1. THE ELECTROPHORETIC CONTRIBUTION TO EQUIVALENT CONDUCTANCE USING THE COMPLETE EXPONENTIAL DISTRIBUTION FUNCTION: 1-1 SALTS IN DIOXANE-WATER MIXTURES

11. TRANSFERENCE NUMBERS AND ACTIVITY COEFFICIENTS OF AQUEOUS SOLUTIONS OF TRIS-(ETHYLENEDIAMINE) COBALT (III) CHLORIDE AT TWENTY-FIVE DEGREES CENTIGRADE

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David J. Karl

AN ABSTRACT

Submitted to the School for Advanced Graduate Studies
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ABSTRACT

An outline of the Onsager theory of conductance is presented as an introduction to the study of this difficult treatment.

Higher order concentration dependent terms of the electrophoretic effect, which are neglected in the usual treatment, have been evaluated, using a digital computer, for 1-1 salts in water and in 10% to 70% dioxane-water mixtures. Significant differences are found to occur between the Onsager and the extended electrophoretic expressions. These differences increase rapidly with decreasing ion size and with decreasing solvent dielectric constant.

The electrophoretic calculations are applied to equivalent conductance data in several dioxane-water mixtures for tetraisoamylammonium nitrate and tetra-n-butylammonium bromide taken from the literature. For these data it is found that deviations from the Onsager-Fuoss conductance equations, which previously have been attributed to ion-pair formation, can be interpreted instead using two constant distance parameters; the minimum distance of approach, and the cation hydrodynamic radius. It is concluded that much of the deviation from theory, heretofore ascribed to electrostatic aggregation of ions, arises from an incomplete treatment of the model used rather than from physical phenomena which cause the model to be inaccurate. The program developed to compute the electrophoretic higher terms is also applicable to other charge types.

In addition to these theoretical considerations, experimental data are presented for aqueous solutions of tris-(ethylenediamine) cobalt (III) chloride: transference number values obtained by the moving boundary method and activity coefficients determined from the electromotive force of concentration cells with transference. Deviations from the predictions of theory occur for both ion mobilities and activity coefficients.

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PART I

THE ELECTROPHORETIC CONTRIBUTION TO EQUIVALENT CONDUCTANCE USING THE COMPLETE EXPONENTIAL DISTRIBUTION FUNCTION: 1-1 SALTS IN DIOXANE-WATER MIXTURES

I. INTRODUCTION

Solutions of ionophores (1) or "strong" electrolytes consist of ions dissolved in dielectric media. The electrical conductivity of such solutions clearly indicates that the ions are free to move more or less independently. For completely independent ions, the equivalent conductance should be independent of concentration for a given electrolyte and solvent. Actually this quantity varies markedly with concentration. This behavior has been the subject of intense experimental and theoretical study for over sixty years.

The modern theory of electrolytic solutions is based on the interionic attraction theory of Milner (2) as formulated by Debye and Hückel (3). According to this view, coulombic forces between ions cause any chosen reference ion to be surrounded by an excess of ions of opposite charge, and this ion excess can be treated as a uniform charge cloud or "atmosphere." Using the Debye-Hückel theory together with statistical and hydrodynamical considerations, Onsager (4), and Onsager and Fuoss (5) proposed a general theory for irreversible processes in electrolytic solutions and derived a limiting expression for the equivalent conductance as a function of concentration and other pertinent variables. The recent extension of this theory by these same authors (6, 7, 8, 9) has resulted in an expression which accurately predicts the conductance of symmetrical salts under conditions which satisfy the physical and mathematical assumptions and approximations.

Rather large differences between observed and calculated conductances appear when the theory is applied to solutions whose solvents have low dielectric constants. Following the idea of Bjerrum (10) who postulated the existence of non-conducting "ion-pairs," Fuoss (11, 12) has extended the range of utility of the theory.

The Onsager-Fuoss treatment does not take into account the possible dependence of conductance upon higher powers of concentration than the first. It is demonstrated in this thesis that complete neglect of higher order terms, even at very low concentrations can be extremely hazardous and can indeed lead to very questionable conclusions regarding the nature of certain solutions. This is shown by an extensive study of the higher order terms of the electrophoretic correction to conductance for symmetrical univalent salts in a variety of solvents. The significance of these terms for the case of unsymmetric electrolytes in water has been pointed out by Dye and Spedding (13).

A number of excellent reviews and expositions of the many-faceted development of the theory ionic solutions are available in the literature (14, 15, 16, 17). Accordingly only a brief account of the most recent contributions to the theory of conductance will be presented.

II. THE INTERIONIC ATTRACTION THEORY OF CONDUCTANCE

A. Introduction

The equivalent conductance (λ_j) of a given type of ion in solution may be defined as the current, at a potential gradient of one volt per centimeter, produced by one gram equivalent of the ion. The ionic equivalent conductance is simply related to the average ionic velocity $\underline{\vec{v}_j}$ through the average mobility $\underline{u_j}$ by the equations

$$\lambda_j = 96,500\ u_j \tag{1}$$

and

$$\vec{u}_j = \vec{v}_j/300\ X \qquad (2)$$

where X is the electric potential gradient in volts per centimeter. The total equivalent conductance (Λ) or simply the equivalent conductance is obtained by summing ionic conductances over all types of ions in a given solution.

$$\Lambda = \sum_j \lambda_j = (96,500/300\ X) \sum_j \bar{v}_j \qquad (3)$$

The central problem in conductance theory is, therefore, to find the average ionic velocities through the statistical equations of motion. In order to find the average velocities it is necessary to know the distribution of the ions relative to one another and the electrical potential at any point in the solution. These quantities, together with the hydrodynamic equation of continuity are sufficient to derive the Onsager conductance equation.

The Debye-Hückel model and the resulting distribution function and electrical potential between ions are used as a starting point and the average ionic velocities are found by considering the perturbing effects of an external electric field. From the Debye-Hückel concept two major factors affecting conductance are recognized: the electrophoretic effect and the time of relaxation effect. A third effect, kinetic in nature, has recently been recognized by Onsager (9). Before discussing these three terms, the treatment of Debye and Hückel for the equilibrium case will be briefly presented.

B. The Equilibrium Distribution Function and Potential

The general interionic attraction theory initially assumes that known numbers of hard spherical, uniformly charged particles are present, in a ratio preserving charge balance, in a dielectric medium. This medium is assumed to be structureless and non-interacting.

The average configuration of the entities in such a solution can be described by an average distribution of the ions. Since the equations of motion for the system are ultimately desired, the logical choice for this description is the *time average distribution*. A reference volume element of the solution, located in space by the vector $\vec{r}_1$ from a fixed origin, is considered to contain, on the average (over a "sufficiently" long period of time), n_j ions of type j. A second volume element, located by $\vec{r}_2$ from origin and $\vec{r}_{21}$ from the reference element then contains an average of n_{ji} ions of type i and the desired distribution function is defined by equation (4).

$$f_{ji} = n_j n_{ji}(\vec{r}_1, \vec{r}_{21}) \tag{4}$$

The quantity n_{ji} gives the number of i-ions per unit volume at the distance r_{12} from a single reference or "central" j-ion. This distribution of i-ions about a central ion is called the ionic "atmosphere." Since n_{ji} has this meaning, the symbol f_{ji} is read as the time average distribution of i-ions in the vicinity of n_j central j-ions. An expression similar to equation (4) may be written for f_{ij}, the distribution of j-ions about central i-ions, and since material must be conserved in the system equation (5) must hold.

$$f_{ji} = n_j n_{ji}(\vec{r}_1, \vec{r}_{21}) = f_{ij} = n_i n_{ij}(\vec{r}_2, \vec{r}_{12}) \tag{5}$$

For the equilibrium case (denoted by superscript zero) Debye and Hückel assumed that the quantity n_{ji} is governed by the Boltzmann law and is given by

$$n_{ji}^{0} = n_i \exp[-U_{ji}^{0}/kT] \tag{6}$$

where U_{ji}^{0} is the potential energy of an i-ion when it is located in the solution at a distance r_{12} from a j-ion, and n_i is the average concentration of i-ions computed assuming completely uniform distribution.

If the approximation

$$U_{ji}^{o} \cong e_i \Psi_j^{o} \tag{7}$$

is made, where e_i is the charge on an ion of type i and Ψ_j^{o} is the time average electrical potential at a distance r_{21} from the j-ion for the unperturbed system, the equilibrium distribution function f_{ji}^{o}, can be written as equation (8).

$$f_{ji}^{o} = n_j n_i \exp[-e_i \Psi_j^{o}/kT] \tag{8}$$

The expression (7) is known as the linear superposition of fields approximation and is tantamount to assuming that a partially complete assembly of i-ions about a central j-ion will not rearrange as the remainder of the atmosphere ions are brought into place. It is this assumption which seriously limits the range of validity of the final Debye-Hückel expression.

The Poisson equation from electrostatics relates the electrical potential Ψ to the charge density ρ through the dielectric constant D according to equation (9).

$$\nabla^2 \Psi = -4 \pi \rho / D \tag{9}$$

For the case at hand the charge density may be written in terms of n_{ji}.

$$\rho = \sum_j n_{ji} e_i \tag{10}$$

A series of straightforward substitutions gives a second order non-linear differential equation in the potential Ψ_j^{o}.

$$\nabla^2 \Psi_j^{o} = -(4 \pi / D) \sum_i n_i e_i \exp[-e_i \Psi_j^{o}/kT] \tag{11}$$

No general solution of this equation is known. Furthermore it is mathematically inconsistent in that equation (7) requires that Ψ_j^{o} be a linear function of e_j, while equation (11) is linear in e_j on the left hand side and exponential in e_j on the right hand side. These difficulties may be circumvented by expanding the exponent in equation (11).

$$\nabla^2 \Psi_j^o = (4\pi/D) \sum_i n_i e_i \left[(e_i \Psi_j^o/kT) - 1/2(e_i \Psi_j^o/kT)^2 + \cdot \cdot \cdot \right] \quad (12)$$

The leading term of the expansion vanishes since electrical neutrality requires that

$$\sum_i n_i e_i = 0 \quad (13)$$

If the condition

$$e_i \Psi_j^o >> kT \quad (14)$$

is met, the terms in equation (12) other than the first may be neglected and one may write

$$\nabla^2 \Psi_j^o = \kappa^2 \Psi_j^o \quad (15)$$

where

$$\kappa \equiv \left[\frac{4\pi}{DkT} \sum_i n_i e_i^2 \right]^{\frac{1}{2}} \quad (16)$$

It should be noted that κ has the units of reciprocal length and is proportional to the square root of the concentration through n_j. Because of the symmetrical nature of the equilibrium distribution, Ψ_j^o depends only on $r = |\vec{r}_{21}|$. The general solution of equation (15) is then

$$\Psi_j^o = \frac{Ae^{-\kappa r}}{r} + \frac{Be^{\kappa r}}{r} \quad (17)$$

The boundary condition $\Psi_j^o \rightarrow 0$ as $r \rightarrow \infty$ requires that B = 0. To maintain charge balance, the total charge outside the central j-ion must be equal and opposite to its own charge. This statement may be formulated as

$$-e_j = \int_a^\infty 4\pi r^2 \rho \, dr \qquad (18)$$

where a is the distance of closest approach of the ions. A comparison of equations (9) and (15) gives

$$\rho = -D\kappa^2 \Psi_j^o/4\pi \qquad (19)$$

Combination of (18) and (19) with equation (15) yields

$$e_j = AD\kappa^2 \int_a^\infty e^{-\kappa r} r \, dr \qquad (20)$$

Integration of this expression serves to evaluate the constant A as

$$A = e_j e^{\kappa a}/D(1 + \kappa a) \equiv e_j/D\mu \qquad (21)$$

The final expression for the potential then becomes

$$\Psi_j^o = \left[\frac{e_j e^{\kappa a}}{D(1 + \kappa a)} \right] \frac{e^{-\kappa r}}{r} \qquad (22)$$

The physical significance of κ can best be illustrated for the simple case in which the ions are considered as point changes $(a = o)$. Equation (22) becomes, upon expansion of the exponent

$$\Psi_j^o \approx e_j/Dr - e_j \kappa/D$$

This is the simple expression for the potential due to two point charges e_j and $-e_j$, at distances r and $(1/\kappa)$ from origin. Accordingly, $(1/\kappa)$ has been called the "radius" of the atmosphere. A more refined analysis shows that the charge density is a maximum at this distance.

A useful form of the distribution function f_{ji}^o can be obtained by expansion of the exponential equation (8) using Ψ_j^o from equation (22)

$$f_{ji}^o = n_j n_i \left[1 - \frac{e_j e_i e^{\kappa a}}{DkT(1 + \kappa a)} \cdot \frac{e^{-\kappa r}}{r} + \frac{e_j e_i^2 e^{2\kappa a}}{2Dk^2T^2(1+\kappa a)^2} \cdot \frac{e^{-2\kappa r}}{r^2} - \cdot \cdot \cdot \right] \qquad (23)$$

This expression for the equilibrium distribution function is the one used by Onsager in his treatment of the conductance problem.

With these background considerations completed, a discussion of conductance theory itself will now be presented.

C. The Form of the Conductance Equation

From a qualitative discussion of the two major effects considered by Onsager, the conductance equation can be written in symbolic form. This result helps to clarify the logic of the detailed development.

If an unsymmetrical force, such as an electric field, is applied to a solution of an electrolyte, the average velocity of all ions of a given type becomes non-zero. An ion, which is "wet" by the solvent, moving through a solution will drag solvent with it. The ions of opposite charge in its atmosphere will be moving in the opposite direction and will, in effect, be moving against a local solvent flow. The effect is reciprocal and the net result is a lowering of the average speed of all ion types. This is known as the electrophoretic effect.

A second effect is produced when the external force is an electric field. The tendency of a given central ion and its oppositely charged atmosphere to move in opposite directions leads to an asymmetric distribution about the central ion. A finite time (the "relaxation time") is required for the atmosphere to build up and decay about the moving ion. The net result may be pictured as an excess of oppositely charged ions behind a given ion. This effect can be treated as a small restoring force opposite in direction to the applied force. In the case of conductance, the applied force on an ion is just the product of the charge of the ion and the potential gradient $\underline{X}$. The small restoring force is described in terms of a correction to the field, $\underline{\Delta X}$, called the relaxation field.

A symbolic conductance equation may now be formulated. If a force $\underline{K}_j$ were applied to an isolated $\underline{j}$-ion in a solvent, the ion would assume a velocity $\vec{\underline{v}}_j$.

$$v_j = K_j\omega_j \tag{24}$$

Here ω_j is the reciprocal of the coefficient of friction of the ion. In the case of conductance the force is given by equation (24)

$$K_j = e_jX \tag{25}$$

In a solution of many ions, the average force felt by the j-ions is $(X + \Delta X)e_j$ and the average velocity is

$$v_j = v_{js} + (X + \Delta X)e_j\omega_j \tag{26}$$

where the term v_{js} is the retarding velocity of the solvent in the neighborhood of the j-ions which results from the electrophoretic solvent drag by atmospheric i-ions. The above velocity expression is easily converted to an equation for equivalent conductance through equation (3) to give

$$\lambda_j = \frac{96,500}{300} \left(1 + \frac{\Delta X}{X}\right) |e_j| \omega_j - \frac{96,500}{300\ X} |v_{js}| \tag{27}$$

Since the solvent velocity (v_{js}) depends upon the velocity of ions of type i, which in turn depends upon the field $(X + \Delta X)$, the last term on the right may be written as

$$\frac{96,500\ |v_{js}|}{300\ X} = \Delta\lambda_j^{e} \left(1 + \frac{\Delta X}{X}\right) \tag{28}$$

where $\Delta\lambda_j^{e}$ is the electrophoretic contribution to the conductance. If only non-interacting j-ions were present in the solution (an infinitely dilute solution) the equivalent conductance would be

$$\lambda_j^{o} = \frac{96,500}{300} |e_j| \omega_j \tag{29}$$

where λ_j^{o} is called the equivalent conductance at infinite dilution. Equation (27) may now be written as

$$\lambda_j = (\lambda_j^{o} - \Delta\lambda_j^{e}) \left(1 + \frac{\Delta X}{X}\right) \tag{30}$$

or, for all types of ions in the solution

$$\Lambda = (\Lambda^o - \Delta\Lambda_e)(1 + \frac{\Delta X}{X}) \quad (30a)$$

The explicit evaluation of the electrophoretic term $\underline{\Delta\Lambda}_e$, different from that of Onsager, is the major concern of this work. The derivation of an expression for the relaxation term $\underline{(\Delta X/X)}$ is both difficult and lengthy. Accordingly, only an outline of the Onsager procedure will be presented here. For anyone seriously interested in the details it is recommended that the following presentation be regarded as an introduction to be read prior to the study of the original papers of Onsager and Fuoss and their amplification by Fuoss and Accascina (19).

D. The Onsager Conductance Equation

1. General Approach

In order to find the ionic velocity $\underline{\vec{v}}_j$, and from this the equivalent conductance, it is necessary to find $\underline{\vec{v}}_{js}$, the local solvent velocity, and the relaxation field $\underline{\Delta X}$. The first of these quantities, $\underline{\vec{v}}_{js}$, involves the solution of a hydrodynamic problem and may be found either by use of Stokes Law (an integration treatment) or through the general hydrodynamic equations of motion (a differential treatment).

The relaxation field $\underline{\Delta X}$ is more difficult to evaluate. This field is obtained from the negative gradient of the asymmetric potential $\underline{\Psi}_j$ evaluated at the surface of the ion, or more properly, at the distance of closest approach of the ions

$$\Delta X = -(\nabla\Psi)_a \quad (31)$$

It is assumed that the potential function $\underline{\Psi}_j$ can be written in terms of an asymmetric distribution function $\underline{f}_{ji}$ through a Poisson equation analogous to equation (9, 10). In order to find $\underline{f}_{ji}$, a general expression for $\underline{\vec{v}}_{ji}$ the velocity of an i-ion relative to that of a neighboring j-ion is

written. This expression contains $\underline{f}_{ji}$ and $\vec{\underline{v}}_{js}$ (which can be evaluated by hydrodynamic equations). The final link in the chain is provided by the equation of continuity which relates $\vec{\underline{v}}_{ji}$ and $\underline{f}_{ji}$. Solution of the resulting differential equation with suitable boundary conditions gives $\underline{f}_{ji}$. Integration of the Poisson equation leads to the evaluation of the potential $\underline{\Psi}_j$ from which the relaxation field $\underline{\Delta X}$ is easily found.

The general expression for the relative velocity $\underline{v}_{ji}$ may be written as

$$\vec{v}_{ji}(\vec{r}_1, \vec{r}_{21}) = \vec{v}_{js}(\vec{r}_2) + \omega_i(K_{ji} - kT\nabla_2 \ln f_{ji}) \tag{32}$$

where

$\vec{v}_{js}$ = the solvent velocity in the neighborhood

ω_i = reciprocal of the coefficient of friction of ions of type $\underline{i}$

K_{ji} = total force on an i-ion in the neighborhood of a j-ion

The last term on the right of equation (32) arises from the Brownian motion of the ions which tends to restore symmetry to the ionic distribution. It was this term which was overlooked in an early attempt by Debye and Hückel (20) to solve the conductance problem. The subscript on the gradient operator is due to the use of two volume elements with different sets of coordinates in defining the distribution function. A completely analagous expression for $\vec{\underline{v}}_{ij}$, the average velocity of a j-ion near an i-ion may be written,

$$\vec{v}_{ij}(\vec{r}_2, \vec{r}_{12}) = \vec{v}_{is}(\vec{r}_1) + \omega_j(K_{ij} - kT\nabla_1 \ln f_{ij}) \tag{32a}$$

It is assumed that the distribution functions and potentials may be treated as the sum of a symmetric part (denoted by superscript zero) and a perturbation term (denoted by primes) due to an external force.

$$f_{ji} = f_{ji}^{o} + f_{ji}' \tag{33}$$

$$\Psi_j = \Psi_j^{o} + \Psi_j' \tag{34}$$

The asymmetric (primed) quantities are then related through Poisson equations, for example

$$\nabla^2 \Psi_j' = -(4\pi/D) \sum_{i=1}^{s} f_{ji}' \, e_i/n_j \tag{35}$$

The total force $\overline{K}_{ji}$ can be specified in terms of external and internal forces.

$$\vec{K}_{ji} = e_i X \vec{\imath} - e_i \nabla_2 \Psi_i'(a) - e_i \nabla_2 \Psi_j(\vec{r}_1, \vec{r}_{21}) \tag{36}$$

The first term on the right is the external force and is chosen to have only an <u>x</u> component ($\vec{i}$ is the unit vector in the <u>x</u> direction). The second term represents the force on an i-ion due to its own atmosphere and third term is the force on the i-ion due to the neighboring j-ion and the atmosphere of this j-ion. The symmetric part of <u>$\nabla_2 \Psi_i(a)$</u> cancels out since it represents a balanced force and can produce no net motion. Combination of equations (32) and (36) gives

$$\vec{v}_{ji}(\vec{r}_2, \vec{r}_{12}) = \vec{v}_{js}(\vec{r}_2) + \omega_i[e_i X \vec{\imath} - e_i \nabla_2 \Psi_i'(a) - e_i \nabla_2 \Psi_j(\vec{r}_1 \vec{r}_{21}) \\ -kT \nabla_2 \ln F_{ji}] \tag{37}$$

A companion expression for $\vec{v}_{ji}(\vec{r}_1 \vec{r}_{21})$ may also be written. To relate the relative velocities and distribution functions, the hydrodynamic equation of continuity for stationary states is used in the form

$$\nabla_2 \cdot (f_{ji} \vec{v}_{ji}) + \nabla_1 \cdot (f_{ij} \vec{v}_{ij}) = 0 \tag{38}$$

When integrated, this is merely a statement of charge conservation: the net flux of charge through the system is zero for a system in a steady state. The complicated expression which results upon combination of equations (37) and (38) may be greatly simplified by using the <u>Onsager symmetry relations.</u> If the solution as a whole is fixed in space, the potentials and distribution functions can be described by the relative distance between any chosen pair of ions. Accordingly $\underline{\vec{r}_1}$ is chosen as a

new origin and the system is described by the vector $\vec{r}$.

$$\vec{r}_1 = 0$$
$$\vec{r} = \vec{r}_{12} = -\vec{r}_{21}$$
$$\vec{r}_2 = \vec{r} \tag{39}$$

Since the applied field is in the x-direction, the perturbed potentials and distribution functions will be symmetric about the x-axis and can be written in terms of the variable $\vec{r}$ without complication:

$$\Psi_i'(-\vec{r}) = -\Psi_i'(\vec{r})$$
$$f_{ij}'(-\vec{r}) = -f_{ij}'(\vec{r})$$
$$f_{ji}'(\vec{r}) = f_{ij}'(-\vec{r})$$
$$f_{ji}'(\vec{r}) = -f_{ij}'(\vec{r}) \tag{40}$$

The operators can also be simplified:

$$\nabla = \nabla_2 = -\nabla_1$$
$$\nabla_1 \cdot \nabla_1 = \nabla_2 \cdot \nabla_2 = \nabla^2 \tag{41}$$

The array of terms which arises from the combined equations (37) and (38) are then taken pair-wise (one from each of the two terms in equation 38 and simplified by the symmetry relations (40) with the aid of equations (39) and (41). Further, all terms which are quadratic in the field are neglected; for example, terms such as $\underline{\vec{v}_s \cdot \nabla f'}$ and $\underline{X\left(\frac{\partial f}{\partial x}\right)}$. Terms which are completely symmetric such as $\underline{f^o \nabla \Psi^o}$ can have no effect on the asymmetry properties and therefore vanish. Assembling all the terms, the continuity equation may be written in the form of equation (42).

$$
\begin{array}{ll}
X\,(e_i\omega_i - e_j\omega_j)\,(\partial f_{ji}^{\,o}/\partial x) & T_x \\
-\,kT(\omega_i + \omega_j)\nabla^2 f_{ji}' & T_k \\
-\,f_{ji}^{\,o}(e_i\omega_i\nabla^2\Psi_j' - e_j\omega_j\nabla^2\Psi_i' & T_g \\
\quad = (e_i\omega_i\nabla\Psi_j' - e_j\omega_j\nabla\Psi_i')\cdot\nabla f_{ji}^{\,o} & T_g \\
\quad + f_{ji}'(e_i\omega_i\nabla^2\Psi_j^{\,o} + e_j\omega_j\nabla^2\Psi_j^{\,o}) & T_g \\
\quad + (e_i\omega_i\nabla\Psi_j^{\,o} + e_j\omega_j\nabla\Psi_i^{\,o})\cdot\nabla f_{ji}' & T_g \\
\quad - [e_i\omega_i\nabla\Psi_i'(a) - e_j\omega_j\nabla\Psi_j'(a)]\cdot\nabla f_{ji}^{\,o} & T_a \\
\quad + (v_{is} - v_{js})\cdot\nabla f_{ji}^{\,o} & T_v
\end{array}
\qquad (42)
$$

The column of symbols on the right indicates the origin of the terms in the nomenclature of the original paper (9). The terms $\underline{T_x}$ are called the field terms; $\underline{T_k}$, the Boltzmann terms; $\underline{T_v}$, the velocity field terms; and $\underline{T_a}$, the terms containing $\underline{\nabla\Psi'(a)}$. The remaining terms are designated by $\underline{T_g}$.

The quantity which is ultimately sought, the relaxation field, will be given by

$$\Delta X = -\nabla\Psi'(a) = -\left(\frac{\partial\Psi'}{\partial x}\right)_a \qquad (43)$$

Dependence upon $\underline{x}$ only arises for the conductance case since the distribution function and potential are axially symmetric with respect to the direction of the field.

2. The Boundary Conditions

Inspection shows that equation (42) is a fourth order non-linear, non-homogeneous differential equation in the asymmetry potentials $\underline{\Psi'}$, since the quantity $\underline{\nabla^2 f'}$ appears and $\underline{f'}$ itself is proportional to $\underline{\nabla^2\Psi'}$. The solution of the differential equation therefore requires four boundary conditions. Three of the conditions are simple electrostatic requirements:

1. The field of the central ion must vanish at infinity

$$\left(\frac{\partial \Psi_j'}{\partial r}\right)_{\infty} = 0$$

2. The potential must be continuous across the boundary at $r = a$,

$$\Psi_j'(a-o) = \Psi_j'(a+o)$$

3. The field strength must be continuous at $r = a$

$$\left(\frac{\partial \Psi'}{\partial r}\right)_{a-o} = \left(\frac{\partial \Psi'}{\partial r}\right)_{a+o}$$

The fourth condition is hydrodynamic in nature and while simply stated is very complicated when put into useful mathematical form:

4. The radial components of the relative velocities of any two ions must vanish on contact

$$\left[\left(f_{ij}\vec{v}_{ij} - f_{ji}\vec{v}_{ji}\right)\cdot\vec{r}\right]_a \equiv (\vec{Y}\cdot\vec{r})_a = 0$$

By further defining the function $Z(r)$ by

$$Z(r) = (\vec{Y}\cdot\vec{r})/x = |\vec{Y}|/\cos\theta \tag{44}$$

This condition may be stated as a scalar equation.

$$Z(a) = 0 \tag{45}$$

To be of use, equation (45) must be expanded in the same manner as was the equation of continuity. A complicated eight-term expression containing f^o, f' and Ψ' as well as the local solvent velocities $\vec{v}_{is}$ and $\vec{v}_{js}$ results. The second and third (electrostatic) boundary conditions may be conveniently combined. If the ions are considered as conducting spheres, then for $r < a$ the asymmetric part of the solution of the LaPlace equation ($\nabla^2\Psi_j = 0$) gives

$$\Psi_j'(a-o) = |Br\cos\theta|_{a-o} = \left[r\frac{\partial \Psi_j'}{\partial r}\right]_{a-o} \tag{46}$$

Rearrangement with use of the second and third conditions $[\Psi_j'(a - o) = \Psi_j'(a + o)]$ gives equation (47)

$$\left[r \frac{\partial \Psi_j'}{\partial r} - \Psi_j' \right]_{a + o} = 0 \qquad (47)$$

The four boundary conditions may be summarized by the three equations (48)

$$(\partial \Psi_j' / \partial r) = 0$$

$$[r (\partial \Psi_j' / \partial r) - \Psi_j']_a = 0$$

$$Z(a) = 0 \qquad (48)$$

3. Order of Terms and Method of Solution of the Continuity Equation

The differential equation (42) has been arranged so that the terms of higher order in the charges are collected on the right. The reason for this division can be clearly shown only after an approximate solution is obtained. Initially it assumed that the primed potentials are proportional to the first power of the corresponding charges. Since $\underline{\nabla} f_{ji}^{o}$ starts proportional to $e_i e_j$ the terms on the right are all of order $e_i^2 e_j^2$, $e_i e_j^3$, $e_i^3 e_j$. The last term on the left is of order $e_i e_j$ and is assumed to give the leading term of the solution. The problem is now specified to a solution of a single electrolyte giving only two kinds of ions. Accordingly let $i = 1$; $j = 2$. Equation (42) can then be written as

$$X(e_1\omega_1 - e_2\omega_2)(\partial f_{21}/\partial x) - kT(\omega_1 + \omega_2)\nabla^2 f_{21}'$$
$$- f_{21}^{o}(e_1\omega_1\nabla^2 \Psi_2' - e_2\omega_2\nabla^2\Psi_1') = \sum_i T_i \qquad (49)$$

where $\sum_i T_i$ denotes the higher order terms. An approximate solution for the asymmetric distribution function is then found ignoring the higher order terms. Let

$$\psi_2' = \Psi_2 + p_2 \tag{50}$$

and

$$f_{21}' = F_{21} + g_{21} \tag{51}$$

where $\underline{\Psi}$ and $\underline{F}$ are the first order approximate asymmetric potential and distribution function obtained by solution of equation (49) without the terms $\sum_i T_i$. The contributions of these terms are denoted by $\underline{p}$ and $\underline{g}$ respectively. The potentials and distribution functions are assumed to be related by Poisson equations:

$$\nabla^2 \Psi_2 = -4\pi F_{21}/D\, n_1 \tag{52}$$

and

$$\nabla^2 p_2 = -4\pi g_{21}/D\, n_1 \tag{53}$$

From equation (49) making use of equation (52) and rearranging terms, the differential expression to be solved for $\underline{F_{21}}$, the first order approximation to the distribution functions, becomes

$$\nabla^2 F_{21} - \left[\frac{4\pi f_{21}^{\,o}}{DkT(\omega_1 + \omega_2)} \right] \left[\frac{e_1^2\omega_1}{n_2} + \frac{e_2^2\omega_2}{n_1} \right] F_{21} = \frac{X(e_1\omega_1 - e_2\omega_2)}{kT\ (\omega_1 + \omega_2)} \left(\frac{\partial f_{21}^{\,o}}{\partial x} \right) \tag{54}$$

Having obtained $\underline{F}_{21}$, the potential $\underline{\Psi}_2$ is found by solution of the Poisson equation (52). Differentiation of $\underline{\Psi_2}$ gives the first order approximation to the relaxation field, $\underline{\Delta X_1}$. Then, the expression for $\underline{F_{21}}$ is substituted, with equation (51), into the differential equation (49) keeping the higher terms $\underline{T_i}$. This gives a differential equation, the solution of which is $\underline{g}_{21}$. The potential $\underline{p}_2$ is then found from the Poisson equation (53). A correction to the first order relaxation field is then obtained from $\underline{p}_2$. A glance at the form of the higher terms (shown in equation 42), clearly indicates that the second order solution is not easy to find. The method actually used by Onsager consists of splitting $\underline{g}_{21}$ into four

parts and treating each part as a separate problem. Further comments about the higher-order terms will be reserved until after the first order solution is set down.

4. First Order Approximation to the Distribution Function and Relaxation Field

To obtain the first order solution F_{21} from equation (54) it is necessary to know f_{21}^{o}, the equilibrium distribution function. The complete function was derived above and is given by equation (8). Onsager and Fuoss, in stressing consistency of the order of terms, used the expanded forms of f_{21}^{o} given by equation (23) to various degrees of accuracy. For example, for the derivative term of equation (54), two terms of f_{21}^{o} are used:

$$f_{21}^{o} \simeq n_1 n_2 (1 - e_1 e_2 e^{-\varkappa r}/\mu D k T r) \tag{55}$$

where

$$\mu \equiv (1 + \varkappa a)/e^{\varkappa a} \tag{56}$$

To this approximation $(\partial f_{21}^{o}/\partial x) \sim e_1$ and the term of the right of equation (54) begins proportional to e_1^2. The second term of the left is already proportional to e_1^2 so that in this term the approximation

$$f_{21}^{o} \approx n_1 n_2 \tag{57}$$

is used. Making these substitutions and the electrical neutrality requirement (equation 13), equation (42) to first order reduces to

$$\nabla^2 F_{21} - \gamma^2 F_{21} = \left[\frac{n_1 e_1 \gamma^2 X}{4\pi\mu k T}\right]\left[\frac{\partial}{\partial x}\left(\frac{e^{-\varkappa r}}{r}\right)\right] \tag{58}$$

where

$$\gamma^2 = q^2 \varkappa^2 = \left[\frac{4\pi}{DkT(\omega_1 + \omega_2)}\right]\left[n_1 e_1^2 \omega_1 + n_2 e_2^2 \omega_2\right] \tag{59}$$

Subject to the first boundary condition $(\partial\Psi'/\partial r)$ = 0, this equation has the solution:

$$F_{21} = \left[\frac{n_1 e_1 q^2 X}{4\pi\mu kT(1-q^2)}\right]\left[\frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r} - \frac{Ae^{-\gamma r}}{r}\right)\right] \tag{60}$$

Substitution of this expression into the Poisson equation (52) and subsequent integration gives the potential

$$\Psi = \left\{\frac{e_1 e_2 g^2 X}{\mu DkT(1-q^2)}\right\}\left\{\frac{\partial}{\partial x}\left[\frac{e^{-\kappa r}}{\kappa^2 r} - \frac{Ae^{-\gamma r}}{\gamma^2 r} + \frac{B}{r}\left(\frac{1}{\gamma^2} - \frac{1}{\kappa^2}\right)\right]\right\} \tag{61}$$

where A and B are constants of integration. Since this solution contains the charges only as the product e_1e_2, the solutions for Ψ_1 and Ψ_2 are identical and are denoted by Ψ. The combined form of the second and third boundary conditions serves to evaluate A in terms of B. The constant B is obtained from the fourth boundary condition in which higher-order terms are neglected. The relaxation field is found from the relation

$$\Delta X = -\nabla_x \Psi(a) = -(\partial\Psi/\partial x)_a \tag{62}$$

For the simple case of point charges ($a = o$) A and B are both unity. The field for point charges, ΔX_0, is given by

$$\Delta X_0 = \left[\frac{e_1 e_2 g^2 X}{DkT(1-q^2)}\right] \lim_{r \to o}\left[\frac{e^{-\kappa r}(1+\kappa r)}{\kappa^2 r^3} - \frac{e^{-\gamma r}(1+\gamma r)}{\gamma^2 r^2} + \frac{1}{\gamma^2 r^3} - \frac{1}{\kappa^2 r^3}\right] \tag{63}$$

Expansion of the factors $e^{-\kappa r}$ and $e^{-\gamma r}$ to order r^2, and taking the indicated limit (triple differentiation of numerator and denominator) leads to

$$\frac{\Delta X_0}{X} = \frac{e_1 e_2 q^2 \kappa}{3\, DkT(1+q)} \tag{64}$$

This is the classic result obtained by Onsager in 1927 and is usually written as

$$\frac{\Delta X_0}{X} = -a\,c^{*\frac{1}{2}} \tag{64a}$$

where c^* is the normality of the solution and a is a constant.

For the case in which the ions are represented by hard spheres with minimum distance of approach a, the constants A and B of equation (61) are complicated functions of κa. From equations (61) and (62) an expression for ΔX for this model is obtained. The result may be expressed as a correction, $-\Delta X_0 \Delta_1$, to the solution for point charges. Accordingly Δ_1 is defined by the relation

$$\Delta X = \Delta X_0 \,(1 - \Delta_1) \tag{65}$$

So that

$$\Delta_1 = 1 - (\Delta X / \Delta X_0) \tag{66}$$

The ratio $(\Delta X / \Delta X_0)$ is found to be

$$\frac{\Delta X}{\Delta X_0} = \frac{1 + (\frac{\kappa a}{2})\,(1 + q)\left[1 - \frac{1 + \kappa a}{b}\right]}{(1 + \kappa a)\, p_3} \tag{67}$$

where

$$b = |e_1 e_2| \,/\, aDkT \tag{68}$$

and

$$p_3 = 1 + q\,\kappa a + q^2 \kappa^2 a^2/3 \tag{69}$$

The quantity Δ_1 may be written

$$\Delta_1 = \frac{\kappa a(1 + q)}{p_3(1 + \kappa a)} + \frac{\kappa a(1 + q)}{2bp_3} + \frac{\kappa^2\, a^2}{p_3(1 + \kappa a)}\left[q + q^2/3\right] \tag{70}$$

At this point Onsager and Fuoss specialize to the case of symmetrical electrolytes, for which $q^2 = 1/2$, and to the approximation that $(1 + 6q)/3\,(1 + q) \approx 1$, The expression for Δ_1 can be written in the much simpler form of equation (71).

$$\Delta_1 = \kappa a(1 + q)\,(1 + b)\,/2\,bp_3 \tag{71}$$

It should be pointed out that with equations (65) and (70), the relaxation field to first approximation may be calculated for any electrolyte charge type. The result is consistent to terms of order κ^2. The quantity of interest $(\Delta X/X)$ can now be written to first approximation as

$$\frac{\Delta X_1}{X} = \frac{e_1 e_2 q^2 \quad (1 - \Delta_1)}{3DkT\ (1 + q)} = - \quad \alpha\, c^{*\frac{1}{2}}\ (1 - \Delta_1) \tag{72}$$

5. The Second Order Approximation to the Relaxation Field

The second order approximation to f_{ji}' and $\Delta X/X$ is now found by returning to the continuity equation (42), (49) including higher terms. Substitutions of equation (51)

$$f_{21}' = F_{21} + g_{21} \tag{51}$$

into equation (49) gives a differential equation in g_{21}. Expansion of the higher terms, T_i, leads to a multiplicity of inhomogeneous terms of unknown order insofar as they will effect the solution of the equation. An ingenious method of classifying these terms was devised by Onsager and Fuoss. It consists of writing the unknown solution of the differential equation in g_{21} as a product of an unknown dimensionless function U and a determinable power of κ. The part of the complete solution which will result from each term can then be expressed as $\kappa^n U$ where n is the lowest power of κ which will appear in the solution from the term in question. When the method is applied to the single inhomogeneous term retained in the first order solution, it is found that $F_{21} \sim \kappa^4 U$. For the second order solution all terms which give $\kappa^5 U$ are retained and those giving $\kappa^6 U$ and higher are neglected. The terms T_i, when examined in this manner, are all of order κ^5. This justifies the initial separation of terms according to equation (42). It should be noted that while this procedure separates terms of higher order, no information is obtained concerning the relative magnitude of the terms.

When the distribution function in the T_i terms is expressed as $(F_{21} + g_{21})$, all the terms in g_{21} are, by definition, of higher order in κ than those in F_{21}

and may be neglected. This tremendous simplification has the effect of changing the form of the equation to be solved from

$$\nabla^2 g_{21} - \gamma^2 g_{21} = \sum_i G_i\,(r, \cos\theta) \qquad (73)$$

in which the G_i are unknown functions, to the form

$$\nabla^2 g_{21} - \gamma^2 g_{21} = \sum_i \mathfrak{F}_i\,(r, \cos\theta) \qquad (74)$$

in which the $\underline{\mathfrak{F}_i}$ involve only known functions of the variables evaluated through the use of $\underline{F_{21}}$ and $\underline{\Psi}$. The equilibrum distribution function is again used in various approximate forms, the number of terms used always being one more than was used in the corresponding location in the first order solution. It is important to note that this requires retension, in one instance, of the quadratic term in the distribution function. In all cases, the equilibrum potentials are represented by the Debye-Hückel expression.

If the radial functions $\underline{h_{21}(r)}$ and $\underline{\Phi\,(r)}$ are defined by

$$\begin{aligned} F_{21}(r,\theta) &= h_{21}(r)\cos\theta \\ \Psi(r,\ \theta) &= \Phi\,(r)\cos\theta \qquad (75) \end{aligned}$$

The expanded equation in g_{21} is

$$\begin{aligned}
\nabla^2 g_{21} - \gamma^2 g_{21} = & \\
&+ \frac{n_2 e_1 e_2{}^2 \gamma^2 X}{8\pi D \mu^2 k^2 T^2} \; \frac{\partial}{\partial x} \left(\frac{e^{-2\kappa r}}{r^2} \right) && (T_x,\ g_B) \\
&- \frac{e_1 e_2 \gamma^2 e^{-\kappa r} F_{21}}{\mu D k T r} - \frac{e_1 e_2 \kappa^2 e^{-\kappa r} F_{21}}{\mu D k T r} && (T_g,\ g_{23}) \\
&+ \frac{n_2 e_2 \gamma^2}{4\pi \mu k T} \left[\frac{d}{dr} \left(\frac{e^{-\kappa r}}{r} \right) \right] \left[\frac{\partial \Phi}{\partial x} \right] && (T_g,\ g_{23}) \\
&- \frac{e_1 e_2}{\mu D k T} \left[\frac{d}{dr} \left(\frac{e^{-\kappa r}}{r} \right) \right] \left[\frac{\partial h_{21}}{\partial x} \right] && (T_g,\ g_{23}) \\
&- \left(\frac{n_2 e_2 \gamma^2}{4\pi \mu k T} \right) \left[\frac{d}{dr} \left(\frac{e^{-\kappa r}}{r} \right) \right] \left[\frac{\partial \Phi}{\partial x} \right]_a && (T_a,\ g_a) \\
&+ \left[\frac{n_1 n_2 e_1 e_2 \,(v_{1s} - v_{2}s)}{\mu D k^2 T^2 (\omega_1 + \omega_2)} \right] \left[\frac{d}{dr} \left(\frac{e^{-\kappa r}}{r} \right) \right] && (T_v,\ g_v) \qquad (76)
\end{aligned}$$

The boundary conditions applied to this equation becomes

$$\nabla p_j(\infty) = 0$$

$$[r \; \partial p_j / \partial r - p_j]_a = 0$$

$$Z'(a) = 0 \tag{77}$$

The function Z'(r) is obtained from the expression for Z(r) in the same manner in which the differential equation for g_{21} was obtained from the continuity equation.

Rather than attempt to solve equation (76) directly for g_{21}, Onsager and Fuoss have devised a method whereby the result can be obtained from the particular solutions found for certain groups of inhomogeneous terms. They therefore divide g_{21} into the sum of four terms.

$$g_{21} = g_B + g_{2,3} + g_a + g_v \equiv \sum_j g_j \tag{78}$$

The first symbol to right of the inhomogeneous terms of equation (76) indicates the origin of the term in the continuity equation (T_i) and the second indicates the part of g_{21} to which each term gives rise.

The problem then is divided into four simpler ones. Rather than finding the potentials p_j from Poissan equations in g_j and differentiating to get the second order parts of the relaxation field (ΔX_j), the latter are found directly from the boundary conditions. In order to find the solution g_v, it is necessary to first find the radial components of the local solvent velocities v_{1r} and v_{2r}. These quantities also appear in the boundary condition $[Z'(r)]_a$.

6. Solvent Velocities and the Electrophoretic Effect

It may be well, at this point, to recall that v_{is} is the velocity produced in the solvent at a distance r from an i-ion by a j-ion, and that these velocities have come into the equation from the velocity field terms.

$$(v_{is} \cdot \nabla f_{ij} - v_{js} f_{ji})$$

When reduced to the single variable $\vec{r}$, and the problem is specified to $i = 1$, $j = 2$, these terms are denoted by

$$(\vec{v}_{1r} - \vec{v}_{2r}) \cdot \nabla f_{21}$$

These solvent velocities describe the very important electrophoretic effect as well as being necessary for the evaluation of part of the relaxation field. Insofar as electrophoresis is concerned, a rather simple method based on the integration of Stokes Law in differential form is sufficient. This method is presented later.

In order to find suitable expressions for $\vec{v}_{1r}$ and $\vec{v}_{2r}$ for use in finding the potential g_v and the part of the relaxation field ΔX_v, it is necessary to start with the general hydrodynamic equation of motion

$$\eta \nabla^2 \vec{v} = \nabla p - F \tag{79}$$

where

η = viscosity
$\vec{v}$ = solvent velocity at distance r from a selected ion
p = pressure
F = volume force (force per unit volume of solution)

The ionic subscripts are dropped for convenience. A scheme for separating the pressure and force terms of equation (79) is then devised. Since the solvent velocity must satisfy the continuity equation,

$$\nabla \cdot \vec{v} = 0 \tag{80}$$

equation (79) may be written as

$$\eta \nabla \times \nabla \times \vec{v} = \vec{F} - \nabla p \tag{81}$$

By defining the axial vector $\vec{u}$ by

$$\eta \vec{v} = \nabla(\nabla \cdot \vec{u}) - \nabla^2 \vec{u} \tag{82}$$

and constructing $\underline{\nabla \times \nabla \times \vec{v}}$ in terms of $\vec{u}$, equation (81) becomes

$$\nabla^2\nabla^2\vec{u} - \nabla(\nabla\cdot\nabla^2\vec{u}) = F - \nabla p \tag{83}$$

The form of equation (83) allows the identifications

$$\nabla^2\nabla^2\vec{u} = \vec{F} \tag{84}$$

$$\nabla(\nabla\cdot\nabla^2\vec{u}) = \nabla p \tag{85}$$

The problem is now reduced to finding $\underline{\vec{u}}$ from a knowledge of $\underline{\vec{F}}$. The desired quantity, $\underline{\vec{v}}$, is then constructed from $\underline{\vec{u}}$ according to equation (82). Since the force may be expressed as

$$\vec{F} = X\rho\vec{i} \tag{86}$$

where $\underline{\rho}$, the charge density, is approximately given by the Poisson equation

$$\rho = -(D/4\pi)\nabla^2\Psi^0 \tag{87}$$

The differential equation in $\vec{u}$ becomes

$$\nabla^2\nabla^2\vec{u} = -(DX\vec{i}/4\pi)\nabla^2\Psi^0 \tag{88}$$

A part of $\underline{\Psi}^0$ is due to the central ion and part is due to its atmosphere. It is expected that the resulting velocity, $\underline{\vec{v}}$, will contain a term describing the local disturbance of the solvent due to the central ion as well as the comparatively long range effect of its atmosphere. In relation to the relaxation field, the use of the equilibrium potential $\underline{\Psi}^0$ is justified since the solvent velocities enter as a part of the second order solution (g_V), and $\underline{\Psi}'$ would lead to an even higher-order term. The effect on the electrophoretic term is negligible by hypothesis since this leads to a term which is quadratic in the field.

Integration of equation (66) gives

$$\nabla^2\vec{u} = -(DX\vec{i}/4\pi)\Psi^0 + \nabla^2\vec{w} \tag{89}$$

where $\underline{\nabla^2\vec{w}}$ is the general solution of the homogeneous equation $\underline{\nabla^2\nabla^2\vec{u} = 0}$.

Through rather subtle reasoning concerning symmetry and boundary conditions, it is concluded that the vector $\vec{w}$ and $\nabla^2 \vec{w}$ may be disregarded. The potential Ψ^0 is then split into two terms representing the contribution from the atmosphere

$$\Psi_A = (e/D)\,(e^{-\kappa r}/\,\mu r - 1/r) \tag{90}$$

and one representing the central ion

$$\Psi_c = e/Dr \tag{91}$$

The solutions $\vec{u}_A$ and $\vec{u}_c$ are found from equation (89), and the velocity vector $\vec{v} = \vec{v}_A + \vec{v}_C$ is constructed according to equation (82). The integration constants that appear from the solution for $\vec{u}_A$ are found by requiring that $\vec{u}_A$ and its first derivative be continuous at $r = a$

$$\left(\frac{d\vec{u}_A}{dr}\right)_{a\,-\,o} = \left(\frac{d\vec{u}_A}{dr}\right)_{a\,+\,o} \tag{92}$$

One of the two constants disappears upon differentiation of construct $\vec{v}_A$. and its evaluation is not necessary. The solution $\vec{u}_C$ is found by requiring the disappearance of the radial component of $\vec{u}_C$ at $r = R$, where R is the hydrodynamic radius of the ion. The radial component of the solvent velocity in the neighborhood of an ion is simply found from the relation $v_r = \vec{r}_1 \cdot \vec{v}$ (where $\vec{r}_1$ is the unit vector in the r direction) and is

$$v_r = \frac{X\,e\cos\theta}{4\,\pi\,\eta}\left\{[2(1 + \kappa a + \kappa^2 a^2/2 + \kappa^3 a^3/6] - \frac{2e^{\kappa(a-r)}(1 - \kappa r)}{\kappa^3 r^3 (1 + \kappa a)} - \frac{R^2}{3r^3}\right\} \tag{93}$$

In the 1957 treatment of Onsager and Fuoss (8), the hydrodynamic radius R is, very reasonably, set equal to $a/2$, thus eliminating an added distance parameter. A more recent modification by Fuoss and Accascina (19) uses $R = a$. This seemingly contradictory choice comes about through a consideration of the expression for $\vec{v}$ evaluated at $r = a$.

$$\vec{v}\,(a) = \frac{Xe}{4\pi\eta}\left\{ i\left[\frac{R^2}{6a^3} + \frac{1}{2a} - \frac{2\kappa}{3(1+\kappa a)}\right] + \vec{r}_1\left[\cos\theta\left(\frac{1}{2a} - \frac{R^2}{2a^3}\right)\right]\right\} \tag{94}$$

Since one of the boundary conditions used to obtain $\vec{v}$ requires the radial component to vanish at $r = a$ and $\cos\theta$ not always zero, it must be concluded that $R = a$ in order that the radial term of equation (94) vanish unequivocally. This same requirement can be shown to be mathematically necessary in several similar ways. While this result is operationally satisfying, physical justification necessitates a modification of the model. If it is assumed that the kinetic entity called a "free ion" is really the ion plus a solvation sheath (22), the dilemma can be rationalized by allowing that the solvent molecules are "squeezed out" upon contact of the ions so that two solvated ions of radii R_j and R_i, upon contact, have a minimum distance of approach $a_j + a_i = a$. If $a_j = a_i = a/2$ and if the solvation sheath is assigned a thickness $a/2$, the desired result $R = a$ is obtained. This explanation is not altogether satisfactory since it requires a "thicker" solvation sheath for larger ions--a condition which is hardly a general truth! It should be pointed out that this difficulty arises from the boundary condition which requires the vector $\vec{u}_A$ to have a continuous derivative at $r = a$ (equation 71). The only alternative is to require continuity at $r = R$ and to proceed under the aesthetically distressing circumstance of requiring two distance parameters. Fortunately it turns out that the value of R used in the relaxation term affects the final calculated conductances only slightly.

If it is conceded that $R = a$, the x-component of $\vec{v}\,(a)$ (equation 94) becomes

$$v(a) = \frac{X\,e}{6\pi\,\eta a} - \frac{X\,e\,\kappa}{6\pi\eta(1+\kappa a)} \tag{95}$$

This expression gives the velocity of the solvent at the surface of the ion, which must also be the velocity of the ion itself. The first term is just the velocity of an isolated ion of radius $\underline{R} = \underline{a}$ as given by Stokes Law

$$v = \frac{F}{6\pi\eta R} \tag{96}$$

The second, concentration dependent, term must then be a slowing effect produced by other ions in the vicinity. This is exactly the description of the electrophoretic effect given previously; hence the second term of equation (74) is identified with the electrophoretic velocity correction

$$v_s = \frac{-X e \kappa}{6\pi\eta(1+\kappa a)} \tag{97}$$

The contribution to the equivalent conductance becomes

$$\Delta\lambda_j = \frac{-96500\,|e_j|}{1800\,\pi\,\eta} \cdot \frac{\kappa}{1+\kappa a} \tag{98}$$

For the simple case $\underline{a} = \underline{o}$ (point charges), the correction may be written

$$\Delta\lambda_j = \frac{-96500\,|e_j|\kappa}{1800\,\pi\,\eta} \equiv -\beta_j\, c^{*\frac{1}{2}} \tag{99}$$

This is the limiting form obtained in the original Onsager treatment (4) while the result expressed by equation (98) is used in the new treatment.

A different derivation of the electrophoretic correction, based on Stokes Law is presented below in section (8) of this chapter.

Having obtained the expression for the radial component of the local solution velocity (equation 93), the part of the relaxation field due to these and other terms of higher order in the continuity equation are found.

7. Higher Terms in the Relaxation Field

The final step in the evaluation of the relaxation field is the solution of equation (76) for second order correction to the asymmetric distribution function $\underline{g_{21}}$.

Integration of the Poisson equation (53) would give the corresponding potential p_2, from which the higher order correction to the relaxation field could be found. As described above $\underline{g_{21}}$ is divided into four parts

according to equation (78), and each part is found separately. Rather than integrating the Poisson equation $\underline{g}_j$ in $\underline{p}_j$ and to expressions for $\underline{p}_j$, and then differentiating to find $\underline{\Delta X}_j$, a method was devised whereby the parts of the relaxation field were expressed directly in terms of the boundary conditions and particular integrals of equation (76). The details of the method have been presented by Fuoss and Accascina (23).
The results are summarized by the following formulae:

$$\frac{\Delta X_B}{X} = -\left(\frac{e_1 e_2 \kappa}{3DkT}\right)\left[\frac{b\kappa a}{p_2(1+\kappa a)^2}\right]\left[\frac{1}{8} - \frac{1+\kappa a}{4b} + \frac{T_2}{4}\right] \qquad (100)$$

$$T_2 = \mathrm{Tr}\,[\,(2+q)\,\kappa a]$$

$$\mathrm{Tr}(x) = e^{x}\int_{x}^{\infty} e^{-t}/t = e^{x}\,\mathrm{Ei}(x)$$

$$\frac{\Delta X_A}{X} = -\left[\frac{e_1 e_2 \kappa}{3DkT}\right]\left[\frac{b\kappa a}{p_2 p_3\,(1+\kappa a)^2}\right]\left[q^2 - \frac{g}{3}\right] \qquad (101)$$

$$p_3 = 1 + \frac{g\kappa a}{2} + \frac{g^2\kappa^2 a^2}{3} = 1 + \frac{2^{\frac{1}{2}}\kappa a}{2} + \frac{\kappa^2 a^2}{6}$$

$$p_2 = 1 + \frac{2^{\frac{1}{2}}\kappa a}{2} + \frac{\kappa^2 a^2}{4}$$

$$\frac{\Delta X_{2,3}}{X} = -\left[\frac{e_1 e_2 \kappa}{3DkT}\right]\left[\frac{b\kappa a\,\zeta_5(\kappa a)}{p_2 p_3(1+\kappa a)^2}\right] \qquad (102)$$

$$\zeta_5 = \frac{2^{\frac{1}{2}}\,9-9}{16} + \frac{3p_3T_2}{16} + \frac{p_1p_3T_1}{16} - p_1p_2p_3\frac{T_0}{4}$$

$$p_1 = 1 + \kappa a + \frac{\kappa^2 a^2}{4}$$

$$T_0 = \mathrm{Tr}(\kappa a) = e^{\kappa a}\ \mathrm{Ei}\,(\kappa a)$$

$$T_1 = \mathrm{Tr}[(1+q)\,\kappa a]$$

Since each of these three terms contains the factor ΔX_0, they are conveniently combined

$$\Delta X_B + \Delta X_a + \Delta X_{2,3} = \Delta X_0 \Delta_2 \qquad (103)$$

The value of $\underline{\Delta_2}$ is then

$$\Delta_2 = \left[\frac{b(1+q)\kappa a}{(1+\kappa a)^2}\right]\left[\frac{2^{\frac{1}{2}}\,11-3}{24\,p_2p_3} + \frac{1}{4p_2} + F(\kappa a)\right] - \frac{(1+q)\kappa a}{2p'_2(1+\kappa a)} \qquad (104)$$

where

$$F(\kappa a) = (7\,T_2 + p_1T_1 - 4p_1 \cdot p_2T_0)/8p_2$$

It should be remembered that this equation (104) is valid only for symmetrical electrolytes ($q^2 = 1/2$). The relaxation field, except for the part due to the velocity field, may be written as

$$\frac{\Delta X}{X} = \alpha\, c^{*\frac{1}{2}}(1 - \Delta_1 + \Delta_2) \qquad (105)$$

The part of the relaxation term due to the velocity field (using $\underline{R} = \underline{a}$) is given by

$$\frac{\Delta X_v}{X} = \left[\frac{ab\kappa^2}{6\pi\eta\,(1+\kappa a)^2\,(\omega_1+\omega_2)}\right]\left[\frac{13 + 3\cdot 2^{\frac{1}{2}}}{48\,p'_2} + \frac{F(\kappa a)}{2}\right] - \left[\frac{\kappa^2 a}{36\pi\eta\,p_2\,(1+\kappa a)\,(\omega_1+\omega_2)}\right] \qquad (106)$$

Factoring the quantity $\underline{\beta\, c^{*\frac{1}{2}}/\Lambda^0}$,

where

$$1/(\omega_1+\omega_2) = 96,500\,|e|/300\,\Lambda^0 \qquad (107)$$

and

$$\beta\, c^{*\frac{1}{2}} = (\beta_1 + \beta_2)\, c^{*\frac{1}{2}} = \frac{96,500\,(\,|e_1| + |e_2|)\kappa}{1800\,\pi\,\eta} \qquad (108)$$

one obtains

$$\frac{\Delta X_v}{X} = \left\{\frac{b\,\kappa a}{(1+\kappa a)^2}\left[\frac{13 + 3\cdot 2^{\frac{1}{2}}}{96p'_2} + \frac{F(\kappa a)}{4}\right] - \left[\frac{\kappa a}{12\,p_2(1+\kappa a)}\right]\right\}\frac{\beta\, c^{*\frac{1}{2}}}{\Lambda^0} \qquad (109)$$

The term in braces is defined as $\underline{\Delta_3'}$

so that

$$\frac{\Delta X_v}{X} = \frac{\Delta_3' \, \beta \, c^{*\frac{1}{2}}}{\Lambda^0} \tag{109a}$$

The complete relaxation term is expressed as

$$\frac{\Delta X}{X} = \alpha \, c^{*\frac{1}{2}} \left(1 + \Delta_1 - \Delta_2 + \beta \, \Delta_3' / \alpha \Lambda^0 \right) \tag{110}$$

Further discussion of this expression will be reserved until after an alternate treatment of electrophoresis is presented.

8. The Electrophoretic Effect

The electrophoretic effect is usually treated by the following method based on the integration of Stokes Law.

Consider a volume element, $\underline{dV}$, near a central j-ion. The number of ions in excess of the stoichiometric average is

$$\sum_{i=1}^{s} (n_{ji} - n_i) \, dV$$

and the net force on the volume element is

$$X \sum_{i=1}^{s} (n_{ji} e_i - n_i e_i) \, dV$$

Similarly, the force on a spherical shell at a distance $\underline{r}$ from the central ion, and of thickness $\underline{dr}$, is

$$dF = 4\pi \, r^2 \, X \sum_{i=1}^{s} (n_{ji} e_i - n_i e_i) \, dr \tag{111}$$

This force is in the direction of the field and is distributed evenly over the surface of the shell. According to Stokes Law, the force $\underline{dF}$ will cause the spherical shell to move with a velocity $\underline{dv}$, opposed to the direction of motion of the central ion.

$$dv = \frac{dF}{6 \pi \eta \, r} \tag{112}$$

The solution inside the shell will then move with this velocity also,

imparting it to the central ion so that $\underline{dv} = \underline{dv_j}$. To obtain the total decrease in velocity $\underline{\Delta v_j}$ equation (92) is integrated from the distance of closest approach $\underline{a}$ to infinity. Combination of equation (111) and (112) gives

$$\Delta v_j = \frac{2X}{3\eta} \int_a^\infty r \sum_i e_i (n_{ji} - n_i)\, dr \tag{113}$$

or, with $\underline{n_{ji}}$ obtained from equation (23)

$$\Delta v_j = \frac{2Xe_j (\sum_i n_i e_i^2) e^{\kappa a}}{3\eta\, DkT\, (1 + \kappa a)} \int_a^\infty e^{-\kappa r}\, dr + \frac{Xe_j^2 (\sum_i n_i e_i^3) e^{2\kappa a}}{3\eta\, [DkT\, (1 + \kappa a)]^2} \int_a^\infty \frac{e^{-2\kappa r}}{r}\, dr \tag{114}$$

The integration yields:

$$\Delta v_j = - \frac{2X(\sum_i n_i e_i^2) e_j}{3\eta\, DkT\, (1 + \kappa a)} + \frac{X(\sum_i n_i e_i^3)}{3\eta} \left[\frac{e_j e^{\kappa a}}{DkT(1 + \kappa a)} \right]^2 \mathrm{Ei}(2\kappa a) \tag{115}$$

In the cases treated by Onsager, the presence of the second term is purely formal; for point charges it was ignored as being small and for symmetrical salts it vanishes because $\underline{e_i} = -\underline{e_j}$ and $\underline{\sum_i' n_i e_i^3 = 0}$. Using the definition of $\underline{\kappa}$ given by equation (16), the first term gives

$$\Delta v_j = - \frac{X\, e_j \kappa}{6\pi\eta\, (1 + \kappa a)} \tag{116}$$

which is seen to be identical with the relation obtained above (equation 97) in the discussion of the velocity field.

The correction to the equivalent conductance is given by equation (98) and is repeated here for clarity.

$$\Delta\lambda_j^e = \frac{-96,500\, |e_j| \kappa}{(1 + \kappa a)} \tag{98}$$

For two kinds of ions, the expression is

$$\Delta\Lambda_e = \frac{-96,500\,(|e_1| + |e_2|)\,\kappa}{1 + \kappa a} \equiv -\beta c^{*\frac{1}{2}} / (1 + \kappa a) \qquad (117)$$

It will be noted that in equation (111) the force on each i-ion was taken to be e_iX. Stokes and Robinson (24) have pointed out that it should be more correct to use $e_i(X + \Delta X)$ since the force actually felt by the ion is the external force e_iX diminished by an amount $e_i\Delta X$ because of the relaxation effect. This leads to the conclusion that $v_{js} \sim (X + \Delta X)$ which was assumed in obtaining the symbolic conductance equation (30). This is equivalent to introducing the cross-term, $\Delta\lambda_j^e(\Delta X/X)$, into conductance equation.

The terms of the symbolic conductance equation (30a) are now known, and the equation in the form presented by Onsager and Fuoss in 1957 can be written. Two additional terms have since been recognized and evaluated, however, and the writing of the explicit conductance equation will be postponed until after their discussion.

E. Recent Modifications of the Onsager Equation

1. The Kinetic Effect

As discussed above, an applied electric field produces an asymmetric distribution of ions of opposite charge about a chosen central ion. There is, in essence, a larger number of atmosphere ions "behind" the central ion so that thermal motions will cause the central ion to be struck from behind, more often than from the front, by these ions (9). The result is an increase in the velocity of the central ion. This effect is described by a small virtual force in the direction of the field or as an osmotic pressure on the reference ion which moves it with the field.

The osmotic pressure π, due to the field, is given by equation (118).

$$\pi = (n_{12} - n_{12}^{0})\, kT = (f_{21} - f_{21}^{0} / n_1)\, kT \qquad (118)$$

If the approximation $f_{21} \cong f_{21}^{0} + F_{21}$ is used, the pressure is

$$\pi = F_{21}\, kT/n_1 \qquad (119)$$

The force on the central ion, due to this pressure is found by integrating π over the surface of a sphere of radius a corresponding to a region into which no ions can penetrate.

The resulting force, ΔP, in the direction of the field is

$$\Delta P = X \left[\frac{\kappa^2 a^2 (b - 1)}{12b}\right] \qquad (120)$$

The conductance equation (30a), with the inclusion of this effect, becomes

$$\Lambda = (\Lambda^0 - \Delta\Lambda_e)(1 + \Delta X/X + \Delta P/X) \qquad (121)$$

The $\Delta P/X$ term is clearly linear in concentration through $\kappa^2 a^2$.

2. Einstein Viscosity Correction

It has been shown above that the electrophoretic term $\Delta\Lambda_e$ is inversely proportional to the viscosity. Similarly, if an isolated ion obeys Stokes Law, Λ^0 has the same dependence. It is concluded then that

$$\Lambda \sim 1/\eta$$

The original model used in conductance theory considers the solvent as a continuum. At finite concentrations, an ion moving with the field through the (assumed) structureless solvent will "see" ions of opposite charge as obstacles to be passed if it is to continue its course. This effect can be treated as a correction to the viscosity (11). The Einstein viscosity expression (25, 26), serves to evaluate this correction.

$$\eta = \eta_0 (1 + 5\varphi/2) \qquad (122)$$

where

η = "solution" viscosity

η_0 = solvent viscosity

φ = ion volume fraction

The volume faction is given by

$$\varphi = \frac{4\pi R^3}{3} \left(\frac{NC}{1000} \right) \equiv Fc \qquad (123)$$

where N is Avogadro's number and c is the molarity of the ions which contribute to this effect. Since, in reality, many ions are not much larger than the solvent molecules, Fuoss recommends that only "bulky" ions (such as quaternary ammonium cations) be considered as "contributing" ions.

The problem of distance parameters is again introduced. Consistent with the choice made in the velocity field terms, the value $R = a$ is taken. The effect of this term on the calculated conductance is, in some cases, much larger than is generally supposed. The effect of the value of R on the course and shape of some phoreograms (1) (plots of Λ vs. $c^{\frac{1}{2}}$) will be shown in Chapter 4.

3. The Effect of the Relaxation Field on the Electrophoretic Term

In the discussion of the electrophoretic effect, it was noted that the assumption that the force per atmosphere ion in a spherical shell about a central ion is given by $e_j(X + \Delta X)$ leads to the cross-term $(\Delta\lambda_i^e)(\Delta X/X)$ in the conductance equation. If, however, the atmosphere is represented as a charge cloud, as is the case, Dye (27) has taken the view that the correction to the force $e_j\Delta X$ should not be treated as constant but as a function of r and θ. The term ΔX is regarded as shielding of an ion by its atmosphere and changes as r and θ are varied. This effect can be expressed as a correction to the cross-term and is, of course, very small. Using the asymmetric potential for point charges (28) to obtain $\Delta X(r, \theta)$, the cross-term correction is shown to be

$$- \mid (\Delta_{+}) (\Delta\lambda^{e}) (\Delta X/X) \mid \qquad (124)$$

where

$$\Delta_{+} = \frac{e^{\kappa a}}{1 - q} \quad E_i[(1 + q)\,\kappa a] - E_i\,[2\,\kappa\,a] \qquad (125)$$

F. The Complete Onsager Conductance Equation and Its Limitations

The complete conductance equation may be written in the form

$$\Lambda = \frac{(\Lambda^{0} - \Delta\Lambda_{e})\,(1 + \Delta X/X + \Delta P/X)}{(1 + F\,c)} \qquad (126)$$

Values of Λ may be calculated using the various expressions for the terms of (126) given above. A more convenient expression is obtained by expansion of this equation. The relaxation field through the terms Δ_2 and Δ_3' contains several transcendental functions all of which are related to the function

$$E_i(x) = \int_{x}^{\infty} (e^{-t}/t)dt \qquad (127)$$

For small values of x, this function may be approximated by

$$E_i(x) \cong \Gamma - \ln x + x \ldots \qquad (128)$$

in which $\Gamma = 0.5772$. Using this approximation and

$$(1 + Fc)^{-1} \cong F\,c \qquad (129)$$

the conductance equation may be written

$$\Lambda = \Lambda^{0} - S\,c^{*\frac{1}{2}} + E\,c^{*} \log c^{*} + J\,c^{*} - F\,\Lambda^{0}\,c \qquad (130)$$

where all terms of order $c^{*\frac{3}{2}}$ and higher have been dropped. The expressions for the constants S, E, J and F are summarized by Fuoss and Accascina (29). The first two terms of equation (130) give the Onsager limiting law. The higher terms give theoretical justification for the long-standing practice (30, 31) of fitting conductance data with empirical terms of the form *Dclogc* and *Bc*.

The conductance equation (126, 130) is completely consistent to terms linear in the concentration. Higher order concentration dependence is ignored. The results are limited to solutions of completely dissociated symmetrical salts. Mathematical approximations limit the range of applicability to values of $\kappa a < 0.2$ or approximately 0.1 normal for 1-1 electrolytes in water. This limit is also physically reasonable since the representation of the ionic atmosphere as a charge cloud certainly becomes invalid at higher concentrations. The equation contains at least two parameters, Λ^0 and the distance of closest approach a. The relationship between the hydrodynamic radius R, and a, should be clarified by extensive studies of viscosity effects as suggested by Stokes (32).

G. Ion Association and Conductance

The idea of ion-association was first suggested by Bjerrum (10) as a means of explaining observed deviations from the Debye-Hückel expression for activity coefficients. The postulation of an equilibrium caused solely by electrostatic interactions between "free" ions and neutral ion-pairs according to the scheme

$$C^+ + A^- \underset{}{\overset{K}{\rightleftharpoons}} (C^+ A^-)^0$$

leads to an expression for the association constant K

$$K = (1 - \gamma) / c\, \gamma^2 f^2 \qquad (131)$$

where γ is the fraction of ions which are free and f is the ionic activity coefficient given by the Debye-Hückel expression. The activity coefficient of the neutral species is assumed to be unity. Bjerrum obtained a theoretical value for K by considering the probability of finding an anion in a spherical shell of thickness dr and radius r around a reference cation. The resulting expression for the association constant is

$$K = \frac{4\pi N}{1000} (ab)^3\, Q(b) \qquad (132)$$

where

$$Q(b) = \frac{1}{6}\left\{e^2 - \mathrm{Ei}(2) + \mathrm{Ei}(b) - (e^b/b)(1 + 1/b + 2/b^2)\right\} \qquad (133)$$

and b has been previously defined by equation (68) as $|e_1e_2|/aDkT$. This expression suffers from the mathematical necessity of considering ions which are not in physical contact, (less than the distance $ab/2$ apart), as pairs. Furthermore it predicts abrupt cessation of ion pairing at a critical value of the dielectric constant. For large values of b

$$K \approx \frac{4\pi a^3 N}{1000} \cdot \frac{e^b}{b} \qquad (134)$$

Using a thermodynamic approach, Denison and Ramsey (33) and Gilkerson (34) conclude that K is proportional to e^b. The Gilkerson expression is

$$K = [G \exp(-Ap_S/kT)]e^b \qquad (135)$$

where G and A are constants and p_S is the dipole moment of a solvent molecule. The quantity Ap_S represents the difference in solvation energies of the ions and the ion pair. In a mechanistic treatment, Fuoss (35) has also reached the conclusion that

$$K \sim e^b.$$

The application of the concept of ion pairing to conductance is obvious. The concentration terms in the Onsager expression refer to ion concentrations. The presence of a pairing equilibrium means that the average concentration of ions is less than the stoichiometric amount and that c^* everywhere, except in the viscosity correction, in the conductance equation should be replaced by the ion concentration $c_i = \gamma c$. The observed conductance for 1-1 electrolytes where $c = c^*$, is given by $\underline{\Lambda = \gamma\ \Lambda}_{calc.}$ or in the expanded form of equation (130)

$$\Lambda = \frac{\Lambda^0 - S c_i^{\frac{1}{2}} + E c_i \log c_i + J c_i - K c_i f^2 \Lambda (1 + Fc)}{1 + Fc} \qquad (136)$$

Unfortunately, the theoretical expressions for K prove to be unreliable. For solutions of low dielectric constant, the best numerical values are given by the Bjerrum equation (132). However, recent careful examination (12) has shown that K is more nearly proportional to e^b than e^b/b. As a result the ion pairing constant is now treated as a parameter chosen to give the best fit to the data. Fuoss (36) has outlined several graphical methods for the selection of the parameters Λ^0, a, and K of equation (136).

It should be noted, that through the linear superposition of fields approximation, (equation 7), only approximate expressions for the ionic potential and distribution function are obtainable. If exact expressions were known, and the model of non-polarizable spherical ions represented real ions accurately, there would be no need for consideration of ion pairing. Since, in reality, ions are polarizable, the introduction of ion-pairing equibria must be considered to represent in part real phenomena and in part a device to hide inherent mathematical inadequacies.

In the hope of bringing to light the effect of some of the mathematical approximations, the following study of the higher terms of the electrophoretic effect is presented.

III. The Effect of Higher Terms in the Distribution Function on the Electrophoretic Effect for 1-1 Salts in Dioxane-Water Mixtures

A. Introduction

When the Onsager equation is applied to aqueous solutions of multiple-charged ions or to nonaqueous solutions of univalent ions, large discrepancies between observed and calculated values of conductances often occur. Much better agreement was obtained for aqueous solutions of certain multivalent ions, whose activity coefficients obey the Debye-Hückel equation,

when the complete electrophoretic effect was employed by Dye and Spedding (13). This treatment of electrophoresis uses an exponential distribution function. Since the extended Onsager expression for the time of relaxation effect is specialized to symmetrically charged ions, it seemed desirable to study the complete electrophoretic effect for symmetrical salts for which a suitable account of the relaxation contribution to conductance may be taken. Accordingly, an examination of the magnitude of the higher terms of the electrophoretic effect of "uni-univalent" salts in dioxane-water mixtures has been made and is presented after a brief *rationale* of the Dye-Spedding treatment.

B. The Extended Electrophoretic Effect

1. The Exponential Distribution Function

Onsager (37) has shown that the statistically correct expression for the equilibrium distribution function f_{ji}^0 is

$$f_{ji}^0 = n_j n_i \exp [- U_{ji}^0 / kT] \qquad (137)$$

where U_{ji}^0 is the time-average energy required to charge an *i*-ion at a distance *r* from a *j*-ion, less the time average energy required to charge the *i*-ion at an infinite distance from the *j*-ion (but still in the solution). The linear superposition of fields approximation

$$U_{ji}^0 = e_i \Psi_j^0 \qquad (7)$$

gives

$$f_{ji}^0 = n_i n_j [\exp(-e_i \Psi_j^0 / kT)] \qquad (138)$$

It is not until the Poisson equation (11) is used to obtain Ψ_j^0 that it becomes mathematically necessary to expand the exponent in equation (138). Consistency requires the retension of the first two terms only.

$$f_{ji}^0 = n_i n_j [1 - e_i \Psi_j^0 / kT] \qquad (139)$$

A comparison of the forms of equation (137), (138), and (139) suggests that much of the difficulty may lie in the use of the Poisson equation rather than in the linear superposition of fields "approximation." It should be emphasized that the latter is a statement about time-average energies and time-average potentials, and while instantaneous values may differ greatly, the time average potential energy $\underline{U_{ji}}^0$ may be very closely approximated by equation (7). The Poisson equation, on the other hand, is known to be valid only for static systems and may also be regarded as an approximation when applied to non-equilibrium processes in electrolytic solutions. While these statements do not really help the mathematical situation, the conceptual distinction allows one to adopt the best (even though approximate) expression available for the energy $\underline{U_{ji}}^0$. This "best" expression is obtainable through the Poisson equation.

$$U_{ji}^0 = e_i \psi_j^0 = \frac{e_i e_j e^{\kappa a}}{D(1+\kappa a)} \cdot \frac{e^{-\kappa r}}{r} \qquad (140)$$

For point charges

$$U_{ji}^0 = e_i e_j e^{-\kappa r}/Dr$$

which, as $\underline{r}$ becomes small, approaches the simple expression for the pairwise energy between two charges:

$$U_{ji}^0 \longrightarrow e_i e_j/Dr \qquad \text{as} \quad r \longrightarrow 0$$

Combination of equation (140) and (137) give the "complete" distribution function

$$f_{ji}^0 = n_i n_j \exp\left[- \frac{e_i e_j e^{\kappa a}}{DkT(1+\kappa a)} \cdot \frac{e^{-\kappa r}}{r} \right] \qquad (141)$$

An alternative argument for the use of this expression has been made by Kirkwood (38) who pointed out that, while the Poisson equation may be an incorrect expression for the second derivative of the potential $\underline{\nabla^2 \psi_j^0}$, the resulting value of the potential itself may be only slightly in error.

It is interesting to compare the exponential distribution function (equation 138) and the linearized form (equation 139) with the function

$$f_{ji}^{0} = n_i n_j \exp\left[- e_i e_j / DrkT \right]$$

which was used by Bjerrum (19) in his treatment of ion pairs. Figure 1 is a sketch of the radial function $\underline{(f_{ji}^{0}/n_j)\ 4\ \pi\ r^2}$ for various distribution functions. The plot refers to a 1-1 electrolyte at $\underline{c} = \underline{0.01}$ with the contact distance $\underline{a} = 4.0$ Å. It is clear from the figure that the linearized function ignores a large interaction force between oppositely charged ions at closed distances. The Bjerrum function accounts for these forces at small distances but diverges at large values of $\underline{r}$. The exponential function, however, gives the correct limiting behavior at both large and small distances. It is this distribution which is used in the Dye-Spedding treatment of electrophoretic theory.

2. Formulation of the Electrophoretic Term

In the preceding treatment of the electrophoretic effect, the expression for the ionic velocity correction due to this effect is given by equation (113)

$$\Delta v_j = \frac{2X}{3\eta} \int_a^{\infty} r \left[\sum_i (n_{ji} - n_i) e_i \right] dr \qquad (113)$$

The correction to the conductance is, then

$$\Delta \lambda_j = \frac{96,500}{450\ \eta} \int_a^{\infty} r \left[\sum_i (n_{ji} - n_i) e_i \right] dr \qquad (142)$$

Using the value of $\underline{n_{ji}}$ given by the exponential distribution function (equation 141) ($\underline{n}_{ji} = f_{ji}^{0}/n_j$), one obtains

$$\Delta \lambda_j = \frac{96,500}{450\ \eta} \int_a^{\infty} r \sum_i n_i e_i \left[\exp\left(- \frac{e_i e_j e^{\kappa a}}{DkT(1+\kappa a)} \cdot \frac{e^{-\kappa r}}{r}\right) - 1 \right] dr \qquad (143)$$

For convenience, the following quantities are defined:

$\rho = \kappa r$

$x = \kappa a$

$e_i = Z_i \epsilon$

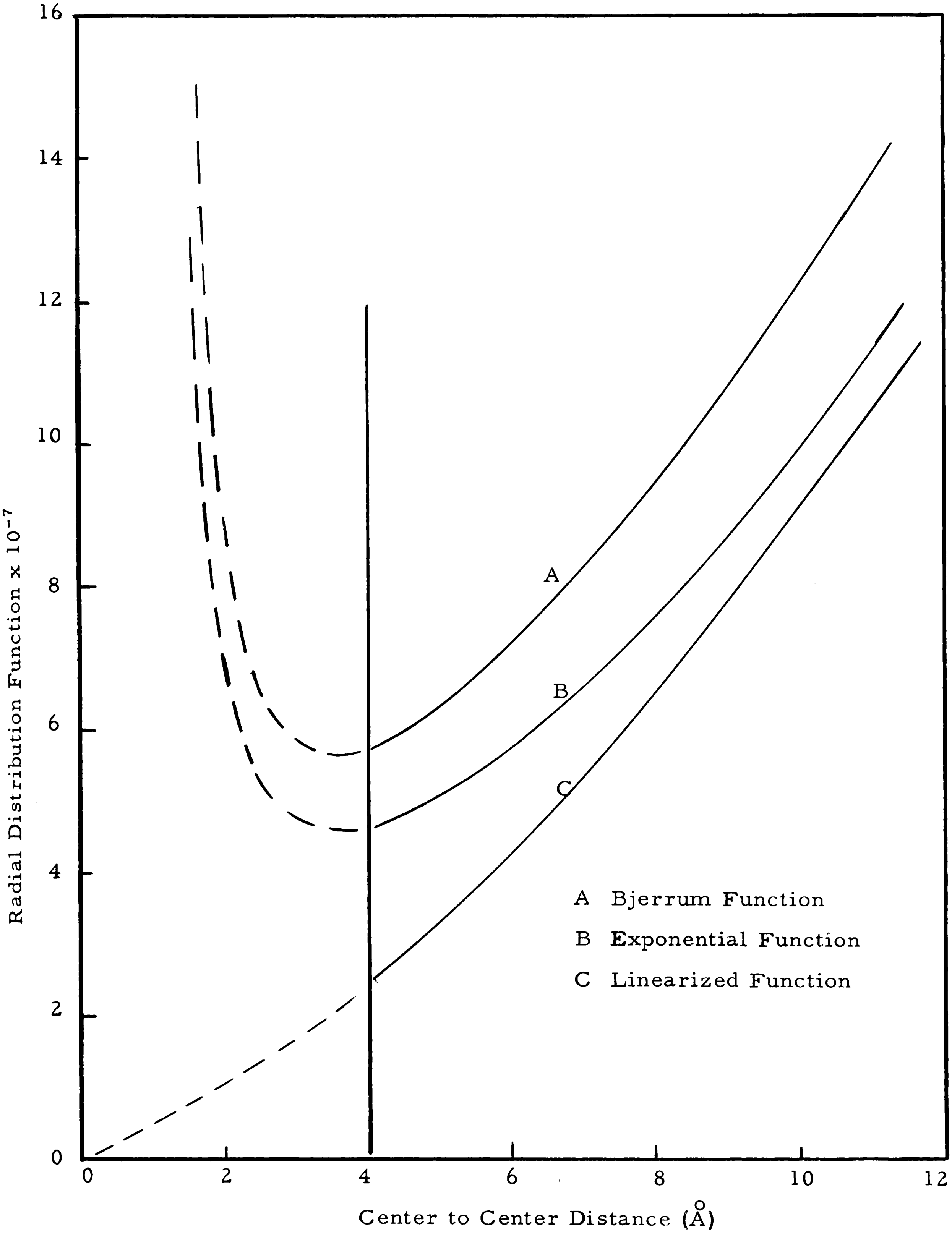


Figure 1. Comparison of several radial distribution functions for 0.01 normal solution of a 1-1 electrolyte in water at 25°C: a = 4.0 Å.

where ϵ is the charge on the electron and Z_i is the signed number of charges carried by an ion of type i.

Equation (143) then becomes

$$\Delta\lambda_j = \frac{96,500}{450\,\eta\kappa^2} \int_x^\infty \rho \sum_i n_i e_i \left[\exp(Z_i Z_j \frac{e^x \epsilon^2}{DkT(1+\kappa a)} \cdot \frac{e^{-\rho}}{\rho}) - 1\right] d\rho \tag{144}$$

For an electrolyte which dissociates into only two kind of ions according to the scheme,

$$M_{\nu_+} A_{\nu_-} \longrightarrow \nu_+ M^{Z_+} + \nu_- A^{Z_-}$$

equation (144) may be specialized to

$$\Delta\lambda_+ = \frac{96,500}{450\,\eta\kappa^2} \int_x^\infty \Big\{ n_+ e_+ \rho [\exp(-Z_+^2 P e^{-\rho}/\rho) - 1] + n_- e_- \rho [\exp(-Z_+ Z_- P e^{-\rho}\;\rho) - 1] \Big\} d\rho \tag{145}$$

where P is defined as

$$P \equiv \kappa e^x / DkT\,(1+x) \tag{146}$$

Using the relationships

$$n_+ e_+ = \frac{\nu_+ Z_+ \, cN\epsilon}{1000} \qquad n_- e_- = \frac{\nu_- Z_- cN\epsilon}{1000} \tag{147}$$

and

$$\nu_+ Z_+ = -\nu_- Z_-$$

$$|\,\nu_+ Z_+\,| = |\,\nu_- Z_-\,| \tag{148}$$

where c is the stoichiometric molarity and N is Avogadro's number, one obtains

$$\Delta\lambda_+ = \frac{96,500\; cN\epsilon\, \nu_+ Z_+}{10^3 \cdot 450\,\eta\kappa^2} \int_x^\infty \rho \Big\{ \exp[-Z_+^2 P e^{-\rho}/\rho] + \exp[\,|Z_+ Z_-|\, P e^{-\rho}/\rho\,] \Big\} d\rho \tag{149}$$

The definition of κ is given by equation (16) and may be written as

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT}\sum_i n_i Z_i^2 = \frac{4\pi\epsilon^2 N c}{10^3 DkT}\left[\nu_+ Z_+^2 + \nu_- Z_-^2\right] \tag{150}$$

Combination of equations (149) and (150), making use of (148), gives

$$\Delta\lambda_+ = M\int_x^\infty \rho\left\{\exp\left[-Z_+^2 P e^{-\rho}/\rho\right] - \exp\left[Z_+ Z_- P e^{-\rho}/\rho\right]\right\} d\rho \tag{151}$$

where

$$M \equiv \frac{96,500\ DkT}{1800\ \pi\eta\epsilon\left(|Z_+| + |Z_-|\right)} \tag{152}$$

A similar expression for $\Delta\lambda_-$ is

$$\Delta\lambda_- = M\int_x^\infty \rho\left\{\exp\left[-Z_-^2 P e^{-\rho}/\rho\right] - \exp\left[|Z_+ Z_-|\, P e^{-\rho}/\rho\right]\right\} d\rho \tag{153}$$

Equations (151) and (153) are the final expressions obtained by Dye and Spedding. These integrals are functions of the charge type, dielectric constant, viscosity, temperature, concentration and, the minimum distance of approach a. It should be noted that κ appears alone through the exponential coefficient P (equation 146) so that several values of an integral can occur for a given κa.

3. The Evaluation of Extended Electrophoretic Effect for Univalent Electrolytes in Dioxane-Water Mixtures

In order to evaluate the electrophoretic integrals (equations 151, 153), a program was written for the Michigan State University *MISTIC* high speed digital computer. A description of this program is given in Appendix I. Tables 1 through 9 give the electrophoretic correction $\Delta\Lambda_e$ to the equivalent conductance of 1-1 salts in water and dioxane-water mixtures from 10 to 70 weight percent dioxane. The dielectric constants and viscosities are taken from several sources and have been summarized by Fuoss and Accascina (19). The computational accuracy of the $\Delta\Lambda_e$ values is 0.004 conductance units. For 1-1 salts $\Delta\lambda_+ = \Delta\lambda_- = \Delta\Lambda_e/2$. Because of the method used in computing these values, the single ion conductances are accurate to ± 0.002 units. (See Appendix I.) The extended term is compared with the Onsager electrophoretic term ($\beta c^{\frac{1}{2}}/1 + \kappa a$) and the ratio [$\Delta\Lambda_e(1 + \kappa a)/\beta c^{\frac{1}{2}}$] is given for a series of concentrations at each of several values of the distance parameter a. Figure 2 shows the change in the ratio of the extended term $\Delta\Lambda_e$ to the Onsager term $\beta c^{\frac{1}{2}}/1 + \kappa a$ with the square root of the normality for various values of a in 60% dioxane ($D = 27.21$). Plots for the other solvent mixtures exhibit the same features. In all cases for which values were obtained, the extended term is larger than the Onsager term. The ratio of the terms rapidly increases from unity at $c^{\frac{1}{2}} = 0$ and passes through a maximum in the neighborhood of $\kappa a \approx 0.35$.

Figure 3 is a plot of $\Delta\Lambda_e(1 + \kappa a)/\beta c^{\frac{1}{2}}$ *vs.* a for several values of $c^{\frac{1}{2}}$ in 60% dioxane - 40% water. The extended term becomes larger as a decreases. Evidently the ratio approaches unity as a approaches infinity. As $a \rightarrow 0$, the Onsager term approaches $\beta c^{\frac{1}{2}}$, while the extended term and ratio become infinite. For the model of hard spheres used in the theory, however, a can never be zero.

Figure 4 shows the increasing importance of the higher terms of the electrophoretic effect as the solvent dielectric constant is decreased. The ratio $\Delta\Lambda_e(1 + \kappa a)/\beta c^{\frac{1}{2}}$ *vs.* dielectric constant is plotted at $c^{\frac{1}{2}} = 0.07$ for water ($D = 78.54$) and dioxane-water mixtures from 10% ($D = 70.33$) to 70% dioxane ($D = 19.07$). Curves at a values of 4.0, 5.0 and 6.0 Å are shown. Below $D = 70$ (10% Dioxane), the curves increase smoothly with decreasing dielectric constant. In the region $80 > D > 40$, β decreases since the drop in dielectric constant is overpowered by an increase in the viscosity. As a result both $\beta c^{\frac{1}{2}}/(1 + \kappa a)$ and $\Delta\Lambda_e$ decrease with decreasing D. The extended term decreases more slowly,

TABLE 1

THE EXTENDED ELECTROPHORETIC CONDUCTANCE TERM FOR 1-1 ELECTROLYTES AT 25°C.: WATER

$D = 78.54$ $\eta = 0.8937$ $\beta = 60.19$ $10^{-8}\kappa/\sqrt{c} = 0.3286$

$\mathring{a}$	$\sqrt{c}$	$\Delta\Lambda_e$	$\frac{\beta\sqrt{c}}{1+\kappa a}$	$\frac{\Delta\Lambda_e(1+\kappa a)}{\beta\sqrt{c}}$
7.0	0.07	3.678	3.629	1.014
	0.04	2.228	2.205	1.010
	0.02	1.160	1.151	1.008
	0.01	0.592	0.588	1.007
6.0	0.07	3.764	3.702	1.017
	0.04	2.258	2.232	1.012
	0.02	1.168	1.158	1.009
	0.01	0.594	0.590	1.007
5.0	0.07	3.862	3.778	1.022
	0.04	2.294	2.260	1.015
	0.02	1.178	1.166	1.010
	0.01	0.598	0.592	1.010
4.5	0.07	3.914	3.818	1.025
	0.04	2.313	2.274	1.017
	0.02	1.182	1.169	1.011
	0.01	0.598	0.593	1.008
4.0	0.07	3.974	3.858	1.030
	0.04	2.335	2.288	1.021
	0.02	1.191	1.173	1.015
	0.01	0.600	0.594	1.010
3.5	0.07	4.040	3.899	1.036
	0.04	2.361	2.302	1.026
	0.02	1.197	1.177	1.017
	0.01	0.602	0.595	1.012

TABLE 2

THE EXTENDED ELECTROPHORETIC CONDUCTANCE TERM FOR 1-1 ELECTROLYTES AT 25°C.: 10% DIOXANE-90% WATER

D = 70.33 η = 1.073 β = 53.08 $10^{-8}\kappa/\sqrt{c}$ = 0.3275

$\overset{\circ}{a}$	$\sqrt{c}$	$\Delta\Lambda_e$	$\frac{\beta\sqrt{c}}{1+\kappa a}$	$\frac{\Delta\Lambda_e(1+\kappa a)}{\beta\sqrt{c}}$
7.0	0.07	3.224	3.202	1.006
	0.04	1.958	1.944	1.007
	0.02	1.021	1.015	1.005
	0.01	0.522	0.518	1.003
6.0	0.07	3.308	3.280	1.072
	0.04	1.989	1.968	1.010
	0.02	1.031	1.022	1.008
	0.01	0.522	0.520	1.003
5.0	0.07	3.400	3.333	1.020
	0.04	2.023	1.992	1.015
	0.02	1.038	1.028	1.009
	0.01	0.525	0.522	1.005
4.5	0.07	3.452	3.368	1.024
	0.04	2.043	2.004	1.019
	0.02	1.046	1.032	1.013
	0.01	0.527	0.522	1.009
4.0	0.07	3.512	3.403	1.032
	0.04	2.063	2.017	1.022
	0.02	1.050	1.035	1.014
	0.01	0.529	0.523	1.011
3.5	0.07	3.581	3.439	1.041
	0.04	2.089	2.030	1.029
	0.02	1.057	1.038	1.018
	0.01	0.529	0.524	1.009

TABLE 3

THE EXTENDED ELECTROPHORETIC CONDUCTANCE TERM FOR 1-1 ELECTROLYTES AT 25°C.: 30% DIOXANE-70% WATER

$D = 53.28$ $\eta = 1.505$ $\beta = 44.69$ $10^{-8}\kappa/\sqrt{c} = 0.3286$

$\overset{\circ}{a}$	$\sqrt{c}$	$\Delta\Lambda_e$	$\frac{\beta\sqrt{c}}{1+\kappa a}$	$\frac{\Delta\Lambda_e(1+\kappa a)}{\beta\sqrt{c}}$
7.0	0.07	2.613	2.548	1.026
	0.04	1.598	1.565	1.021
	0.02	0.835	0.824	1.013
	0.01	0.427	0.423	1.009
6.0	0.07	2.699	2.608	1.035
	0.04	1.632	1.588	1.028
	0.02	0.845	0.830	1.018
	0.01	0.429	0.425	1.009
5.0	0.07	2.800	2.672	1.048
	0.04	1.669	1.611	1.036
	0.02	0.856	0.837	1.023
	0.01	0.431	0.426	1.012
4.5	0.07	2.861	2.705	1.058
	0.04	1.692	1.623	1.043
	0.02	0.862	0.840	1.026
	0.01	0.433	0.427	1.014
4.0	0.07	2.934	2.739	1.071
	0.04	1.721	1.636	1.052
	0.02	0.868	0.851	1.020
	0.01	0.436	0.428	1.019
3.5	0.07	3.025	2.774	1.090
	0.04	1.755	1.648	1.065
	0.02	0.879	0.846	1.039
	0.01	0.438	0.429	1.021

TABLE 4

THE EXTENDED ELECTROPHORETIC CONDUCTANCE TERM FOR 1-1 ELECTROLYTES AT 25°C.: 45% DIOXANE-55% WATER

D = 40.20 η = 1.830 β = 41.17 $10^{-8}\kappa/\sqrt{c}$ = 0.4593

$\mathring{a}$	$\sqrt{c}$	$\Delta\Lambda_e$	$\frac{\beta\sqrt{c}}{1+\kappa a}$	$\frac{\Delta\Lambda_e(1+\kappa a)}{\beta\sqrt{c}}$
6.0	0.10	3.458	3.227	1.071
	0.07	2.578	2.415	1.067
	0.04	1.562	1.483	1.053
	0.02	0.808	0.780	1.035
	0.01	0.410	0.400	1.025
5.0	0.10	3.700	3.348	1.105
	0.07	2.720	2.482	1.095
	0.04	1.620	1.508	1.074
	0.02	0.824	0.780	1.056
	0.01	0.414	0.402	1.029
4.5	0.10	3.858	3.411	1.131
	0.07	2.812	2.518	1.117
	0.04	1.656	1.521	1.088
	0.02	0.836	0.791	1.057
	0.01	0.416	0.403	1.032
4.0	0.10	4.064	3.478	1.168
	0.07	2.932	2.553	1.148
	0.04	1.072	1.534	1.109
	0.02	0.842	0.794	1.068
	0.01	0.420	0.404	1.039

TABLE 5

THE EXTENDED ELECTROPHORETIC CONDUCTANCE TERM FOR 1-1 ELECTROLYTES AT 25°C.: 50% DIOXANE-50% WATER

$D = 35.85$ $\eta = 1.913$ $\beta = 41.700$ $10^{-8}\kappa/\sqrt{c} = 0.4863_5$

$\overset{\circ}{a}$	$\sqrt{c}$	$\Delta\Lambda_e$	$\frac{\beta\sqrt{c}}{1+\kappa a}$	$\frac{\Delta\Lambda_e(1+\kappa a)}{\beta\sqrt{c}}$
7.0	0.07	2.510	2.356	1.065
	0.04	1.548	1.467	1.055
	0.02	0.810	0.780	1.038
	0.01	0.413	0.403	1.025
6.0	0.07	2.638	2.423	1.089
	0.04	1.600	1.492	1.072
	0.02	0.826	0.788	1.048
	0.01	0.417	0.407	1.025
5.0	0.07	2.813	2.494	1.128
	0.04	1.672	1.520	1.100
	0.02	0.847	0.795	1.065
	0.01	0.421	0.407	1.034
4.5	0.07	2.931	2.531	1.158
	0.04	1.720	1.533	1.122
	0.02	0.861	0.799	1.078
	0.01	0.426	0.408	1.044
4.0	0.07	3.092	2.569	1.204
	0.04	1.786	1.547	1.154
	0.02	0.880	0.803	1.096
	0.01	0.432	0.408	1.059
3.5	0.07	3.326	2.666	1.248
	0.04	1.880	1.582	1.188
	0.02	0.902	0.811	1.112
	0.01	0.441	0.411	1.073

TABLE 6

THE EXTENDED ELECTROPHORETIC CONDUCTANCE TERM FOR 1-1 ELECTROLYTES AT 25°C.: 55% DIOXANE-45% WATER

$D = 31.53$ $\eta = 1.964$ $\beta = 43.37$ $10^{-8}\kappa/\sqrt{c} = .51861$

$\overset{\circ}{a}$	$\sqrt{c}$	$\Delta\Lambda_e$	$\frac{\beta\sqrt{c}}{1 + \kappa a}$	$\frac{\Delta\Lambda_e(1 + \kappa a)}{\beta\sqrt{c}}$
7.0	0.10	3.457	3.177	1.088
	0.07	2.626	2.417	1.086
	0.04	1.625	1.513	1.074
	0.02	0.852	0.807	1.056
	0.01	0.432	0.418	1.034
6.0	0.10	3.714	3.303	1.124
	0.07	2.787	2.489	1.120
	0.04	1.693	1.540	1.099
	0.02	0.869	0.815	1.065
	0.01	0.436	0.420	1.038
5.0	0.10	4.086	3.439	1.188
	0.07	3.018	2.566	1.176
	0.04	1.791	1.569	1.142
	0.02	0.899	0.823	1.092
	0.01	0.444	0.422	1.052
4.5	0.10	4.360	3.511	1.242
	0.07	3.187	2.606	1.223
	0.04	1.862	1.584	1.175
	0.02	0.919	0.827	1.111
	0.01	0.450	0.423	1.064
4.0	0.10	4.744	3.596	1.323
	0.07	3.423	2.647	1.293
	0.04	1.958	1.599	1.224
	0.02	0.949	0.831	1.141
	0.01	0.458	0.424	1.081
3.5	0.10	5.341	3.665	1.457
	0.07	3.791	2.689	1.409
	0.04	2.113	1.614	1.309
	0.02	0.997	0.835	1.194
	0.01	0.472	0.425	1.111

TABLE 7

THE EXTENDED ELECTROPHORETIC CONDUCTANCE TERM FOR 1-1 ELECTROLYTES AT 25°C.: 60% DIOXANE-40% WATER

D = 27.21 η = 1.980 β = 46.24 $10^{-8}\kappa/\sqrt{c}$ = .55827

$\overset{\circ}{a}$	$\sqrt{c}$	$\Delta\Lambda_e$	$\frac{\beta\sqrt{c}}{1+\kappa a}$	$\frac{\Delta\Lambda_e(1+\kappa a)}{\beta\sqrt{c}}$
7.0	0.10	3.727	3.324	1.121
	0.07	2.852	2.541	1.123
	0.04	1.770	1.600	1.106
	0.02	0.923	0.858	1.076
	0.01	0.465	0.445	1.048
6.0	0.10	4.068	3.463	1.175
	0.07	3.070	2.622	1.171
	0.04	1.868	1.631	1.146
	0.02	0.953	0.867	1.100
	0.01	0.473	0.448	1.059
5.0	0.10	4.600	3.615	1.272
	0.07	3.413	2.707	1.261
	0.04	2.018	1.664	1.213
	0.02	1.001	0.875	1.144
	0.01	0.487	0.449	1.085
4.5	0.10	5.015	3.695	1.357
	0.07	3.681	2.752	1.337
	0.04	2.136	1.680	1.271
	0.02	1.038	0.880	1.180
	0.01	0.497	0.451	1.103
4.0	0.10	5.640	3.780	1.492
	0.07	4.082	2.799	1.458
	0.04	2.314	1.697	1.364
	0.02	1.090	0.885	1.232
	0.01	0.512	0.452	1.130
3.5	0.10	6.703	3.784	1.771
	0.07	4.767	2.847	1.674
	0.04	2.614	1.715	1.524
	0.02	1.185	0.890	1.331
	0.01	0.538	0.453	1.187

TABLE 8

THE EXTENDED ELECTROPHORETIC CONDUCTANCE TERM FOR 1-1 ELECTROLYTES AT 25°C.: 65% DIOXANE-35% WATER

$D = 23.14$ $\eta = 1.962$ $\beta = 50.60$ $10^{-8}\kappa/\sqrt{c} = .60537$

$\mathring{a}$	$\sqrt{c}$	$\Delta\Lambda_e$	$\frac{\beta\sqrt{c}}{1+\kappa a}$	$\frac{\Delta\Lambda_e(1+\kappa a)}{\beta\sqrt{c}}$
7.0	0.10	4.168	3.554	1.172
	0.07	3.219	2.732	1.178
	0.04	2.011	1.730	1.162
	0.02	1.042	0.933	1.117
	0.01	0.521	0.486	1.072
6.0	0.10	4.662	3.712	1.256
	0.07	3.552	2.824	1.255
	0.04	2.169	1.768	1.227
	0.02	1.094	0.943	1.160
	0.01	0.537	0.489	1.099
5.0	0.10	5.506	3.885	1.417
	0.07	4.121	2.923	1.410
	0.04	2.435	1.805	1.349
	0.02	1.183	0.950	1.245
	0.01	0.561	0.491	1.144
4.5	0.10	6.225	3.977	1.565
	0.07	4.610	2.974	1.550
	0.04	2.663	1.825	1.459
	0.02	1.258	0.959	1.312
	0.01	0.584	0.493	1.184
4.0	0.10	7.425	4.074	1.822
	0.07	5.411	3.028	1.787
	0.04	3.041	1.846	1.648
	0.02	1.379	0.965	1.363
	0.01	0.618	0.494	1.251

TABLE 9

THE EXTENDED ELECTROPHORETIC CONDUCTANCE TERM FOR 1-1 ELECTROLYTES AT 25°C.: 70% DIOXANE-30% WATER

$D = 19.07$ $\eta = 1.914$ $\beta = 57.11$ $10^{-8}\kappa/\sqrt{c} = .66660$

$\mathring{a}$	$\sqrt{c}$	$\Delta\Lambda_e$	$\frac{\beta\sqrt{c}}{1+\kappa a}$	$\frac{\Delta\Lambda_e(1+\kappa a)}{\beta\sqrt{c}}$
7.0	0.10	4.934	3.896	1.266
	0.07	3.874	3.014	1.285
	0.04	2.447	1.925	1.271
	0.02	1.261	1.045	1.206
	0.01	0.617	0.546	1.130
6.0	0.10	5.756	4.079	1.411
	0.07	4.469	3.123	1.431
	0.04	2.751	1.970	1.397
	0.02	1.367	1.058	1.291
	0.01	0.649	0.549	1.182
5.0	0.10	7.365	4.284	1.719
	0.07	5.641	3.241	1.740
	0.04	3.355	2.016	1.664
	0.02	1.579	1.071	1.474
	0.01	0.713	0.553	1.290
4.5	0.10	8.916	4.394	2.029
	0.07	6.782	3.329	2.037
	0.04	3.948	2.040	1.935
	0.02	1.788	1.077	1.660
	0.01	0.776	0.544	1.400

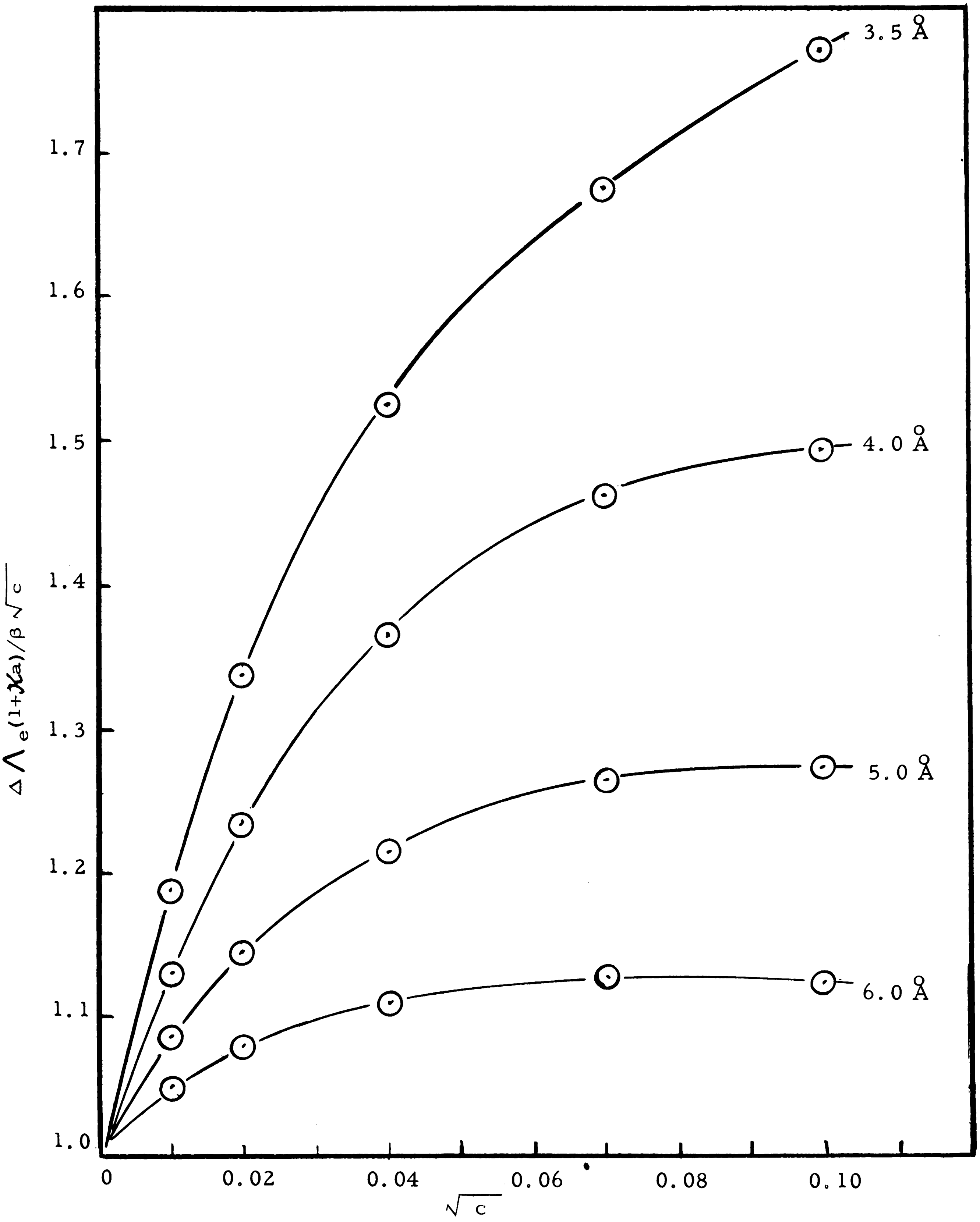


Figure 2. The ratio of the extended and Onsager electrophoretic terms versus the square root of concentration at several values of a: 60% dioxane-40% water solution of a 1-1 salt at 25°C.

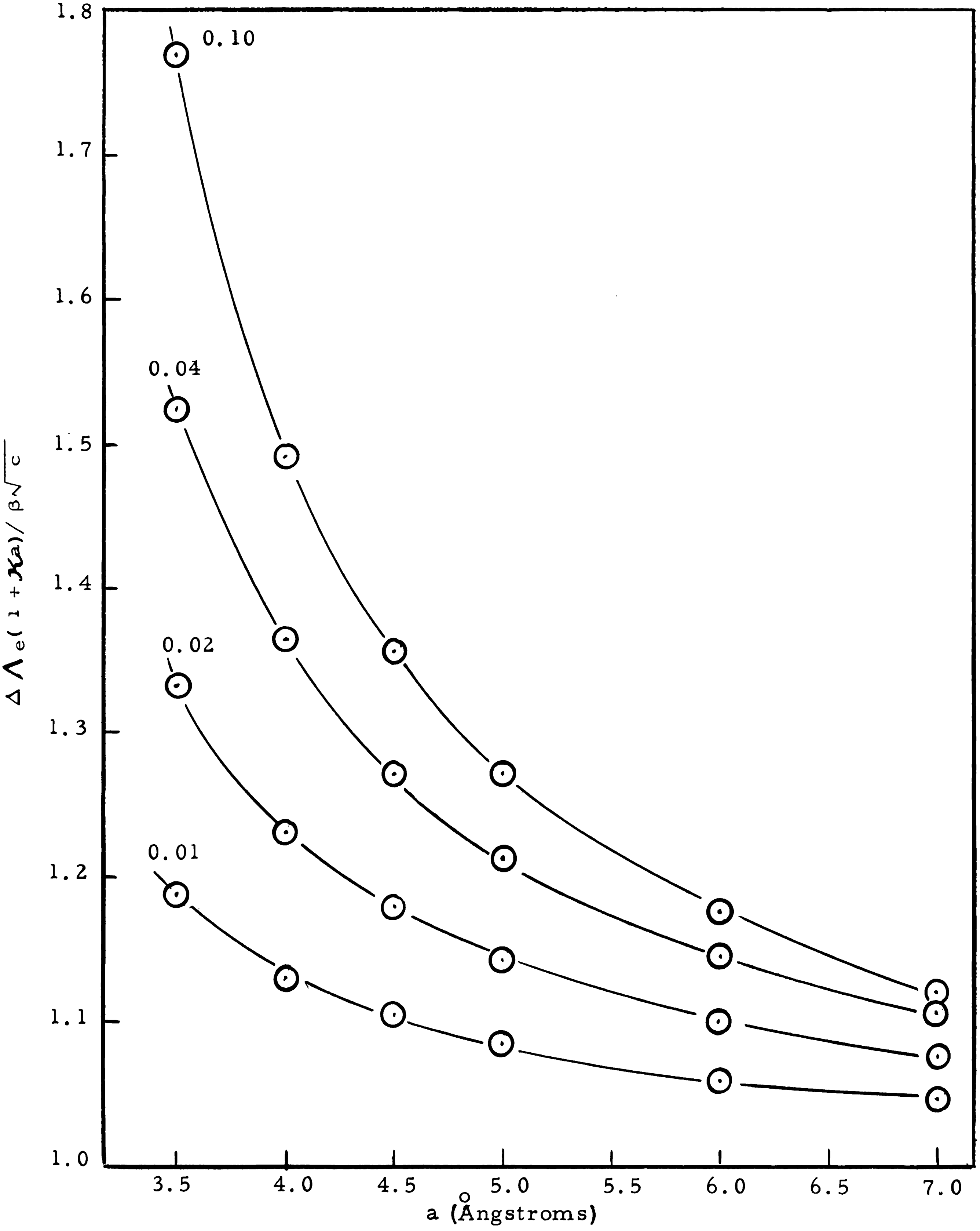


Figure 3. The ratio of the extended and Onsager electrophoretic terms versus a at several values of the square root of concentration: 60% dioxane-40% water solution of a 1-1 salt at 25°C.

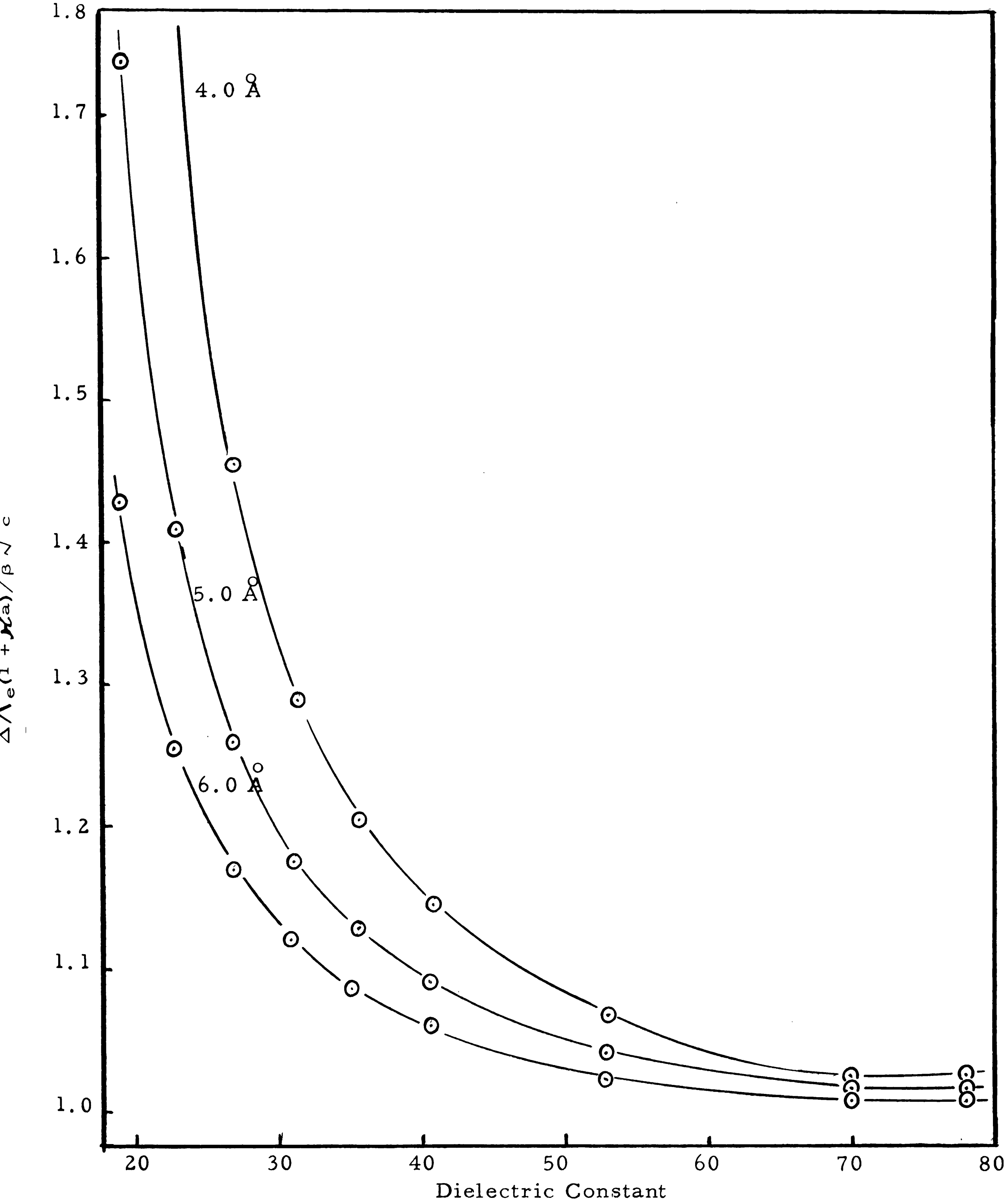


Figure 4. The ratio of the extended and Onsager electrophoretic terms versus dielectric constant for 1-1 salts in dioxane-water mixtures at 25°C.: $\sqrt{c} = 0.07$; a = 4.0 Å, 5.0 Å, 6.0 Å.

however, giving a slight increase in the ratio. Below $D \simeq 40$ (45% dioxane), the viscosity increase is less important than the decrease in dielectric constant, and both terms become larger. The extended term increases very rapidly in the region $40 > D > 20$ (45 to 70% dioxane), giving rise to the large slopes seen in Figure 4.

For $a = 4.0$ Å and $c^{\frac{1}{2}} = 0.07$ in 70% dioxane, the extended term is more than twice the Onsager term--a difference of 4.5 conductance units between the two values. This *difference* in electrophoretic terms represents about 50% of the total change in conductance with concentration which is usually observed with this solvent!

The differences in the magnitudes of the Onsager and extended electrophoretic terms having been established, some comparisons of calculated conductances with experiment follow.

C. Applications and Conclusions

In order to test the utility of the extended electrophoretic correction, equivalent conductances were computed with the aid of *MISTIC* according to equation (154).

$$\Lambda = \frac{(\Lambda^{o} - \Delta\Lambda_{e})\,(1 + \Delta X/X + \Delta P/X) - |\Delta_{+}\Delta\Lambda_{e}(\Delta X/X + \Delta P/X)|}{(1 + (10/3)\,\pi\, N\, R^{3}\, c)} \tag{155}$$

using $\Delta\Lambda_e$ values from the above tables. The relaxation expression of Fuoss and Onsager,

$$\frac{\Delta X}{X} = -\ \alpha c^{\frac{1}{2}}(1 - \Delta_1 + \Delta_2) - \Delta'_3\ \ \beta c^{\frac{1}{2}}/\Lambda^{0} \tag{156}$$

was employed. The expressions for Δ_1 Δ_2 and Δ'_3 are given by equations (71), (104), and (109). The kinetic term $\Delta P/X$ has been defined by equation (120). The denominator of equation (155) represents the Einstein viscosity term which corrects for the presence of "bulky" ions of hydrodynamic radius *R* and concentration *c*. The term $|\Delta_{+}\Delta\Lambda_{e}(\Delta X/X + \Delta P/X)|$ is the correction to the cross-term discussed

above. In the calculations discussed in this thesis, this term was never larger than 0.01 conductance units and could well have been dropped. A description of the MISTIC program for the computation of conductances is given in Appendix II.

Before presenting a comparison of conductance values calculated by equation (155) with some observed values, it is of interest to briefly note the relative importance of some of the terms in the theoretical expression. For illustrative purposes, partial conductance functions have been calculated for 60% dioxane-40% water as the solvent (D = 27.21) with $\Lambda^0 = 39.75$, $a = 5.0$ Å at $c^{\frac{1}{2}} = 0.07$ and 0.04. Table 10 gives a summary of these calculations and the various functions are sketched in Figure 5. A comparison of the simple limiting law relaxation correction (Curve B), $\Lambda^0(1 - \alpha c^{\frac{1}{2}})$, with the extended relaxation and kinetic effect function $\Lambda^0(1 + \Delta X/X + \Delta P/X)$, (Curve E), shows that the simple function accounts for nearly 75% of the change in conductance due to these effects. For $c^{\frac{1}{2}} = 0.07$ it is found that

$$- (\Delta X/X + \Delta P/X) = 0.08685$$

The velocity field contribution to $\Delta X_V/X$ is

$$\Delta X_V/X = 0.00524$$

or approximately 6% of the total. Under the conditions of this example, the velocity field term increases the calculated conductance by about 0.028 units. The change from $R = a/2$ to R represents a change in conductance of only +0.004 units, so that no serious operational difficulties are introduced by this modification. The difference between the Onsager and the extended electrophoretic contributions (Curves C and D), while not extremely large, is certainly significant. Curves D and E show that the extended electrophoretic term and relaxation-kinetic term contribute approximately equally to the total calculated change in conductance. Curve A shows the viscosity correction term for $R = 7.5$ Å. This contribution increases rapidly above

TABLE 10

CONTRIBUTION OF VARIOUS PARTIAL CONDUCTANCE FUNCTIONS TO A CALCULATED PHOREOGRAM FOR A 1-1 SALT IN 60% DIOXANE-40% WATER SOLVENT

$D = 27.21$ $\Lambda^0 = 39.75$ $a = 5.0$ Å $R = 7.5$

Function $\Delta\Lambda$	$\sqrt{c}$	$\Delta\Lambda$	$(\Lambda^0 - \Delta\Lambda)$	Description
$\Lambda^0/(1 + 2.5\,\varphi)$	.07	39.33	0.42	Viscosity correction
(R = 7.5 Å)	.04	39.61	0.14	
$\Lambda^0(1 - \alpha\sqrt{c})$	.07	37.26	2.49	Limiting relaxation correction
	.04	38.33	1.43	
$\Lambda^0 - \beta\sqrt{c}/1 + \kappa a$	.07	37.04	2.71	Onsager electrophoretic correction
	.04	38.09	1.66	
$\Lambda^0 - \Delta\Lambda_e$	.07	36.43	3.32	Extended electrophoretic correction
	.04	37.73	2.02	
$\Lambda^0(1 + \frac{\Delta X}{X} + \frac{\Delta P}{X})$	.07	36.30	3.45	Relaxation and kinetic terms
	.04	37.49	2.26	

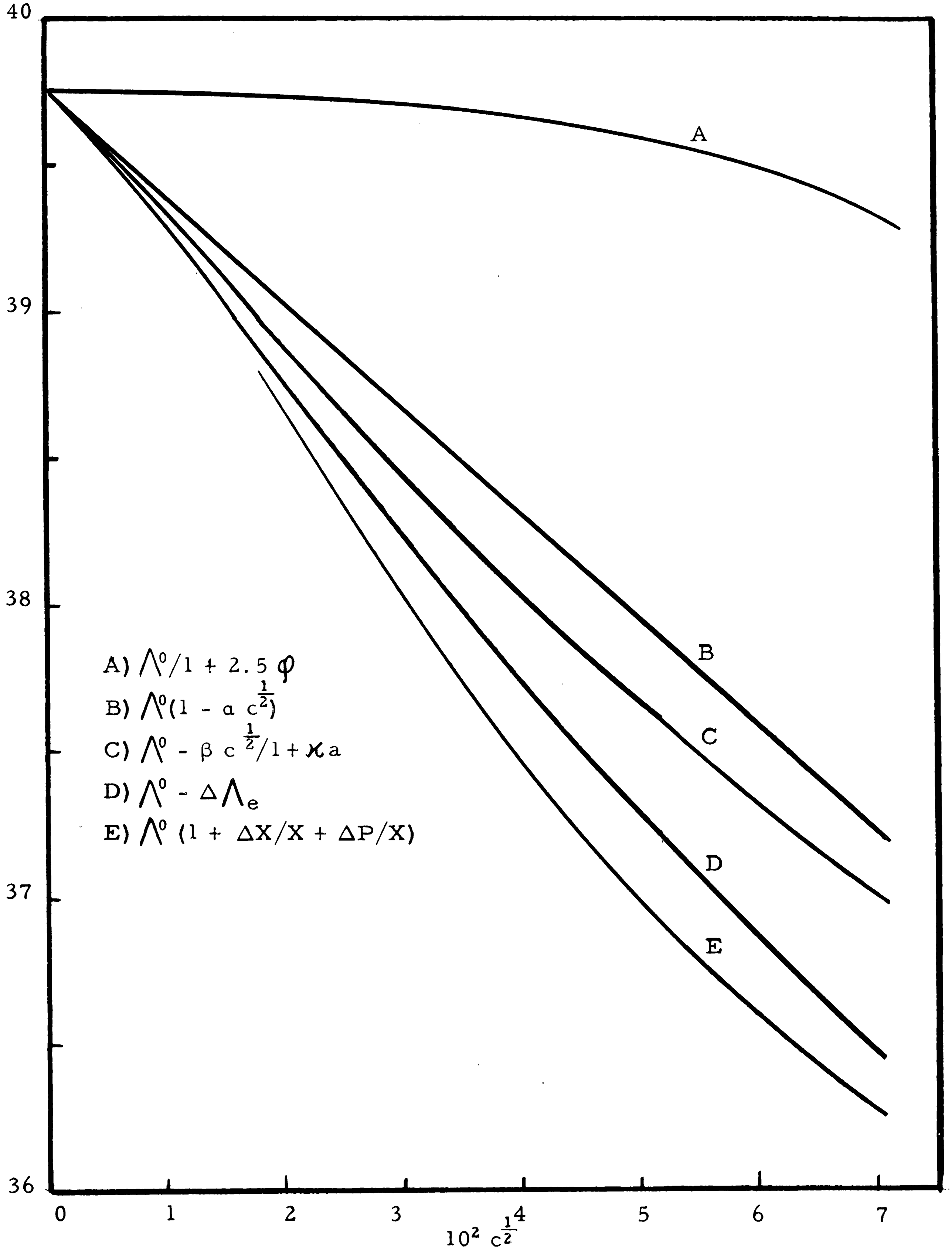


Figure 5. The contribution of several terms to the calculated conductance of a 1-1 salt in 60% dioxane-40% water solution *versus* the square root of concentration: a = 5.0 Å.

a radius value of $\underline{R} \approx 6.0$ Å. At $\underline{c}^{\frac{1}{2}} = 0.07$ the term amounts to about 0.4 conductance units and cannot be dismissed as a small correction.

Conductance data for salts in dioxane-water mixtures are available in the literature. While limited in quantity, these data are of high quality and, in general, are accurate to about 0.01 conductance units. Martel and Kraus (39) have reported values of the equivalent conductance of tetraisoamylammonium nitrate ($i\text{-}Am_4NNO_3$) in water and in 10% to 50% dioxane-water mixtures. These data have been treated by Fuoss (12) using the expanded Onsager equation (with $R = a/2$) and including a consideration of ion pairing (equation 136). The data were fit with one constant parameter ($\underline{a} = 5.83$ Å) and three variable parameters: $\underline{R}$ values of 7.3 Å in water to 8.4 Å in 50% dioxane (D = 35.85); association constants from 1.2 to 5.2; and the best value of Λ^0 for each solution. Conductance values for this salt have been calculated for water, 10%, 30% and 50% dioxane-water mixtures using the complete equation (155). All four sets of data can be reproduced using a variable Λ^0 for each solvent mixture and two constant distance parameters: $\underline{a} = 4.50$ Å and $\underline{R} = 7.50$ Å. Table 11 gives observed and calculated values of Λ for these cases. The "observed" values were obtained from large plots of the original data. A parenthesis around the "observed" value at $\underline{c}^{\frac{1}{2}} = 0.07$ indicates that a rather long extrapolation was necessary. The average deviation for the twelve compared points of water, 30% and 50%, is ± 0.03 conductance units. The deviation for 10% data is +0.06 units, the calculated curve lying slightly above the experimental data. The Fuoss treatment experiences the same difficulty in that a larger association constant was required for the 10% dioxane data than for the data in water. Figure 6 shows the phoreograms for water and 10% dioxane. Similar plots for 30% and 50% dioxane are given by Figure 7. The broken curve above the 30% data represents the calculated conductance values with $\underline{R} = 0$. This curve lies above the limiting law slope while the data are below. The importance

TABLE 11

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF THE CONDUCTANCE OF SOLUTIONS OF i-Am$_4$NNO$_3$ IN DIOXANE-WATER MIXTURES AT 25°C.: $\underline{a}$ = 4.50 Å ; $\underline{R}$ = 7.50 Å

Water D = 78.54 Λ^0 = 89.30			10% Dioxane D = 70.33 Λ^0 = 74.55		
$\sqrt{c}$	Λobs.	Λcalc.	$\sqrt{c}$	Λobs.	Λcalc.
0.01	88.45	88.47	0.01	74.12	74.10
0.02	87.60	87.62	0.02	73.31	73.32
0.04	85.79	85.85	0.04	71.69	71.73
0.07	82.95	83.06	0.07	69.09	69.25

30% Dioxane D = 53.28 Λ^0 = 74.85			50% Dioxane D = 35.85 Λ^0 = 42.55		
$\sqrt{c}$	Λobs.	Λcalc.	$\sqrt{c}$	Λobs.	Λcalc.
0.01	53.34	53.33	0.01	41.77	41.77
0.02	52.65	52.64	0.02	40.96	40.94
0.04	51.24	51.25	0.04	39.30	39.27
0.07	49.07	49.11	0.07	36.94	36.91

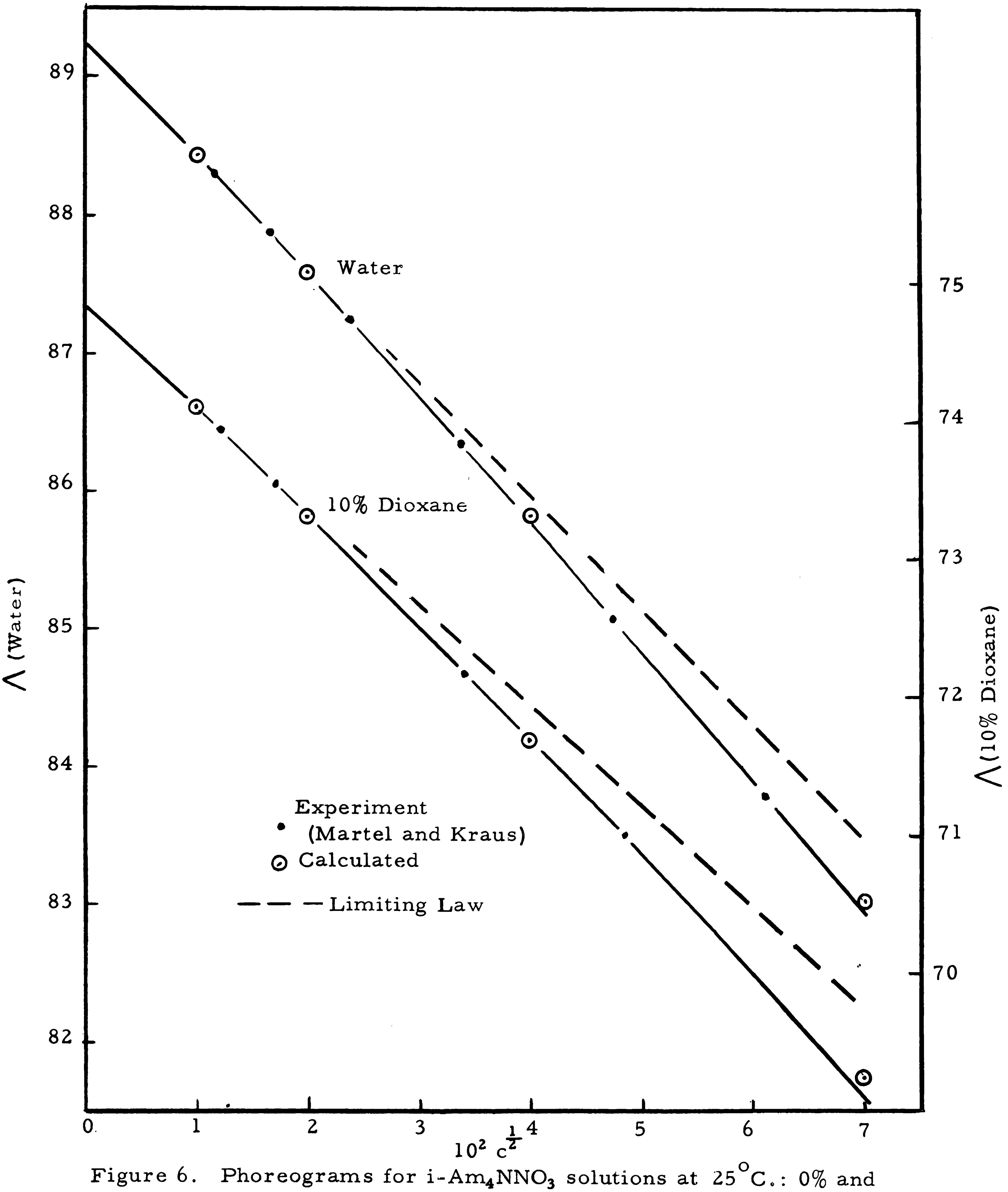


Figure 6. Phoreograms for i-Am_4NNO_3 solutions at 25°C.: 0% and 10% Dioxane.

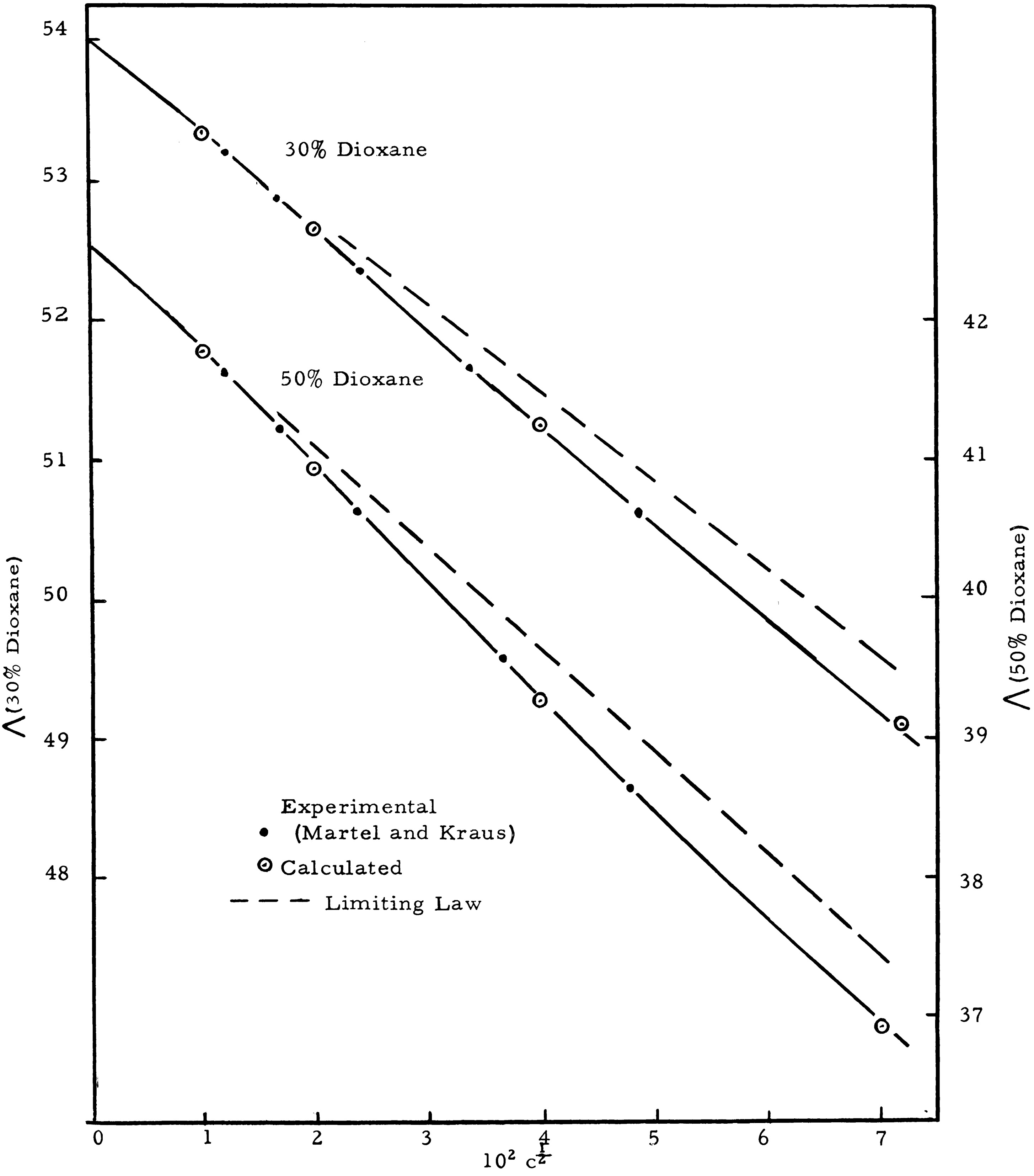


Figure 7. Phoreograms for i-Am_4NNO_3 solutions at 25°C.: 30% and 50% Dioxane.

of the viscosity term is evident. At first glance, the distance parameters $R = 7.5$ Å and $a = 4.50$ Å seem rather contradictory. Molecular models (Stuart-Briegleb type) show, however, that the outer radius of the cation is about 7.3 Å. Further, the ion is not completely spherical but a shorter anion-cation contact distance of about 3.6 Å is possible. If all anion-cation collisions are random, an average a of 4.50 Å is only slightly smaller than one would expect. The "planer" nature of the nitrate ion may cause some unusual effects.

A more critical test of the conductance equation (155), using the complete electrophoretic term, is provided by the data of Mercier and Kraus (40) for tetra-*n*-butylammonium bromide (Bu_4NBr) in water and 10% to 70% dioxane-water mixtures. The original analysis of these data by Fuoss (12) was performed in two parts. The data for 0% to 45% dioxane were fit with a constant a of 5.5 Å; variable association constants from *0.6* to *3.16*; and variable values of R from 6.0 Å to 7.2 Å. The data for the same salt in 50% to 70% dioxane were fit with K values from *4.6* to *103*; R was held constant at *6.0* Å and a varied from *5.22* Å to *8.12* Å. In a more recent analysis (41), using $R = a$ in the velocity field term of the relaxation effect and ignoring all terms of higher order than $c^{\frac{3}{2}}$ in the expanded equation, the data from 0% to 55% dioxane were fit with $a = R = 4.8$ Å and K varies from *1.3* to *6.9*. In the 60%, 65% and 70% solutions, $a = R$ values are *5.4*, *4.88* and *5.00* respectively, while the K's are *12.7*, *24*, and *80*. By allowing $a = R$ to vary in the latter solvents, the values of K for 15% to 70% dioxane can be expressed as $K = K_0 e^{b}$. The water and 10% data require larger K values than expected. In all cases Λ^0 is treated as an adjustable parameter for each solvent.

Conductances for Bu_4NBr have been calculated for water and seven dioxane-water mixtures from 10% to 70% dioxane using the complete electrophoretic effect. With a "best" value for each solvent all *eight* sets of data can be reproduced with *two constant* distance parameters:

$a = 5.00$ Å and $R = 7.00$ Å. Table 12 shows "observed" and calculated values of Λ. The observed values at round $c^{\frac{1}{2}}$'s were obtained graphically as described above. Excluding the point at $c^{\frac{1}{2}} = 0.07$ for 60% dioxane, the average deviation between the observed and calculated values for thirty-one points in eight different solvents is only ± 0.023 conductance units. Models of the *n*-butylammonium ion give $R = 6.7$ Å and a shortest ion contact distance of about 3.7 Å. An average a value of 5.0 Å seems quite reasonable. Figures 8 through 11 show the phoreograms for these solutions. Figure 12, pertinent to the data in 60% dioxane, is a plot of several conductance functions *vs.* $c^{\frac{1}{2}}$ for $\Lambda^0 = 39.75$. The broken line is the limiting Onsager tangent; the upper curve (A) represents the calculated conductances using the Onsager electrophoretic term [$\beta c^{\frac{1}{2}}(1 + \kappa a)$] with $a = 5.00$ Å and $R = 0$; ; the lower curve (B), with the same parameters, uses the extended electrophoretic term. The effect of the viscosity correction with $R = 7.0$ Å is inferred by the experimental points which are reproduced by the complete conductance expression including the Einstein term.

While these applications are by no means comprehensive, they serve to illustrate that it is unnecessary to invoke ion pairing to explain all deviations from the Onsager theory in its present form. The advantages of using constant parameters directly related to the dimensions of the ions rather than variable "association constants" is obvious.

It is not implied that ion association never occurs, but that properly "pairing" should describe only non-coulombic interactions which are not considered by the hard sphere model. Data for Bu_4NI (39) in dioxane-water mixtures cannot be fit by the above treatment using reasonable and constant values of a and R. Undoubtedly the highly polarizable iodide ion (42) gives rise to ion-induced dipole interactions which cause some "pairing." It is expected that sodium bromate (39) solutions would

TABLE 12

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF THE CONDUCTANCE OF SOLUTIONS OF Bu_4NBr IN DIOXANE-WATER MIXTURES AT 25°C.:a = 5.00 Å, R = 7.00 Å

Water			10% Dioxane		
D = 78.54	Λ^0 = 97.45		D = 70.33	Λ^0 = 80.85	
$\sqrt{c}$	$\Lambda_{obs.}$	$\Lambda_{calc.}$	$\sqrt{c}$	$\Lambda_{obs.}$	$\Lambda_{calc.}$
0.01	96.64	96.61	0.01	80.09	80.08
0.02	95.75	95.75	0.02	79.29	79.31
0.04	93.97	94.00	0.04	77.68	77.74
0.07	91.3	91.31	0.07	75.4	75.35

30% Dioxane			50% Dioxane		
D = 53.28	Λ^0 = 57.25		D = 35.85	Λ^0 = 43.70	
$\sqrt{c}$	$\Lambda_{obs.}$	$\Lambda_{calc.}$	$\sqrt{c}$	$\Lambda_{obs.}$	$\Lambda_{calc.}$
0.01	56.57	56.57	0.01	42.90	42.92
0.02	55.88	55.88	0.02	42.10	42.10
0.04	54.51	54.50	0.04	40.48	40.50
0.07	52.50	52.49	0.07	38.30	38.31

55% Dioxane			60% Dioxane		
D = 31.53	Λ^0 = 41.56		D = 27.21	Λ^0 = 39.75	
$\sqrt{c}$	$\Lambda_{obs.}$	$\Lambda_{calc.}$	$\sqrt{c}$	$\Lambda_{obs.}$	$\Lambda_{calc.}$
0.01	40.71	40.69	0.01	38.75	38.75
0.02	39.77	39.78	0.02	37.65	37.66
0.04	37.98	37.98	0.04	35.54	35.54
0.07	35.60	35.59	0.07	32.65	32.82

65% Dioxane			70% Dioxane		
D = 23.14	Λ^0 = 38.30		D = 19.07	Λ^0 = 37.05	
$\sqrt{c}$	$\Lambda_{obs.}$	$\Lambda_{calc.}$	$\sqrt{c}$	$\Lambda_{obs.}$	$\Lambda_{calc.}$
0.01	37.05	37.07	0.01	35.43	35.43
0.02	35.69	35.64	0.02	33.48	33.55
0.04	33.03	33.08	0.04	29.97	29.97
0.07	29.70	29.74	0.07	25.90	25.94

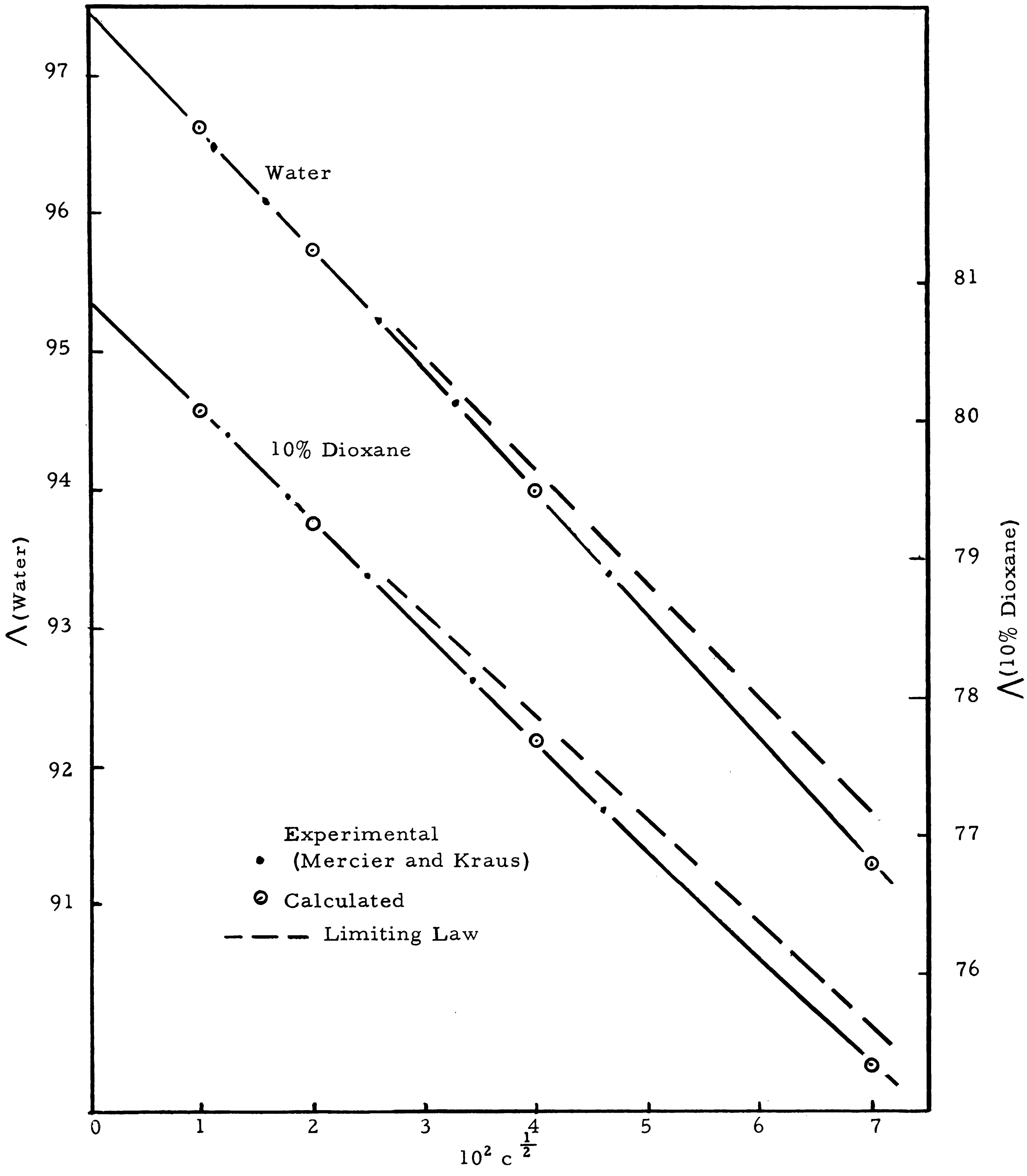


Figure 8. Phoreograms for Bu4NBr solutions at 25°C.: 0% and 10% dioxane.

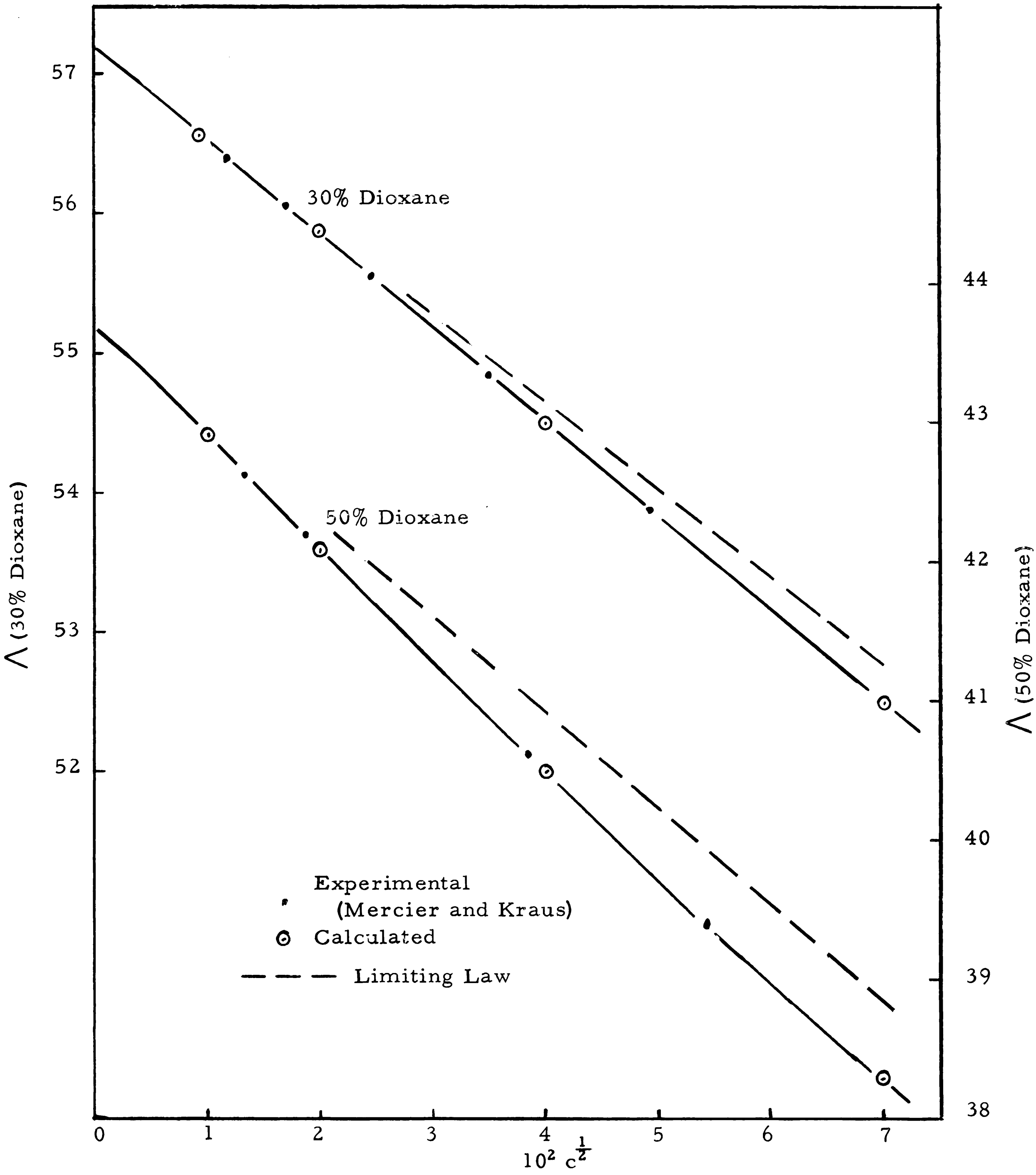


Figure 9. Phoreograms for Bu_4NBr solutions at 25°C.; 30% and 50% dioxane.

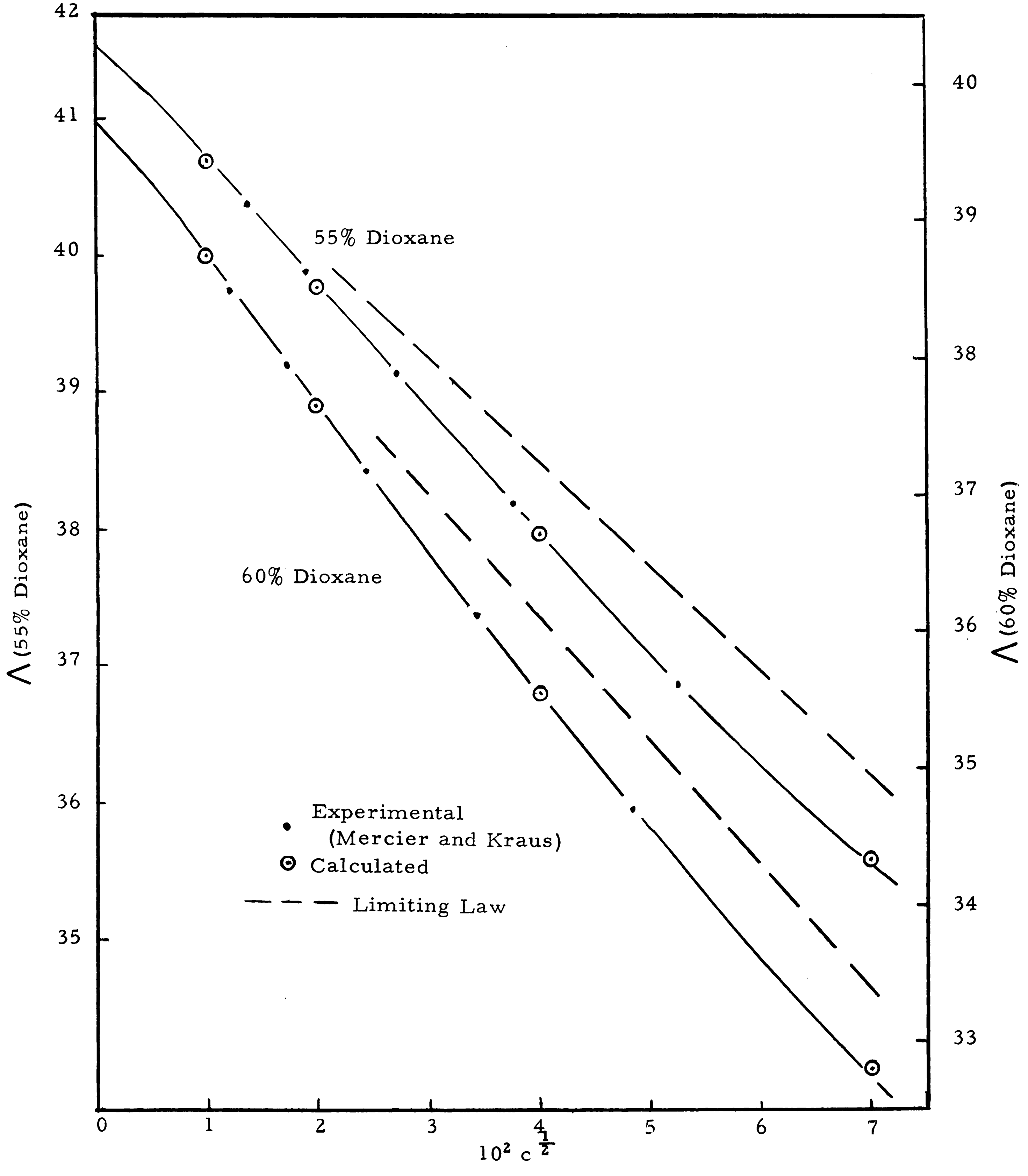


Figure 10. Phoreograms for Bu_4NBr solutions at 25°C.:55% and 60% dioxane.

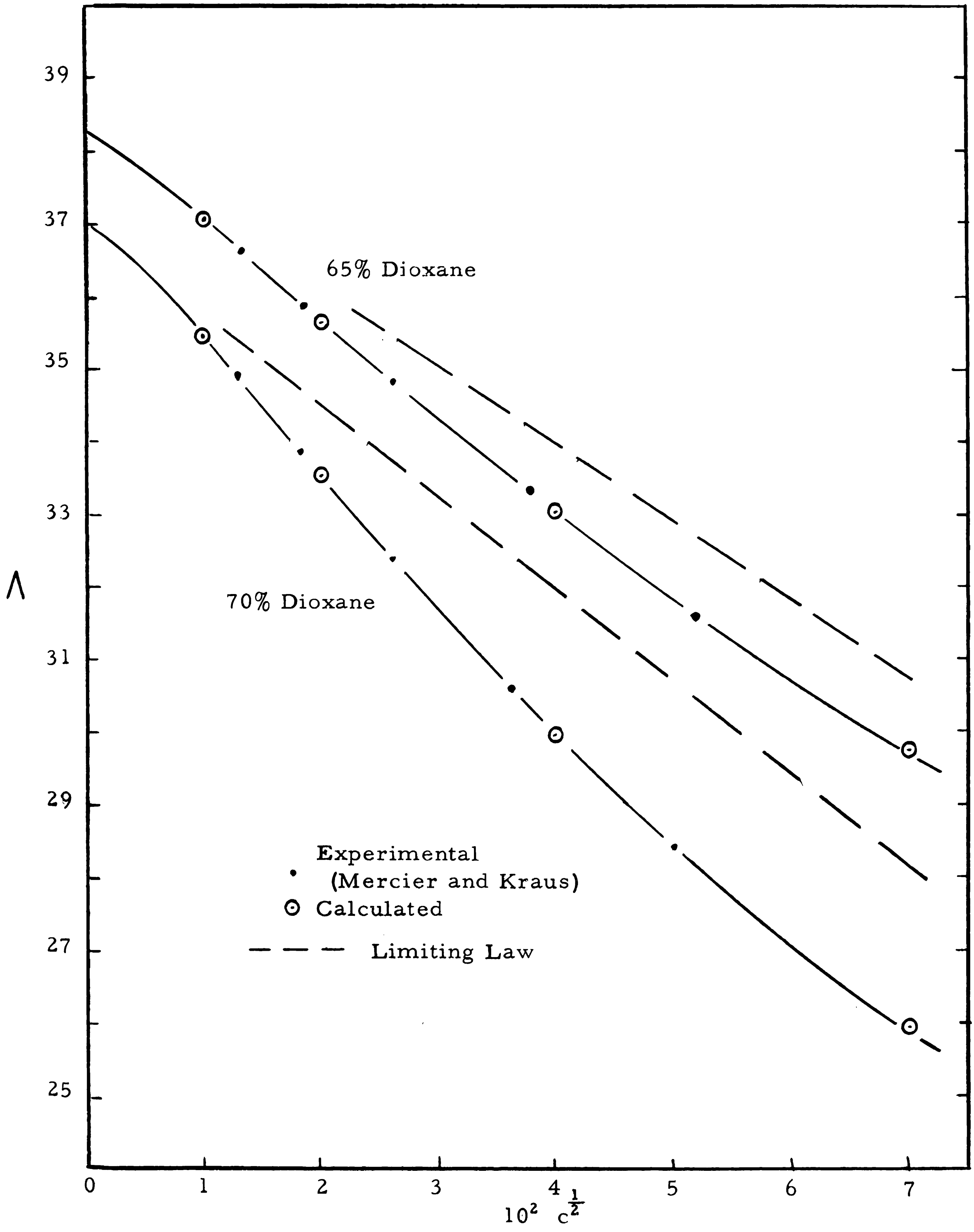


Figure 11. Phoreograms for Bu_4NBr solutions at 25°C.:65% and 70% dioxane.

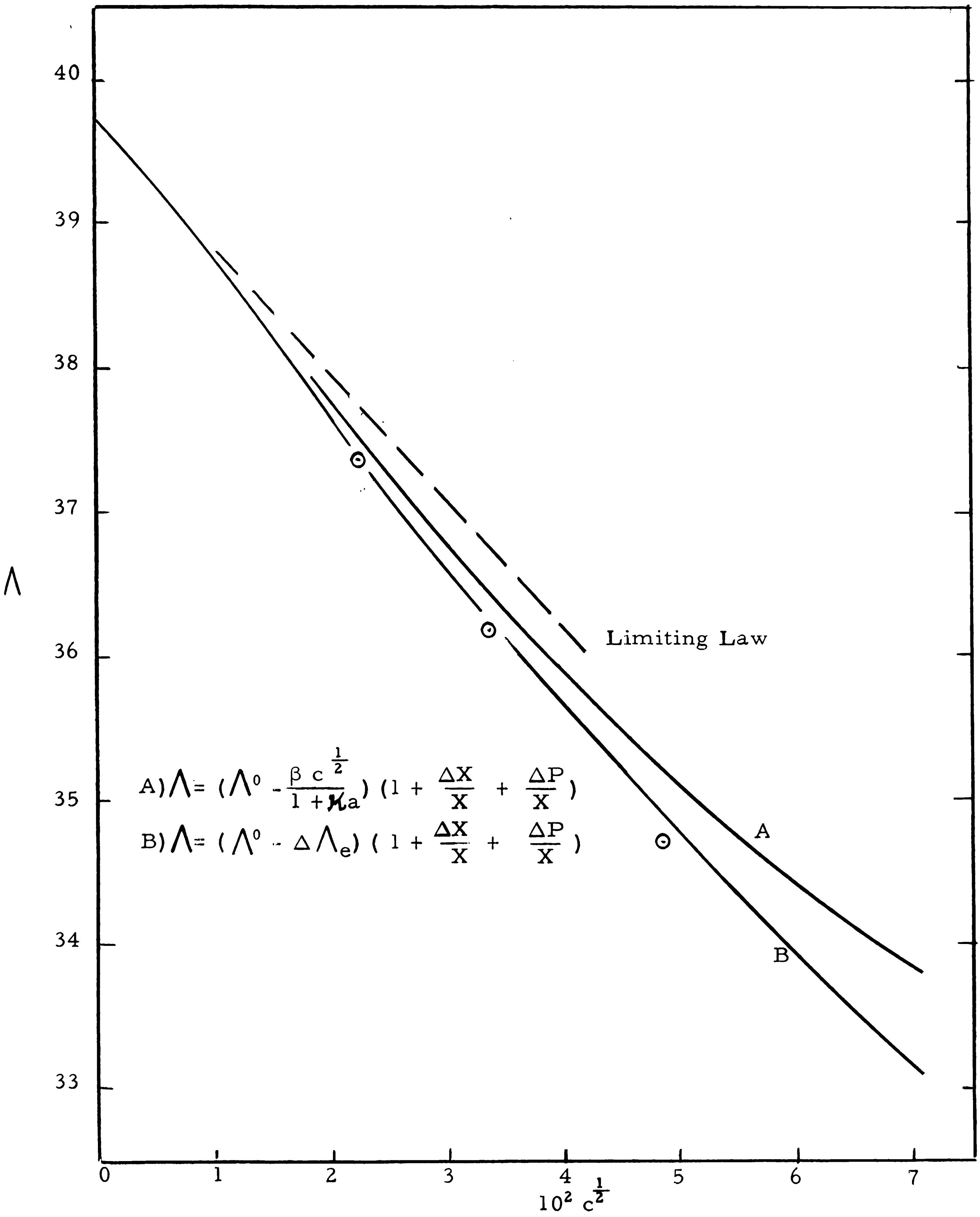


Figure 12. Various theoretical phoreograms for a 1-1 salt in 60% dioxane-40% water solution at 25°C.: $\underline{\Lambda}^0 = 39.75$, $\underline{a} = 5.0$ Å.

also require pairing considerations since the bromate ion possesses a permanent dipole which should give rise to ion-dipole interactions.

The only other accurate data available over a sufficiently large range of dielectric constant in dioxane-water mixtures are for tetramethylammonium picrate (40). An analysis by Fuoss (12) indicates that no ion pairing takes place in 0% to 70% dioxane. The necessary a values ranged from 8.0 Å to about 7.0 Å, systematically decreasing with decreasing solvent dielectric constant. The average R value was about 4.5 Å for each ion. Although the calculations using the extended electrophoretic effect were not performed, it is certain that these data can be treated successfully. For the large value of $a = 8.0$ Å the difference between the extended and Onsager electrophoretic terms is negligible in water, and although it remains relatively small, increases as the dielectric constant decreases. This behavior is exactly the form that would be required to fit all the data for the picrate with a constant value of a.

Many more data must be gathered and examined to assure the generality of the above results. Studies of simple spherical ions should help one decide at what radius ions can be considered "sufficiently bulky" to require the use of the Einstein viscosity correction. Tests of the correction by viscosity measurements would be of some help. The relationship between the minimum distance of approach a and the hydrodynamic radius R should also be clarified. Until the generalization of the Onsager relaxation expression to unsymmetrical salts can be made, work with symmetrical 2-2 and 3-3 salts should be of great help along these lines.

Finally, the above calculations are not considered to be exact, since higher order terms in the relaxation field of unknown magnitude resulting from the complete exponential distribution function, remain unevaluated and also because of errors introduced by the linear superposition approximation. In view of the complexity of the Onsager treatment outlined above, it would seem that a fresh approach is needed.

At the very least, this study shows that the terms in the electrophoretic effect which are usually neglected are not negligible, and, indeed, their inclusion can in some cases eliminate the need for introducing an association constant.

IV. Summary

An outline of the Onsager theory of conductance has been presented which, it is hoped, will be of value as an introduction to the study of this difficult treatment.

Higher order concentration dependent terms of the electrophoretic effect, which are neglected in the usual treatment, have been evaluated for 1-1 salts in water and in 10% to 70% dioxane-water mixtures. Significant differences between the Onsager and extended electrophoretic expressions occur which increase rapidly with decreasing ion size and with decreasing dielectric constant. The complete term is always larger than the simpler function and in extreme cases is more than twice the value of the Onsager correction.

The electrophoretic calculations were applied to equivalent conductance data for tetraisoamylammonium nitrate and tetra-n-butylammonium bromide taken from the literature. In both cases significant deviations from the previous theoretical expressions have been attributed to ion pair formation. The present work shows that, if higher electrophoretic terms are included, the $i\text{-}Am_4NNO_3$ data for the four solvents (0% to 50% dioxane in water) can be interpreted without the concept of ion pairing using two constant distance parameters: the minimum distance of approach $a = 4.50$ Å, and the cation hydrodynamic radius $R = 7.5$ Å. In a similar manner the data for Bu_4NBr in eight solvents (0% to 70% dioxane in water) require no association constant and involve the constant parameters, $a = 5.00$ Å and $R = 7.0$ Å.

It is concluded that much of the deviation from the Onsager theory, heretofore ascribed to electrostatic aggregation of ions, arises from incomplete treatment of the model used rather than from physical phenomena which cause the model to be inaccurate.

PART II

TRANSFERENCE NUMBERS AND ACTIVITY COEFFICIENTS OF TRIS-(ETHYLENEDIAMINE) COBALT (III) CHLORIDE IN WATER AT 25°C.

I. Introduction

The interionic attraction theory of electrolytes, as formulated by Debye, Hückel, and Onsager and Fuoss has met with great success in aqueous solutions of 1-1 electrolytes. In solution of higher charge types, however, theoretical predictions often deviate from experiment. To permit an adequate evaluation of the cause of these discrepancies, an extensive study of the properties of multicharged electrolytes has been undertaken in this laboratory (43, 44, 45, 46, 47).

As a part of this program, the transference numbers and activity coefficients of solutions of *tris*-(ethylenediamine) cobalt (III) chloride have been measured.

II. Transference Numbers

A. Introduction

The transference number of an ion is defined as

$$T_j = \frac{i_j}{\sum_i i_i} \qquad (158)$$

where i_j is the current carried by ions of type *j* and $\sum_i i_i$ is the total current carried by all types of ions in the solution. Alternatively the transference numbers may be expressed as

$$T_j = \frac{u_j}{\sum_i u_i} = \frac{\lambda_j}{\sum_i \lambda_i} = \frac{\lambda_j}{\Lambda} \qquad (159)$$

so that a correct theory of conductance should also yield the correct transference number. From equations (30) and (30a) for λ_j and $\underline{\Lambda}$, it is seen that the relaxation terms cancel and $\underline{T}_j$ is given by

$$T_j = \frac{\lambda_i^0 - \Delta\lambda_j^e}{\Lambda^0 - \Delta\Lambda_e} \qquad (160)$$

transference measurements, then, help to provide a critical test of the electrophoretic part of conductance theory but suffer the disadvantage that they must be measured at concentrations which are higher than would be desirable for a test of the theory.

Experimentally, transference numbers may be obtained in three ways:

(1) The Hittorf method, (48, 49, 50, 51, 52), which depends upon concentration changes in a cell during electrolysis.

(2) The electromotive force method, (53, 54, 55, 56), which requires measurement of the potentials of cells with and without transference.

(3) The moving boundary method.

The Hittorf method is tedious, inaccurate, and today, is rarely used. The electromotive force (E.M.F.) method is less accurate and not generally applicable since it requires electrodes which are reversible to both anion and cation, or else independent activity measurement. The moving boundary method, while limited in concentration range, is capable of a high degree of accuracy and is now in general use. This method was used in the present work and is described below.

B. The Moving Boundary Method

Since several excellent reviews of the history and theory of the moving boundary method (57, 58, 59) are available, only the most important features of the theory will be presented.

The method consists in forming a boundary between two solutions which may or may not have an ion in common. For the purpose of the present work it is sufficient to consider the case of solutions of two electrolytes $\underline{C^+A^-}$ and $\underline{B^+A^-}$ with the common anion $\underline{A^-}$. Let the two solutions be placed in an electrolysis cell.

A line (x - x) gives the initial position of the boundary between the solutions. If a steady current $\underline{i}$ is passed through the cell for a given time, and the mobility of ions $\underline{C}^+$ is greater than that of ions $\underline{B}^+$, the boundary between the solutions will move to the final position as represented by (y-y). Though all negative ions move toward the anode, and all positive ions toward the cathode, the two solutions remain separated since the $\underline{C}^+$ ions move faster. If the $\underline{B}^+$ ions lagged far behind, the solution would become more dilute and the increased resistance and (at constant current) increased potential gradient would cause the $\underline{B}^+$ ion velocity to increase. In this way the boundary is "self-sharpening." The $\underline{C^+A^-}$ solution is designated the "leading solution," and $\underline{B^+A^-}$ the "indicator" or "following solution." If the boundary moves a distance $\underline{d}$ cm. in $\underline{t}$ seconds, the average velocity of positive $\underline{C}^+$ ions, $\underline{v_+}$, is $\underline{d/t}$. Since $\underline{v_+ = Xu_+}$ where $\underline{u_+}$ is the mobility and X is the potential gradient in volts/cm.,

$$u_+ = d/Xt \tag{161}$$

Further,

$$X = i/A.L \tag{162}$$

where $\underline{i}$ is the current in amperes, $\underline{A}$ the cross-sectional area of the cell and $\underline{L}$ the specific resistance of the solution. Since

$$\Lambda = 1000\ L/c^* = F\ (u_+ + u_-) \tag{163}$$

where F is the Faraday, then

$$L = c^*\ F(u_+ + u_-)/1000 \tag{164}$$

Combining these statements

$$u_+ = d/Xt = dAL/it = \frac{dAc^* F(u_+ + u_-)}{1000\ it} \qquad (165)$$

The quantity (dA) is just the volume V, swept out by the boundary, and since

$$T_+ = \frac{i_+}{i_+ + i_-} = \frac{u_+}{u_+ + u_-}$$

we obtain for the transference number of leading solution cation

$$T_+ = \frac{c^* F\ V}{1000\ it} \qquad (166)$$

In the first theoretical treatment of moving boundaries, Kohlrausch (60) deduced that, in order to obtain a stable boundary, the condition

$$\frac{c^*}{c^*_f} = \frac{T_+}{(T_+)_f} \qquad (167)$$

must be met. Here, c^*_f is the normality of the following solution and $(T_+)_f$ its cation transference number. This relationship is known as the Kohlrausch ratio. According to the Kohlrausch treatment, the concentration of the indicator solution will automatically adjust to that given by the Kohlrausch ratio under the influence of an electric field. In an extensive study by MacInnes and Smith (61), it was found that the following solution concentration must be within three to eight per cent of the Kohlrausch ratio in order that the concentration adjustment can take place properly. The necessary properties of an indicator solution may be summarized as follows:

(1) The solution must not react with the ion under investigation.

(2) The transference number of the indicator ion must be less than that of leading ion.

(3) The density of the following solution must be less than that of the leading solution for falling boundaries and greater for rising boundaries.

(4) There must be sufficient difference in some property of the two solutions, such as color or refractive index, to permit the observation of the boundary motion.

In the above discussion of the moving boundary method, no mention was made of the electrode processes which necessarily occur. Equation (166) gives the transference number with respect to a fixed mark on a transference cell. Any change in volume caused by an electrode reaction will necessitate a correction to volume swept out by the boundary since the bulk of the solution moves to accommodate the volume change. The necessity of this correction was recognized by Miller (62) and first calculated by Lewis (63). The computation is greatly simplified (64, 65) if one side of the cell is left open to the atmosphere and the other side is closed since only the volume changes which occur between the closed side and boundary need then be considered.

As an example of the computation of the volume correction, consider a cell employing a descending or "falling" boundary between lithium chloride and tris-(ethylenediamine) cobalt (III) chloride (abreviated $Co(en)_3Cl_3$). Let the side of the cell containing silver-silver chloride cathode be closed, and side with a cadmium anode be open to the atmosphere. The volume changes which take place between the boundary and closed cathode during the passage of one Faraday of electricity are:

(1) Loss of one mole of AgCl(s) $\Delta V = -V_{AgCl}$
(2) Gain of one mole of Ag $\Delta V = +V_{Ag}$
(3) Gain of one mole of Cl^- ions $\Delta V = +\bar{V}_{Cl^-}$
(4) Gain of $T_+/3$ moles of $Co(en)_3^{+++}$ ions $\Delta V = +T_+\left(\frac{\bar{V}_{Co(en)_3^{+++}}}{3}\right)$
(5) Loss of T_- moles of Cl^- ions $\Delta V = -T_-\bar{V}_{Cl^-}$

Summing the volume changes (1) through (5) the total volume change between the closed side and the boundary is

$$\Delta V = V_{Ag} - V_{AgCl} + T_+ \left(\frac{\bar{V}_{Co(en)_3^{+++}}}{3}\right) \qquad (168)$$

If this volume change ΔV turns out to be positive (as indeed it does), this means that, effectively, the boundary has swept out a volume $(V + \Delta V)$ rather than the smaller observed volume V so that the corrected transference number is larger than the "observed" value. For the passage of one Faraday equation (166) becomes

$$T_+ = \frac{c^* V}{1000} = \frac{(V' + \Delta V)\, c^*}{1000} = T_+' + \frac{c^* \Delta V}{1000} \qquad (169)$$

A similar analysis,, taking the cadmium anode as the closed side, shows that for this case

$$\Delta V = \frac{\bar{V}_{CdCl_2}}{2} - \frac{V_{Cd}}{2} - T_+ \left(\frac{\bar{V}_{Co(en)_3Cl_3}}{3} \right) \qquad (170)$$

An additional correction has been pointed out by Longsworth (64). Realizing that a small fraction of the total current passed through a cell is carried by conducting impurities in the solvent, he derived the expression

$$\Delta T_+ = T_+ \,(L_{solvent} / L_{solution}) \qquad (171)$$

where ΔT_+ is the correction to the transference number T_+; $L_{solvent}$ is the specific conductance of the solvent; and $L_{solution}$ is the specific conductance of the solution. The final expression for the transference number becomes

$$T_+ = \frac{F\ c^*\ V}{1000\ it} - \frac{c^* \Delta V}{1000} + T_+ \left(\frac{L_{solvent}}{L_{solution}} \right) \qquad (172)$$

C. Experimental

1. Materials

Tris-(ethylenediamine) cobalt (III) chloride was prepared according to the method of Work (66). The crude product was recrystallized three times from ethanol and dried in a vacuum oven at 55°C. Chloride analysis of the semi-pure product gave 30.59 ± 0.01% compared to the theoretical value of 30.78%. A four step fractional recrystallization of the salt by dissolving in a minimum volume of water and adding an equal volume of ethanol, was then undertaken. Solutions of constant molality were prepared as the recrystallization progressed and their conductivity measured. Constant conductances were found for the third and fourth fractions. Chloride analysis of the pure salt gave 30.79 ± 0.02% chloride. Solutions were made by weight dilutions of a stock solution.

Potassium Chloride, used for secondary calibration of the transference cell was prepared by recrystallizing Baker C. P. salt twice recrystallized from conductivity water followed by fusion in platinum ware under an atmosphere of nitrogen.

A Lithium Chloride stock solution was prepared according to the method of Scatchard and Prentice (67). The necessary following solutions were prepared by volume dilution of this stock solution.

Conductivity water, used in the preparation of all solutions, was obtained by distillation of demineralized water from alkaline permanganate and subsequent redistillation. The specific conductance of the water was never greater than 2×10^{-6} ohm^{-1} cm^{-1}.

2. Apparatus

The transference numbers reported in this thesis were obtained using the sheared boundary technique (59).

The equipment used is a modification of that of Spedding, Porter and Wright (68, 69) and is described in the literature (43).

A diagram of the transference cell is shown in Figure 13. The cell was constructed of Pyrex. The measuring tube was constructed from a two millimeter pipette (Corning "redline"). Fine semi-circular

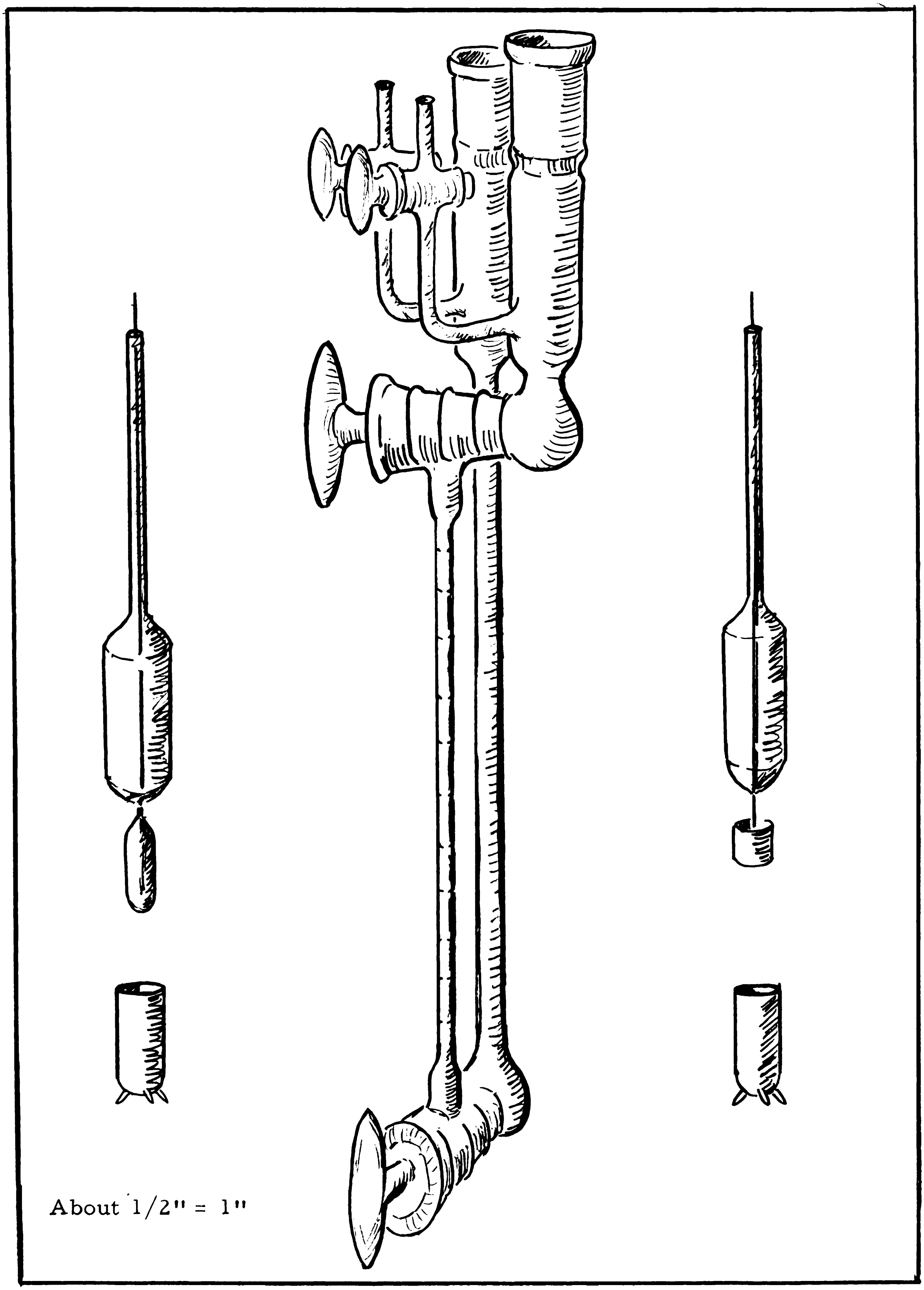


Figure 13. Moving Boundary Transference Cell

grooves were cut in the tube at constant intervals using a diamond stylus with the tube mounted in a milling machine. Gaps were left in the markings to facilitate timing of the boundary. The tube was twice calibrated with mercury as recommended by Longsworth (64). This tube was connected to a hollow bore stopcock at which the boundary was formed.

The electrodes are connected at the bottom of the cell by a second hollow bore stopcock to permit use with rising boundaries. The anode and cathode compartments were equipped with female ground glass joints to accommodate the male joints into which the electrodes were sealed. Side tubes with stopcocks which could be closed were attached to the electrode compartments for ease in filling the cell. Removable electrode cups were used to prevent the products of the electrode reactions from reaching the measuring tube.

The anode consisted of a copper wire sealed into a ground glass joint. The copper wire was immersed in a small test tube of cadmium metal which was melted under a stream of nitrogen. Upon cooling, the test tube was broken away leaving a smooth cadmium plug electrode.

The silver-silver chloride cathode was made by sealing a platinum wire into a ground glass joint. Corrugated silver sheet was then fused to the wire and cylindrically wrapped to a diameter of about one-half inch. The electrode was "plated" with silver chloride by electrolyzing in a one normal solution of hydrochloric acid.

The position of the boundary was detected by means of a narrow slit of light placed behind the transference tube with a telescope focused on the tube from the front. The light source was a vertically mounted fluorescent lamp, covered vertically by a movable, slotted cloth blind. The blind was raised and lowered by attachment to the drive shaft of a 110 volt reversible D. C. motor. Motor power was provided from the A. C. line voltage, converted by selenium rectifiers.

The motion of the boundary was timed with two stopwatches mounted in a stand with a hinged lid. The lid extended over both watches so that one watch could be started and the other stopped by pressing down on the lid. The watches were checked with the standard WWV signal and were accurate to three seconds over a twenty-four hour period.

A large aquarium-type water both, into which the cell was placed during experiments, was maintained at 25.00 ± 0.05°C.

Constant currents were obtained with an electronic controller and balancing motor. The current was determined from the potential drop across a standard resistor in series with the cell. Compensation for minor fluctuations not eliminated by the electronic apparatus was made by feeding the unbalance from a Leeds and Northrup type K-1 potentiometer to a Brown "electronik" 356358-1 amplifier which was used to drive a Brown 76750-3 balancing motor. A diagram of the current controlling apparatus is given in Figure 14.

The entire apparatus was checked at intervals by measuring the transference number of potassium chloride followed by lithium chloride. These results agreed with published values to within 0.05%.

3. Procedure

The transference cell was "quick-rinsed" with warm alkaline cleaning solution followed by acid-chromate cleaner. The cell was thoroughly rinsed and filled with distilled water and allowed to stand for twenty-four hours to insure complete removal of acid from the glass. The dried hollow-bore stopcocks were uniformly coated with a silicone grease and carefully seated. Since only falling boundaries were used, the stopcock at the bottom of the cell was always open. With the upper stopcock open, the cathode compartment was rinsed at least five times with the solution to be measured. The cell was then filled with the solution; the electrode cup, and the silver-silver chloride cathode were

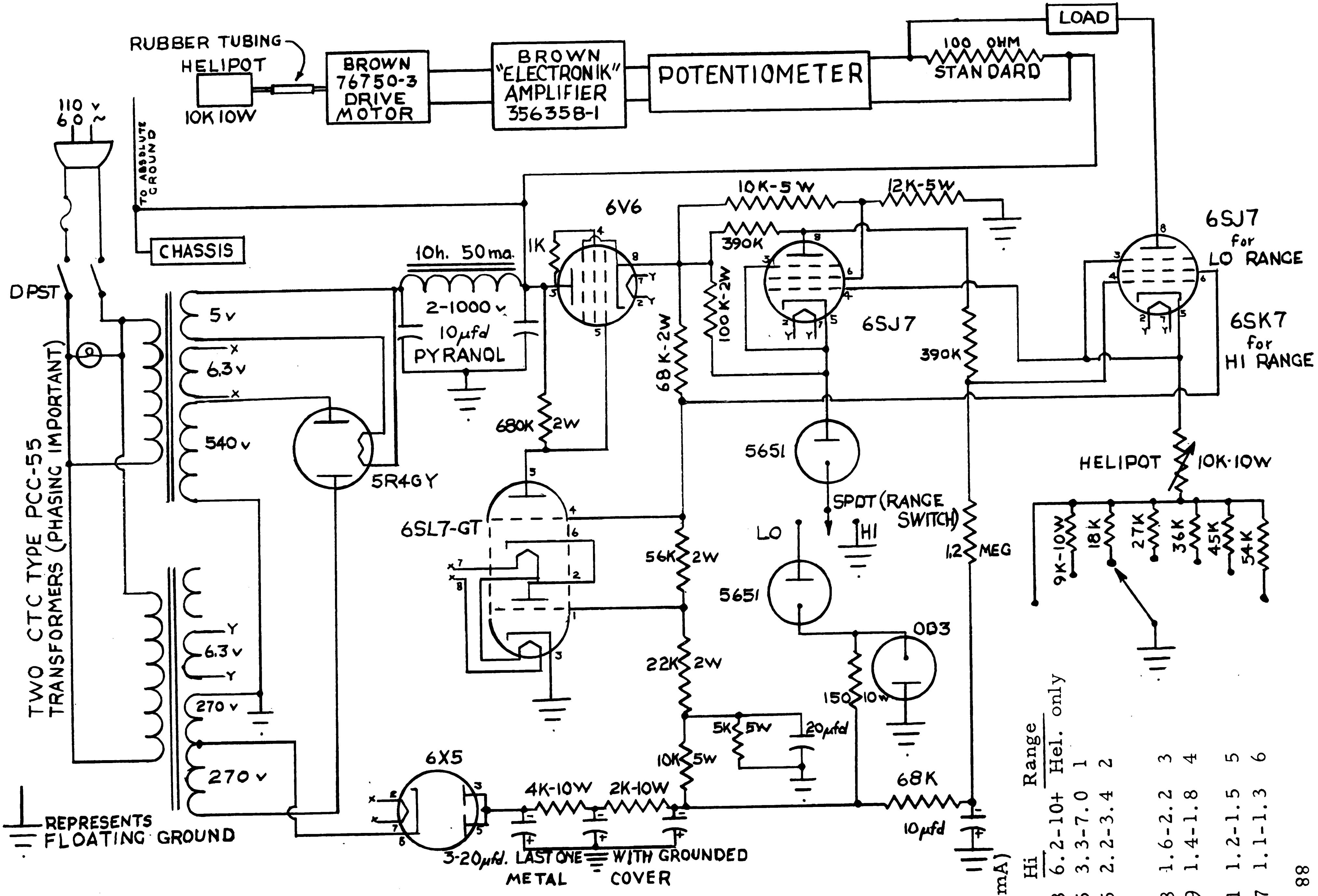


Figure 14. Constant Current Apparatus

Current (mA)

Lo	Hi	Range
1.4-2.8	6.2-10+	Hel. only
.74-1.5	3.3-7.0	1
.48-.75	2.2-3.4	2
.36-.48	1.6-2.2	3
.31-.39	1.4-1.8	4
.26-.31	1.2-1.5	5
.23-.27	1.1-1.3	6

inserted, and the side arm stopcock and upper hollow-bore stopcock were closed. The anode compartment was rinsed with water and, at least three times, with the lithium chloride following solution. The following solution was made up to the concentration given by the Kohlrausch ratio with an estimated value of the transference number of the complex cobalt cation. The anode compartment was then filled with the lithium chloride solution; the electrode cup and cadmium anode were inserted; and the cathode side arm was opened.

The cell was placed in the water bath and checked for electrical leaks to the bath with an ohmmeter. The cell was then aligned vertically and the light and telescope arranged so as to form a straight line with the cell. After waiting thirty minutes for temperature equilibrium, one side arm was closed to the atmosphere, the other left open. The Leeds and Northrup potentiometer was then balanced against a standard cell, the leads to the cell were connected, the hollow-bore stopcock was opened, and the current turned on. The current was adjusted to such a value that the boundary required from 200 to 250 seconds to traverse the distance between each pair of tube makings ($\Delta V = 0.1$ ml.). The time required for the boundary to pass each mark was measured with the stop-watches.

The $\underline{Co(en)_3Cl_3}$ solutions were made up by weight dilution of a stock solution. In order to calculate the normality of the solutions, the densities of the solutions were measured with a 50 ml. pycnometer. The densities were also used to calculate values of the partial molar volume of the salt, which were necessary for the evaluation of the volume correction to the observed transference number.

4. Results

The cation transference numbers of *tris*-(ethylenediamine) cobalt (III) chloride solutions were measured using lithium chloride following solutions. The concentration of the following solution was determined by an estimate of the transference number of the leading ion and transference numbers of the lithium ion given by Longsworth (64). The following solution concentration was found to be within the prescribed limits by changing the concentration by several per cent and repeating the determination.

Volume corrections were calculated according to equations (168) and (170) using the following values:

$V_{Cd} = 13.0$ ml. (Reference 64)
$\bar{V}_{ClCl_2} = [23.24 + 8.8 \,(\text{molality})^{\frac{1}{2}}]$ ml. (Reference 70)
$V_{Ag} = 10.3$ ml. (Reference 64)
$V_{AgCl} = 25.8$ ml. (Reference 64)

The densities of the $Co(en)_3Cl_3$ solutions were determined using a 50 ml. calibrated pycnometer. The results are described by the expression

$$\rho = 0.99707 + 0.1555 \,(\text{molality})$$

The average deviation of five points from this straight line was ± 0.00001 g./ cc. Partial molar volumes were calculated from the expression.

$$\bar{V} \approx \phi_V = \frac{1000}{c\rho_0}(\rho_0 - \rho) + \frac{M_2}{\rho_0} \qquad (173)$$

where

$\bar{V}$ = partial molar volume of $Co(en)_3Cl_3$

ϕ_V = apparent molar volume
c = molarity of the solution
$\rho_0 = 0.99707$
ρ = density of the solution
M_2 = molecular weight of $Co(en)_3Cl_3$

The average value 189 ± 1 cc./mole was used for the partial molar volume of $Co(en)_3Cl_3$ in calculating the volume corrections. Solvent corrections were calculated from measured conductances which supplement those in the literature (71). A Leeds and Northrup "Type A" cell, platinized according to the recommendations of Jones and Bollinger (72), was used. The A. C. bridge employed was designed by Thompson and Rogers (73). The resistances, measured at 400 to 2000 cps., were independent of frequency and the oil bath employed was maintained at 25.00 ± 0.02° C. The results are summarized in Table 13. **Figure 15** is plot of transference number versus $c^{*\frac{1}{2}}$, extrapolated to 0.4939, the value calculated from the conductance data of Jenkins and Monk (71). Curves calculated using the Onsager-Fuoss and the extended electrophoretic terms are also shown. Further discussion of the deviation from theory is reserved until after the presentation of activity coefficient data.

In view of the disagreement between theory and experiment, it is difficult to estimate the accuracy of these transference data. The four factors which influence the accuracy of the data are: (1) the timing of the boundary; (2) current; (3) volume of the tube; (4) concentration of the solution. The average precision of observed transference numbers and the maximum current fluctuation within each run was ± 0.04%. In view of the agreement of transference number arising from the various components of the apparatus is estimated to be ± 0.05%. Since the salt was carefully purified and the solution conductances form a smooth extension to literature data, the total maximum error in the reported transference numbers is estimated to be ± 0.1%.

III. Activity Coefficients

A. Definitions

The concept of activity was introduced in 1907 by G. N. Lewis (74, 75) as a means of precisely treating the thermodynamic behavior of

TABLE 13

CATION TRANSFERENCE NUMBERS AND EQUIVALENT CONDUCTANCES OF *TRIS*-(ETHYLENEDIAMINE) COBALT (III) CHLORIDE SOLUTIONS AT 25°C.

Normality	$(\text{Normality})^{\frac{1}{2}}$	$T_+(\text{obs.})$	ΔT_+ (Vol.)	ΔT_+(Solv.)	T_+	Λ
0.0059155	0.07691	0.4867	+ 0.0001	+ 0.0004	0.4872	125.0
0.014033	0.1183	0.4846	+ 0.0002	+ 0.0002	0.4850	114.3
0.023199	0.1523	0.4828	+ 0.0006*	+ 0.0002	0.4836	107.1
		0.4827	+ 0.0006*	+ 0.0002	0.4835	
0.046011	0.2145	0.4810	+ 0.0013*	+ 0.0001	0.4824	96.74
		0.4812	+ 0.0008	+ 0.0001	0.4821	
0.070953	0.26637	0.4800	+ 0.0011	--	0.4811	90.38

*Closed anode compartment.

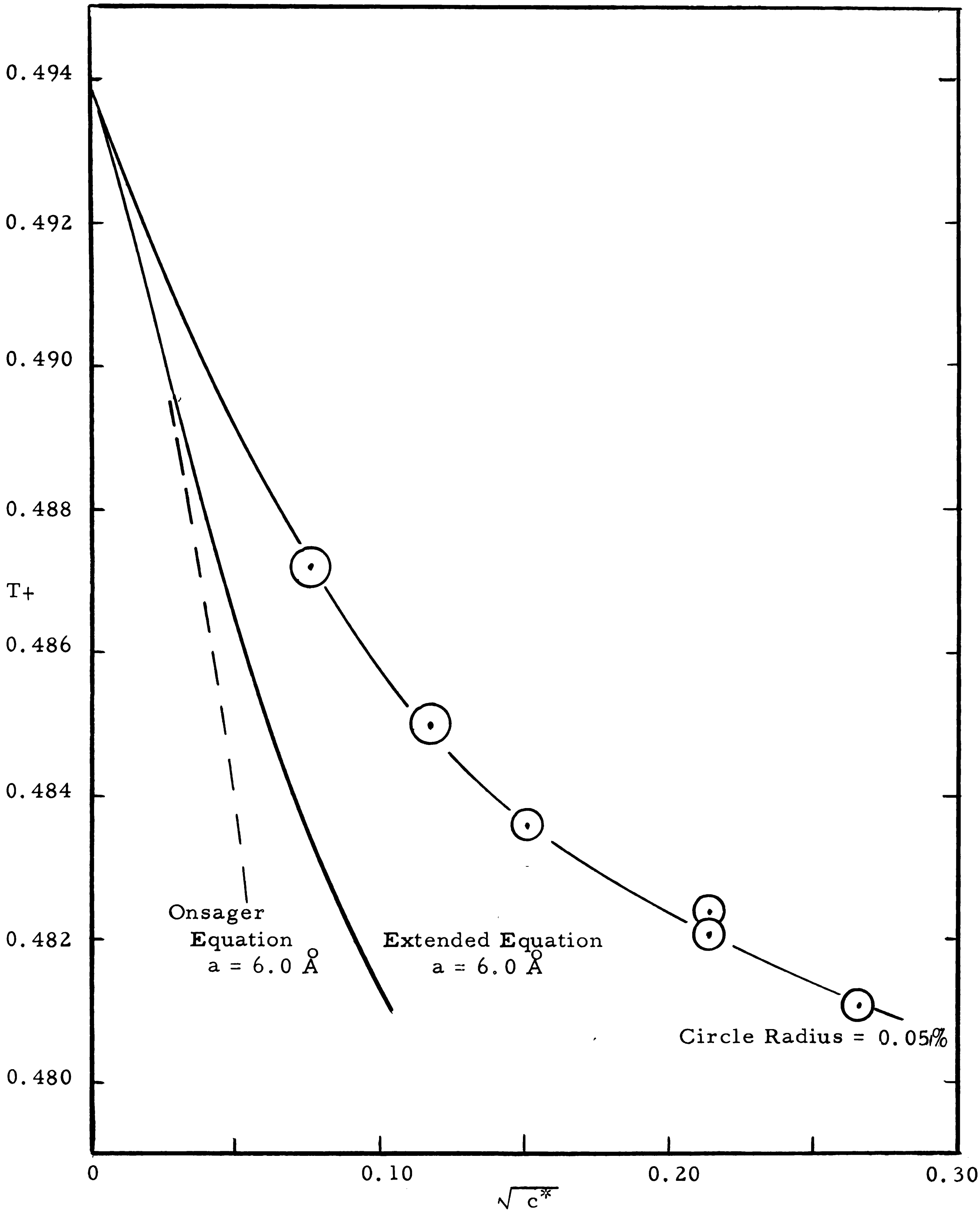


Figure 15. Cation transference number of tris-(ethylenediamine) cobalt (III) chloride versus the square root of normality in aqueous solution at 25°C.

non-ideal solutions. The activity $\underline{a_i}$ of component $\underline{i}$ in a solution may be defined through the relation

$$\overline{\mu_i} = \mu_i^0 + RT \ln a_i \qquad (174)$$

where $\overline{\mu_i}$ is the "chemical potential" of the i-component, and μ_i^0 the chemical potential in the standard state. Clearly, the value of the activity depends on the standard state chosen. The chemical potential is a measure of the escaping tendency of the species and

$$\overline{\mu_i} = \left(\frac{\partial E}{\partial n_i}\right)_{s, v, n_{k \neq i}} = \left(\frac{\partial F}{\partial n_i}\right)_{T, p\, n_{k \neq i}} \qquad (175)$$

where

E = The internal energy of the system

F = The Gibbs free energy

S = The entropy

P, V, T, = The pressure, volume and absolute temperature of the system

n_i = The number of moles of component $\underline{i}$ in a system of $\underline{k}$ components

An <u>ideal solution</u> is defined as one for which the activity is equal to the mole fraction at all concentrations. Accordingly, the activity coefficient $\underline{f_i}$ is defined as

$$f_i = \frac{a_i}{X_i} \qquad (176)$$

where X_i is the mole fraction of component $\underline{i}$. The chemical potential becomes

$$\begin{aligned} \overline{\mu_i} &= \mu_i^0 + RT \ln X_i + RT \ln f_i \\ &= \overline{\mu_i}\,(\text{ideal}) + RT \ln f_i \qquad (177) \end{aligned}$$

It is found that in very dilute solutions the activity approaches the concentration. It is, therefore, customary to chose the standard state

in such a way that

$$f_i = \frac{a_i}{X_i} \longrightarrow 1 \quad \text{as } X_i \longrightarrow 0 \ .$$

The thermodynamic properties of solutions of electrolytes are determined by the properties of the ions and of the solvent. Since the principle of electrical neutrality forbids the forming of solutions of single types of ions, the thermodynamic properties of a single type of ion can never be measured. Theoretically, however, it is advantageous to define hypothetical individual ionic quantities which are related to measureable properties. Consider an electrolyte which dissociates according to the scheme:

$$M_{\nu+} A_{\nu-} \longrightarrow \nu_+ M^{Z+} + \nu_- A^{Z-}$$

Individual ionic activities, $\underline{a_+}$ and $\underline{a_-}$, are defined by the relation

$$a \equiv (a_+^{\nu+} \ a_-^{\nu-}) \equiv a_\pm^{\nu} \qquad (178)$$

where

$$\nu = \nu_+ + \nu_-$$

$\underline{a}$ is the activity of the salt; and $\underline{a_\pm}$ is called the mean ionic activity. On this basis, the rational activity coefficient, $\underline{f_\pm}$, is defined as

$$f_\pm \equiv \frac{(a_\pm)_X}{X_\pm} \qquad (179)$$

where

$$X_\pm \equiv (X_+^{\nu+} \ X_-^{\nu-})^{1/\nu}$$

The standard state is chosen so that

$$f_\pm \longrightarrow 0 \qquad \text{as } X_\pm \longrightarrow 0$$

Since mole fraction is not always a convenient concentration unit for ionic solutions, activities and activity coefficients are defined for molal concentrations:

$$\gamma_{\pm} = \frac{(a_{\pm})_m}{m_{\pm}} \quad ; \quad m_{\pm} = (m_+^{\nu_+} \, m_-^{\nu_-})^{1/\nu} = m \, (\nu_+^{\nu_+} \, \nu_-^{\nu_-})^{1/\nu} \tag{180}$$

and molar concentrations

$$y_{\pm} = \frac{(a_{\pm})_c}{c_{\pm}} \quad ; \quad c_{\pm} \quad (c_+^{\nu_+} \, c_-^{\nu_-})^{1/\nu} = c(\nu_+^{\nu_+} \, \nu_-^{\nu_-})^{1/\nu} \tag{181}$$

The respective standard states are chosen so that

$$\gamma_{\pm} \longrightarrow 1 \qquad \text{as} \qquad m_{\pm} \longrightarrow 0$$

$$y_{\pm} \longrightarrow 1 \qquad \text{as} \qquad c_{\pm} \longrightarrow 0$$

Since the chemical potential must have the same value, regardless of the standard state chosen,

$$\begin{aligned} \bar{\mu} = \mu_x^0 + \nu RT \ln (f_{\pm} X_{\pm}) &= \mu^0_m + \nu RT \ln (\gamma_{\pm} \, m_{\pm}) \\ &= \mu_c^0 + \nu RT \ln (y_{\pm} \, c_{\pm}) \end{aligned} \tag{182}$$

At infinite dilution

$$f_{\pm} = y_{\pm} = \gamma_{\pm} = 1$$

With introduction of the limiting values $X_{\pm} / m_{\pm} = M_1 / 1000$ and

$X_{\pm} / c_{\pm} = M_1 / 1000 \, \rho_0$, one obtains

$$\mu_x^0 = \mu_m^0 + \nu RT \ln \frac{1000}{M_1} = \mu_c^0 + \nu RT \ln \frac{1000 \rho_0}{M_1} \tag{183}$$

where ρ_0 and M_1 are the density and molecular weight of the solvent respectively. By combining equations (184) and (185), the various

activity coefficients may be related:

$$\begin{aligned}\ln\ f_{\pm} &= \ln \gamma_{\pm} + \ln\,(1 + m\,\nu M_1/1000)\\ \ln\ f_{\pm} &= \ln y_{\pm} + \ln\,(\rho/\rho_0 + c(\nu M_1 - M_2)/1000\rho_0)\\ \ln\ \gamma_{\pm} &= \ln y_{\pm} + \ln\,(\rho/\rho_0 - cM_2/1000\rho_0)\end{aligned} \qquad (184)$$

where $\underline{\rho}$ is the density of the solution and $\underline{M_2}$ is the molecular weight of the solute.

The theoretical expression of Debye and Hückel (3) for ionic activity coefficients is obtained by assuming that all deviations in the chemical potential of electrolyte solutions arise from the charges of the ions. By considering the difference in the energy necessary to charge an isolated ion, and the energy necessary to charge an ion in a potential field $\underline{\Psi_j^0}$ (Equation 22) the result is

$$\ln\ f_j = \frac{-e_j^2\,\kappa}{2DkT(1 + \kappa a)} \qquad (185)$$

where $\underline{f_j}$ is the activity coefficient of ions of type j. For an electrolyte which dissociates into two kinds of ions, combination of the individual ionic activity coefficients given by equation (185) leads to

$$\log\ f_{\pm} = \frac{-S_f\,\sqrt{c}}{1 + \mathring{a}\,B\sqrt{c}} \qquad (186)$$

where

$$S_f = 0.5091\ \omega'$$

$$\mathring{a}\,B = a/\sqrt{c} = 10^8\ a\,(0.3286\ \omega'')$$

and

$$\omega'' = \left(\tfrac{1}{2}\sum_i \nu_i Z_i^2\right)^{\frac{1}{2}}$$

$$\omega' = \frac{1}{\nu\sqrt{2}}\left(\sum_i \nu_i Z_i^2\right)^{\frac{3}{2}}$$

The symbol $\underline{\mathring{a}}$ denotes $\underline{10^8 a}$, or $\underline{a}$ in Ångstrom units.

The various methods of experimentally determining activity coefficients are adequately reviewed in the literature (75, 76, 77, 78). Accordingly, only the use of E.M.F. cells with transference will be discussed below.

B. Activity Coefficients from the E.M.F. of Cells with Transference

The early theoretical work of Helmholtz (79) and Nernst (80) concerning the nature of the E.M.F. of concentration, received partial confirmation from the experiments of Moser (81, 82), Miesler (83, 83) and Jahn (85). With the introduction of the concept of activity by G. N. Lewis (74), the calculations were brought to their modern form. The first adequate treatment of the junction potentials involved in this type of cell was made by Brown and MacInnes (86), using transference numbers obtained from moving boundary measurements. Thus, the accurate evaluation of activity coefficients was made possible.

The calculations involved in the determination of activity coefficients from E.M.F. measurements using cells with transference may be illustrated by considering the following general cell:

$$\text{M-MX} \mid A_{\nu+}^{Z+} \; X_{\nu-}^{Z-} \; (c_1) \;\vdots\; A_{\nu+}^{Z+} \; X_{\nu-}^{Z} \; (c_2) \mid \text{MX - M} \tag{187}$$

where $M\text{-}MX$ represents an electrode which is reversible to X^- ions, and the molarity c_1 is greater than c_2. Consider the changes which occur in left hand side of cell (anode) when one Faraday of electricity passes through the cell: T_+ equivalents of A^{Z+} will be lost by migration across the junction; T_- equivalents of X^{Z-} will be gained by migration; and one equivalent of X^- will be removed by the electrode reaction. The sum of all the changes is a loss of T_+ equivalents of $A_{\nu+}^{Z+} X_{\nu-}^{Z-}$. A similar analysis of the right hand side gives a net gain of T_+ equivalents of $A_{\nu+}^{Z+} X_{\nu-}^{Z-}$, so that the total "reaction" is a transfer of

T_+ equivalents of salt from the more concentrated to the dilute solution. The free energy change for this process, if c_1 and c_2 differ infinitesimally is

$$dF = nRT\ d\ (\ln a) = \frac{T_+}{\nu_+ Z_+}\ RT\ d\ (\ln a) \tag{188}$$

where n is the number of *moles* of salt transferred and da is the change in the activity of the electrolyte. Since $dF = -nFd\mathcal{E}$ where $\mathcal{E}$ is the potential of the cell

$$\frac{d\mathcal{E}}{T_+} = -\left[\frac{RT}{\nu_+ Z_+ F}\right] d\ (\ln a) \tag{189}$$

For a finite difference in concentration Equation (189) becomes

$$\int_{\mathcal{E}(c = c_1)}^{\mathcal{E}(c = c_2)} \frac{d\mathcal{E}}{T_+} = -\left[\frac{RT}{\nu_+ Z_+ F}\right] \ln \frac{a_2}{a_1} \tag{190}$$

The integral on the left cannot be evaluated analytically since the transference number is a function of concentration. In order to evaluate the integral, the function

$$\delta = \frac{1}{T_+} - \frac{1}{T_{+\,(\mathrm{ref})}} \tag{191}$$

is defined.

If c_1 is taken as the concentration of the reference solution, c_{ref}, for which the cation transference number is $T_{+(\mathrm{ref})}$, then

$$\log \frac{y_\pm}{y_{\pm(\mathrm{ref})}} = \log \frac{c_{\mathrm{ref}}}{c} - \frac{\nu_+ Z_+ F \mathcal{E}}{2.303\ \nu RT T_{+(\mathrm{ref})}} - \frac{\nu_+ Z_+ F}{2.303\ \nu RT} \int_0^{\mathcal{E}} \delta\, d\epsilon \tag{192}$$

since $\mathcal{E}$ at $c = c_{\mathrm{ref}}$ is zero. Converting a to $a_\pm$ by equation (178), equation (192) may be written as

$$\log \frac{y_\pm}{y_{\pm(\mathrm{ref})}} = \log \frac{c_{\mathrm{ref}}}{c} - \frac{\nu_+ Z_+ F \mathcal{E}}{2.303\ \nu RT T_{+(\mathrm{ref})}} - \frac{\nu_+ Z_+ F}{2.303\ \nu RT} \int_0^{\mathcal{E}} \delta\, d\mathcal{E} \tag{193}$$

For $Co(en)_3Cl_3$; $\nu_+ = 1$, $\nu = 4$, $Z_+ = 3$.

Equation (193) shows that, with the aid of accurate transference data, ratio of the activity coefficients $y_\pm / y_{\pm(ref)}$ may be calculated from the E.M.F. of cells with transference. The ratio $f_\pm / f_{\pm(ref)}$ may be calculated from equation (184).

Individual activity coefficients $f_\pm$ may be obtained using the Debye-Hückel expression (186). By subtracting $\log f_{\pm(ref)}$ from both sides of equation (186) and multiplying both sides by $(1 + \overset{\circ}{a} B \sqrt{c})$, one obtains

$$\left[\log \frac{f_\pm}{f_{\pm(ref)}} + S_f \sqrt{c} \right] = - \log f_{\pm(ref)} - \overset{\circ}{a} B \left[\sqrt{c} \left(\log f_{\pm(ref)} + \log \frac{f_\pm}{f_{\pm(ref)}} \right) \right] \tag{194}$$

If the left side is denoted by Y and the bracketed term on the right by X, the intercept of a plot of Y vs. X gives $- \log f_{\pm(ref)}$ providing the solutions obey the Debye-Hückel equation. In order to obtain this value, a successive approximation method must be used since X contains $\log f_{\pm(ref)}$. The value of $\overset{\circ}{a}$, the minimum distance of approach may be obtained from the slope of the plot.

The requirements for the successful determination of activity of coefficients by this method may be summarized as follows:

(1) No changes take place in the cell without passage of current.

(2) Every change which takes place during the passage of current may be reversed by reversing the direction of the current.

(3) The measured potential must depend only on the concentrations of the solutions in contact with the electrodes and not upon the distribution of concentration gradients at junction of the solutions.

Extensive studies of the third criterion have been made (53, 54, 87, 88, 89). It has been found that reproducible potentials are obtained provided the area of junction is at least 12 mm.^{2} and that the concentration of the solution in contact with the electrodes remains unchanged.

C. Experimental

1. Materials

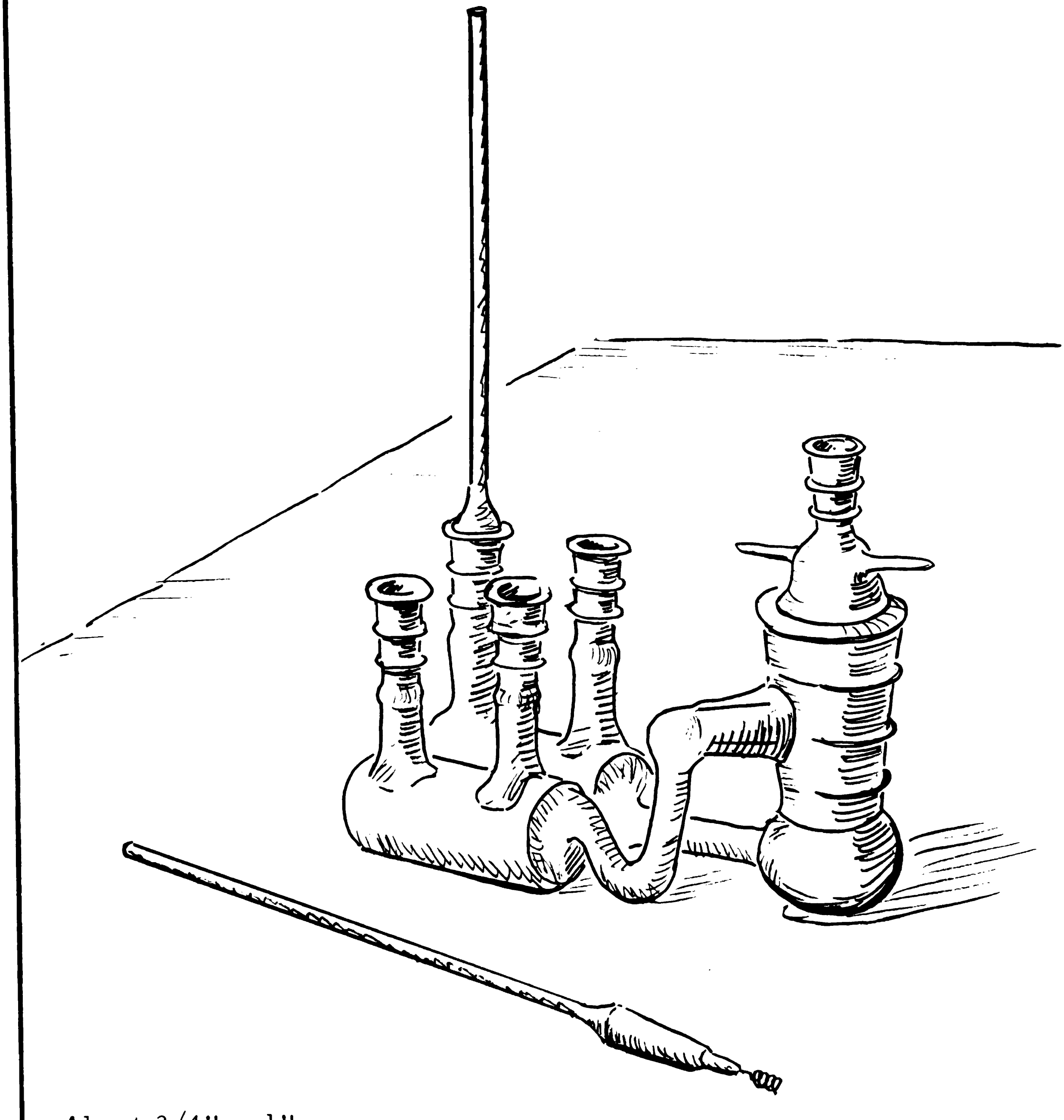
Solutions of $Co(en)_3Cl_3$ were prepared in the manner described in the section of this thesis on transference numbers.

Traces of bromide in potassium chloride were removed by the method of Pinching and Bates (90). The salt was then recrystallized three times from hot conductivity water and fused in platinum ware under a nitrogen atmosphere. Hydrous silver oxide was prepared by the addition C. P. silver nitrate to a boiling solution of potassium hydroxide. The resulting precipitate was washed fifty times with hot conductivity water to remove any potassium carbonate present.

Baker reagent grade hydrochloric acid was used without further purification.

2. Apparatus

The cell and electrodes used in this work were essentially the same as those used by Spedding, Porter and Wright (68). The cell (shown in Figure 16) consisted of two compartments joined by a high-vacuum hollow-bore stopcock (H. S. Martin Co.). Each compartment was equipped with two female ground glass joints to hold the electrodes. A trap was placed between one of the compartments and the stopcock to prevent diffusion. The silver-silver chloride electrodes were prepared by the thermal-electrolytic method of Smith and Taylor (91). About three inches of number 26 C. P. platinum wire was sealed into a standard 12/30 male taper. The wire was then coiled by tightly winding it on a two millimeter



About 3/4" = 1"

Figure 16. Concentration Cell with Transference

glass rod, and cleaned by heating to redness, plunging into concentrated nitric acid, and rinsing with conductivity water. This cleaning process was repeated several times.

The electrodes were then coated with a paste of silver oxide which was ignited to silver at 400° C. Three or four coats of the oxide, and subsequent ignitions, produced a complete covering of silver. After filling with mercury, the electrodes were "plated" with silver chloride by electrolyzing in a one normal solution of hydrochloric acid for forty-five minutes at a current of eight milliamperes per electrode. A convenient source of current was provided by a six volt battery eliminator and a 3,000 ohm rheostat.

A Leeds and Northrup type K-2 potentiometer was used to measure the potentials developed in the cells. The null point was determined with a Leeds and Northrup type R galvanometer (catalog number 2284C) which had a sensitivity of 0.077 μv/mm. The potentiometer was checked against a calibrated Eppley type standard cell.

3. Procedure

After electrolysis, the silver-silver chloride electrodes were connected in parallel and allowed to stand in 0.1 normal bromide-free potassium chloride solution until they reached a nearly constant potential when measured against one another. If the potential of any electrode in a set of ten differed from the mean of the remainder of the set by more than 0.02 mv., it was discarded. Three to four days were usually required for this equilibration.

The electrodes were soaked in conductivity water for eight hours followed by three two-hour soakings in the solution to be measured before being placed in the cell.

The electrode compartment containing the trap was rinsed four times and filled with the more dilute of the solutions to be measured,

and the electrodes were inserted. The remainder of the cell was rinsed and filled in the same way with the more concentrated solution. No stopcock grease was used, the ground glass plug being tight enough to prevent diffusion. The cell was then placed in a large water bath at $25.00 \pm 0.02^{\circ}$ C. One hour was allowed for temperature equilibration. The stopcock was then opened and the E.M.F. measured with the potentiometer. To correct for possible differences, between electrodes each determination was repeated using the electrodes in the more concentrated solution which were originally in the more dilute solution and *vice versa*. Since each compartment contained two electrodes, eight values of the E.M.F. were measured for each pair of solutions. All dilutions were measured against the same reference solution.

4. Results

The potentials of cells with transference were measured for solution of *tris*-(ethylenediamine) cobalt (III) chloride. A typical set of data is shown in Table 14. Values of $\log \left[y \pm / (y\pm)_{ref} \right]$ were calculated from equation (192) in the form

$$\log \frac{y_{\pm}}{(y_{\pm})_{ref}} = \log \frac{c_{ref}}{c} - \frac{3F\mathcal{E}}{9.212\ RT(T_{+})_{ref}} - \frac{3\ F}{9.212\ RT} \int_{0}^{\mathcal{E}} \delta\, d\mathcal{E} \qquad (195)$$

Values of $\log \left[f_{\pm}/(f_{\pm})_{ref} \right]$ were obtained from equation (184). In order to determine $\log (f_{\pm})_{ref}$, the Debye-Hückel equation in the form (194) was employed.

$$\left[\log \frac{f_{\pm}}{(f_{\pm})_{ref}} + S_f \sqrt{c} \right] = - \log (f_{\pm})_{ref} - \mathring{a} B \left[\sqrt{c} \left(\log (f_{\pm})_{ref} + \log \frac{f_{\pm}}{(f_{\pm})_{ref}} \right) \right] \qquad (194)$$

TABLE 14

A TYPICAL SET OF DATA FOR A CONCENTRATION CELL WITH TRANSFERENCE. TRIS-(ETHYLENEDIAMINE) COBALT (III) CHLORIDE

Concentration: 0.0014805 molar
Reference Concentration: 0.0033735 molar

Electrodes	EMF (millivolts)	Average E.M.F. (millivolts)
2 vs. 4	12.502	12.496
4 vs. 2	12.491	
2 vs. 3	12.501	12.494
3 vs. 2	12.486	
1 vs. 3	12.482	12.475
3 vs. 1	12.468	
1 vs. 4	12.473	12.467
4 vs. 1	12.461	

Average: 12.483 mv.
Average deviation: 0.012 mv.
Maximum deviation: 0.016 mv.

Figure 17 is a plot of the left side of this equation versus the bracketed term on the right. The smooth extrapolation to zero absissa requires the unreasonably small value of $\overset{\circ}{a} = 2.0$ Å. A larger $\overset{\circ}{a}$ causes the curve to drop abruptly in the region corresponding to very small concentrations. The curvature of the plot indicates that solutions of $Co(en)_3Cl_3$ do not obey the Debye-Hückel theory. Attempts to fit the data using larger values of $\overset{\circ}{a}$ and an ion-pairing constant were unsuccessful. The method used, however, may be of interest.

Consider the following pairing scheme:

$$Co(en)_3^{+3} + Cl^- \rightleftharpoons [Co(en)_3Cl]^{+2} \tag{195}$$

The association constant, K, for this "reaction" is

$$K = \frac{a_{+2}}{a_{+3}\, a_{-1}} = \frac{c_{+2}}{c_{+3}\, c_{-1}} \cdot (y_\pm)_R \tag{196}$$

where the signed subscripts denote the species of corresponding charge, a their activities and c their molar concentrations. The symbol y_R denotes the activity coefficient ratio

$$(y_\pm)_R = \frac{y_{+2}}{y_{+3}\, y_{-1}} = \frac{(y_\pm)^3_{2-1}}{(y_\pm)^4_{3-1}} \tag{197}$$

where $(y_\pm)_{i-j}$ is the stoichoimetric mean ionic activity coefficient of a "salt" of charge type i-j. Let α be the fraction of the salt associated, and c be the stoichiometric concentration $Co(en)_3Cl_3$. The concentrations of the various species are, then,

$$\begin{aligned} c_{+3} &= c\,(1 - \alpha) \\ c_{+2} &= c\ \alpha \\ c_{-1} &= 3c(1 - \alpha) \end{aligned} \tag{198}$$

and the association constant is given by

$$K = \frac{\alpha}{3c\,(1 - \alpha)^2} \cdot (y_\pm)_R \tag{199}$$

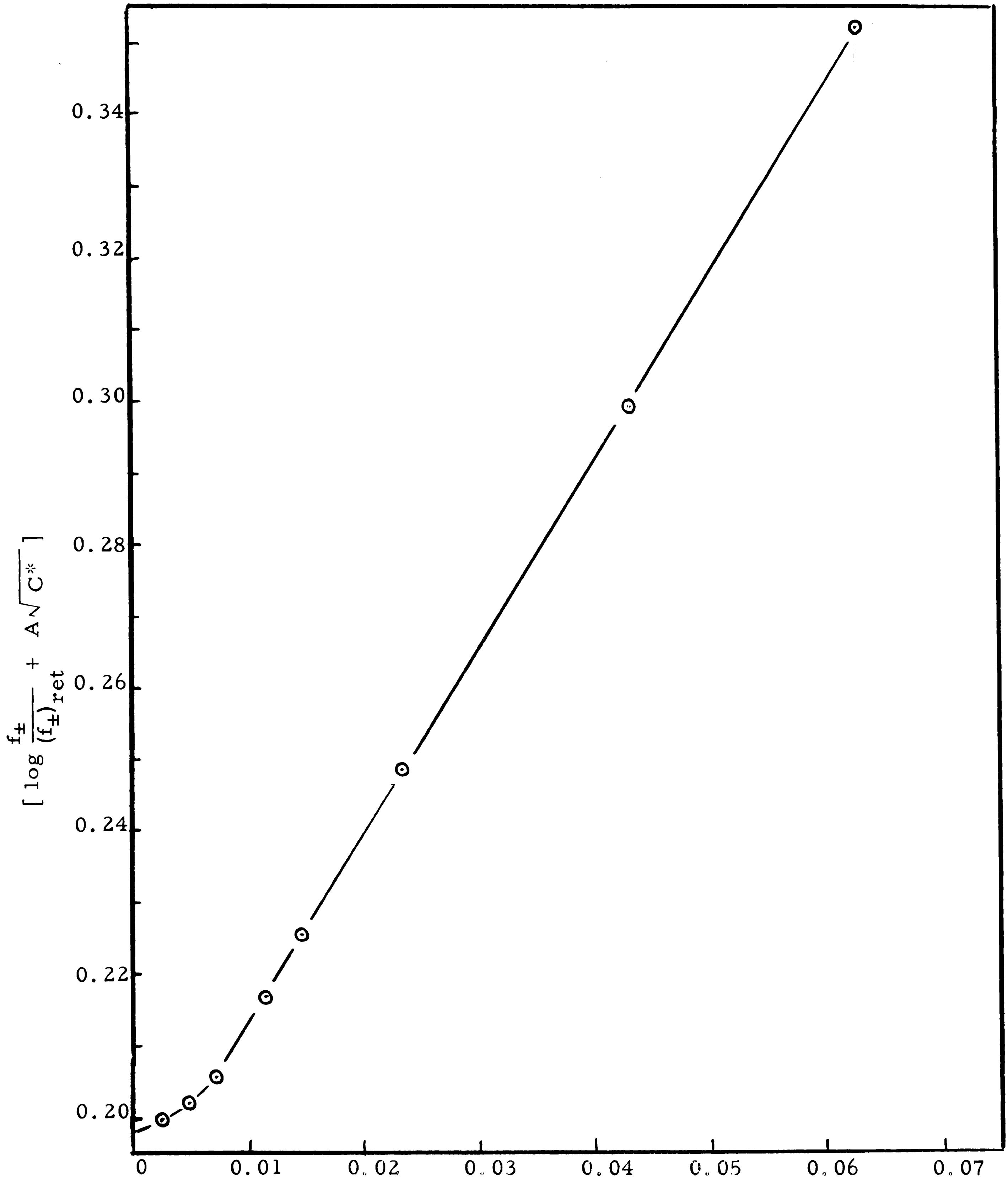


Figure 17. Debye-Hückel plot of activity coefficient data for aqueous tris-(ethylenediamine) cobalt (III) chloride solution at 25°C.

The ionic strength, Γ, of the solution is defined as

$$\Gamma = \sum_i c_i Z_i^2 \tag{200}$$

which, for this system becomes

$$\Gamma = 8\,c\,(3/2 - \alpha) \tag{201}$$

Further, the observed mean activity coefficient, $(y_\pm)$, is related to the value calculated by the Debye-Hückel theory for a 3-1 salt, $(y_\pm)_{DH}$, by equation (202).

$$(y_\pm) = (1 - \alpha)\,(y_\pm)_{DH} \tag{202}$$

or

$$\alpha = 1 - (y_\pm)/(y_\pm)_{DH} \tag{202a}$$

The quantity $(y_\pm)_{DH}$ may be obtained from

$$\log\,(y_\pm)_{DH} = - \frac{S_\Gamma\,\Gamma^{\frac{1}{2}}}{1 + \mathring{a}\,B'\,\Gamma^{\frac{1}{2}}} \tag{203}$$

A method of successive approximations was then carried out. Choosing a concentration c, at which the activity coefficient was experimentally obtained, and $\mathring{a}$ for the salt and a trial value of α, $(y_\pm)_{DH}$ was calculated from equation (201) and (203). A second approximation to α was then obtained from equation (202a), using the experimental value of $(y_\pm)$. This cycle of calculations (equations 201, 203, 202a) was repeated until a constant value of α was obtained. Equations (200) and (204)

$$\log\,(y_\pm)_R \quad \frac{[\,4(S\,)_{3-1} - 3(S\,)_{2-1}]\,\Gamma^{\frac{1}{2}}}{[\,1 + \mathring{a}\,B'\,\Gamma^{\frac{1}{2}}]} \tag{204}$$

serve to evaluate $\underline{(y_\pm)_R}$.

To facilitate calculation, $\mathring{a}$ for the salt and the ion pair were considered to be equal. Using this scheme, then, a K was obtained to "force-fit" the data for the chosen $\mathring{a}$ at the first concentration considered. With

the value of $\underline{K}$ so obtained, $\underline{(y_\pm)_{ref}}$ was calculated by estimating $\underline{(y_\pm)_R}$, calculating $\underline{a}_{ref}$ using equations (199) and (204), and iterating until a constant $\underline{a}_{ref}$ was obtained. Equations (202) and (203) yield $\underline{(y_\pm)_{ref}}$. Points at other concentrations were calculated in the same manner so that several values of $\underline{y_\pm/(y_\pm)\ ref}$ were compared with experiment. As $\underline{\mathring{a}}$ and $\underline{K}$ were decreased, the calculated values more closely approximated the observed quantities. Though unsuccessful, this calculation points out the difficulties involved in the application of the ion pair concept to solutions of unsymmetrical salts.

A second attempt was made to explain the data using the extended equation of LaMer, Gronwall and Grieff (92). This expression for the activity coefficient of unsymmetrical electrolytes, arises from the solution of the Poisson-Boltzmann equation (12) with retention of terms to order $\underline{\Psi_j}^3$. The calculation proved to be completely unsatisfactory when applied to the data for $Co(en)_3Cl_3$ solutions.

Since no theoretical expression adequately explains the data, the value of $\underline{\log (f_\pm)_{ref}}$ from the intercept of the Debye-Hückel plot was used to calculate $\underline{f_\pm}$ for each solution the mean molar $(\underline{y_\pm})$ and molal $(\underline{\gamma_\pm})$ activity coefficients were calculated from equation (184). Table 15 gives the observed E.M.F. and calculated quantities for the solutions.

The measured potentials were precise to ± 0.1% or better. With the lack of a suitable theoretical function with which to compare the results, it is difficult to obtain a good estimate of the accuracy of the data, however, the values of $\underline{y_\pm/(y_\pm)_{ref}}$ are probably accurate to about ± 0.2%.

IV. Discussion of Results

Activity coefficients of $Co(en)_3Cl_3$ in concentrated solutions have been measured by Brubaker (46) using the isopiestic method. These data

TABLE 15

E.M.F. DATA AND ACTIVITY COEFFICIENTS OF TRIS-(ETHYLENEDIAMINE) COBALT (III) CHLORIDE AT 25°C.

(Molarity)10^4	E.M.F. (Millivolts)	$y_\pm$	$f_\pm$
6.7897	22.830	.8019	.8022
13.805	12.483	.7318	.7319
19.718	7.428	.6933	.6934
33.735*	0.000	$.6328_5$	$.6328_5$
46.677	-4.253	.5908	.5904
77.330	-10.732	.5268	.5263
153.37	-18.869	.4344	.4333
236.10	-23.793	.3802	.3787

*Reference Solution

were fit with $\overset{\circ}{\underline{a}} = 3.5$ Å and an empirical linear concentration term. A large plot of $\underline{\log\ \gamma_{\pm}}$ vs. $\underline{m}$ for the E.M.F. and isopiestic data indicates that the chosen reference values are compatible, since, as nearly as one can tell, the two sets of data form a smooth curve.

As indicated above, both transference number and activity coefficient data deviate from all available theoretical expressions. The lack of agreement with theory of the activity coefficients is the more fundamental discrepancy. Since the theory of ionic mobilities is based upon the Debye-Hückel theory, it is not surprizing that differences between observed and calculated transference numbers occur. It is interesting to note that the transference number calculation improves somewhat as larger $\overset{\circ}{\underline{a}}$ values are used and that the extended electrophoretic correction gives a closer fit than the Onsager expression. The activity coefficient data, however, are best approximated with an $\overset{\circ}{\underline{a}}$ value which is certainly too small. A consideration of multiple ion aggregation might improve the situation, however, it seems more likely that the observed deviations are due to other unknown, non-coulombic interactions of the complex cation.

Although the interionic attraction theory is limited, it has met with considerable success when applied to systems which more closely approximate the model of hard spherical ions. Solutions of rare earth chlorides serve to illustrate this behavior. The activity coefficients of such salts obey the Debye-Hückel theory. Further, the difference in observed conductance, and that calculated by the limiting law (usually designated as $\underline{\Lambda_0'}$, shows monatonic dependence upon the square root of the concentration. This behavior is anomolous, in the sense that for a great many other unsymmetrical salts of high charge type, including $Co(en)_3Cl_3$ solutions, $\underline{\Lambda_0'}$ $\underline{\text{versus}}$ $\underline{c}^{*\frac{1}{2}}$ plots exhibit a pronounced minimum. The more usual behavior, then, is deviation from the simple theory which is currently available.

V. Summary

Experimental data have been presented for aqueous solutions of *tris*-(ethylenediamine) cobalt (III) chloride. Transference numbers were obtained by the moving boundary method and activity coefficients were determined from the electromotive force of concentration cells with transference. Both properties show marked deviations from the predictions of theory. Unknown specific interactions of the complex cation are believed to be the cause of the discrepancies.

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APPENDIX I

A DESCRIPTION OF THE PROGRAM FOR THE EVALUATION OF THE COMPLETE ELECTROPHORETIC EFFECT

The expressions for the electrophoretic contribution to the equivalent conductance are given by equations (151) and (153) and are of the form

$$\Delta\lambda_+ = M \int_x^\infty \rho \left\{ \exp\left(-B_+ e^{-\rho}/\rho\right) - \exp\left(B_\pm e^{-\rho}/\rho\right) \right\} d\rho \qquad \text{(a)}$$

$$\Delta\lambda_- = M \int_x^\infty \rho \left\{ \exp\left(-B_- e^{-\rho}/\rho\right) - \exp\left(B_\pm e^{-\rho}/\rho\right) \right\} d\rho \qquad \text{(b)}$$

where

$$B_+ = Z_+^2 P$$

$$B_- = Z_-^2 P$$

$$B_\pm = |Z_+ Z_-| P \qquad \text{(c)}$$

and $\underline{P}$, $\underline{M}$, , and $\underline{x}$ are defined in Chapter III. The quantities $\underline{\Delta\lambda_+^+}$, $\underline{\Delta\lambda_-^-}$ and $\underline{\Delta\lambda_\pm}$ are defined as

$$\Delta\lambda_\pm = M \int_x^\infty \rho \left[\exp\left(B_\pm e^{-\rho}/\rho\right) - 1\right] d\rho$$

$$\Delta\lambda_+^+ = -M \int_x^\infty \rho \left[\exp\left(-B_+ e^{-\rho}/\rho\right) - 1\right] d\rho$$

$$\Delta\lambda_-^- = -M \int_x \rho \left[\exp\left(-B_- e^{-\rho}/\rho\right) - 1\right] d\rho \qquad \text{(d)}$$

so that

$$\Delta\lambda_+ = \Delta\lambda_\pm + \Delta\lambda_+^+$$

$$\Delta\lambda_- = \Delta\lambda_\pm + \Delta\lambda_-^-$$

$$\Delta\Lambda_e = \Delta\lambda_+ + \Delta\lambda_- \qquad \text{(e)}$$

The program accepts, as parameters, ten values of $\underline{c}^{\frac{1}{2}}$, six values of $\underline{a}$, the quantities $\underline{M}$, $\underline{1/DT}$, $|Z_+|$, and $|Z_-|$ and prints out $\underline{a}$, $\underline{c^{\frac{1}{2}}}$, $\underline{\Delta\lambda_\pm}$, $\underline{\Delta\lambda_+^+}$, $\underline{\Delta\lambda_-^-}$ for each combination of $\underline{a}$ and $\underline{c^{\frac{1}{2}}}$.

The following method was used to evaluate the integrals (e). Taking the expression for $\Delta\lambda_{\pm}$ as an example, one may expand the lower exponent in the integrand

$$f(\rho) = \rho[\exp(B_{\pm} e^{-\rho}\ \rho) - 1] \approx -B_{\pm} e^{-\rho} + B_{\pm}^{2} e^{-2\rho}/2\rho - \ldots \tag{f}$$

so that for some large value of $\rho \equiv R$

$$\int_{x}^{\infty} f(\rho)\, d\rho \quad \int_{x}^{R} f(\rho)\, d \ - \int_{R}^{\infty} B_{\pm}\ e^{-\rho}\, d\rho$$

$$= \int_{x}^{R} f(\rho)\, d\rho + B_{\pm}\ e^{-R} \tag{g}$$

The finite upper limit is chosen such that the ratio of the second and the first terms in the expansion (f) is less than some small number ϵ at $\rho = R$.

$$Be^{-R}/2R < \epsilon \tag{h}$$

The integrals of $f(\rho)\, d\rho$ are thus reduced to forms with finite limits. For each integral the value of B is calculated. With this and $\epsilon = 10^{-3}$, the upper limit R and the "tail" Be^{-R} are determined. The major portion of the integral

$$I_{\pm} = \int_{x}^{R} \rho\ [\exp(B_{\pm} e^{-\rho}/\rho) - 1\ ]\, d\rho \tag{i}$$

is then numerically integrated using a MISTIC library subroutine which employs the Newton-Cotes quadrature formula "Q_{66}" (93). For small values of ρ , $f(\rho)$ becomes very large and changes very rapidly with ρ . In order to insure "fitting" of function, the integral is re-evaluated using successively smaller increments (with a larger number of points) until

$$M[\ |(I_{\pm})_{n+1}| - |(I_{\pm})_{n}|\ ] < \epsilon = 10^{-3}$$

The accuracy of the results is limited by this step. The choice of $\epsilon = 0.001$ implies an error of ± 0.001 conductance units in each $\overset{\pm}{\Delta\lambda_{\pm}}$, or ± 0.002

in $\Delta\lambda_+$ and $\Delta\lambda_-$, and finally ± 0.004 units in $\Delta\Lambda_e$. The convergence of the integral is also a time-consuming operation, the average integral requiring about three minutes of machine time. Because of the magnitude of $f(\rho)$ at small values of ρ , the routine is written in *binary floating point* form, which accommodate numbers in the range $10^{\pm 37}$, and is subject to restriction

$$|Z_+ \ Z_-| / aDT < 5 \times 10^4$$

The routine was code checked with values of $\Delta\lambda_+$ and $\Delta\lambda_-$ which had been graphically evaluated and others which were calculated with an IBM 604 calculator.

Copies of the complete program are available from Professor James L. Dye, Department of Chemistry, Michigan State University, East Lansing, Michigan.

APPENDIX II

A DESCRIPTION OF THE PROGRAM USED TO CALCULATE THE RELAXATION FIELD AND THE EQUIVALENT CONDUCTANCES

The equivalent conductances, Λ, of symmetrical electrolytes reported in this thesis were calculated according to equation (155)

$$\Lambda = \frac{(\Lambda^0 - \Delta\Lambda_e)\,(1 + \ X/X + \Delta P/X) - |\,\Delta_+\,\Delta\Lambda_e\,(\Delta X/X + \Delta P/X)\,|}{(1 + (10/3)\,\pi\,NR^3\,c)}$$

by the MISTIC computer. The various symbols are defined in Chapter II. A binary floating point routine was written, which, given the parameters, a, $c^{\frac{1}{2}}$ and R, printed out values of a, $c^{\frac{1}{2}}$, $(\Delta X/X + \Delta P/X)$ the cross-term correction $-|\,\Delta_+(\Delta\Lambda_e)\,(\Delta X/X + \Delta P/X)|$, the equivalent conductance with $R = 0$; and the complete value of Λ according to equation (155). Computations were executed in blocks with the following imput parameters:

a) Up to ten values of Λ^0

b) Up to six values of a

c) Up to ten values of $c^{\frac{1}{2}}$

d) Up to sixty values of $\Delta\Lambda_e$ corresponding to the combinations of a and $c^{\frac{1}{2}}$

e) Z^2 $(= |\,Z_+ Z_-\,|)$

f) DT

g) $\kappa/c^{\frac{1}{2}}$

h) α

i) β

j) R^3

A built in alarm was provided so that the calculation is performed only if $\kappa a \leq 0.50$.

Since exponential integrals related to Ei(x) occur frequently in the calculation of the relaxation term, a closed binary floating point subroutine

was written to evaluate these functions. The subroutine uses the formula

$$Ei(x) = \int_{x}^{\infty} (e^{-t}/t)\, dt \quad -0.57722 - \ln x + x(1-0.2500\, x\, (1-0.2222\, x(1-0.1875\, x))) + \epsilon$$

where $\epsilon \leq x^5/600$, and operates in connection with the MISTIC library arithmetic and logarithm routines. Quantities calculated by this routine were found to agree with careful hand calculations to at least four significant figures. Complete copies of the routine are available.