These and other recognized imperfections of the model described above may, in principle at least, be eliminated by more elaborate mathematical methods, but for the present we shall use the simple model.

We consider then a solution containing N ions of charge $+\epsilon$ and N ions of charge $-\epsilon$ in a total volume V. The contribution to the free energy due to electrostatic forces is given by the equation

$$e^{-F/kT} = V^{-2N} \int \cdots \int e^{-E/kT} (\mathrm{d}V)^{2N} \tag{1}$$

where the total electrostatic potential energy may be written

$$E = \tfrac{1}{2} \sum_{ij}{}' u_{ij} \tag{2}$$

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[3] Very interesting and suggestive results are obtained by setting $D = D(r)$, where r is the distance between two ions. The function $D(r)$ is probably an S-function, which may be approximated by a step function: $D(r) = 1$, $a \leqslant r \leqslant a + a'$; $D(r) = n^2$, $a + a' \leqslant r \leqslant d$; $D(r) = D$, $d \leqslant r < \infty$, where d is a distance equal in order of magnitude to the distance from an ion at which a solvent dipole of strength μ has an even chance of assuming a random orientation, i.e., where $\epsilon\mu/r^2D(r)kT = 1$.

[4] Kirkwood (18) has discussed a model in which the ionic charge distribution is arbitrary, and has applied his results to the case of zwitterions.

if u_{ij} represents the mutual energies of ions i and j. For the i^{th} ion, we have as its total potential energy

$$E_i = u_{i1} + u_{i2} + \cdots + u_{i,\,i-1} + u_{i,\,i+1} + \cdots + u_{i,\,2N} \tag{3}$$

Now many terms of E_i may be entirely negligible compared to kT, because

$$u_{ij} = \epsilon_i \epsilon_j / D r_{ij} \tag{4}$$

and r_{ij} has as its maximum value a distance of the order of $V^{\frac{1}{3}}$. In fact, u_{ij} will converge to zero much faster than $1/r$, because, if we anticipate somewhat, the electrostatic screening due to ions between i and j, when $r_{ij} \gg a$, will lead to a potential

$$\psi_i = \epsilon_i e^{-\kappa r} / Dr \tag{5}$$

around the i^{th} ion, thus multiplying the Coulomb $1/r$ potential by a negative exponential. For practical purposes, we could approximate the sum (equation 3) very closely by neglecting all terms u_{ij} for which r_{ij} was greater than say six or a dozen times $1/\kappa$. Now in the remaining terms, we may expect to find several relative orders of terms. If no particular ion j happened to be near (i.e., $r \approx a$) ion i in the configuration selected, many of the terms u_{ij} would be of equal magnitude, although smaller than kT. On the other hand, we might find one particular ion $j = k$, such that $r_{ik} \approx a$, in which case u_{ik} would be much larger than all the other terms of E_i. This term would then control the contribution of ion i to F. Another case would be when two ions l and m were near i, so that $(u_{il} + u_{im})$ would make up the main contribution to E_i. Even in the first case (many u_{ij}'s approximately equal), we should be able to select one term which was larger than the others, although perhaps only infinitesimally so. We are thus led to seek a classification of the ions which will permit an ordering of their energies in sequences, such that the largest term (which may also be the leading term) of E_i can be selected.

Let us consider a particular instantaneous configuration of the ions in the total volume V, which temporarily will be chosen so large that groups containing three ions at distances of the order of a will be negligibly rare. Let each positive ion be surrounded by a concentric sphere of radius $a/2$, and then let all the spheres expand at a uniform rate, until a distance of the order of $V^{\frac{1}{3}}$ is reached. As soon as the sphere for a given positive ion cuts the center of a negative ion, we shall count these two ions as a pair, provided that the negative ion has not already been counted at some smaller distance as the partner of some other positive ion. In this way, we are able to assign a unique partner to each positive ion, namely, that negative ion which is nearest to the central ion, provided that the former ion is not nearer to some other positive ion than to the reference positive ion. If the nearest ion has already been assigned to a partner, then the next nearest is counted, and so on. We may define an ion pair of this type as follows: a positive ion and a negative ion, the center of which lies in dr at a distance r from the positive ion are counted as an ion pair, provided that no other unpaired negative ion lies within a sphere of radius r drawn around the positive ion (7).

The probability $G(r)\mathrm{d}r$ for such a configuration is proportional to $4\pi r^2\mathrm{d}r/V$, the ratio to the total volume of the volume which is to contain the partner ion; to N, the total number of negative ions present; to the Boltzmann factor, exp (ϵ^2/DkT); and to the probability $f(r)$ that an unpaired ion is not already in the sphere $4\pi r^3/3$. The chance that another ion at x, $a \leqslant x \leqslant r$, should have been counted as the partner of the central ion is $[(N-1)/N]\ G(x)\mathrm{d}x$, and the probability that no such ion is anywhere in the sphere $4\pi r^3/3$ is

$$f(r) = 1 - \frac{N-1}{N}\int_a^r G(x)\mathrm{d}x \tag{6}$$

giving the following integral equation for $G(r)$:

$$G(r) = \frac{4\pi N}{V} r^2 e^{\beta/r}\left(1 - \frac{N-1}{N}\int_a^r G(x)\mathrm{d}x\right) \tag{7}$$

where

$$\beta = \epsilon^2/DkT \tag{8}$$

The solution of equation 7 is

$$G(r) = \frac{4\pi N}{V} r^2 \exp\left(\frac{\beta}{r} - \frac{4\pi N}{V}\int_a^r e^{\beta/x}x^2\,\mathrm{d}x\right) \tag{9}$$

We note that

$$\int_a^\infty G(r)\,\mathrm{d}r = 1 \tag{10}$$

The above derivation contains the approximation that the potential around the central ion is ϵ^2/Dr; in other words, the screening effects due to possible ions between the two ions of the pair, which would cause the insertion of a factor exp $(-\kappa r)$, are neglected. This approximation is not serious for our present purpose, because the function will be used primarily to classify the ions into several groups, and the general character of $G(r)$ for this purpose is not changed by inserting the correction factor.

As a function of r, $G(r)$ may have two peaks. If we assume low concentrations, and have

$$b = \epsilon^2/aDkT > 2 \tag{11}$$

the first is an exponential peak at $r = a$ and the second is a maximum at a distance

$$\rho = \sqrt[3]{V/2\pi N}\,(1 - \beta\,\sqrt[3]{V/2\pi N} + \cdots) \tag{12}$$

which is in order of magnitude the distance between uniformly distributed particles.

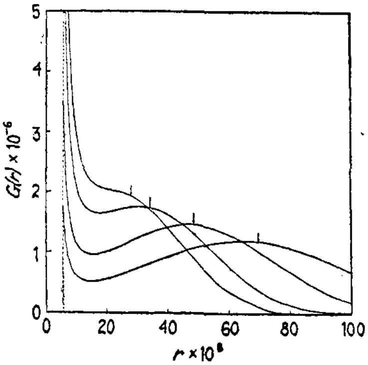

FIG. 1. Distribution curves for c = 5, 10, 20, and 30 $\times 10^{-4}$, $a = 5.57 \times 10^{-8}$, $D = 20$, $t = 25°C$. Arrows mark the distance $1/\kappa$.

Between $r = a$ and $r = \rho$ is a minimum which comes approximately at the Bjerrum radius

$$q = \epsilon^2/2DkT = \beta/2 \tag{13}$$

Up to $r = \beta/2$, the function $G(r)$ approximates the Bjerrum distribution function; beyond $r = \beta/2$, $G(r)$ resembles roughly the distribution curve for a pairwise selection of uncharged particles.

An example of the distribution curve is given in figure 1, where $D = 20$, $t = 25°C.$, $a = 5.57 \times 10^{-8}$, $\beta = 27.8 \times 10^{-8}$, and c = 5, 10, 20, and 30 $\times 10^{-4}$. If we consider only the lower concentrations, we find that the ions present may be divided into several groups: those which find partners near $r = a$, those with partners near $r = \beta/2$, and those with partners near $r = \rho$. (In view of the definition of $G(r)$, the fraction of all the positive ions which find partners between r_1 and r_2 is obviously

$$\int_{r_1}^{r_2} G(r)\,dr$$

i.e., the area under $G(r)$ between r_1 and r_2; cf. equation 10.) The group for which $r \approx \beta/2$ will represent a small fraction of the total, because they correspond to a *minimum* probability; the ions in this group are ions in transition from short to long range pairs, through the probability barrier at $r \approx \beta/2$.

The ions in the short range pairs are ions which are near together on account of Coulomb attraction. By far the largest term in their total potential energy is the contribution from their mutual interaction. Their net external field, as far as other ions are concerned, is essentially a dipole field, which corresponds to a $1/r^2$ energy. Compared to the $1/r$ energies of ion–ion interaction, we are led to neglect in first approximation the interaction of ions in such short range pairs with ions at large distances from either. In other words, we count ions in short range pairs as associated, as was first suggested by Bjerrum (3), and assume them to act approximately like single particles of an ideal solute. If we assume that ions for which $a \leqslant r \leqslant d$ are associated, where d is a distance[5] of the order of several times a and has its upper limit $\beta/2$, then the fraction of solute associated is given by

$$1 - \gamma = \int_a^d G(r)\mathrm{d}r = 1 - \exp\left(-\frac{4\pi N}{V}\int_a^d e^{\beta/r}r^2\,\mathrm{d}r\right) \tag{15}$$

In the limit of zero concentration, we have

$$\lim_{c\to 0}\frac{1-\gamma}{c} = \frac{4\pi L}{1000}\int_a^d e^{\beta/r}r^2\,\mathrm{d}r \tag{16}$$

Now if we had a mass action equilibrium between free and associated ions of the type

$$\mathrm{A}^+ + \mathrm{B}' \rightleftharpoons \mathrm{AB} \tag{17}$$

the left side of equation 16 defines the reciprocal of the mass action constant K for equation 17, and the right side of equation 16 evaluates K^{-1} in terms of parameters characteristic of solvent and solute.

The ions in the long range pairs (those whose partner is found at distances of the order of ρ) must be treated in a different way. Here the interaction with all the neighboring ions (except with those in short range pairs within the present approximation) rather than with merely the nearest

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[5] For a discussion of d, see reference 7. As a matter of fact, the association calculated is not very sensitive to the value of d on account of the exponential peak in $G(r)$ at $r = a$. For practical purposes, it is sufficient to choose d equal to two or three times a; or, for the sake of uniformity with earlier work, to take $d = \beta/2$. Halpern's objections (J. Chem. Physics **2**, 85 (1934)) to the latter choice are unfounded; the proper volume to exclude as belonging to ion pairs is $(4\pi/3)\int_a^d r^3G(r)\mathrm{d}r$, and the ratio of this to V is always small in the range of concentration over which the equations derived from $G(r)$ apply. The "thermodynamic" objection is likewise groundless, because the free energy of a single ion pair has no more meaning than the temperature of a single molecule.

ion of opposite charge must be taken into account. A simple calculation shows that

$$\epsilon^2/\rho DkT \ll 1 \tag{18}$$

when the concentration is small, so that the potential energy of an ion in this group with respect to the nearest otherwise unpaired ion is small compared to the energy of thermal motion. There will be in its potential energy many terms of the same order of magnitude all of which, however, are small. This situation suggests that a time average treatment be applied to the calculation of the mutual energy of ions in long range pairs, and we are naturally led to the Poisson-Boltzmann equation derived by Debye and Hückel. Fluctuation terms are due to ions for which $r \approx \beta/2$; their effects are negligible at low concentrations (8). The ions for which $r \approx a$, and which would represent very serious fluctuation terms in any time average treatment, are handled separately by means of the association hypothesis.

On the basis of the distribution function $G(r)$, we have thus divided the ions in solution into three groups: short range pairs or associated ions, long range pairs or free ions, and ions in transition. The latter group will always represent a small fraction of the total at low concentrations, and for the sake of simplicity may be included with the free ions, which will then be defined as all ions whose distance to the nearest unpaired ion of opposite sign is greater than d, a distance equal to several ionic diameters. Furthermore, we have seen that, according to equation 16, the relative concentrations of free and bound ions satisfy the formal laws of dissociation theory. Let us now calculate the conductance as a function of concentration. The total current i for unit field between unit electrodes is given by the product of the number of conducting ions per unit volume times charge times mobility. If we assume that a fraction $(1 - \gamma)$ of the total solute is associated and hence non-conducting for direct current, we have

$$i = Fc\gamma(v_+ + v_-)/1000 \tag{19}$$

where $F = 96{,}494$ coulombs, $c =$ concentration in equivalents per liter, and v is mobility. The mobility of the free ions at finite concentrations is less than v^0, the limiting mobility, on account of long range interionic effects, and it has been shown (24) that for low free ion concentrations,

$$v = v^0 - A\sqrt{c} \tag{20}$$

Combining equations 19 and 20 and recalling the definition of equivalent conductance, Λ, we have

$$\Lambda = \gamma(\Lambda_0 - \alpha\sqrt{c\gamma}) \tag{21}$$

where α is the Onsager coefficient and Λ_0 is the limiting conductance. Equation 21 represents a combination of two effects which can change Λ with changing concentration; both the actual relative number of conducting particles, as well as their mobilities, are assumed to be functions of concentration. The equation thus combines the original ideas of Arrhenius with the modern notions of interionic forces.

If we know Λ_0 and α and measure Λ as a function of c, equation 21 permits us to determine γ, the "degree of dissociation," as a function of c. Formally, we can solve equation 21 for γ by the usual algebraic methods, but a slight transformation gives a much more convenient form. If we define a new variable z by the relation

$$z = \alpha\Lambda_0^{-3/2}\sqrt{c\Lambda} \tag{22}$$

we find

$$\Lambda = \gamma\Lambda_0 F(z) \tag{23}$$

where

$$F(z) = \tfrac{4}{3}\cos^2 \tfrac{1}{3}\cos^{-1}(-3\sqrt{3}\,z/2) \tag{24}$$

$$= 1 - z(1 - z(1 - z(1 - \cdots)^{-1/2})^{-1/2})^{-1/2} \tag{25}$$

The function $F(z)$ has been calculated (11) and tabulated for a series of values $0 \leqslant z \leqslant 0.209$. Consequently, the solution of equation 21 for γ, given α, Λ_0, Λ, and c can be carried out very simply. But obtaining numerical values for γ does not furnish a test of the equation; rather it is necessary to find some other relationship which γ must satisfy, and then to make the test by means of the second equation. The further connection between γ and concentration is suggested by equation 16. If we assume an equilibrium between long and short range pairs, controlled by the balance between Coulomb forces and thermal motion, then we have the mass action equation

$$c\gamma^2 f^2/(1 - \gamma) = K \tag{26}$$

where K^{-1} is given by equation 16. The term f^2 is included in equation 26 to account for the effect of long range free ion–free ion interaction on the thermodynamic potentials involved in the derivation of equation 26. Following Debye and Hückel, we may set

$$-\ln f^2 = 2\beta'\sqrt{c\gamma} \tag{27}$$

because free ions, defined as those for most of which $r \gg d$, satisfy the Debye-Hückel approximation

$$\epsilon\psi/kT \ll 1 \tag{28}$$

necessary for the simplification of the Poisson-Boltzmann equation to a linear differential equation, and equation 27 is the direct result of this step.

Equations 21, 26, and 27 together then give conductance as a function of concentration, and aside from universal constants, two arbitrary constants, Λ_0 and K appear. It should therefore be possible to rearrange the equations so that conductance data can be plotted in such a way that a straight line is obtained, provided all our assumptions are correct. This form is readily found; as a matter of fact, it is simply the function used by Kraus and Bray (20) twenty years ago, modified to take into account long range interionic effects. By rearrangement of the fundamental equations, we obtain

$$\frac{F}{\Lambda} = \frac{1}{K\Lambda_0^2}\frac{c\Lambda f^2}{F} + \frac{1}{\Lambda_0} \tag{29}$$

so that F/Λ plotted against $c\Lambda f^2/F$ gives a straight line with slope $1/K\Lambda_0^2$ and intercept $1/\Lambda_0$. In figure 2 are given some examples for salts in liquid ammonia (17) ($D = 22$) at −33°C., and in figure 3 for salts in ethylene chloride (6) ($D = 10.23$) at 25°C. Over a wide range of concentration, the plot is linear as required by equation 29.[6]

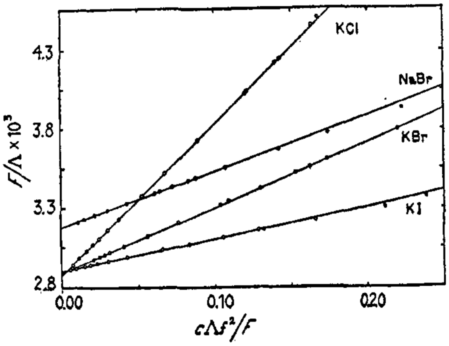

FIG. 2. Conductance function in liquid ammonia at −33°C.

We may reverse the procedure and calculate the conductance curve, once values of the constants are obtained. In figure 4 are given calculated $\Lambda - \sqrt{c}$ curves for a variety of conducting systems (12) covering a wide range of all the variables. The solid curves are calculated; the circles represent

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[6] The procedure for making the plot, given experimental $\Lambda - c$ values is as follows. First, a free-hand extrapolation of a $\Lambda - \sqrt{c}$ curve or of a $(\Lambda + \alpha\sqrt{c}) - c$ curve is made, in order to obtain a tentative value Λ_0' for the limiting conductance. Using this value, z is computed for each point, and the corresponding F is interpolated from the table (reference 6) or calculated by equation 24 or 25. Then γ is computed from equation 23, and with this value of γ, equation 27 is used to obtain f^2. Now both f^2 and F will be somewhat in error if Λ_0' does not equal the true value of the limiting conductance, but these errors do not seriously affect the extrapolation for Λ_0. Then F/Λ is plotted against $c\Lambda f^2/F$, and the line constants are determined. If the value of Λ_0 obtained from the intercept is more than a per cent or so different from Λ_0', the calculation is repeated to obtain a second approximation, because the slope of the curve is affected by the Λ_0 value used in the computation.

observed points. It should be noted that in principle two points are sufficient to determine the entire conductance curve, because only two arbitrary constants are involved. All the curves approach Λ_0 along the Onsager tangent; in solvents of higher dielectric constant, the deviation from the limiting law

$$\Lambda = \Lambda_0 - \alpha\sqrt{c} \tag{30}$$

is small at low but accessible concentrations, because γ is nearly unity. In solvents of dielectric constant less than about 30, an inflection point appears at a concentration

$$c_{inf} = 0.2165\ K/f^2_{inf} \tag{31}$$

near which the curve is, of course, approximately linear. It is the appearance of this inflection point which has led to the statement appearing

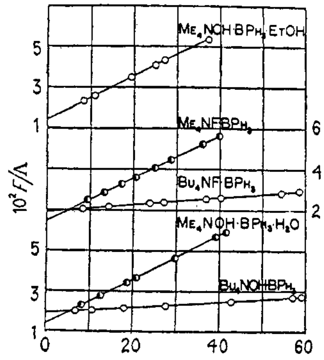

FIG. 3

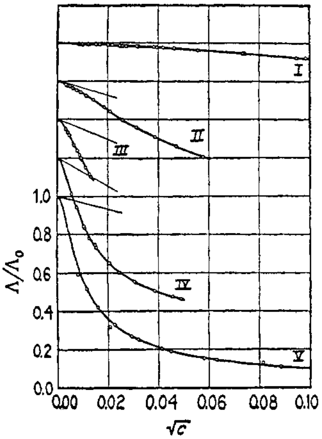

FIG. 4

FIG. 3. Conductance function in ethylene chloride at 25°C.

FIG. 4. Calculated and observed conductance values. Curve I, HIO_3 in water: curve II, $NaBrO_3$ in ammonia; curve III, NaI in amyl alcohol; curve IV, $(C_5H_{11})_4N \cdot NO_3$ in ethylene chloride; curve V, KNH_2 in ammonia.

frequently in the literature that, in non-aqueous solvents, conductance curves approach linearity on a $\sqrt{c}$ scale, but with a slope much greater than α.

We must inquire how the constants Λ_0 and K vary with more fundamental parameters. In first approximation, Λ_0 depends primarily on the viscosity, η, of the solvent, as required by Walden's application of Stokes' law,

$$\Lambda_0\eta = \text{constant} \tag{32}$$

but it is probable that this product also depends on temperature, viscosity, and dipole moment of the solvent (4, 26). Also, in first approximation,

K varies with ion size, dielectric constant, and temperature (13) in accordance with the following equation:

$$K^{-1} = \frac{4\pi L}{1000}\left(\frac{\epsilon^2}{DkT}\right)^3 [P(b) - P(\epsilon^2/DkTd)] \tag{33}$$

where

$$P(x) = Ei(x) - \frac{e^x}{x}\left(\frac{1}{x} + \frac{2}{x^2} + 1\right) \tag{34}$$

For example, figure 5 shows the variation of the dissociation constant of tetraisoamylammonium nitrate in dioxane–water mixtures (21) over the range $D = 2.38$ to $D = 38$. The circles are experimental values; the curve is calculated according to equation 33 with $d = \beta/2$ and $a = 6.40 \times 10^{-8}$ cm.

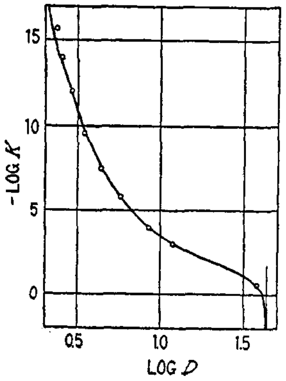

FIG. 5

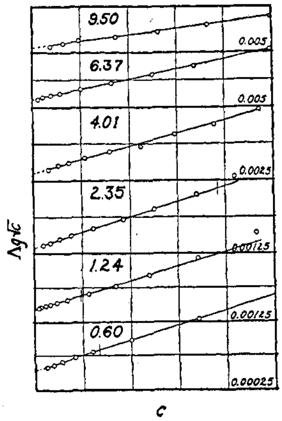

FIG. 6

FIG. 5. Calculated and observed dissociation constants for tetraisoamylammonium nitrate in dioxane–water mixtures.

FIG. 6. Test of the triple ion conductance function

At low concentrations, therefore, we may, with a reasonable degree of certainty, describe and predict electrolytic properties. The next question deals, of course, with higher concentrations. It must be pointed out immediately that the meaning of the phrase "at low concentrations" depends on the solvent. For example, the behavior of 0.001 N aqueous solutions is fairly well understood, but at the same concentration in benzene, electrolytic properties are far too complicated for analysis with any of our present methods.

The applicability of the hypothesis made above—namely, a combination of the effects of long range interionic forces with the effects due to ionic association—depends for its success, obviously enough, on the presence of free ions and associated pairs in the solution. Now as concentration is increased, we find a shift of the distribution curve $G(r)$, as is shown in figure 1, which eventually eliminates the long range maximum. At a concentration given by

$$c_{crit} = 3.2 \times 10^{-7} D^3 \text{ at } 25°\text{C}. \qquad (35)$$

the maximum of $G(r)$, the minimum and the included inflection point coincide. Above this concentration, there is no relative maximum probability for the free ions; the shorter the pairwise distances, the greater the probability. As a matter of fact, the simple conductance equation (equation 21) is found to fail at concentrations of the order of that given in equation 35; at higher concentrations, Λ (observed) is always greater than Λ calculated from equation 21. Frequently the observed curves show a minimum in conductance, beyond which Λ increases with c, while equation 21 calls for a decrease of Λ with increasing c as long as the equation has any physical meaning (i.e., as long as $3\sqrt{3}z/2 \leqslant 1$).

It is therefore necessary to find some additional process which is taking place in the solution, in order to account for the positive deviations from equation 21. A suggestion regarding this is found in the restrictions involved in deriving the distribution function. We assumed that V was so large that short range three-ion configurations were negligibly rare, so that no $1/r^2$ terms in ionic energies would be comparable with the $1/r$ terms. At concentrations greater than that given in equation 35, many ions will be near short range pairs, because the distribution curve calls for a large fraction of the solute existing as short range pairs (cf. figure 1). The potential energy of a single ion in contact with an ion pair is, in the ideal case, one half the potential energy of the ion pair, and may therefore also be large compared to kT. Consequently, short range three-ion configurations will be stable to thermal impact, and we must re-define the distribution, in order to take these groups into account. Let us define a free ion as one which is relatively far from either another free ion or from a short range ion pair. Then, by an analysis entirely analogous to the one which led to $G(r)$, we find that short range triple ion groups have a relative maximum in probability when the dielectric constant becomes small or the concentration large. Furthermore, if we consider part of the solute to exist as triple ions, we are removing a part of the solute from the ion–ion equilibrium (17), and the net result is to remove some area from the $G(r)$ curve near $r = \beta/2$, which restores the long range maximum. We now have five individual species of solute particles: $(+)$, $(-)$, $(+\ -)$, $(+\ -\ +)$, and $(-\ +\ -)$.

It is easy to compute the effect of the presence of triple ions on the conductance (14). These groups have a net charge of $\pm\epsilon$ and hence are conducting. Also the equilibrium between triple ions, ion pairs, and free ions obeys the formal laws of dissociation theory; the proof is analogous to that leading to equation 16. If, for the sake of simplicity, we assume that $(+ - +)$ and $(- + -)$ groups are equally probable,[7] we find the conductance equation

$$\Lambda \sqrt{c}\, g(c) = \Lambda_0 \sqrt{K} + \frac{\lambda_0 \sqrt{K}}{k_3}\left(1 - \frac{\Lambda}{\Lambda_0}\right) c \qquad (36)$$

Here λ_0 is the limiting conductance of the hypothetical salt $(+ - +)$ $(- + -)$. The function (14) $g(c)$ approximates the long range interionic effects; in it, total ion concentration is set equal to $c\Lambda/\Lambda_0$ and cross terms in the mobility correction, caused by the difference between Λ_0 and λ_0, are neglected (25). According to equation 36, we should obtain a straight line when $\Lambda\sqrt{c}g(c)$ is plotted against $c(1 - \Lambda/\Lambda_0)$. In figure 6 are shown the corresponding curves for tetraisoamylammonium nitrate in dioxane–water mixtures (14) over the appropriate ranges of concentration. It will be seen that all the plots are linear. The line constants evaluate $\Lambda_0\sqrt{K}$ and $\lambda_0\sqrt{K}/k_3$ as intercept and slope. Now the triple ion hypothesis brings in three new arbitrary constants. By assuming $(- + -)$ and $(+ - +)$ groups equally probable, we reduce the number to two, λ_0 and k_3. We may estimate λ_0, and thus determine k_3, or else make conductance measurements at at least two temperatures, which will then determine the two constants (2).

In the same way that K was expressed as a function of D, T, and a, we find for k_3

$$k_3^{-1} = \frac{2\pi\beta a^3}{1000} I(b) \qquad (37)$$

The function $I(b)$ has been tabulated for a series of b-values. When the parameter b is large compared to unity, we may use the asymptotic expansion (10).

$$I(b) \sim 32e^{b/2}/3b^2 \qquad (38)$$

Equation 37 may be tested by plotting observed values of log k_3 against D and comparing with a log k_3–D curve calculated from equation 37, using a fixed a-value. In figure 7, we have such a plot for the data of figure 6,

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[7] An inequality in probability causes a shift of the minimum to higher concentrations, other variables remaining constant. In the limiting case where one triple species does not form at all, the conductance curve approaches asymptotically a constant value, provided higher association does not produce a minimum.

with $a = 9.0 \times 10^{-8}$ cm. The agreement is satisfactory over a wide range of the variables.

The development sketched above serves to account quantitatively for conductance curves up to concentrations of the order of that corresponding to the minimum in conductance, when a minimum appears, i.e., in solvents of dielectric constant less than about 10. For solvents of higher dielectric constant, triple ion energies are fairly small, and this type of interaction[8] cannot be treated by association theory, just as short range pairwise interaction cannot be so treated for strong electrolytes in solvents of high dielectric constant; and for the same reason, the energy is only of the same order as kT. The general problem of concentrated solutions of electrolytes is as yet practically untouched.

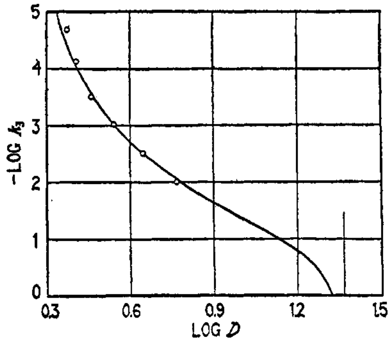

FIG. 7. Calculated and observed triple ion dissociation constants

In solvents of very low dielectric constant, association increases very rapidly with increasing concentration, if we base our opinion on molecular weight (1, 23) and dielectric constant measurements (22). The next simplest association after the triple ion is the quadrupole type, and it is possible to set up a system of equations which describes the limiting behavior of a pair–pair association in solvents of low dielectric constant (9). The agreement between theory and experiment is fairly satisfactory (16), but not many data are yet available and the theory is still in the process of development. The greatest practical difficulty in the treatment of even moderately concentrated electrolytic solutions in solvents of low dielectric constant lies in the fact that, with increasing order of association, the excess potential energy of the last ion added to a cluster becomes less and less. Consequently, the binding energy decreases with increasing

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[8] The three-ion interaction in solvents of higher dielectric constant could probably be handled best by starting with the equations of motion (Fuoss: Physik. Z. **35**, 59 (1934)).

order of association, and, furthermore, it becomes difficult to separate individual orders, because their relative energies, and hence probabilities, are nearly equal. We can only draw the conclusion that association will increase very rapidly once the triple ion stage is passed; this conclusion is confirmed by experimental data on conductance (15), freezing points (1, 23), and dielectric constant (22). It is, however, quite possible that the conductance mechanism in concentrated solutions in solvents of low dielectric constant is different from the simple migration type characteristic for low concentrations, and an exchange of ions between neighboring clusters, corresponding to a rapid increase of effective mobility with increasing concentration, might easily be involved. Again we are faced with a lack of experimental data on which to base deductions. It is interesting to note that the high concentration ends of conductance curves for a given salt in solvents of low dielectric constant all tend to converge to the same region, which is presumably the conductance of the fused salt at the experimental temperature. This fact suggests that the best approach to the problem might be through the theory of the conductance in fused salts, another field which has been investigated in only a preliminary way.

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