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IONIC CONDUCTIVITIES AND SOLVENT PROPERTIES

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CHRISTOPHER JOHN JAMES, B.Sc.

Department of Physical and Inorganic Chemistry

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SUMMARY

Conductivities of KCl and KBr have been measured at 25°C in 80%, 60%, 40% and 20% water/N,N-dimethylformamide, DMF, mixtures and KCl in a 31% water/DMF mixture. Λ^o for each electrolyte-solvent system was evaluated with the full Pitts and the Fuoss-Hsia conductivity equations. If the electrolytes were assumed to be non-associated, the distance of closest approach of the ions, the a parameter, was found to systematically decrease with decreasing solvent dielectric constant, D, more rapidly in the case of the Pitts than the Fuoss-Hsia theory. This observation suggested that ionic association was responsible. Upon the basis of the Fuoss-Hsia theory the electrolytes were subsequently found to be slightly associated in DMF/water mixtures. The Fuoss-Hsia theory for the associated case returned reasonable values for a but this quantity still was found to depend upon the value of D - a increasing with decreasing D. Computing the mean ionic activity coefficient with the Debye-Hückel equation rather than the Debye-Hückel limiting law reduced, but did not eliminate, the dependence of a on D. No physical significance was attached to this last dependence.

Cationic transport numbers of KBr were measured in 80%, 60%, 40% and 20% and KCl in 40% water/DMF mixtures at 25°C thus permitting the evaluation of individual ionic conductivities in this solvent system. The limiting equivalent conductivities of the K^+ ion, $\lambda^o_{K^+}$, derived from KBr and KCl in a 40% water/DMF mixture were found to be equal within 0.12%.

The Stokes radius of the K^+, Cl^- and Br^- ions in water/DMF mixtures have been computed. In addition, the dependence of the Stokes radius of the K^+ ion and $\lambda^o_{K^+}$ upon solvent composition in aqueous mixtures of ethanol, methanol, tetrahydrofuran, dioxane, iso-propanol and acetone have been examined. On the basis of current models there is no evidence to suggest that the passage of an ion through the solvent induces the phenomenon of the dielectric relaxation of the solvent. Also there appears to be little

correlation between changes in the viscosity of a solvent and $\lambda^{o}_{K^+}$. There seems to be, however, a greater correlation between volume changes in the solvent system and $\lambda^{o}_{K^+}$. In the region of pure water the larger depression in $\lambda^{o}_{K^+}$, from its value in water, is brought about by the added non-electrolyte having the larger molecular size. A qualitative explanation is given for this observation on the basis of current proposals relating to the effect of added non-electrolyte upon the structure of liquid water.

Densities of KCl and KBr in DMF/water mixtures were measured in order to convert the molality of an electrolyte solution to its corresponding molarity. Root's equation is also demonstrated to describe the concentration dependence of the densities of these electrolyte solutions. In addition, extensive density data for DMF/water mixtures are also reported.

Procedures for the evaluation of the kinetic energy correction coefficient of capillary kinematic viscometers have been examined in this research. The kinetic energy term for a long-flared Ubbelohde viscometer was shown to be negligible for flow times corresponding to water between 0° and 60°C. Consequently, by neglecting this correction term, the viscosity of water in this temperature range has been evaluated to a precision of better than 0.1%, the values obtained being based solely upon the absolute viscosity of water at 20°C. The determination of the instrument constants of a second viscometer with which the flow times of DMF/water mixtures had been measured was made by utilising the values for the viscosity of water obtained in this research. Hence the viscosities of the DMF/water mixtures reported in this thesis have a precision of better than 0.1%.

This research is, in part, a continuation of a previous study by the author of this thesis in which the dependence of the energy of activation for the conductance process, Ea, upon density changes in aqueous solution in the vicinity of the maximum density of the solution were examined. Conductance data for an aqueous 0.001N CsCl solution between 0° and 10°C are presented. The temperature dependence of Ea for this salt decreases linearly with temperature in the region in which the density of the solution attains its maximum value: that is, Ea is independent of the influences which give rise to the maximum density of the solution. This finding corroborates those of the previous research in which Ea for the K^+ and Cl^- ions at infinite dilution and at a finite concentration were also shown to be independent of density changes in the system with temperature. Using the previously reported conductance data for aqueous KCl solutions, Ea is shown to be concentration dependent for the K^+ and Cl^- ions and, in addition, Ea for the Cl^- ion is greater than K^+ at infinite dilution and at a finite concentration.

DECLARATION

I hereby certify that this thesis contains no material which has been accepted for the award of any other degree or diploma in any other University, and to the best of my knowledge contains no material previously published or written by any other person, except where due reference is made in the text.

Christopher J. James

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GLOSSARY OF PRINCIPAL SYMBOLS

These symbols are applicable to the entire thesis - others are defined locally and their significance is restricted to the chapter in which they appear.

A_1, A_2	Coefficients of the Root equation.
a	The distance of closest approach between ions.
B	Coefficient of ion-size term in the Debye-Hückel theory.
B_1	Coefficient of the relaxation term of the Robinson and Stokes conductivity equation.
B_2	Coefficient of the electrophoretic term in the Robinson and Stokes conductivity equation.
C	Concentration in equivalents per 1000 cm^3 of solution normality.
C	The principal coefficient of the Poiseulle-Hagenbach equation in the theory of viscometry.
D	Dielectric constant.
d	In chapter 1 and equation 3.6 - the differential, while in the remainder of the thesis - density.
E	The FORTRAN notation used to denote the exponent in the tables of this thesis, e.g. $10^{-6} \equiv$ E-6.
EXP	The exponent, e.
e	The protonic charge.
F	The Faraday.
f	The mean rational activity coefficient.
K	The kinetic energy correction coefficient in the theory of viscometry.
Ka	The association constant in the theory of conductivity.
Ksp	Specific conductance.
k	Boltzmann's constant.
log	Logarithms to the base 10.
ln	Logarithms to the base e.
M	Concentration in moles per 1000 cm^3 of solution - molarity.

m	Concentration in moles per 1 Kg of solvent-molality.
N	Concentration in equivalents per 1000 cm^3 of solution-normality.
N	Avagadro number.
O	'Of the order of'.
R	The gas constant.
T	Absolute temperature.
t_+, t_-	Transport or transference numbers of cation and anion respectively.
z_1, z_2	Algebraic valencies of cations and anions respectively.
γ	Fraction of solute existing as non-associated ions.
$\delta\mu$	The difference between the experimental value of the quantity μ and that computed from an empirical or theoretical equation.
∂	Partial differential.
η	Viscosity.
κ	Quantity proportional to the square root of ionic strength.
Λ	The equivalent conductance of an electrolyte.
λ_-, λ_+	The equivalent conductivities of anion and cation respectively.
$\sum$	Summation.
σ	The standard error of the fit of the data to an empirical or theoretical equation.
$\sigma\mu$	The standard error of the coefficient μ.
Ω	Resistance, ohms.

General Introduction

In the study of electrolyte solutions that of conductance is unique, because the measured conductivity can be explicitly divided into anionic and cationic contributions with transport number data. This situation may be contrasted with viscometric studies in which the B coefficient of the Jones-Dole equation is divided into its individual ionic contributions on an arbitrary basis (1). In activity coefficient studies, the quantity that is measured is a mean property of the cation and anion; individual ionic activity coefficients cannot be measured experimentally (2). When spectroscopy is employed in the study of ion-solvent interactions, the results obtained are complicated by the presence of ion-ion interactions as the measurements must be carried out at concentrations of electrolyte at which the strength of ion-ion interactions are considerable (3). However, by evaluating individual ionic conductivities at infinite dilution, the effect of ion-ion interactions is eliminated. Since limiting ionic conductivities depend solely upon the strength of ion-solvent interactions (4), conductivity measurements thus provide an unique means of research in the investigation of the variation of ion-solvent interactions with solvent properties.

The properties of the solvent can be varied in a number of ways two of which were employed in this research. A series of pure liquids may be chosen as solvents and measurements made at constant temperature or, alternatively, a single liquid may be employed at varied temperatures. In the latter instance, a study could be made of the dependence of conductivity on the structure of the solvent as intermolecular associations are sensitive to temperature changes. Alternatively a mixed solvent could be employed, the components of which are chosen, so that a series of solvents are prepared with particular properties, such as a large charge in viscosity compared with dielectric constant or the reverse as the composition of the solvent is varied. The strength of intercomponent interactions can also be varied by the choice of suitable components for the mixed solvent.

At 4°C the well known maximum density of water is exhibited. On the basis of models that have been proposed for liquid water (5) (6), this is interpreted as being due to structural changes occurring near this temperature. Horne and co-workers (7-13) reported that the Arrhenius activation energy for the conductance process of some electrolytes but not others attained a maximum in the region of the maximum density of the solution. An earlier study (14) by the author of this thesis found that ion-solvent interactions of K^+ and Cl^- ions in this temperature region were independent of the influences which gave rise to the maximum density of water. These findings were corroborated by a concurrent study of KCl at a finite concentration in the temperature region of -1°C to 10°C. This last result for KCl is contrary to that reported by Horne et al (7) (8) (9) for this salt. The present research is, in part, a continuation of that already undertaken, as it reports the experimental findings obtained from a study of a CsCl solution. Horne et al (10) have reported that this salt exhibits a maximum in the energy of activation between 0° and 9°C.

The most extensively studied solvent property and its relationship to conductance has been that of solvent viscosity. One proposed relationship is Walden's Rule - $\lambda^0\eta$ is constant. It is conceded that compliance with this relationship is the exception rather than the rule (15). In some systems the Walden product increases, while in others it decreases with changing solvent composition. In this research, the last dependence on solvent composition and the explanation for its occurrence proposed by Fuoss (15) is of prime interest. Fuoss explained this observation by suggesting that the ions were moving in a medium of greater viscosity-rather than in one defined by the macroscopic viscosity of the pure solvent - as a result of ion-solvent interactions between the ion and the dipoles of the solvent molecules. Fuoss proposed an empirical relationship based on heuristic arguments describing the dependence of the Stokes radius of the ion, R, on the dielectric constant of the solvent, D, thus -

$$R = R_\infty + {}^{S}/_{D} \qquad 1$$

where R_∞ is the Stokes radius of the ion in a solvent of infinite dielectric constant in which electrostatic forces are absent. Boyd (16) (17) and Zwanzig (18) (19) later confirmed theoretically Fuoss's arguments and evaluated the terms comprising the coefficient, S, and found that it was related to the dielectric relaxation time of the solvent.

Several interesting papers by Justice and Fuoss (20) and Treiner and Justice (21) led to a study by Mewett (22) and to the major topic to be discussed in this thesis. These authors (20) (21) reported that the coefficient S for the K^+ ion in aqueous solvent mixtures of glycine, β-alanine and dioxane was identical. Hence they proposed that a single ion initiated solvent relaxation process was common to these solvent systems - that of water molecules. It was also concluded that the added component did not participate in the relaxation process. However, the conclusions of Justice et al (20) and Treiner et al (21) are based upon their assumption that transport numbers are independent of solvent composition. The glycine/water results of Justice and Fuoss (20) were re-examined by Mewett (22) who found S for this system was not equal to that for dioxane/water, when ionic conductivities for KCl were evaluated with transport number data. Scrutiny of the literature reveals from the work of Steel and Stokes (23) (24), Erdey-Gruz et al (25-30) and Fredriksson (31) that transport numbers are not independent of solvent composition, even in the dioxane/water system (29). Consequently, wherever possible, ionic conductivities have been computed with transport number data in this research.

In the Fuoss-Boyd-Zwanzig model, FBZ, the significance of the coefficient, S, is two-fold. Firstly, it is related to the solvent relaxation time since the passage of the ion through the liquid induces the solvent relaxation phenomenon. Secondly, as a result of the electrostatic interaction between the ion and the dipoles ionic motion is retarded to a greater extent than predicted by Stokes law. Therefore S should be related and, in turn, be relatable to the strength of solvent-solvent and ion-solvent interactions. Examination of the literature reveals that no study has yet been made of the relationship between the strength of solvent-solvent, defined by the values of the relaxation times, and ion-solvent interactions defined by ionic conductances and the coefficient, S, for an ion in a number of mixed solvents. In this research this point has been examined by evaluating S for the potassium ion in aqueous mixtures of N, N-dimethylformamide (DMF), ethanol, methanol, acetone, isopropanol and tetrahydrofuran. Conductances of KCl and KBr together with transport numbers of the potassium ion were measured in DMF/water mixtures. Values of $\lambda^{o}_{K^+}$ in other aqueous solvent mixtures were computed from literature data. The full Pitts (32) (33) and Fuoss-Hsia (34) conductivity equations were employed to evaluate Λ^{o} for KBr and KCl in DMF/water mixtures. Since S depends upon the magnitude of ion-solvent interactions, the DMF/water system is particularly interesting, as Fratiello and co-workers (35-37) have reported in their numerous N.M.R. studies that cations interact strongly with DMF in aqueous mixtures.

Originally this research was concerned with the conductance and transport numbers of KCl and KBr in aqueous mixtures of formamide and DMF. The amides are a particularly interesting series of compounds because, by successively substituting the amide hydrogens with an alkyl group, a series of molecules, e.g. N-methylformamide, formamide and DMF, are obtained which differ dramatically in their physical properties, e.g. viscosity and dielectric constant. This last property is explained in terms of the liquid structure and the degree of mutual orientation of the molecular dipoles (38-42) - being greatest for N-methylformamide and intermediate for formamide and least for DMF. For the last liquid the dipoles are described as being chaotically orientated (42) showing that the liquid possesses little structure. In contrast water and formamide are complex liquids, the last having a number of different types of intermolecular associations co-existing in the liquid state (38) (42). Of interest is the influences that structural changes, which occur when DMF or formamide is added to water, may have upon ionic transport. Similar reasoning applies when water is added to formamide. Hence this research is, in part, a continuation of the study of ionic conductance in the region of another proposed structural change - water in the vicinity of $4^{o}C$.

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CHAPTER 1

ELECTROLYTIC CONDUCTANCE

ITS THEORETICAL BASIS

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Introduction

"Modern" theories relating to the properties of electrolyte solutions, such as, activity coefficients and conductance, have as their common foundation, the evaluation of the ionic atmosphere potential due to Debye and Hückel.

1.1 Debye and Hückel's Expression for the Potential

(a) The Ionic Atmosphere

Debye and Hückel evaluated the electrical potential ψ at a point in the solution by using Poisson's equation for the electrical potential, and Boltzmann's expression to describe the ionic distribution about this point.

In the absence of external forces, e.g. an electrical field as in conductance, the solution around the central ion, j, can be considered as a series of spherical shells at varying distances r from their common centre, this ion. On a time average basis, upon which this model is based, these shells will contain more ions of **opposite** charge to the j ion; that is, each shell will have a nett charge of opposite sign to j. Invoking the condition of electrical neutrality for the system, the sum of the nett charge on each shell for the system must be equal and opposite to the j ion's charge.

1.1 (b) Distribution Functions

Debye and Hückel used the Boltzmann expression (1) 1.1 to relate the average local concentration of ionic species i, n_i', to its bulk concentration, n_i, and the electrical potential energy of the i ion $z_i e\psi_j$ thus

$$n_i' = n_i \quad \text{EXP} \left[\frac{-z_i e\,\psi_j}{kT}\right] \qquad 1.1$$

The charge density, ρ_j, at any point in the system whose centre is the j ion, is thus related to the potential ψ_j by the following relationship.

$$\rho_j = \sum_i n_i\, z_i\, e \quad \text{EXP} \left[\frac{-z_i e\,\psi_j}{kT}\right] \qquad 1.2$$

Equation 1.2 can be expanded as a series:-

$$\rho_j = \sum n_i z_i e - \sum n_i z_i e \left[\frac{z_i e\ \psi_j}{kT}\right] + \sum \frac{n_i z_i e}{2!} \left[\frac{z_i e\ \psi_j}{kT}\right]^2 - \sum \frac{n_i z_i e}{3!} \left[\frac{z_i e\ \psi_j}{kT}\right]^3 + \ldots\ldots \qquad 1.3$$

If we assume that the electrical potential energy of the majority of the i ions, $z_i e\ \psi_j$ is small compared with their thermal energy kT, then the third term of 1.3 can be neglected. This approximation is justifiable in <u>dilute</u> solutions where the separation between the majority of the i ions and the reference ion j is large. This approximation becomes more reasonable for symmetrical electrolytes, since even powers of the potential vanish. Finally, it can be stated that the assumption in question is not justifiable for i ions close to j with $\Sigma n_i z_i = 0$, the electrical neutrality condition, and if $kT \gg z_i e\ \psi_j$ 1.3 simplifies to

$$\rho_j = -\sum \frac{n_i z_i^2 e^2\ \psi_j}{kT} \qquad 1.4$$

1.4, unlike equation 1.2, is consistent with the principle of linear superposition of fields, that is ρ_j being directly proportional to ψ_j.

The approximate distribution functions used to reconcile the exponential Boltzmann function, equation 1.1, with the principle of linear superposition of fields are as follows. Firstly, for unsymmetrical electrolytes equation 1.5a is used, while for symmetrical electrolytes an additional term can be taken in the expansion of the Boltzmann function because the third term in the expansion, 1.3, of the expression for the charge density is zero. Equation 1.5b is thus a better approximation to the original function 1.1.

$$n_i' = n_i \left[1 - \frac{z_i e \psi_j}{kT} \right] \qquad 1.5a$$

$$n_i' = n_i \left[1 - \frac{z_i e \psi_j}{kT} + \frac{1}{2} \left[\frac{z_i e \psi_j}{kT} \right]^2 \right] \qquad 1.5b$$

1.1 (c) The Expression for the Potential

Poisson's equation for the case of spherical symmetry, relating the charge density, ρ, at a point to the point's potential ψ, can be written in the form (1):

$$\frac{1}{r^2} \frac{d}{dr} \left[r^2 \frac{d \psi_j}{dr} \right] = - \frac{4\pi\rho}{D} \qquad 1.6$$

By substituting the linear equation, 1.4, for ρ_j to 1.6 the latter becomes

$$\frac{1}{r^2} \frac{d}{dr} \left[\frac{r^2 \, d\psi_j}{dr} \right] = \kappa^2 \psi_j \qquad 1.7$$

where

$$\kappa^2 = \frac{4\pi e^2 \, \Sigma n_i z_i^2}{DkT} \qquad 1.8$$

It can be shown (1) that the solution of 1.7 is

$$\psi_j = A^* \, \frac{\mathrm{EXP}(-\kappa r)}{r} + B^* \, \frac{\mathrm{EXP}(\kappa r)}{r} \qquad 1.9$$

The evaluation of the constants A* and B* is achieved by invoking two boundary conditions (2) and, having substituted the resulting expression for A*, B* being zero, into equation 1.9, the resulting, equation 1.10, is Debye and Hückel's equation for the time averaged potential, ψ_j, at a distance r from the j ion in the absence of external forces

$$\psi_j = \frac{z_j e}{D} \frac{\mathrm{EXP}(\kappa a)}{1+\kappa a} \frac{\mathrm{EXP}(-\kappa r)}{r} \qquad 1.10$$

The expression for the potential 1.10 and those for Boltzmann's distribution 1.1 and its approximate forms 1.5, are the starting points for the discussion presented here, limited though it may be, on activity coefficients and electrical conductance.

1.2 Activity Coefficients

In many systems in which conductance measurements are made, activity coefficient determinations have yet to be reported. Therefore, an expression is required that will yield reasonable values for the activity coefficient, $f\pm$, in the concentration range of interest. Some expressions for $f\pm$ will now be examined with this in mind.

1.2(a) The Debye-Hückel Expression for the Mean Ionic Activity Coefficient

The potential ψ''_j at a distance r from the isolated reference j ion is (3)

$$\psi''_j = \frac{z_j e}{Dr} \qquad 1.11$$

Again invoking the principle of linear superposition of fields, the potential ψ_j can be split into two terms; one due to the isolated j ion, 1.11, the second due to the remaining ions in the system, ψ'_j. That is, the potential due to the j ion's atmosphere

$$\psi_j = \psi''_j + \psi'_j \qquad 1.12$$

combining of equations 1.10, 1.11 and 1.12 leads to

$$\psi_j' = \frac{z_j e}{Dr}\left[\frac{\mathrm{EXP}\ (\kappa a)}{1 + \kappa a}\ \mathrm{EXP}\ (-\kappa r)\ -1\right] \qquad 1.13$$

The effect on the potential of the central ion due to the remaining ions in the system can be gauged by setting $r = a$ in 1.13 which becomes,

$$\psi_j' = -\frac{z_j e}{D}\ \frac{\kappa}{1+\kappa a} \qquad 1.14$$

The result of the interaction of the j ion with its neighbouring ions is to reduce the electrical energy of the j ion. This reduction is given by the product of the j ion's charge and the potential due to the remaining ions in the system given by equation 1.14. It is assumed that in the absence of these interionic interactions the electrolyte solution would exhibit ideal behaviour hence the rational activity coefficient for the j ion, f_j, may be expressed in the following way (3)

$$-\ln f_j = \frac{z_j^2\ e^2}{2DkT}\ \frac{\kappa}{1+\kappa a} \qquad 1.15$$

Since f_j cannot be experimentally determined, it can be replaced by f±, the mean rational activity coefficient (3).

$$\ln f_{\pm} = -\frac{|z_1\ z_2|e^2}{2DkT}\ \frac{\kappa}{1+\kappa a} \qquad 1.16$$

It can be stated that by equating $(1+\kappa a) \simeq 1$, that is for very dilute solutions, equation 1.16 reduces to the Debye-Hückel limiting law (3).

1.2(b) Discussion of Expressions for the Activity Coefficient, $f_{\pm}$

With regard to equation 1.16, within the concentration range of its validity, agreement between experimental and predicted values of $f_{\pm}$ is somewhat dependent upon the value assigned to a(3). To be frank, although a is meaningful from a theoretical point of view, in practice it is determined by "curve fitting criteria". However, 1.16 has two important features: firstly, the order of magnitude of a is known (3) and, secondly, the functional form of this equation is also known (4).

The realm of applicability of equation 1.16 can be extended by the addition of further terms, for example, a linear term in concentration (3) (4). The coefficients of the additional term(s) in concentration are determined by fitting the experimental data to the equation in question. It is more logical, therefore, to restrict the activity coefficient expression 1.16 to the region of known behaviour (4), that is, disregarding the higher terms in concentration.

1.3 The Distance of Closest Approach

(a) Activity Coefficient Expressions

It has already been stated that individual ionic activity coefficients cannot be determined experimentally: rather the measured quantity is regarded as being a mean property of the anion and cation. By analogy, therefore, the same argument could be applied to the distance of closest approach that appears in the mean ionic activity coefficient expression 1.16. That is, a separation between the centres of anion and cation that can be expressed in terms of their ionic radii.

1.3 (b) The Theory of Conductivity

It is convenient to discuss at this point the distance parameter's role in some theoretical models proposed by others to describe the phenomenon of electrolytic conductance.

The a parameter must be considered from the theoretical and experimental viewpoints. In the first instance, its function is well defined - it is the quantity that is involved with some of the boundary conditions, invoked for the evaluation of the constants of integration for the equations, related to expressions for the potential (5). However, from the second viewpoint, experimentally the order of magnitude of a is known, but its value is determined by comparing the theoretical function of the concentration dependence of Λ with that determined experimentally. Hence, to some degree, a has the role of a "curve fitting parameter". The reader's attention has already been drawn to the similar case of the activity coefficient expression 1.16. Further, returning to the case of conductance, the magnitude of a determined by such a procedure is dependent, for a given system, upon the model used, which also effects the interpretation given to a. Our attention now focuses upon the latter point.

Both the Fuoss-Onsager (6) and Pitts (7) treatments regard a as being the distance separating the centres of rigid charged spheres in contact, their so-called collision diameter. It is also relevant to compare their interpretations of the hydrodynamic radii of the charged spheres used in their hydrodynamic models. Firstly, Pitts (8) regards the two distance quantities as being basically independent, the hydrodynamic radius in his model being approximated by the Stokes radius. Fuoss (9), on the other hand, equates the average hydrodynamic radius of the two ions with their collision diameter, a.

1.4 Contributing Terms to a Conductance Equation

So far discussion has been concerned with a system unperturbed by external forces. We shall now discuss such a force, an electric field.

The principal experimental observation related to the conductance of an electrolyte solution is that Λ, the equivalent conductance of an electrolyte solvent system, decreases with increasing concentration. The problem has been, and still is, to account theoretically for this observation (10), although advances have been made in this respect (7) (11).

Various contributing terms have been proposed to account for the concentration dependence of Λ, namely, the electrophoretic effect $\Delta\Lambda$, the time of relaxation effect ${}^{\Delta X}/_{X}$, an osmotic term ${}^{\Delta P}/X$, a viscosity term $(1 + FC)$ and ionic association represented by the fraction of solute that exists as non-associated ions, γ, in the symbolic equation 1.17. Summarized in this equation are these terms together with Λ^0, the limiting equivalent conductance.

$$\Lambda = \gamma(\Lambda^0 + \Delta\Lambda)\ (1 + \Delta X/X + \Delta P/X)\ (1 + FC) \qquad 1.17$$

Ionic association will be considered later; in the interim, complete dissociation will be assumed i.e. $\gamma = 1$.

1.4(a) The Electrophoretic Effect

The atmosphere is considered to be a series of spherical shells whose thickness is such that each point within a shell moves with the same velocity under the influence of a force. The central j ion will move under the influence of the external force dragging its atmosphere along with it. However, the hydrodynamic resistance of the solvent retards the motion of each shell. The central ion, in dragging its atmosphere with it, must overcome the viscous resistance that is experienced by each shell of its atmosphere as they move through the medium. Therefore the sum total of these retardation terms, due to all shells in the system, sums to an effective counter velocity to the j ions' limiting ionic velocity.

1.4(b) The Relaxation Effect

Influenced by the electrical field the j ion will move, in the direction of the field, with the result that the j ion no longer occupies the central point of the atmosphere. However, the atmosphere tends to adjust itself to a new equilibrium position, but this process takes a finite time, the relaxation time, to occur. The situation can be pictured as being a continual decay and reformation of the atmosphere as the j ion moves through the medium. An external force denoted by the field strength X has a reaction, the relaxation effect ΔX, regarded as being the time averaged restoring field the j ion experiences when the atmosphere and the reference ion are in an asymmetric orientation one to the other.

1.4(c) The Osmotic Term

The osmotic term of Onsager (27) arises from the asymmetry of the ionic atmosphere of the j ion. Since there is a greater concentration of ions of opposite charge in the direction opposed to the motion of the j ion, there will be a greater probability of collisions with the j ion, arising from coulombic attraction, from the rear part of the ionic atmosphere, thus leading to a nett increase in conductance.

1.4 (d) The Viscosity Term

In the concentration range of applicability of the Fuoss-Onsager equation, i.e. $\kappa a<0.2$, if one or both of the ionic species are large compared with the solvent molecules, Fuoss (6) (12)(13) (14) reasons that a viscosity correction factor should be introduced to account for the increase in the local viscosity due to the solute. Thus the central ion and its co-sphere, of radius Θ, are moving in a medium described by η' and not by η, the bulk solvent viscosity, the two can be related by Einstein's expression (45), (13) :

$$\eta' = \eta\ (1 + 2.5\ \Phi) \qquad 1.18a$$

For example, if one ionic species is large compared with the other the volume fraction of this species Φ is given by equation 1.18b thus (13):

$$\Phi = \frac{4\pi\ \Theta^3\ NC}{3000} = \frac{2\ FC}{5} \qquad 1.18b$$

Since, to a good approximation, Λ varies inversely with viscosity, the decrease in conductance, due to the increase in local viscosity above the bulk value η, can be accounted for from equations 1.18a and 1.18b by the term $(1 + FC)$. For the concentration range considered above, such a correction term is considered negligible in the case where Θ is of the same order of magnitude as the size of the solvent molecules (6). Another effect which also depends upon the magnitude of Φ can be mentioned here. When the solute concentration is such that Φ, even for small ions, can no longer be regarded as being a negligible component of the total volume, as in the concentration range of applicability of the Fuoss-Hsia equation, allowance is made for the fact that the ions, being in close proximity, will obstruct each other's motion. The term $(1 + 1.5\Phi)$ makes allowance for the obstruction effect (46), Φ being in this instance the volume fraction of one ionic species (40).

The Evaluation of the Electrophoretic Effect

To illustrate how the concepts of Debye and Hückel can be applied to the theoretical treatment of conductance, the expression for the potential and the distribution functions used in the evaluation of ψ will be applied to the derivation of an expression for the electrophoretic counter velocity.

Robinson and Stokes (15) consider a solution containing a single electrolyte, cationic and anionic properties being denoted by subscripts 1 and 2 respectively. A shell of the ionic atmosphere is defined by its thickness dr and a distance r from j, so that within this volume each point has a constant velocity. Further, it is assumed that given an expression for the force acting on each shell, the velocity of this shell can be calculated from Stokes' law. The total counter velocity, that the central ion experiences as it and its atmosphere moves through the solvent medium, is obtained by integrating over all the shells in the system.

$$\Delta V_1 = \frac{2}{3\eta} \int_{r=a}^{\infty} \left[(n_1^1 - n_1)\, K_1 + (n_2^1 - n_2)\, K_2 \right] r\,dr \qquad 1.19$$

K_1 and K_2, the forces acting on the ions, will be evaluated later.

Robinson and Stokes use the exponential Boltzmann expression, 1.1, rather than the linearized approximation 1.5a, to evaluate the local concentrations of anions and cations n_2^1 and n_1^1 respectively.

For a cation:

$$n_1^1 - n_1 = n_1 \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \left[\frac{z_1 e \psi}{kT} \right]^n \qquad 1.20$$

Via the electroneutrality condition n_1, the bulk concentration of cations, can be expressed in terms of κa which leads to

$$n_1 = \frac{(\kappa a)^2}{4\pi a^2} \left[\frac{e^2}{DkT}\right]^{-1} \frac{1}{z_1^2 - z_1 z_2} \qquad 1.21$$

By substituting equation 1.21 and the <u>linearized</u> Debye-Hückel-Boltzmann expression, 1.10, for the potential into equation 1.20 the result can then be combined with equation 1.19. By applying similar reasoning to equations for the anion, analogous to 1.20 and 1.21, Robinson and Stokes obtain from 1.19 equation 1.22 for the electrophoretic counter velocity of the cation. It must be emphasised here that equation 1.10 was obtained for the special case of spherical symmetry. The asymmetry of the present system is therefore being neglected.

$$\Delta V_1 = \sum \frac{(-1)^n}{6\pi\eta n!} \left[\frac{e^2}{DkT}\right]^{n-1} \frac{z_1^n}{a^n} \frac{z_1^{n-1}K_1 - z_2^{n-1}K_2}{z_1 - z_2} \phi_n\ (\kappa a) \qquad 1.22$$

Where $\phi_n(\kappa a)$ is a function of κa only. Analogous equations for the anion can be obtained for the equations 1.19 to 1.22.

The forces K_1 and K_2, acting upon the ions, are related to the field strength X and the relaxation field ΔX by the following relationships.

$$K_1 = (X + \Delta X)z_1e \text{ and } K_2 = z_2e\ (X + \Delta X) \qquad 1.23$$

Thus, the forces are the product of the effective field strength acting upon the ions and of the ionic charges (15). Hence, replacing K_1 and K_2 in 1.22 by their definitions, expression 1.23,- after making the abbreviation 1.24 (15)- the resulting expression, 1.25, is the electrophoretic counter velocity of the cation.

$$A_n = \frac{(-1)^n}{n!6\pi\eta} \left[\frac{e^2}{DkT}\right]^{n-1} \phi_n\ (\kappa a) \qquad 1.24$$

$$\Delta V_1 = (X + \Delta X)e \sum_{n=1}^{\infty} A_n \frac{z_1^{2n} - z_1^n z_2^n}{a^n (z_1 - z_2)} \qquad 1.25$$

A similar relationship to 1.25 exists for the anion.

Robinson and Stokes obtained a general expression for the electrophoretic effect, equation 1.26, which could be placed in the symbolic equation. Equation 1.26 itself has been discussed in detail in reference (15).

$$\Delta\Lambda = \left[\frac{F^2}{N} \sum_{n=1}^{\infty} A_n \frac{(z_1^n - z_2^n)^2}{a^n (|z_1| + |z_2|)} \right] \qquad 1.26$$

By examining equation 1.26, it can be seen that even order terms vanish for symmetrical electrolytes. Such a result has already been discussed in the expansion, 1.3, of the explicit expression 1.2 for the charge density ρ_j which ultimately led to the expression for the potential.

It will be recalled that, in deriving the expression for the potential, the exponential Boltzmann distribution function was approximated by the first three terms of a series, to reconcile it, and the linear Poisson equation, with the principle of linear superposition of fields. There is no advantage, therefore, in using, as above in the derivation of equation 1.26, the exponential distribution function. The number of terms of 1.26, required for the final expression for the electropheretic effect, should also be consistent with the approximations made in the derivation of the expression for the potential. Robinson and Stokes regard the utilization of the first term of 1.26 for all electrolytes, with regard to valence type, as being a reasonable approximation (15), after considering the approximations made in its derivation. Truncating the series at n = 1 will be a better approximation for symmetrical electrolytes due to the vanishing of the next term.

By equating n = 1, equation 1.26 becomes:-

$$\Delta\Lambda = -\frac{F^2}{6\pi\eta N}\left[|z_1| + |z_2|\right]\frac{\kappa}{1+\kappa a} \qquad 1.27$$

1.5 Conductivity Equations

(a) The Robinson and Stokes Conductivity Equation

By substituting equation 1.27 for $\Delta\Lambda$, and an approximate form of Falkenhagen's expression (15) for the relaxation effect into the symbolic conductance equation, it becomes

$$\Lambda = \left[\Lambda^0 - \frac{F^2}{6\pi\eta N}(|z_1|+|z_2|)\frac{\kappa}{1+\kappa a}\right]\left[1 + \frac{z_1 z_2 e^2}{3DkT}\frac{q}{1+\sqrt{q}}\frac{\kappa}{1+\kappa a}\right] \qquad 1.28$$

If equation 1.28 is expanded, and the cross term neglected in $\Delta\Lambda$ and $\frac{\Delta X}{X}$, equation 1.29 results.

$$\Lambda = \Lambda^0 - \left[\frac{\Lambda^0 z_1 z_2 q\, e^2}{3DkT(1+\sqrt{q})} + \frac{F^2(|z_1|+|z_2|)}{6\pi\eta N}\right]\frac{\kappa}{1+\kappa a} \qquad 1.29$$

It can be stated, at this point, that, by neglecting the term $(1+\kappa a)$ in equation 1.29, the resulting expression is Onsager's limiting law. Hence, by retaining the term $(1+\kappa a)$, the point charge model of Onsager's relationship is refined to allow for the ions having a finite size. To a certain degree, short range coulombic interionic interactions are also accounted for by the retention of this term. For 1 : 1 electrolytes equation 1.29 can be rewritten in its more familiar form namely, the Robinson and Stokes equation, 1.30.

$$\Lambda^0 = \Lambda + \frac{(B_1\Lambda + B_2)\sqrt{C}}{1 + (Ba - B_1)\sqrt{C}} \qquad 1.30$$

In the "derivation" of the Robinson and Stokes equation, 1.30, a number of noteworthy approximations have been made. Firstly, by setting $X \gg \Delta X$ the cross term, in the electrophoretic and relaxation effects, has been neglected. Secondly, the first term of the electrophoretic expression 1.26 is utilized in the symbolic equation, higher terms in the series being neglected. Finally, the symmetrical expression for the potential was used in the derivation of the general expression for the electrophoretic effect. No allowance was made, in the final conductance expression, to account for the asymmetric contribution to the electrophoretic effect. More elaborate theories of conductivity, for example Pitts' (7), calculate the asymmetric contribution to the potential.

The Robinson and Stokes' equation has been extensively discussed elsewhere (15) (16) (17). Λ^0 is evaluated by the extrapolation of Λ^0 (calculated) for each concentration plotted against concentration, assuming a reasonable ion size.

1.5 (b) Pitts Equation

Pitts (7) replaced the earlier point charge model of Debye and Hückel and that of Onsager, with the sphere in continuum model to allow for finite ion size in his theoretical treatment of electrolytic conductance of symmetrical nonassociated electrolytes.

Distances in his account are measured in terms of κ^{-1} which is sometimes referred to as being the thickness of the ionic atmosphere (18). The parameter q, the ratio of electrostatic to thermal energy, is involved in the solution of the Debye-Hückel equation, by the method of Gronwell, Lamer and Sandved, used by Pitts to obtain an expression for the potential (8). The method of Gronwell et al (19) invokes higher terms in the expansion of the exponential Boltzmann distribution function, resulting in an expansion of ψ as a power series in q (8). In the case of symmetrical electrolytes, it has the form of equation 1.31 and also has the further property that for even powers of m, that term is zero.

$$q = \frac{z^2 e^2 \kappa}{DkT}$$

$$\frac{ze\psi}{kT} = \Sigma\, q^m \phi m \qquad 1.31$$

ϕm is a function of a and r.

In the case of symmetrical electrolytes the term $0(q^2)$ is zero, and no higher terms are utilized (8). The solution of the Debye-Hückel equation obtained by Pitts, in the absence of external forces, is identical with that already discussed in this thesis. This equivalent result has been pointed out by Pitts. Therefore, both results are consistent with the linear superposition principle.

Pitts calculated the force K_{ij} on an i ion from Onsager's continuity equation which he (Pitts) expressed as (8).

$$K_{ij} = e_i \left[E - E_i - \text{grad}\ \psi_j \right]$$

Where E is the external field, E_i is the field of the i ions' atmosphere and (- grad ψ_j) is the field arising from the potential. Since there is one reference ion j, Pitts reasons that the remaining ions, i.e. i type ions, are in the j ions' atmosphere and any interactions between the field E and the ionic atmosphere manifest themselves through (- grad ψ_j). E_i is therefore equated to zero. Thus the force acting upon the central ion is calculated in terms of E and the ionic distribution about the j ion.

In his discussion of the hydrodynamic theory of his model, Pitts (8) discusses the significance he attaches to the coefficients of the powers of q. In the case of q the coefficient arises from the spherically symmetrical Debye-Hückel charge distribution. The coefficient of the term $0(q^2)$ has two sources; in the first instance, "interaction of the field arising from the non-centrally-symmetrical ionic distribution and the centrally symmetrical (Debye-Hückel) charge density" (8). While the second is involved with "the field due to the centrally symmetrical ionic distribution acting on the non-centrally-symmetrical charge density" (8). The final equation from his hydrodynamic theory is an expression for the total force yet to be fully evaluated, equated to two terms, one, the Stokes term $6\pi\eta b_j V$ containing the hydrodynamic radius b_j and the ionic velocity V. The second factor is the correction term to this velocity due to the electrophoretic effect.

The total force on the ion has three components, firstly the external field, secondly the field due to the ionic atmosphere, the relaxation effect and the hydrodynamic term involving the electropheretic effect. The effective force acting upon the reference ion, giving rise to its velocity, is calculated by evaluating the effective external field acting upon the j ion, i.e. the applied field that is reduced by the relaxation field of the ionic atmosphere. Such a calculation involves the evaluation of the non-symmetrical charge distribution about the central ion, since the symmetrical Debye-Hückel distribution does not contribute to the force acting on the ion.

Having evaluated the total force, the only remaining unknown is the ionic velocity which ultimately leads to Pitt's conductivity equation (8) ÷ 1.32

$$\Lambda^0 - \Lambda = \Lambda^0 \left[\frac{z^2 e^2 \kappa}{3DkT(1+\sqrt{2})(1+y)(\sqrt{2}+y)} + \frac{z^4 e^4 \kappa^2 S_1}{3D^2 k^2 T^2} \right] + \frac{z^2 e \kappa}{(1+y)} \left[\frac{N\,10^9}{3\pi\eta c} \right] - \frac{z^4 e^4 \kappa^2}{3DkT} \left[\frac{N\,10^9}{3\pi\eta c} \right] \left[\frac{\sqrt{2}-1}{(1+y)^2(\sqrt{2}+y)} + \frac{T_1}{(1+y)} \right] \qquad 1.32$$

where ÷

(1) $y = \kappa a$

(2) S_1 arises from the relaxation effect, terms including $0(q^2)$ being evaluated.

(3) T_1, arises from the interaction between centrally symmetrical and non-centrally symmetrical charge distributions in his hydrodynamic theory, terms including $0(q^2)$ being evaluated.

Also S_1 and T_1, as functions of κa are tabulated in reference (7).

(4) c is the velocity of light and N is Avogadro's number.

The application of Pitts equation to experimental data has been discussed in a second paper by Pitts et al (20), and in papers by Stokes et al (21), Fernandez-Prini and Prue (22) and by Fernandez-Prini (23) (44).

1.5 (c) The Fuoss-Onsager Equations

In 1955 Fuoss and Onsager first published their theoretical account, incorporating the concept of finite ion size, for the decrease in Λ with increasing concentration.

A linearized equation, approximating this 1955 result, was published in 1957 (24), thus allowing their concepts to be more readily applied to conductance data.

As a result of the approximations employed, the range of applicability is such that $\kappa a<0.2$. Later, in 1957 and 1958, papers by Fuoss generalized the Fuoss-Onsager equation to account for ionic association. A revision of the Fuoss-Onsager equation was undertaken, climaxing in the 1965 paper of Fuoss, Onsager and Skinner, in which theoretical justification was given to the ad hoc account of ionic association proposed earlier by Fuoss. Later in 1967 Fuoss and Hsia extended the Fuoss-Onsager treatment to increase the range of applicability in terms of concentration, to include the explicit term in $0(C^{3/2})$.

The exponential Boltzmann distribution function, equation 1.2, was approximated by the first three terms of a series, equation 1.5b, for the ionic distribution, utilized in the expression for the potential (25), (26), and in the equation of continuity.

Having substituted the contributing terms (27)(28) into the symbolic equation, Fuoss describes the result as the "explicit product" (27) which is then expanded, any resulting terms $O(C^{3/2})$ that arise are dropped (27). The individual terms that contribute to the "explicit product" are evaluated, in terms of powers of κa, to include the term $O(C)$, higher powers of concentration being neglected (27). The resulting equation 1.34 is written below.

$$\Lambda = \Lambda^0 - S\sqrt{C} + EC\log C + JC - F^2\, \Lambda^0 C + O(C^{3/2}) \qquad 1.34$$

However, a term $O(C^{3/2})$ still remains in the Fuoss-Onsager equation 1.34. The role of the $O(C^{3/2})$ term in the Fuoss-Onsager equation will be discussed later. Here it suffices to state that it is usually omitted from the equation.

Further, at this juncture, we shall anticipate later work and note that the viscosity term $F\Lambda^0 C$ can be ignored for small ions (6) (29) (47) e.g. the alkali halides whose size is similar to the solvent molecules.
Therefore equation 1.34 becomes

$$\Lambda = \Lambda^0 - S\sqrt{C} + EC\log C + JC \qquad 1.35$$

The Onsager limiting slope S can be calculated from fundamental constants, solvent properties and Λ^0.

E is likewise a known function of Λ^0 and solvent properties and is essentially independent of the ion size term a (30).

The coefficient J is a function of the solvent properties Λ^0 and the ion size term a.

Fuoss' (6) (14) generalization of equation 1.35 to account for ionic association is based on a three fold argument. Firstly the concentration of ion pairs, $(1-\gamma)C$, can be calculated from the mass action equation 1.36, assuming that the activity coefficient of the ion pairs is unity.

$$1 - \gamma = C\gamma^2 f^2 Ka \qquad 1.36$$

Where f is the mean ionic activity coefficient obtained from the Debye-Hückel expression, 1.16, which has been extensively discussed earlier.

(The distinction between mean ionic activity coefficients and mean rational ionic activity coefficients is ignored (31)).

Secondly, using the Arrhenius relationship we may write:

$$\gamma = \Lambda/\Lambda_i \qquad 1.37$$

Where Λ_i is the conductance of the non-associated ions described by equation 1.35. Replacing C by $C\gamma$ in equation 1.35 and combining the result with equations 1.36 and 1.37, the generalized Fuoss-Onsager equation reads:

$$\Lambda = \Lambda^0 - S\sqrt{C}\sqrt{\gamma} + EC\gamma\log C\gamma + JC\gamma - K_aC\gamma f^2\Lambda \qquad 1.38$$

Equation 1.38 is a three parameter equation involving the parameters Λ^0, a and Ka.

The "1965" Fuoss-Onsager Equations

The fifth (26) of a series of papers by Fuoss and Onsager completed a re-investigation of the equations that ultimately led to equation 1.34. These authors felt that the following two points warranted re-examination. Firstly, the ad hoc generalization of equation 1.34 to account for ionic association, hence equation 1.38. Secondly, the systematic increase in the contact distance with decreasing solvent dielectric constant.

The following are some of the major points of their last paper. In the "1957 version" the Boltzmann factor in the equation of continuity was approximated by the first three terms of a power series. However, by retaining this factor in its explicit form, terms emerged in the expression for the relaxation field (32) that could be identified as being of the form of the Ka parameter of the 1957 equation (33). That is, instead of an arbitrary account being made for ionic association, Fuoss et al have shown that ionic association arises from the fundamental equations. An equation of the form of 1.38 is now considered by these authors to be theoretically established.

$$\Lambda = \Lambda^0 - S\sqrt{C}\sqrt{\gamma} + EC\gamma\log C\gamma + JC\gamma - KaC\gamma f^2\Lambda \qquad 1.38$$

The equation they obtained is

$$\Lambda = \Lambda^0 - S\sqrt{C} + E'C\ln\tau + LC - A\Lambda^0 f^2 C \qquad 1.39$$

Where A and L are constants and $\tau^2 = 6E_1'C$ the other terms have their meanings defined in this text. For a discussion of the first two constants, the reader is referred to reference (26). Firstly the coefficient L is composed of two terms, the major one being independent of a. Consequently, a_L, as with the re-examined a_J, is less precisely known than the linear J term of 1957. Apart from the larger uncertainties in the values of a_L and a_J compared with the former a_J, their values still show the same relationship to D^{-1} as previously. Further, if A is identified with Ka equation 1.38 becomes

$$\Lambda = \Lambda^0 - S\sqrt{C}\sqrt{\gamma} + E'C\gamma\ln(6E_1C\gamma) + LC\gamma - KaC\gamma f^2\Lambda \qquad 1.40$$

Consequently, equation 1.40 is regarded as being the general equation with 1.39 being its limit.

Summarizing the Fuoss-Onsager equations discussed in this thesis, we have:

$$\Lambda = \Lambda^0 - S\sqrt{C} + EC\log C + JC \qquad 1.34$$

$$\Lambda = \Lambda^0 - S\sqrt{C}\sqrt{\gamma} + EC\gamma\log C\gamma + JC\gamma - KaC\gamma f^2\Lambda \qquad 1.38$$

$$\Lambda = \Lambda^0 - S\sqrt{C} + E'C\ln\tau + LC - A\Lambda^0 f^2 C \qquad 1.39$$

$$\Lambda = \Lambda^0 - S\sqrt{C}\sqrt{\gamma} + E'C\gamma\ln(6E_1C\gamma) + LC\gamma - KaC\gamma f^2\Lambda \qquad 1.40$$

These equations are related thus

as $\gamma \rightarrow 1$ 1.38 and 1.40 → 1.39, further if $f^2 \simeq 1$ and $Ka \simeq 0$ 1.39 → 1.34 For a given electrolyte solvent system of D>30 Fuoss et al found a large uncertainty in L and a value for A, coupled with an error of the same magnitude as A. Since for $f^2 \simeq 1$ A and L are difficult to separate into two terms consequently by inserting $f^2 \approx 1$ into equation 1.39 is reduced to a two parameter equation, thus -

$$\left.\begin{array}{l} \Lambda = \Lambda^0 - S\sqrt{C} + E'C\ln\tau^2 + (L-A\Lambda^0)C \\ \text{or} \\ \Lambda = \Lambda^0 - S\sqrt{C} + E'C\ln\tau^2 + J'C \end{array}\right] \qquad 1.41$$

The application of the two parameter equation, as expected, reduced the uncertainty in the L coefficient now termed J'. Further, for D>40 1.34 and its successor 1.39 are indistinguishable (34). However, as Fuoss points out the latter equation is more sound theoretically, even though L and A can not be separated. Therefore, for A<10 1.39 reverts to its two parameter version 1.41.

For D between the bounds of about 25 and 30 A and L are distinguishable; hence 1.39 can be utilized. However, below the lower bound, systematic deviations between Λcalc - Λexpt become apparent; hence equation 1.40, accounting for higher order effects in the ion pairing phenomenon, should be used for the analysis of conductance data.

Finally, it can be stated that, since the re-examination of the original equations confirmed their earlier, though more approximate results, the authors concluded that the proposed model was an inadequate representation of the physical system.

1.5 (d) The Fuoss-Hsia Equation

The retention of some $C^{3/2}$ terms, usually omitted, however, has already been noted in this thesis. Berns and Fuoss (35) invoked these terms to "reduce a spurious systematic change of ion size with solvent composition". Such an effect was confirmed and discussed in the 1965 paper of Fuoss, Onsager and Skinner. Fuoss has stated elsewhere (36) that the $C^{3/2}$ terms employed in reference (35) and in the original paper by Fuoss and Onsager are themselves incomplete. We shall now return to the 1965 paper of Fuoss, Onsager and Skinner for a further discussion of the $C^{3/2}$ terms.

In the 1965 revision, the authors investigated terms in $C^{3/2}$ that arose in the expansion of negative exponential functions, which appeared in the relaxation and velocity functions. From their analysis, they concluded that the retention of this term was not justified, since many other terms of this order had already been neglected. Hence, A and L were allowed to absorb the resulting errors. It seemed more consistent to limit again, as in 1957, the range of the equation's applicability to where the effect of the unknown terms in $C^{3/2}$ is neglible. In 1965 as with the 1961 paper of Berns and Fuoss the utilization of some $C^{3/2}$ terms reduced, but did not eliminate, the dependence of a on D.

Fuoss and Hsia (37) re-examined the computations that originally led to the publication of the Fuoss-Onsager conductance equation 1.34, and, by retaining terms $O(C^{3/2})$, their theoretical conductance equation has a range of applicability such that $\kappa a<0.5$. The expressions for the electrophoretic effect, $\Delta\Lambda$, and the time of relaxation effect, $^{\Delta X}/X$ are given in appendices by Fuoss and his co-workers (37)(39)(40). The expression for γ used in the Fuoss-Hsia equation has already been discussed in this thesis, equation 1.36. Fuoss and Hsia use the Debye-Hückel limiting law to evaluate the activity coefficient, rather than equation 1.16, their claim being (reference 40 page 131) "because ions in contact are counted as pairs and long range interactions between free ions cannot depend on the size of the ions but only on their charges."

We shall comment further upon the choice by Fuoss and Hsia of the Debye-Hückel limiting expression for the activity coefficient required for the computation of the association constant, Ka, later in this thesis.

Fuoss and numerous co-workers (37-42)(43) have applied the Fuoss-Hsia equation to experimental data with the evaluation of Λ^0, a and Ka for a number of electrolyte solvent systems.

CHAPTER 1

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CHAPTER 2

CONDUCTANCE - EXPERIMENTAL

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CHAPTER 2

CONDUCTANCE - EXPERIMENTAL

2.1 Materials

Conductance Water

De-ionized water from the bulk laboratory supply was distilled into, and stored, in a plastic container. Freshly distilled water was used for the preparation of all solutions. This water, referred to in this thesis as conductance water, had a specific conductance which varied between 1.1 and 1.4 x 10^{-6} ohms $^{-1}$cm^{-1} at 25°C.

Potassium Chloride

Univar* A.R. potassium chloride was twice recrystallised from conductance water, dried in an air oven at 120°C for 24 hours, followed by a further 12 hours in a vacuum oven at the same temperature. Finally, the solid was fused in a platinum crucible, broken into small lumps with an agate mortar and pestle and stored in a desiccator over silica gel. The purity of the KCl prepared can be gauged by comparing the cell constant for cell A, obtained with a sample of this salt, with values previously reported by others, each worker having used an independently purified sample of salt. On this criterion, the salt was considered to be of high purity. The cell constant data upon which this conclusion is based is presented in table 2.1.

Potassium Bromide

Univar A.R. KBr was twice recrystallized from conductance water acidified with a few drops of A.R. hydrobromic acid. The well washed crystals were later dried in an air oven at 120°C for three days, followed by a further three days at the same

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* Ajax Chemicals Ltd., Sydney Australia

TABLE 2.1

CELL CONSTANTS AT 25°C

OBSERVER	CELL	CALIBRATING SOLUTION	CELL CONSTANT, cm^{-1}
STEEL	A*	0.01D***	15.102_6
	A*	0.1D	15.100_1
	A*	1.0D	15.099_2
	A**	0.01D	15.102_5
	A**	0.1D	15.099_4
	A**	1.0D	15.101_4
PHANG	A**	0.01D	15.102_6
MEWETT	A**	0.1D	15.09_7
	A**	0.01D	15.09_6
THIS WORK	A**	0.1D	15.097_1
	A**	0.0077809N	15.097_0
	A**	0.031513N	15.098_5
	A**	0.0098649N	15.099_3
	A**	0.0078866N	15.099_3
	A**	0.0338241N	15.097_7

TABLE 2.1 - CELL CONSTANTS AT 25°C (continued)

PHANG	B*	0.1D	7.462_8
THIS WORK	B*	0.1D	7.461_9
THIS WORK	C*	0.0077809N	0.2487_7
	C*	0.0078866N	0.2487_8
THIS WORK	D**	0.0078866N	0.4067_7
	D**	0.01D	0.4067_6
MEWETT	SOLVENT	0.0077809N	0.2478_4
	CELLS*	0.01D	0.1819_0

* Bright Electrodes

** Plantinized Electrodes

*** D denotes demal concentration Scale in this table.

temperature in a vacuum oven. The solid was stored over phosphorus pentoxide in an evacuated desiccator.

The concentration dependence of Λ for the KBr/H_2O system at 25^oC was obtained from Owen and Zeldes' (1) conductance measurements with Pitts conductivity equation, 1.32. This step was achieved with program PITTSV2, the output of which is reported in table 2.2 as "Run 1". Summarized in this table is Λ^0, a, the calculated value of Λ from the equation, Λ calc, and the difference between experimentally determined and calculated Λ, $\delta\Lambda$. σ is the standard error of the fit of the experimental data to the equation. Owen and Zeldes' data was resubmitted to the program, together with the conductance data of the aqueous solution prepared from the purified KBr, the result of which is reported in the remaining two columns of table 2.2, headed "Run 2". It can be observed that $\delta\Lambda$ for the test solution is 0.015% of the observed Λ, and Λ^0 and a, within the uncertainties of these quantities, were identical in the two runs. It is therefore concluded that the recrystallized KBr is of high purity.

Cesium Chloride

Mulcahy (2) purified this salt, B.D.H.* laboratory reagent grade material, by recrystallizing it three times from doubly distilled water and subsequently drying it to constant weight in a vacuum oven, prior to storing it over silica gel in an evacuated desiccator. A sample of this salt was submitted for analysis, by flame photometry, to A.M.D.L.** and impurities, in parts per million, were found to be Li (<1), Na (18), K(1) and Rb (40).

Molecular Sieves

B.D.H. molecular sieves, type 3A, in the form of 1/16" pellets were successfully used for the dehydration of the DMF

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* British Drug Houses Ltd., Poole England

** Australian Mineral Development Laboratories, Adelaide South Australia.

TABLE 2.2

CONDUCTOMETRIC ANALYSIS OF THE PURIFIED KBr AT 25^{0}C

EXPERIMENTAL DATA		RUN 1		RUN 2	
10^4C	Λexpt	Λ calc	$\delta\Lambda$	Λcalc	$\delta\Lambda$
13.949 (a)	148.27	148.26	-0.01	148.27	0.00
27.881 (a)	146.91	146.91	0.00	146.91	0.00
42.183 (a)	145.88	145.89	0.01	145.88	0.00
59.155*	144.88	-	-	144.90	0.02
59.269 (a)	144.90	144.90	0.00	144.90	0.00
71.696 (a)	144.30	144.29	-0.01	144.28	-0.02
Λ^0		151.74 ± 0.04		151.74 ± 0.07	
α		3.08 ± 0.04		3.05 ± 0.06	
σ		0.010		0.014	

(a) Data of Owen and Zeldes (1)

* This work

and formamide used in this work.

A cloudy suspension was observed in the solvent being dehydrated if the sieves were used as received. This was overcome by washing the sieves with repeated changes of de-ionized water until the supernatant liquid was almost clear. Regeneration of the sieves was achieved by a procedure that has been described elsewhere (3) (4).

2.2 Water Determination : Karl Fischer's Method

Since Vogel (5) has already discussed the principles and practical details of this technique, only the departures from his text need be considered here.

The components of the apparatus are essentially those depicted in figs XV1, 6, 2 and 3 of reference (5), with ground glass joints replacing the rubber stoppers shown in these diagrams. Dry nitrogen was used to force the reagents from their storage vessels into the burettes prior to a water determination being commenced. The magnetically stirred cell was constructed of a "Quickfit" (6) culture vessel, FV 250, with an added side arm for the introduction of the sample. The vessel was capped with part number MAFO/50, non aqueous grease intervening between the two portions of the vessel. Parafilm*, being placed around all the ground glass joints present in the apparatus, provided a further seal to ensure the exclusion of atmospheric water from the apparatus.

A potential of 80mV across the platinum electrodes was supplied by a Doran potentiometer, the galvanometer of which was also utilised in the detection of the end point of the titration. B.D.H. Karl Fischer reagent, 1 cc of which is approximately equivalent to 5 mgm of water, was periodically celibrated against a standard water/methanol mixture.

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* Parafilm "M", American Can Company, Wisconsin, U.S.A.

2.3 Preparation of Solutions and Mixed Solvents

Manipulation of Vessels during Weighing

All vessels to be weighed were wiped with a clean, damp cotton cloth, followed by clean chamois leather, to ensure that their outer surfaces were free from adhering material.

Weighing bottles were manipulated within the balance case with a pair of long stainless steel forceps, to minimise disturbances during the weighing procedure. Empty flasks or flasks containing solids were similarly treated. Manipulation of the flasks for the remainder of the solution's or solvent's preparation was undertaken with chamois leather placed between the vessels and the experimenter's hands.

Weighing Bottles and Flasks

The opening of the weighing bottle was an extended B24 cone whose extremity, when mated with the B24 socket of the receiving flask, protruded well below the socket of the flask. Such an arrangement ensured that the solid being transferred from the weighing bottle to the flask was quantitatively delivered into the body of the flask. It was found to be necessary to introduce a small vent, approximately 1/16" in diameter, in the cap of the bottle constructed of a B24 socket to facilitate rapid equilibration between the internal and external air pressures. In the absence of this vent, the raising and lowering of the cap of the weighing bottle with a pair of forceps caused inconsistent weights to be recorded over a number of trials. A similar observation was made when the experiment was repeated with a flask equipped with a standard ground glass stopper. Hence, they were abandoned in favour of vented cones during the preparation of an electrolyte solution.

Flasks equipped with ground glass joints were used throughout this research.

Preparation of Mixed Solvents and Electrolyte Solutions

Except where noted in the summarized results, all solutions for conductance, transport number and density determinations were prepared by diluting a single stock electrolyte solution.

For solutions with a DMF rich solvent, the dissolution of the solid was enhanced with the aid of a glass covered soft iron stirrer bar, introduced into the flask prior to the commencement of the stock's preparation. Fused KCl was very slow in dissolving in solvents containing less than 60% water.

Weighing of Solids

Having weighed, on a Mettler B6C200 balance, the weighing bottle containing the solid to constant weight, the contents were transferred to the receiving flask which was tared to constant weight on a Mettler B5C1000 balance. The re-equilibrated vessels were again weighed to constant weight, which was regarded to be within the tolerances quoted by the manufacturers for the optical scales of the balances (7). The agreement between the two values of the solid taken for the preparation of the stock solution was, as an average of 22 preparations 0.003%. The weight of solid used for the preparation of the electrolyte solution, was taken to be the difference between the weight of the weighing bottle before and after delivery of the solid to the receiving flask, the weighing of the latter vessel acting as a check only.

Objects whose masses were greater than, or equal to, 1Kg, or which could not be tared on the Mettler balances, due to their dimensions, were tared instead by the method of swings (8) on a Stanton* H.D.2. beam balance.

A beam error was evaluated by Gauss's method of double weighing, as recommended by Vogel (8), and was found to be 0.0216 ± 0.0005% of the mass of the tare between 100g and 3Kg, the latter value being greater than any recorded under preparative circumstances.

The balance masses were calibrated on the Mettler balances. Since the air density of the balance room at the time of the calibration was 1.19×10^{-3} g/cm^3, no correction was applied to the calibrations because brass masses were being calibrated against the stainless steel masses of the Mettler balances (9). The brass

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* Stanton Instruments Ltd., London, England.

masses were always manipulated with a pair of forceps or a piece of chamois leather.

Preparation of Mixed Solvents

The weighings associated with this procedure were undertaken with the beam balance described above. A single batch of solvent was used for each run. Others (10) (11) (12) have already reported that, in the mixing of DMF with water, considerable heat is evolved. Consequently, only when the solvent had re-equilibrated with the balance room, was the vessel re-weighed. For ease of identification each mixed solvent was numbered in the chronological order of its preparation. The measurements made with each are summarized in appendix 2.1.

Buoyancy Corrections

All solutions and solvents were prepared by weight, vacuum corrections being applied to all weighings.

For weighings made on the Mettler balances the following procedure was used. If an object, whose apparent weight is M_x and whose density is d_x, is weighed in an atmosphere of density d_a, then the weight in vacuo M_v is given by (9) ÷

$$M_v = M_x \left[1 + d_a \left[\frac{1}{d_x} - \frac{1}{d_{ss}}\right] + 0.000012\right]$$

Where d_{ss} is the density of the stainless steel balance masses.

Since the balance masses of the Stanton beam balance are brass, the following relationship was used to convert M_x to M_v.

$$M_v = M_x \left[1 + d_a \left[\frac{1}{d_x} - \frac{1}{d_b}\right]\right]$$

where d_b is the density of brass.

The densities of brass and stainless steel were obtained from reference (9) while the densities of solid KCl, KBr and CsCl and water were obtained from reference (13). The densities of DMF and its mixtures with water were measured in this work.

2.4 Conductance Measurements

2.4 (a) Oil Thermostats

25°C

The oil bath which was earthed contained, as a thermostat medium, a light petroleum oil, Shell Co. "Diala B", which was regulated by a mercury-toluene regulator in conjunction with a pyrotannax heating coil activated by a thyratron control unit. The oil was contained in a cylindrical well with the heater-regulator coils arranged around the circumference from the base to just below the oil level. The stirrer consisted of four variably pitched paddles that approximated to the diameter of the bath. Fluctuations of ±0.002°C were observed with the above arrangement of regulatory components.

0 - 10°C (14)

Conductance cells were immersed in a small stirred oil bath which was, in turn, suspended in a large regulated water bath. This was the most satisfactory arrangement investigated as the temperature of the oil could be regulated to within two hundredths of a degree over a ten hour period.

The cooling unit used as a commercial refrigeration unit which had been modified, so that coolant was continually flowing through the refrigeration coils immersed in the water bath. Ethylene glycol was placed in the water to prevent ice forming on the cooling coils as the water approached freezing point. The water bath was regulated with a base heater in conjunction with a solid state thermistor proportional temperature control unit. By covering the smaller metal oil bath with a perspex cover separate regulator circuitry for this bath was found to be unnecessary.

The oil was changed frequently as it became cloudy after several days, due to the formation of an oil-water emulsion. Dehydration of the oil was achieved by elevating its temperature above 100°C for several hours.

Thermometers

Thermometers, of the bomb calorimeter type, graduated in 0.01 of a degree, were used in this work, 0.001 of a degree being estimated with the aid of a magnifier. A platinum resistance thermometer, calibrated at the National Standards Laboratory - Division of Physics of C.S.I.R.O.* and periodically checked against the ice point of water, was used to calibrate each thermometer at its temperature of utilization.

2.4 (b) Electrical Apparatus

Resistances were measured with a Jones-Dike bridge,** the construction and operation of which has already been discussed in detail by Dike (15). An oscillator, tunable amplifier and a cathode ray oscilloscope (C.R.O.) detector completed the circuit.

A good quality waveform, whose amplitude could be varied, was produced by the oscillator*** within the range of frequencies employed, 1 Kc/s to 20 Kc/s. Connection to the bridge was effected via an isolating transformer. A second output from the oscillator was connected to the horizontal plates of the C.R.O.****

The input lead to the tunable amplifier*** from the bridge also contained an isolation transformer. The pair of transformers mentioned in this thesis were supplied with the bridge. The output signal from the amplifier was fed onto the vertical plates of the C.R.O.

In the case of bridge inbalance the combination of the signals from the bridge-amplifier circuit and the direct connection between the oscillator and C.R.O., produced on the screen of the C.R.O. an ellipsoidal Lissajous figure. When the bridge was balanced, the only signal relayed to the C.R.O. came directly from

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* Commonwealth Scientific and Industrial Research Organisation.

** Manufactured by - Leeds and Northrup Company, Philadelphia, U.S.A.

*** Manufactured by the Electronics, Instrument and Lighting Company - Norwood, South Australia.

**** Serviscope S32A made by Telequipment England.

the oscillator, a horizontal line being observed on the screen of the C.R.O. The sensitivity of the detector circuit was varied by altering the gain of the C.R.O. vertical amplifier, the sensitivity of the amplifier being preset to its maximum workable limit.

Since the amplifier had a broader bandwidth than might be desired, for resistances greater than about IOKΩ the Lissajous figure became "fuzzy" due to the electrical noise present in the signal from the bridge. The primary signal was nullified as the balance point of the bridge was approached; any noise became the larger component of the bridge signal. This noise, probably caused by "pick up", had the effect of reducing the sensitivity of the apparatus at high resistances, due to the lessening of the resolution in the detection of the null point. To lessen the gradual loss in sensitivity of the circuit as the resistance increased a number of precautions were taken. In the first place, direct electrical linkage between the oscillator and the amplifier with the bridge was avoided by the use of isolation transformers. Then cables with grounded shields were used to interconnect the oscillator, amplifier, C.R.O. and bridge. Further, to lessen the interaction between these components, the oscillator and amplifier were separated by approximately twelve feet, the bridge intervening midway between them. Finally the bridge and the metal cases of the oscillator, amplifier, C.R.O. and thermostat were grounded through a common point.

In an attempt to narrow effectively the amplifier's bandwidth, and hence reduce the stray "pick-up" ultimately reaching the screen of the C.R.O., a band pass filter was placed in the output circuit of the amplifier. This step reduced the level of noise in the C.R.O. trace, but had the undesirable effect of drastically reducing the sensitivity of the detector-amplifier circuit. In order to make more effective use of the inherent sensitivity of the amplifier-detector circuit, it was decided to remove the band pass filter permanently from the circuit.

The maximum sensitivity for resistances less than about 3KΩ was several parts in a million, which when 20KΩ was reached, reduced to a part in 100,000 due to a fall in the resolution of the trace of the C.R.O. resulting from electrical noise.

2.4.(c) Frequency Dependence of a Cell's Resistance

One aspect of the measurement of conductances needs to be discussed here, namely, the evaluation of the pure ohmic resistance of the solution or, in other words, accounting for the electrode polarization which, assuming proper cell design, manifests itself in the frequency dependence of the cell's resistance.

Fig 2.1. represents the electrical equivalent of the cell arm of a conductance bridge as proposed by Feates, Ives and Pryor (16). These authors set the "Warburg impedance" depicted in fig 2.1 to zero. Using the model of Feates et al, Robinson and Stokes (17) and Steel (18) have included the "Warburg impedance", W, in their respective analysis of the frequency dependence of alternating current resistance measurements.

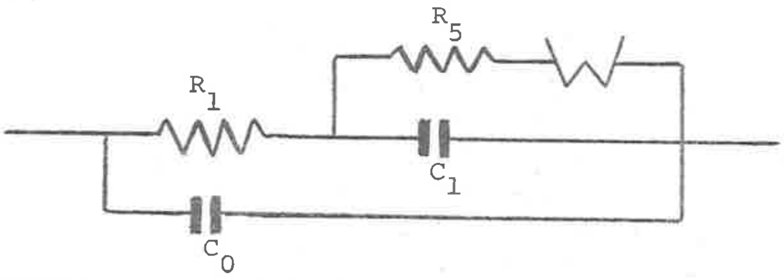


Figure 2.1, Electrical Model for a Conductance Cell

The significance of the circuit elements in fig 2.1 and their frequency dependence is as follows (16) (17):

R_1 is the primary quantity of interest being the pure ohmic resistance of the electrolyte solution in the conductance cell - frequency independent.

C_0 is the capacity of the cell due to the electrolyte solution being a dielectric between the electrodes and the capacity between the cell leads (16).

C_1 represents the capacity of the double layer of ions at the electrode surfaces - frequency independent.

R_5 and W are associated with electrolysis processes. R_5 is frequency independent but W is frequency dependent.

As the electrodes of the conductance cells used in this work were either bright or lightly platinized, the model applicable to these cases will be described. Of the two electrode surfaces, Feates et al apply their model only to the case of "grey platinized electrodes" for which they make these approximations in the simplification of their bridge balance conditions, $R_1 \gg R_5$ and $C_2 \gg C_o$. In his analysis, Steel concludes that the result is equally applicable to the second case (16) (17). The latter author makes the simplifying approximations in his final equation, $R_5 \gg W$ and $R_1 \gg R_5$. Steel's and Feates, Ives and Pryor's result is equation 2.1. describing the frequency dependence, due to electrode polarization, of a cell with lightly platinized or bright electrodes.

$$R_2 = R_1 + \frac{R_5}{1 + \omega^2 C_1^2 R_5^2} \qquad 2.1$$

where R_2 is the measured cell resistance and ω is the frequency of the A.C. potential across the cell.

Stokes and Steel (17) (18) solved equation 2.1 for R_1 at three frequencies. R_1 so obtained agreed well with a linear extrapolation of a plot of R_2 against ω^{-1} for equation 2.2 to infinite frequency, the intercept being R_1. In a recent paper, Hoover (19) has examined empirical and theoratical equations that have been proposed for the attainment of the frequency independent resistance for cells containing aqueous solutions. It can be concluded from Hoover's paper that equation 2.2. is a reasonable method for accounting for electrode polarization considering the approximate nature of this latter function. Hence Hoover has confirmed Steel's earlier result.

$$R_2 = R_1 + \frac{\text{Constant}}{\omega} \qquad 2.2$$

Discussion now centres upon the method used for the attainment of the frequency independent resistance for the conductance cells used in this work.

For conventionally designed cells, A with platinized electrodes and B with bright electrodes, a linear plot was obtained for equation 2.2 for frequencies between 20 Kc/s and 3 Kc/s. Observed values of R_2 for these cells ranged up to 17 KΩ for Cell A and 13 KΩ for Cell B.

R_2 as a function of frequency for the flask cells can be discussed in two segments. In the first case compliance with equation 2.2 over the whole frequency range examined was observed. In the second case, however, equation 2.2 was obeyed at lower frequencies but deviations were noted as the frequency increased, R_2 increasing more rapidly than the frequency.

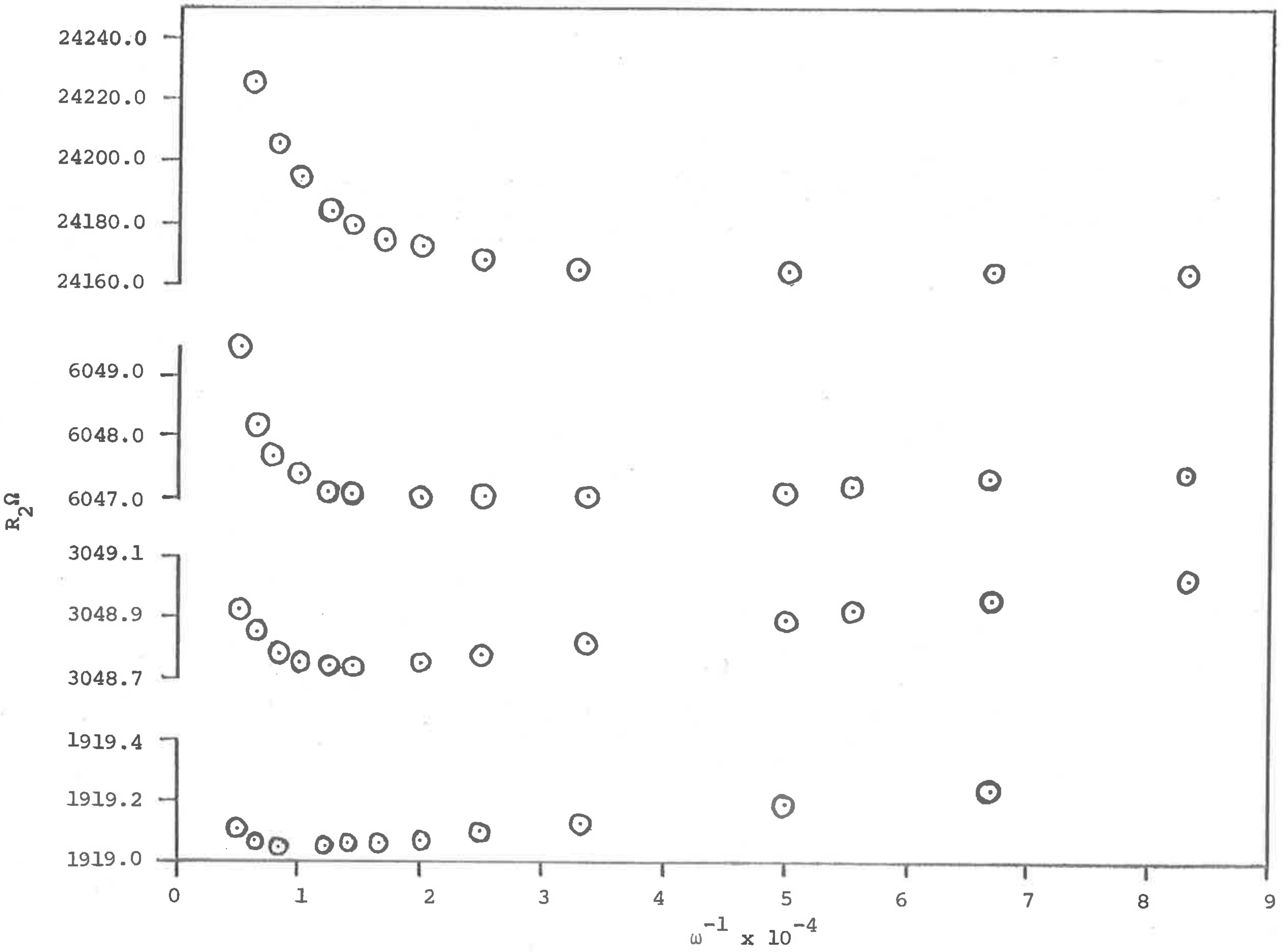
The first case is examplified by flask cell E, of constant ≃ 12 cm^{-1}, for which equation 2.2 was obeyed to the highest measured resistance, 42KΩ, in the frequency range of 20Kc/s to 3Kc/s. Flask cell C, below 3KΩ, also exhibited the same frequency resistance relationship.

The second resistance frequency relationship occurs at resistances above 3KΩ for flask cell C. The plot of equation 2.2 for a given solution can be divided into three stages. At low frequencies the plot is linear, R_2 decreasing with increasing frequency as required for the electrode polarization phenomenon. The second stage is reached when R_2 goes through a minimum as the frequency is increased further before the final step eventuates in which, as the frequency is further increased, R_2 likewise increases. Fig. 2.2 is a plot of R_2 as a function of ω^{-1} illustrating the above description of the frequency dependence of cell C.

Nichol and Fuoss (20), Hawes and Kay (21) and Mysels, Scholten and Mysels (22) have reported increasing values of R_2 with frequency, measurements being made on solutions contained in flask cells. Nichol and Fuoss attribute this behaviour to

FIGURE 2.2

Functional plots of equation 2.2 obtained from resistance-frequency measurements made on KCl/water solutions at 25°C contained in the Erlenmeyer flask cell C.


24240.0
24220.0
24200.0
24180.0
24160.0
6049.0
6048.0
6047.0
3049.1
3048.9
3048.7
1919.4
1919.2
1919.0
$R_2\Omega$
0
1
2
3
4
5
6
7
8
9
$\omega^{-1} \times 10^{-4}$

to terms in ω^2 in the impedence of the cell, resulting from capacitance by-paths between the cell leads and the electrolyte in the cell via the thermostat medium. Hawes and Kay attribute their observations to the polarizability of the glass wall of the cell. However, for solutions in which R_2 decreased with increasing frequency, Hawes and Kay accounted for electrode polarizability by extrapolating to infinite frequency with, in effect, equation 2.2. At higher cell resistances, Hawes and Kay's results are similar to those reported in this thesis i.e. at high frequencies R_2 increases with increasing frequency. However, Hawes and Kay propose that the region where R_2 decreased with increasing frequency could be attributed to electrode polarization. Therefore, they extrapolated this region of the plot to $\omega^{-1} = 0$, not as Mysels et al report Hawes and Kay to have done to zero frequency i.e. $\omega = 0$. In their paper Mysels et al attribute the increase in R_2 to a leakage to ground through a capacitance in series with a resistance, the principal capacitance being, in these authors' opinion, between the base of the flask cell and the magnetic stirrer mechanism. At this point it can be noted that cell C, which exhibited the effect, did not have a magnetic stirrer mechanism.

At this stage some comments can be made about the observed increase in R_2 with frequency. This phenomenon is not necessarily related to the class of cell, i.e. flask or conventional, but rather to the physical dimensions of the particular cell. To illustrate this point, it will be recalled that the flask cell E and the conventional cells did not exhibit this effect whereas flask cell C did. If the forms of cells C, fig 2.3 and 2.4, and E, fig 2.5 and 2.6, are compared the significant difference between them is the larger distance separating, firstly, the leads themselves and, secondly, the leads from the electrolyte solution in the cell. By comparison, therefore, the critical distances separating the leads are greater in the case of cell E than cell C. It is proposed, therefore, that the increase in R_2

FIGURE 2.3

The Erlenmeyer flask cell C - side elevation. The end elevation of this cell is the subject of figure 2.4.

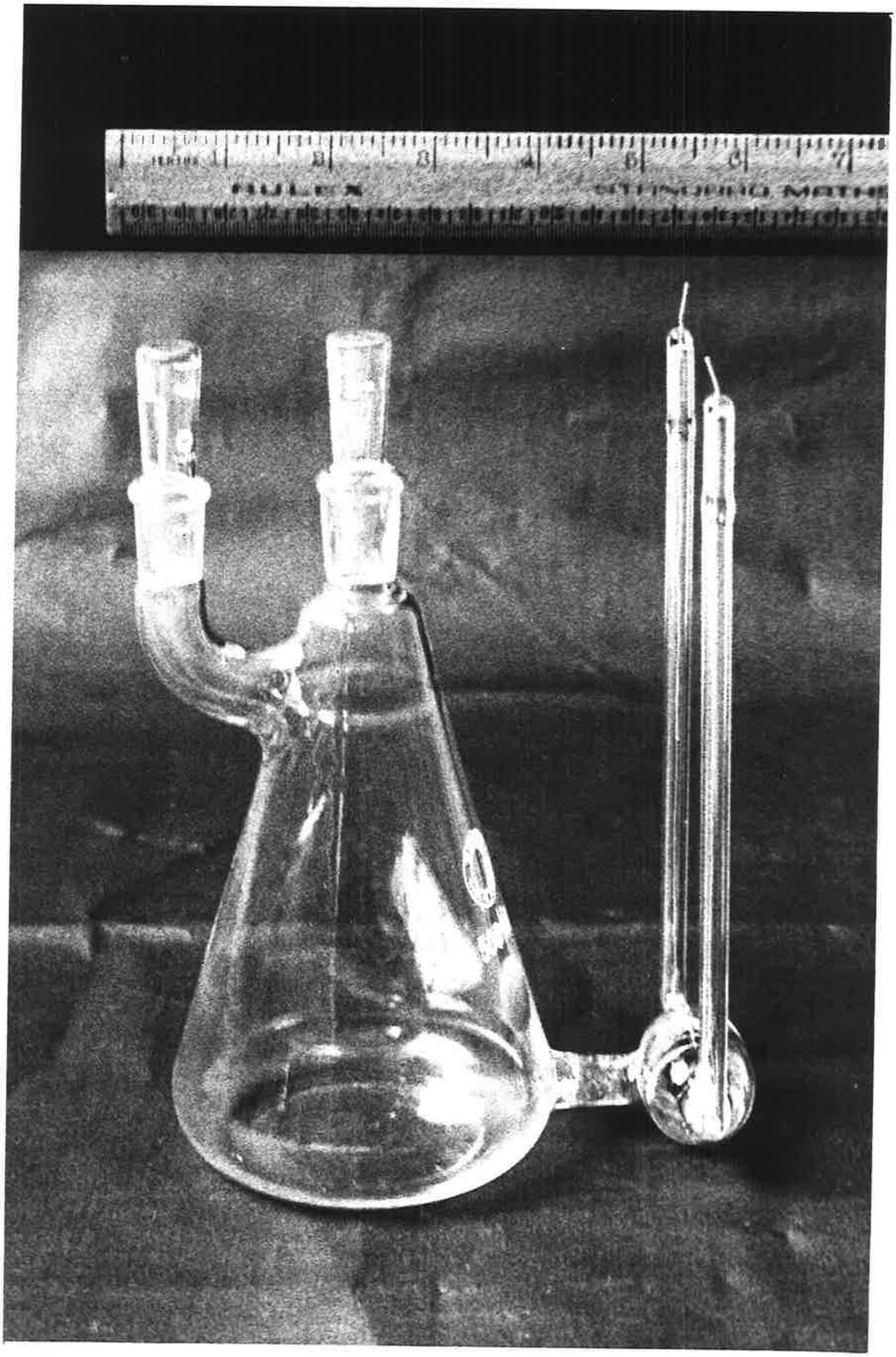

1
2
3
4
5
6
7
RULEX

FIGURE 2.4

The Erlenmeyer flask cell C - end elevation. The side elevation of this cell is depicted in figure 2.3.

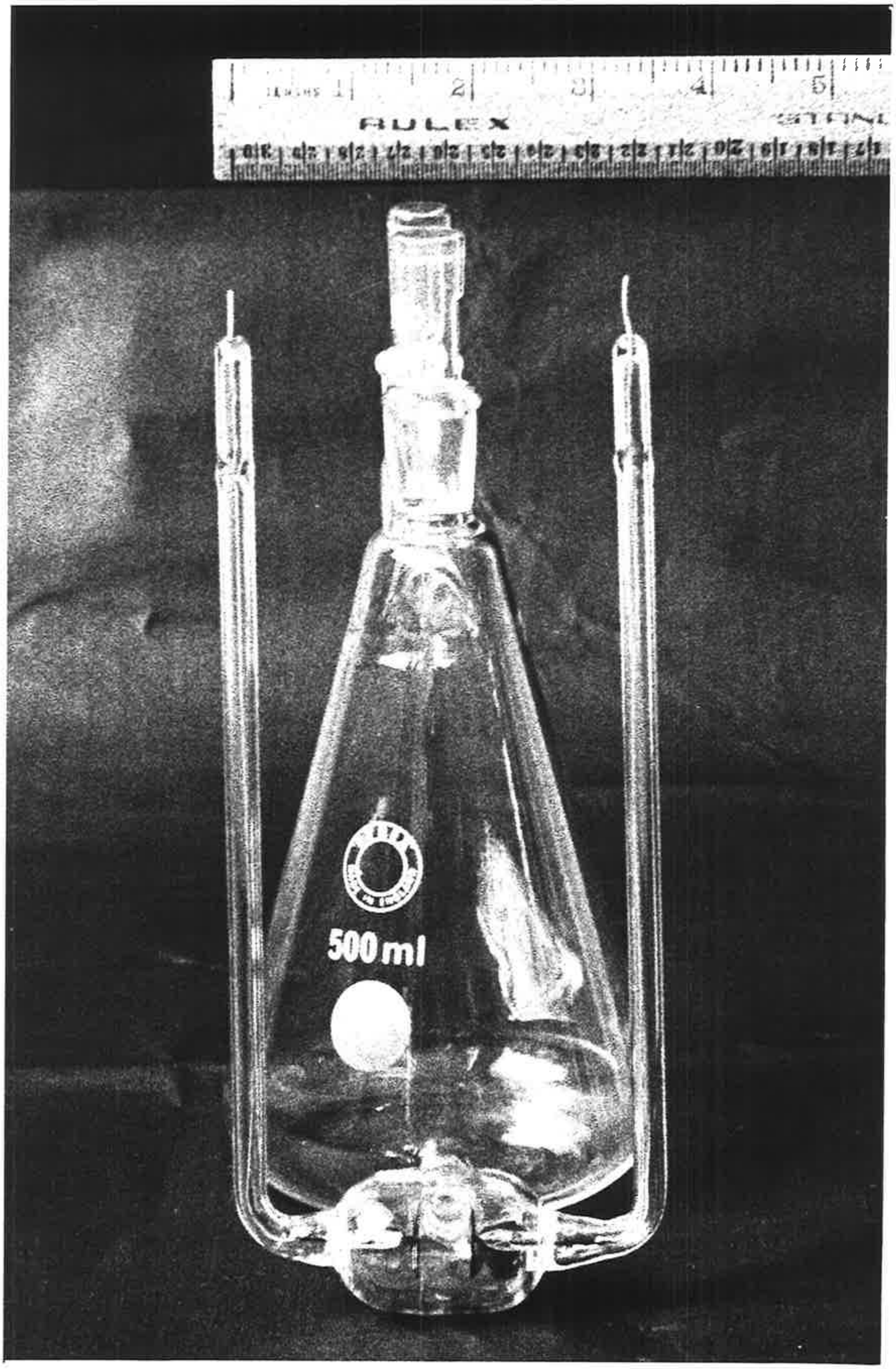

INCHES
1
2
3
4
5
RULEX
500 ml

FIGURE 2.5

The Erlenmeyer flask cell E - side elevation. The end elevation of this cell is the subject of figure 2.6.

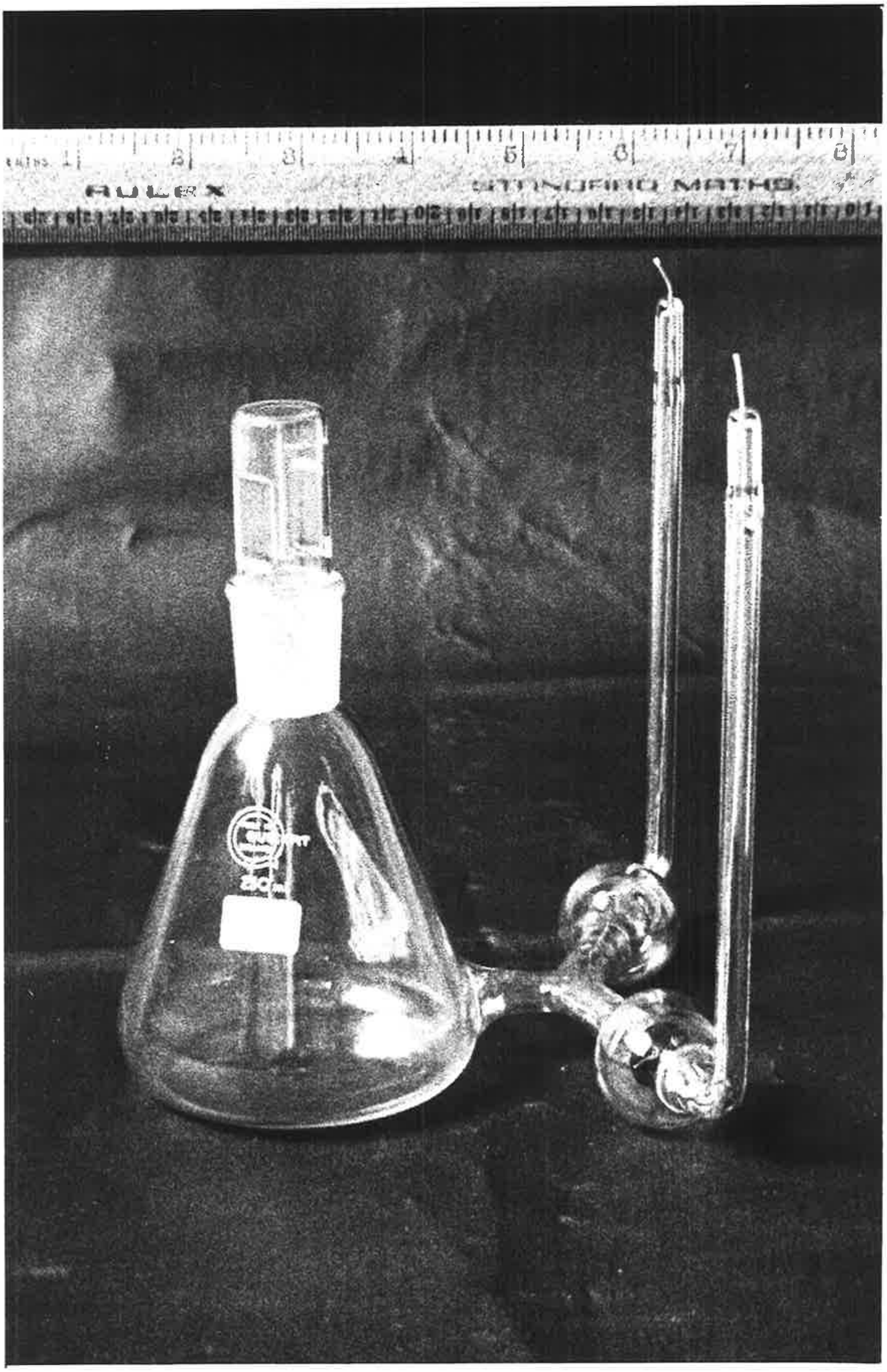
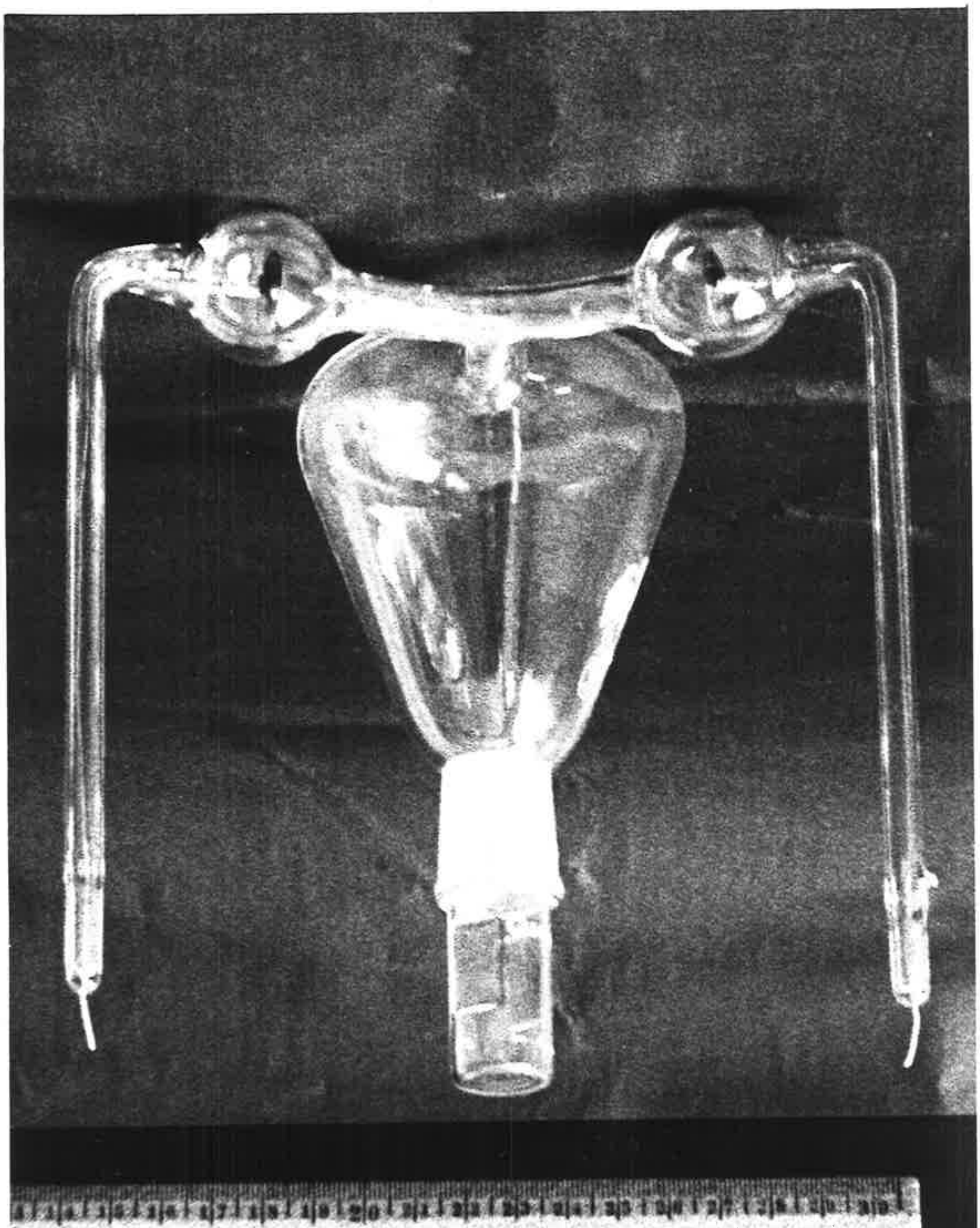

RULEX
STANDARD MATHS

FIGURE 2.6

The Erlenmeyer flask cell E - end elevation.
The side elevation of this cell has been presented in figure 2.5



with frequency is related to these distances. This proposal supports the hypothesis of Nichol and Fuoss that the effect is an interaction between the cell leads and the electrolyte in the cell. Since Nichol and Fuoss's proposal is applicable to cells in general it is to be preferred to that of Mysels et al, which is restricted to cells with a magnetic stirrer mechanism.

Returning to the cells used in this work, the frequency independent resistance was obtained by measuring the cell resistance over a wide range of frequencies and extrapolating a plot constructed for equation 2.2 to infinite frequency, thus accounting for electrode polarization. For cell C the linear stage of the plot of equation 2.2 in which R_2 decreased with increasing frequency, was extrapolated to infinite frequency for the evaluation of R_1. It can be noted that the maximum resistance for cell C encountered in limiting conductance runs was 3.5KΩ.

R_1 was itself corrected for the cell leads.

2.4 (d) Conductance Cells

Construction of Electrode Chamber

Electrodes were made of platinum plate, braced and supported by stout platinum wire. These were in turn, fused to tungsten wire covered with "tungsten sealing glass", to form the metal glass seal between the electrodes and the remainder of the cell. Finer platinum wire formed the cell's internal leads. This arrangement ensured that the only contacts with the cell's contents were platinum and pyrex glass.

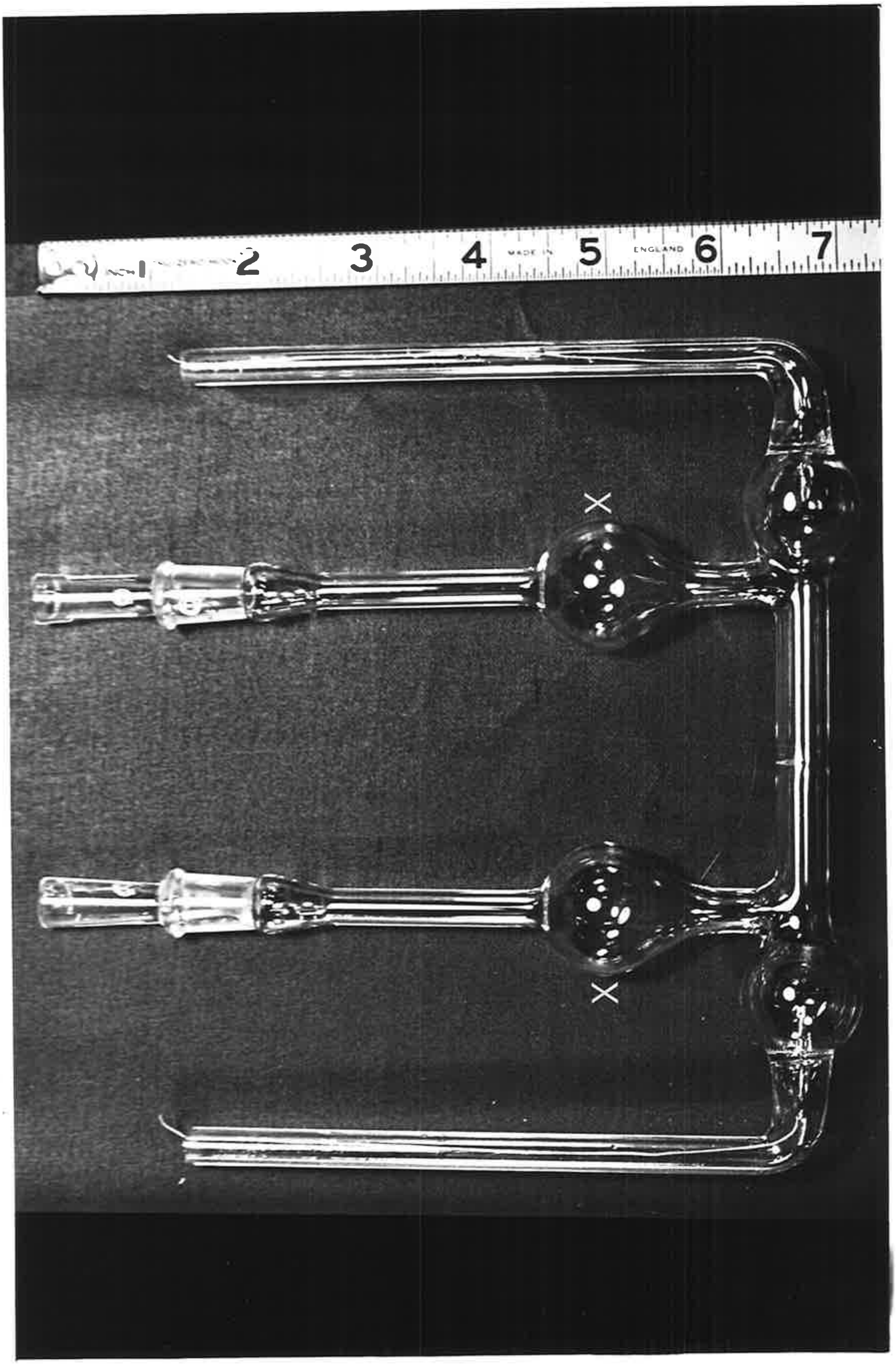
Description and Manipulation

Cells A and B

Figure 2.7 depicts the form of these cells of the conventional design with B 10 ground glass stoppers and sockets capped the inlet tubes. After rinsing the cell five times with the test solution, it was immersed in the appropriate thermostat. Rocking the equilibrated cell with its stoppers removed overcame the Soret (24) and shaking effects (25) reported by others to be sources of error in conductance measurements. The addition of

FIGURE 2.7

Conductivity cell A depicting the mixing bulbs X to facilitate the removal of the Soret effect.


2
3
4
MADE IN
5
ENGLAND
6
7
X
X

the bulbs X as shown in fig 2.7, in contrast to the diagrams of the cells depicted in reference (23), were reported by Stokes (26) in his conductance study of the aqueous HCl system to facilitate the mixing of the cell's contents, thereby removing the Soret effect.

Occasionally, the cell was rinsed and refilled, resistance measurements being repeated on a second sample of the test solution as a check upon the technique.

The electrodes of cell A were platinized whilst those of cell B were bright.

Owing to the nature of these cells's design, the temperature dependence of their cell constants followed case (i) of reference (27). Hence, the constants were regarded as being temperature independent.

Flask Cells

The manipulation of these cells during a limiting conductance run will be discussed later in this chapter.

Cell C

A cell chamber was attached to a 500 ml Erlenmeyer flask as in figs 2.3 and 2.4. For the limiting conductance studies with KCl/H_2O between 0° and 10°C the electrodes were bright platinum, while for the remainder of the work reported in the text involving this cell the electrodes were lightly platinized.

The temperature dependence of this cell's constant was taken into account since the electrode chamber complied with case (ii) of reference (27).

The cell constant was found to be independent of the height of the electrolyte in the cell above a minimum level.

Cell D

This is a 750 ml Erlenmeyer flask cell, fig 2.8, equipped with a stirrer well so that the system could be magnetically stirred. The glass tube, connecting the stirrer well and the electrode chamber, which contained lightly platinised electrodes, was inspired by a paper by Lind and Fuoss (28). It was found

FIGURE 2.8

The Erlenmeyer flask cell D incorporating the well W for the magnetic stirrer bar and the tubes T connecting the cell chamber and the remainder of the cell to facilitate the mixing of the cell's contents with the magnetic stirrer assembly.


FEET
INCH
1
TRU-ZERO HOOK
2
3
4
MADE IN
5
ENGLAND
6
T
W
T

necessary to use a glass encased permanent magnet, instead of a soft iron stirrer bar, in conjunction with the earthed stirring unit situated in the oil bath below the well.

The cell constant was found to be independent of the following factors: the presence of the stirrer bar, the stirrer motor, the combination of the previous two cases and the height of the electrolyte in the cell above a minimum level.

While developmental work was in progress, a standard glass B24 stopper was used. However it was replaced by a teflon stopper, as after several hours in the bath solvent condensate was very noticeable on the base of the glass stopper.

Solvent Cells

Two cells were used, an example of which can be seen in fig 2.9. Having only one inlet tube, the removal of the Soret effect was difficult. Consequently, their use was restricted to the measurement of the solvent correction, yet to be described in this chapter.

2.4(e) The Limiting Conductance Run Using The Flask Cells

The dried and weighed empty conductance cell was rinsed five times before the appropriate amount of solvent required for the run was finally placed in it. Re-weighing of the cell eventually followed on the Mettler B5C 1000 balance. A glass stand was used to support cell D in the balance case. The stirrer bar, being a permanent magnet, was carefully introduced into the cell after the weighing procedure had been completed.

A solution was prepared in the flask section of the cell by the addition of a known weight of stock electrolyte solution, either to the solvent or the previous solution already in the cell. Additions to stock were made from a weight burette, which was tared on the BC6200 Mettler balance. The tared burette was always handled with chamois leather.

The contents of cell C were transferred to the flask portion and thoroughly mixed. This was followed by the rinsing

FIGURE 2.9

A solvent cell for the measurement of the solvent correction.

of the cell chamber. The contents were then returned to the flask for a further mixing period. This sequence of events was repeated approximately ten times. Following equilibration with the bath, the solution was transferred to the flask and swirled. The cell was refilled and, with the Soret and shaking effects thus removed, the flask was returned to the thermostat.

Each new addition of stock to cell D was stirred for approximately 5 minutes after which the cell was removed from the bath so that the flask's walls above the solution could be rinsed. Such a procedure is necessary to prepare a solution homogeneous throughout the total volume of the cell. Stirring ceased after a further 25 minutes. Resistance measurements were always made upon an unstirred equilibrated cell, following the observations of Lind and Fuoss (28). A discrepency between the equilibrium resistance of the stirred and unstirred cell, reported by Lind and Fuoss, was also observed in this work. A consistent resistance was obtained also if the procedure described for cell C was repeated with the contents of cell D, following the resistance determination that climaxed the utilization of the magnetic stirring apparatus.

2.4 (f) Solvent Correction

A sample of the solvent was placed in a solvent cell that had been previously rinsed approximately 5 times with the solvent used to prepare the stock electrolyte solution. Having completed the resistance measurement on an electrolyte solution, 20KΩ was placed in parallel with the solvent cell and the resistance of this combination was determined at 3, 2, 1.8, 1.5, 1.2 and 1 Kc/s. For the 20 KΩ parallel resistors, bridge resistances were used as recommended by Dike (29).

2.4 (g) Cell Constants

The conductance cells were calibrated with the Jones and Bradshaw (30) demal potassium chloride solutions and by the method of Lind, Zwolenik and Fuoss (31) and Chiu and Fuoss (32). The specific conductance of the solute was corrected for the conductance of the solvent.

Table 2.1 presents the cell constant data obtained from each calibrating solution, together with its concentration. In this work, for each calibration reported, the resistance of at least three samples of the test solution was measured to ensure that a constant resistance for each cell was recorded. Since the overall reproducibility obtained for the cell constant of cell A is 0.02%, this can be regarded as an estimate of the probable precision of the conductance measurements made in the present study.

The cell constants recorded by Steel (33) and Phang (34) and Mewett (35) are also reported in this table where applicable. Each worker used different sample of purified KCl to prepare the calibrating solutions.

2.5 The Formamide-Water System

A preliminary Investigation

In this work conductance studies in the solvent system formamide/water were considered. Notley and Spiro (3), Butler (36), Vaughn (37) and Weissberger (38) cite ample references to methods that have been previously employed to purify formamide, by far the most successful being that of Notley and Spiro, who first dried their solvent with 3A molecular sieves, followed by de-ionization of the formamide with a mixed bed resin. This procedure improved by a factor of 10 the lowest previously reported Ksp of formamide. In a later paper, Notley and Spiro (39) used formamide, with a water content between 0.008M and 0.01M and a Ksp of $\simeq 2 \times 10^{-7}$ ohm^{-1} cm^{-1}, in the measurement of the transport numbers of KCl in this solvent by the moving boundary method.

As received, Unilab laboratory reagent formamide was found to have a water content, determined by the Karl Fischer method, between 0.02M and 0.05M and a Ksp of $\simeq 4 \times 10^{-4}$ ohm^{-1} cm^{-1}. Formamide used in this work, purified by the method of Notley and Spiro, had a water content of between 0.002M and 0.005M. When the solvent first emerged from the resin column it had a Ksp of ≃2 x 10^{-7}ohm^{-1}cm^{-1} which rose on standing in 5 days to ≃1.3 x 10^{-5}ohm^{-1}cm^{-1}.

A pilot conductance study was made upon three systems using firstly a 50% water/formamide mixture, secondly a 0.005M KCl/50% water/formamide solution and, finally, for a control, a sample of formamide used to prepare the first two solutions. The Ksp of the three systems measured at 25°C with a Philips conductance bridge, in conjunction with a Philips "dipping cell", expressed as a function of time, are reported in table 2.3.

TABLE 2.3

CONDUCTOMETRIC BEHAVIOUR OF THE FORMAMIDE-WATER SYSTEM

Time after preparation	Ksp ohms^{-1}cm^{-1}				
	≃0	80 mins	2 hrs	8 hrs	20 hrs
Formamide	4.83E-7*	4.68E-7	4.53E-7	6.04E-7	4.39E-6
H_2O/Formamide	4.83E-6	1.67E-5	2.34E-5	7.80E-5	1.69E-4
KCl/H_2O/Formamide	4.39E-4	4.49E-4	4.54E-4	4.83E-4	6.04E-4

* The Fortran notation for designating the exponent is used in this table.

The drift in the solvent Ksp can be attributed (3) to the formation of formic acid and ammonia as a result of the hydrolysis of formamide, which is slow in neutral solution but rapid in the presence of strong acids and bases. Due to the large solvent drift with time, no further work was undertaken in this system.

CHAPTER 2

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CHAPTER 3

ELECTRICAL CONDUCTIVITY IN THE REGION OF THE MAXIMUM DENSITY OF AQUEOUS SOLUTIONS

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3.1 Introduction

Of particular interest in a previous study (1) was the degree of "ice likeness" of liquid water and the phenomenon of the maximum density of an aqueous electrolyte solution and their influences upon ionic conductance. Evidence that water retains some of the characteristic ice structure is provided by X-Ray diffraction studies, I.R. and Raman absorption spectroscopy (2) (3) (4). While a significant amount of short-range order of the ice structure is retained, the long-range order is lost due to thermal motion of the molecules. Some of the models that have been proposed for liquid water and their degree of success in accounting for the diverse properties of water have been discussed by Kavanau (5) and Samoilov (3). The experimental findings of the previous work were interpreted on the basis of the lattice model of Samoilov and the flickering cluster model of Frank and Wen (6).

One aspect of this research is the continuation of the previous study (1) in which the relationship between ionic conductivities and the phenomenon of the maximum density of an aqueous solution was investigated. One of the unique properties of water is the change in density, with temperature, which culminates in the attainment of the maximum density at $4^{o}C$. On the basis of the models that have been proposed for water, this phenomenon has been attributed to competing structural changes in the liquid state in the vicinity of $4^{o}C$. The question is posed as to what influence these density changes, and hence proposed structural changes, might have upon the translational motion of anion.

From the work of Horne and his co-workers it appears that the electrical conductivity of some electrolytes is influenced markedly by the density changes in the solution in the neighbourhood of the temperature of maximum density of the solution. The temperature dependence of the Arrhenius activation energy for the conductance process was interpreted by Horne et al on the basis of the Glasstone, Laidler and Eyring (7) theory for the transport processes, in conjunction with Bernal and Fowler's (3) model for liquid water. Glasstone et al regard the transport processes, e.g. conductivity, viscosity and self-diffusion, as having a common two-step mechanism, which is the creation of a vacancy, or hole, in the solution followed by the activated jump of the reference ion or molecule into the newly formed vacancy. Horne et al report that Ea for some electrolytes attained a maximum value near the temperature of the maximum density of the solution, while for others no maximum was recorded. Some other findings of Horne et al can also be summarised. For a given concentration Ea was found to be larger for the chloride having a structure-making compared with a structure-breaking cation. Also there was no correlation between the structure making or breaking properties of the cation and Ea for the salt attaining a maximum value. For a given electrolyte Ea decreased as the concentration of the electrolyte increased.

Initially the previous research (1) was an extension of the work initiated by Horne et al in that their findings suggested a study of the relationship between density changes in the system and individual ionic conductivities. Since precise limiting transport number data were available for potassium chloride between 0° and 45°C, together with the reported Horne et al Ea maxima for potassium chloride at finite concentrations, this system was considered an obvious choice for a limiting conductance study. The temperature dependence of Ea required for the limiting transport of K^+ and Cl^- ions was found to be independent of density changes that occur between 0° and 9°C. These findings were corroborated by a concurrent study of the conductivity of these ions in the same temperature range at a finite concentration.

In the present research measurements were made on a 1.0×10^{-3}N cesium chloride solution as Horne and Johnson had reported a pronounced maximum in Ea for a cesium chloride solution of similar concentration. Analytical expressions for representing the temperature dependence of the conductance data were re-investigated with the aim of placing the estimation of the uncertainty of Ea on a firmer basis. The evaluation of Λ^o was re-examined using the

Pitts conductivity equation, as was its subsequent effect upon the temperature dependence of Ea. Previously the Robinson and Stokes equation was used to evaluate Λ^{o}. Recently Kay and Vidulich published transport data at 1° and 10°C which showed a different temperature dependence for the limiting transport number of potassium chloride to that previously reported by Steel. It was felt desirable, therefore, to re-examine the energy of activation for the conductivities of the potassium and chloride ions.

3.2 Experimental Measurements

Conductance measurements were made between 0° and 10°C in cell A for an aqueous CsCl solution, 1.3088×10^{-3}N at 25°C, which was prepared by diluting a more concentrated stock solution.

The limiting conductivity of KCl and the conductance of a KCl solution, 0.078323N at 25°C, were measured between 0° and 10°C prior to the commencement of this work (1).

Limiting conductance measurements were made in the flask cells C and E. Cells A and B were utilized for the 0.078323N solution, the temperature range in which each cell was used overlapped, thus providing a useful check of the reproducibility of the two sets of measurements.

Two thermometers with overlapping scales allowed a check to be performed upon the calibration of the 1° range Beckmann thermometer when the work below 0°C was completed.

3.3 Treatment of Data

3.3 (a) Conversion of Molality to Molarity

The density, required to convert the concentration of a solution prepared by weight to a volume basis, was obtained by solving Root's equation, 3.1, (8) (9) by a series of successive approximations for all aqueous solutions studied in this work.

$$d = d_o + A_1C - A_2C^{3/2} \qquad 3.1$$

Equation 3.1 will be introduced in chapter 5. Here it suffices to record that d is the density of the solution, d_o the density of the solvent and C is the solution's normality. A_1 and A_2 are constants, characteristic of the electrolyte, involving the partial molar properties of the solute.

For KCl A_1 and A_2 at 0° and 25°C were calculated from Scott's data (10), while at 10° their values were evaluated from density-concentration data obtained from the International Critical Tables (11). A_1 and A_2 for 0° were used for all points below 5°, while above 5° the values for 10°C were substituted in equation 3.1 for the evaluation of the density of this solution.

In the case of CsCl, A_1 and A_2 were calculated from Scott's data (10) for this salt at 0° and 25°, their value at 0°C being used in conjunction with equation 3.1 between 0° and 10°C. Values of d_o were interpolated from density-temperature data for water presented in reference (12).

3.3 (b) The Evaluation of Λ^o

The limiting equivalent conductance, Λ^o, was evaluated with the Robinson and Stokes equation, 1.30. The values of B, B_1 and B_2 were interpolated from tabulated values of these coefficients (13); a was set to 3.0Å since Λ^o (calc) was then approximately constant to about 0.01N. Hence values of Λ^o (calc) obtained were averaged to evaluate Λ^o.

To ascertain the reliability of the averaging method (1) used previously to evaluate Λ^o, the conductance data were re-examined in this research with the Pitts conductivity equation. Such an undertaking is desirable to show that Λ^o, and hence the energy of activation, is independent of the method used for evaluating Λ^o. The viscosity of water between 0° and 10°C was obtained from Cragoe's (14) interpolation formula, while Malmberg and Maryott's (15) dielectric constant data for water in this temperature range was used. Λ^o for KCl at 0°C could not be re-evaluated on the basis of the Pitts equation, since Λ^o is itself only reported by Lange (16). In a recent paper Pitts, Tabor and Daly (17) have applied the Pitts equation to a number of 1:1 electrolytes in water at various temperatures. For KCl they report a ranging from 2.8 to 3.2 Å, a range in general agreement with that obtained in the present research between 0° and 8°C.

The concentration dependence of Λ from which Λ^o was evaluated is located in appendix 3.1, together with the difference between the experimental value of Λ and that calculated from Pitts equation. Also recorded is the temperature of each point for a given limiting conductance run.

Table 3.1 reports the values of Λ^o obtained from the Robinson and Stokes equation with the arithmetic deviation of the Λ^o (calc) values from their mean, Λ^o. The values of Λ^o at 0° and 5°C result from the measurements of Lange (16) and Owen and Zeldes (18)

TABLE 3.1

VALUES Λ^o FOR KCl, BETWEEN 0^o AND 8.21^oC, EVALUATED FROM THE ROBINSON AND STOKES AND PITTS CONDUCTIVITY EQUATIONS

Temp. °C	Robinson and Stokes	Pitts		
	Λ^o	Λ^o	α	σ
0.0	(81.7)	-	-	-
0.54	83.05 ± 0.03	83.09	2.91	0.018
1.57	85.61 ± 0.021	85.63	2.95	0.021
2.16	87.02 ± 0.035	87.02	3.86	0.030
2.89	88.85 ± 0.01	88.92	2.65	0.017
3.49	90.38 ± 0.013	94.41	3.07	0.015
4.10	92.01 ± 0.02	92.04	2.89	0.020
4.68	93.50 ± 0.023	93.50	3.00	0.041
5.00	94.21	94.27	2.88	-
7.48	100.76 ± 0.04	100.76	2.91	0.052
8.21	102.64 ± 0.05	102.62	3.07	0.026

respectively. The value of Λ^o at 5°C was evaluated with the Robinson and Stokes equation by Robinson and Stokes (19), while the value recorded for the Pitts equation at this temperature was computed by Pitts et al (17).

3.3 (c) The Evaluation of Ionic Conductivities

A combination of the limiting equivalent conductance and transport number data permits the calculation of the limiting ionic conductivities of the K^+ and Cl^- ions at each temperature. Limiting transport number data for each temperature was interpolated, with equation 3.2, from measurements by Steel (20), Longsworth (21) and Allgood, LeRoy and Gordon (22) expressed as a function of temperature, t being °C, thus (23):

$$t^o_{Cl^-} = 0.5046+(1.88\text{x}10^{-4})t \qquad 3.2$$

The values of $\lambda^o_{K^+}$ and $\lambda^o_{Cl^-}$ evaluated on the basis of the above temperature dependence for $t^o_{Cl^-}$ and Λ^o, as calculated from the Robinson and Stokes equation, are presented in table 3.2.

Since the completion of the limiting conductance study, additional transport number data for aqueous KCl solutions to that cited above has been reported by Kay and Vidulich (24). When the measurements of the last authors at 1° and 10°C are combined with other limiting transport number data for this salt above 10°C, a different temperature dependence to that previously reported by Steel results. Table 3.2 also presents a second set of $\lambda^o_{K^+}$ and $\lambda^o_{Cl^-}$ data obtained on the basis of Λ^o evaluated by the Robinson and Stokes equation and the transport number data which resulted when the data of Allgood, LeRoy and Gordon was combined with that of Kay and Vidulich and least-squared to first and second order polynomials, in temperature, which are given below, equations 3.3 and 3.4, with the standard error of fit to each equation, σ.

$$t^o_{K^+} = 0.4963 - (2.10\text{x}10^{-4})t \quad ; \quad \sigma = 4.5\text{x}10^{-4} \qquad 3.3$$

$$t^o_{K^+} = 0.4969 - (2.99\text{x}10^{-4})t + (1.9\text{x}10^{-6})t^2; \quad \sigma = 1.2\text{x}10^{-4} \qquad 3.4$$

Equation 3.4 is the more realistic representation of the data, since σ is comparable with the quoted errors in the measurements.

The transport number for the chloride ion in the 0.078323N KCl

TABLE 3.2

LIMITING CONDUCTIVITIES OF K^+ AND Cl^- IONS BETWEEN 0° AND 8.21°C

Temp.	Robinson and Stokes Equation	Transport Number Data of Steel		Transport Number Data of Kay et al	
°C	Λ^o	$\lambda^o_{K^+}$	$\lambda^o_{Cl^-}$	$\lambda^o_{K^+}$	$\lambda^o_{Cl^-}$
0.0	81.7	40.5	41.2	40.6	41.1
0.54	83.0_5	41.1_4	41.9_2	41.2_7	41.7_8
1.57	85.6_1	42.3_9	43.2_2	42.5_0	43.1_1
2.16	87.0_2	43.0_7	43.9_5	43.1_8	43.8_4
2.89	88.8_5	43.9_7	44.8_8	44.0_7	44.7_8
3.49	90.3_8	44.7_2	45.6_6	44.8_1	45.5_7
4.10	92.0_1	45.5_1	46.5_0	45.6_0	46.4_1
4.68	93.5_0	46.2_4	47.2_6	46.3_3	47.1_7
5.00	94.2_1	46.5_9	47.6_2	46.6_7	47.5_4
7.48	100.7_6	49.7_8	50.9_8	49.8_5	50.9_1
8.21	102.6_4	50.6_9	51.9_5	50.7_7	51.8_9

solution was calculated from equation 3.5 (25) at 5°, 15°, 25° and 35°C. Then t_{Cl^-} at other temperatures were graphically interpolated. Values of Λ^o used to calculate t_{Cl^-} were obtained from reference (19). The values of t_{Cl^-} were calculated on the basis of the temperature dependence for $t^o_{Cl^-}$ defined by equation 3.2.

$$t_{Cl^-} = \frac{\lambda^o_{Cl^-} - \frac{1}{2} B_2\sqrt{C}/(1+Ba\sqrt{C})}{\Lambda^o - B_2\sqrt{C}/(1+Ba\sqrt{C})} \qquad 3.5$$

Appendix 3.2 is a summary of the results obtained with the 0.078323N KCl solution.

Appendix 3.3 likewise summarizes the experimental data for the CsCl solution.

3.3 (d) A Model for the Temperature Dependence of the Conductance Data

The requirements for an analytical expression that will represent the observed temperature dependence of conductance are that the expression be as simple as possible and, further, reflect the experimental error in the original conductance measurements. It was found that polynomials of the form $\Lambda^o = P' + Q't + R't^2$ satisfied these requirements adequately.

All sets of data were fitted to first, second and third order polynomials of conductance as a function of temperature by the method of least squares. The linear regression program, PUTT, furnished the least squares coefficients together with their standard errors and the standard error of fit, S.E., for each system.

Programs which also computed the standard error of the coefficients were written while the present research was in progress. Previously, (1) the most significant order polynomial was selected upon the basis of the standard error of fit reflecting the experimental error of the original conductance measurements.

The record in table 3.3, being representative of the results obtained with the remaining data reported in this work, will suffice to illustrate the criteria by which a polynomial was selected as being the best representation for the temperature dependence of the

TABLE 3.3

THE FIT OF Λ^o TO POLYNOMIALS OF THE FORM

$$\Lambda^o = P' + Q't + R't^2 + S't^3$$

Order	Coefficients	S.E. of Coefficients	S.E. of Fit
1	P' = 8.1611 E* + 1	4.30 E - 2	8.07 E - 2
	Q' = 2.5493 E + 0	9.73 E - 3	
2	P' = 8.1718 E + 1	2.53 E - 2	3.50 E - 2
	Q' = 2.4646 E + 0	1.41 E - 2	
	R' = 1.0295 E - 2	1.63 E - 3	
3	P' = 8.1728 E + 1	3.07 E - 2	
	Q' = 2.4429 E + 0	3.75 E - 2	3.64 E - 2
	R' = 1.7612 E - 2	1.18 E - 2	
	S' = -6.025 E - 4	9.61 E - 4	

* FORTRAN notation for the exponent used in this table.

conductance data under consideration. The second order polynomial was considered to be the best and the most significant representation after comparing, firstly, the magnitude of the standard error of fit of the data to each polynomial and, secondly, the magnitude of each coefficient's standard error to that of the coefficient itself. By referring to table 3.3, in which the standard error is abbreviated S.E., it can be observed that the standard error of fit is better for the second and third orders. However, the last representation can be discounted as being less significant than the second order, because the standard error of the t^3 coefficient is larger than the coefficient itself. The second order polynomial in the case of the Λ^o data can be further supported by the observation that the standard error of the fit of the data is a little larger than the magnitude of the scatter of the Λ^o (calc) values originally averaged to evaluate Λ^o.

3.3 (e) Evaluation of the Energy of Activation, Ea

Since all the experimental quantities were treated alike, the description below will suffice as a "type example". The energy of activation, Ea, for the conductance process was evaluated in two ways.

First, from equation 3.6 given an expression for $\ln\Lambda^o$ as $f(T^{-1})$, T being in degrees Kelvin.

$$Ea = -R\left[\frac{d\ln\Lambda^o}{d(1/T)}\right] \qquad 3.6$$

R is the gas constant, 1.98719 calorie degree^{-1} mole^{-1} (26). An expression for $\ln\Lambda^o$ as $f(T^{-1})$ was obtained by fitting $\ln\Lambda^o$ to first, second and third order polynomials in T^{-1} using the regression program PUTT.

Second, Ea was calculated with the integrated form of the Arrhenius equation (28)

$$Ea = R\,\frac{(\ln\Lambda^o_2 - \ln\Lambda^o_1)T_1T_2}{(T_2 - T_1)} \qquad 3.7$$

Table 3.4 presents the coefficients, their standard errors and the standard error of fit for the three polynomials of $\ln\Lambda^o$ as

TABLE 3.4

THE COEFFICIENTS OF POLYNOMIALS OF THE FORM

$$\ln\Lambda^{o} = P' + \frac{Q'}{T} + \frac{R'}{T^2} + \frac{S'}{T^3}$$

Order of Polynomial	Coefficients	S.E. of Coefficients	S.E. of Fit
1	P' = 1.2216 E + 1	4.31 E - 2	1.288 E - 3
	Q' =-2.1336 E + 3	1.19 E + 1	
2	P' =-1.0304 E + 0	1.41 E + 0	3.929 E - 4
	Q' = 5.2110 E + 3	7.80 E + 2	
	R' =-1.0180 E + 6	1.08 E + 5	
3	P' =-8.3705 E + 1	2.31 E + 2	4.162 E - 4
	Q' = 7.3957 E + 4	1.92 E + 5	
	R' =-2.0072 E + 7	5.32 E + 7	
	S' = 1.7602 E + 9	4.91 E + 9	

$f(T^{-1})$. Although the second and third orders provide a better representation of the data, judged from the view point of their respective standard errors of fit, the significance of some of their coefficients is in doubt due to their large standard errors. Hence these polynomials, in their present form, are not significant representations of the data. However, the important observation from table 3.4 is that the coefficient P' of the second order polynomial is small in relation to the remainder: therefore, it was equated to zero and the data was re-analysed with program DODO 3, the relevant output of which is the subject of table 3.5. The third order case was also included for comparison. By comparing tables 3.4 and 3.5, it can be observed that the standard error of fit is unaltered by setting P' to zero. The remaining coefficients give a more significant overall representation of the data, since their standard errors have become smaller. The second order polynomial has become, by this procedure, highly significant in contrast to the third order case which will not be considered further for the following reasons. The standard error of fit upon the addition of the $S'T^{-3}$ term is approximately the same as for the second order case. Further, the standard errors of the coefficients R' and S' are of the same order of magnitude as the coefficients themselves, and lastly, the third order polynomial, as a representation of the temperature dependence of Λ^{o}, i.e. Λ^{o} as $f(t)$, has already been rejected. Hence, Ea was calculated from the polynomials of the form of 3.8 and 3.9 in conjunction with equation 3.6.

$$\ln\Lambda^{o} = P' + Q'T^{-1} \qquad 3.8$$

$$\ln\Lambda^{o} = 0.0 + Q'T^{-1} + R'T^{-2} \qquad 3.9$$

The coefficients, their standard errors, and the standard error of fit of the data to each polynomial from which Ea was evaluated are located in appendix 3.4

TABLE 3.5

THE COEFFICIENTS OF POLYNOMIALS OF THE FORM

$$\ln\Lambda^{o} = \frac{Q'}{T} + \frac{R'}{T^2} + \frac{S'}{T^3}$$

Order of Polynomial	Coefficients	S.E. of Coefficients	S.E. of Fit
2	P' = 0.0000 E + 0	0.00 E + 0	
	Q' = 4.6397 E + 3	3.56 E + 0	3.827 E - 4
	R' =-9.3880 E + 5	9.85 E + 2	
3	P' = 0.0000 E + 0	0.00 E + 0	
	Q' = 4.3552 E + 3	3.90 E + 2	3.930 E - 4
	R' =-7.8104 E + 5	2.16 E + 5	
	S' =-2.1864 E + 7	3.00 E + 7	

3.4 Results and Discussion

Tabulated in table 3.6 are values of Ea at various temperatures calculated from the polynomial representations of the conductance data, equations 3.8 and 3.9, for the K^+ and Cl^- ions from the limiting conductance study and the stock KCl solution. Also tabulated are values of Ea for Λ^o and Λ of KCl and Λ of CsCl and the estimated error in Ea for each quantity.

From the data presented in table 3.7 it is concluded that Ea evaluated from equation 3.9 for a given ion is independent of the basis for assigning individual ionic conductances from the limiting transport number data cited in this chapter, viz. equations 3.2 or 3.4. Further, the energy of activation of the ion pair is independent of the method of evaluating the limiting conductivity.

A temperature dependence for Ea, depicted in fig 3.1, of the CsCl solution was obtained by taking the experimental values in sequence, with respect to temperature, in pairs and subsequently calculating Ea from the Arrhenius equation. It can be observed that, after consideration of the scatter in Ea obtained, the assignment of a maximum to this plot has little basis: rather, the resultant plot can be best described as a straight line having finite slope. The line of best fit, obtained by expressing Ea as a linear $f(t)$, is indicated on fig 3.1 together with the standard error of fit, namely, ±120 calories/mole. Ea was also calculated with the polynomial representations 3.8 and 3.9, the former giving rise to Ea independent of temperature, while in the latter case, Ea decreases linearly with increasing temperature, both temperature dependences being depicted on fig 3.1. Two observations can be made. First, the two dependences are distinguishable, after taking the error in Ea into account; second, Ea, calculated from the experimental data and the second order polynomial are equivalent within the estimated error of the two representations.

Another important point should be made here in that, by calculating Ea from the experimental points, no temperature dependence could be imposed upon Ea, in contrast to fitting Λ and hence Ea to

TABLE 3.6

TABULATED VALUES OF Ea FOR KCl AND CsCl BETWEEN 0° AND 9°C

		Ea Cals/Mole			
Conductance Quantity	Order of Polynomial	Error in Ea	0°	4°	9°
		Ea FOR 0.001388N CsCl SOLUTION			
Λ	1	±13	4082	4082	4082
Λ	2	±11.3	4327	4133	3898
		Ea FOR LIMITING CONDUCTANCE DATA KCl			
Λ^o	1	±20.9	4246	4246	4246
$\lambda^o_{Cl^-}$	1	±22.7	4306	4306	4306
$\lambda^o_{K^+}$	1	±19.2	4183	4183	4183
Λ^o	2	±24.6	4446	4249	4010
$\lambda^o_{Cl^-}$	2	±29.0	4496	4308	4081
$\lambda^o_{K^+}$	2	±24.3	4370	4186	3963
		Ea FOR 0.078323N KCl SOLUTION			
Λ	1	± 7.9	4160	4160	4160
λ_{Cl^-}	1	± 7.1	4225	4225	4225
λ_{K^+}	1	± 9.2	4093	4093	4093
Λ	2	± 8.0	4327	4135	3903
λ_{Cl^-}	2	±13.8	4384	4201	3980
λ_{K^+}	2	± 9.7	4248	4070	3854

TABLE 3.7

TABULATED VALUES OF Ea DERIVED FROM LIMITING CONDUCTANCE DATA FOR KCl

Ea derived from	Ea Cals/Mole		
	$0^{o}C$	$4^{o}C$	$9^{o}C$
Λ^{o} Robinson and Stokes equation	4446.0	4249.0 ± 20.9	4010.0
Λ^{o} Pitts equation	4440.0	4243.0 ± 21.2	4004.0
K^{+}, $t^{o}_{K^{+}}$ Steel	4370.0	4186.0 ± 19.2	3963.0
K^{+}, $t^{o}_{K^{+}}$ Kay	4341.0	4158.0 ± 22.0	3936.0
Cl^{-}, $t^{o}_{Cl^{-}}$ Steel	4496.0	4308.0 ± 22.7	4081.0
Cl^{-}, $t^{o}_{Cl^{-}}$ Kay	4528.0	4339.0 ± 20.2	4110.0

FIGURE 3.1

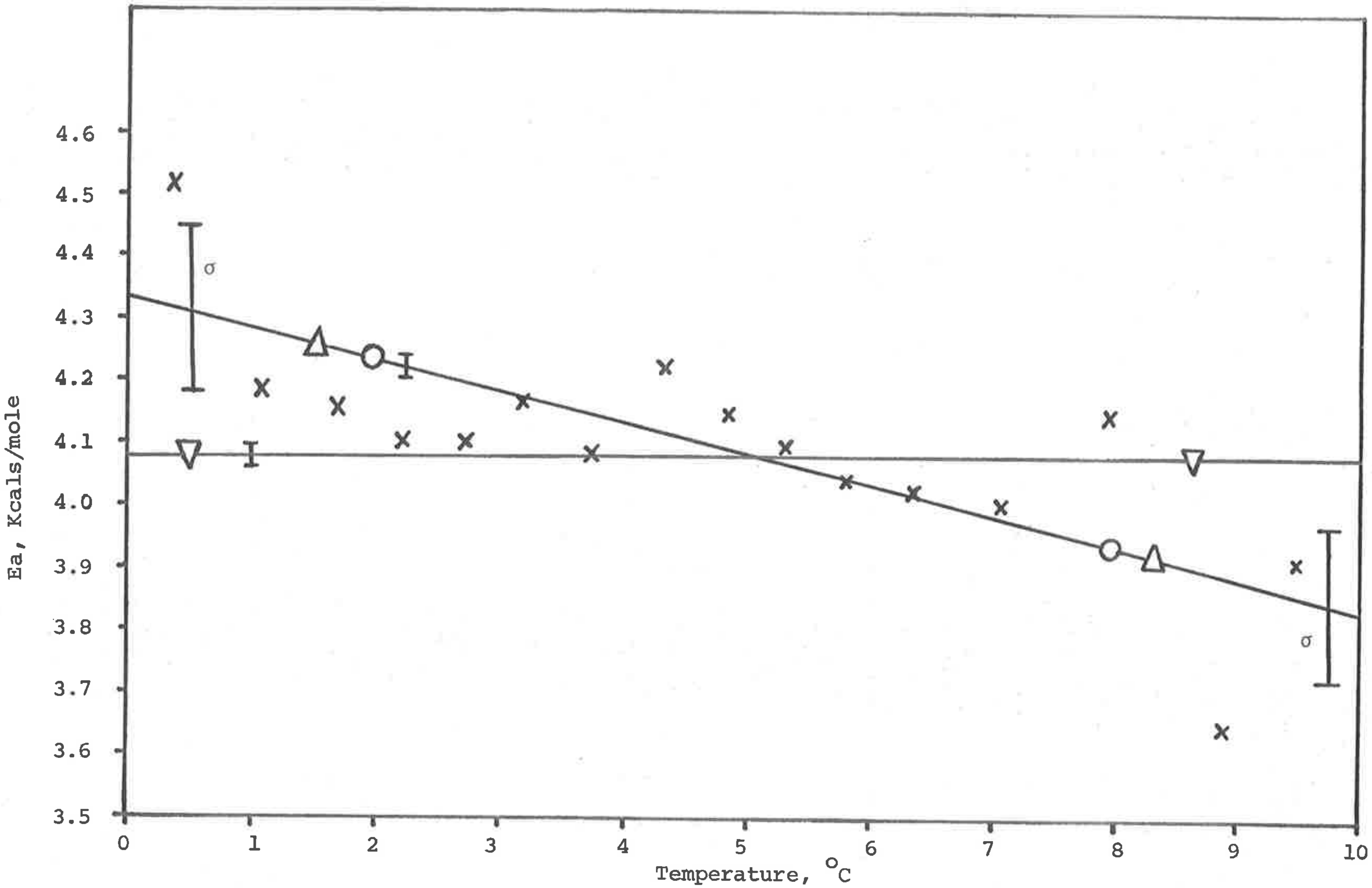
The temperature dependence of Ea for a 0.0013088N CsCl solution derived from the integrated form of the Arrhenius equation, equation 3.7, and the polynomial representations of the conductance data, equations 3.8 and 3.9, in conjunction with equation 3.6.

(a) × Ea computed directly from the experimental conductance-temperature data with the integrated form of the Arrhenius equation, 3.7.

(b) ○ The line of best fit for Ea derived from the experimental points, part (a) above. The standard error of fit, σ, is also denoted.

(c) △ Ea derived from the second order polynomial representation of the conductance-temperature data, equation 3.9, in conjunction with equation 3.6.

(d) ▽ Ea derived from the first order polynomial representation of the conductance-temperature data, equation 3.8, in conjunction with equation 3.6.


4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
Ea, Kcals/mole
0
1
2
3
4
5
6
7
8
9
10
Temperature, °C
σ
σ

a definite function of temperature. It has been shown above that by taking either experimental conductivity-temperature observations, or the polynomial representation of the same data, leads to the same result for the temperature dependence of Ea.

Fig 3.2, constructed from the relevant data from table 3.6, presents the two temperature dependences of Ea for the quantities $\lambda^o_{K^+}$, $\lambda^o_{Cl^-}$ and Λ^o. The conductance quantities, for which Ea was calculated, are based upon the Robinson and Stokes equation and the temperature dependence for the limiting transport number data reported by Steel. It can be observed from fig 3.2 that, for a given quantity, the two temperature dependences of Ea defined by equations 3.8 and 3.9 are distinguishable following the acknowledgement of the estimated error in Ea. From the data presented in table 3.6, for the stock KCl solution, it is likewise concluded that the two representations of Ea for the quantities Λ, λ_{K^+} and λ_{Cl^-} are resolvable.

It will be recalled that the second order polynomial gave a better representation of the conductance data from which Ea was evaluated. However, the decision of which polynomial representations, 3.8 or 3.9, resulted in the more significant representation of Ea as $f(t)$ had to be deferred until the errors of the two representations were evaluated. Since it has been established that the two temperature dependence models for Ea are resolvable, it is now proposed that Ea, for the conductance process between 0° and 9°C, decreases linearly with increasing temperature through the temperature of maximum density of the solution.

Denoted on fig 3.3 is Ea for the K^+ and Cl^- ions at infinite dilution and at the finite concentration. The conclusions that can be drawn from this plot for a given temperature are twofold. First, at infinite dilution, as well as at the finite concentration, Ea required for the transport of the chloride ion is greater than that for potassium ion. Second, for a given ion, Ea is greater at infinite dilution than at the finite concentration, i.e. Ea is concentration dependent.

FIGURE 3.2

The temperature dependence of Ea for the K^+, Cl^- and the ion pair at infinite dilution derived from the polynomial representations of the conductance-temperature data, equations 3.8 and 3.9, in conjunction with equation 3.6.

△ Ea($\lambda^o_{Cl^-}$)

× Ea(Λ^o)

▽ Ea($\lambda^o_{K^+}$)

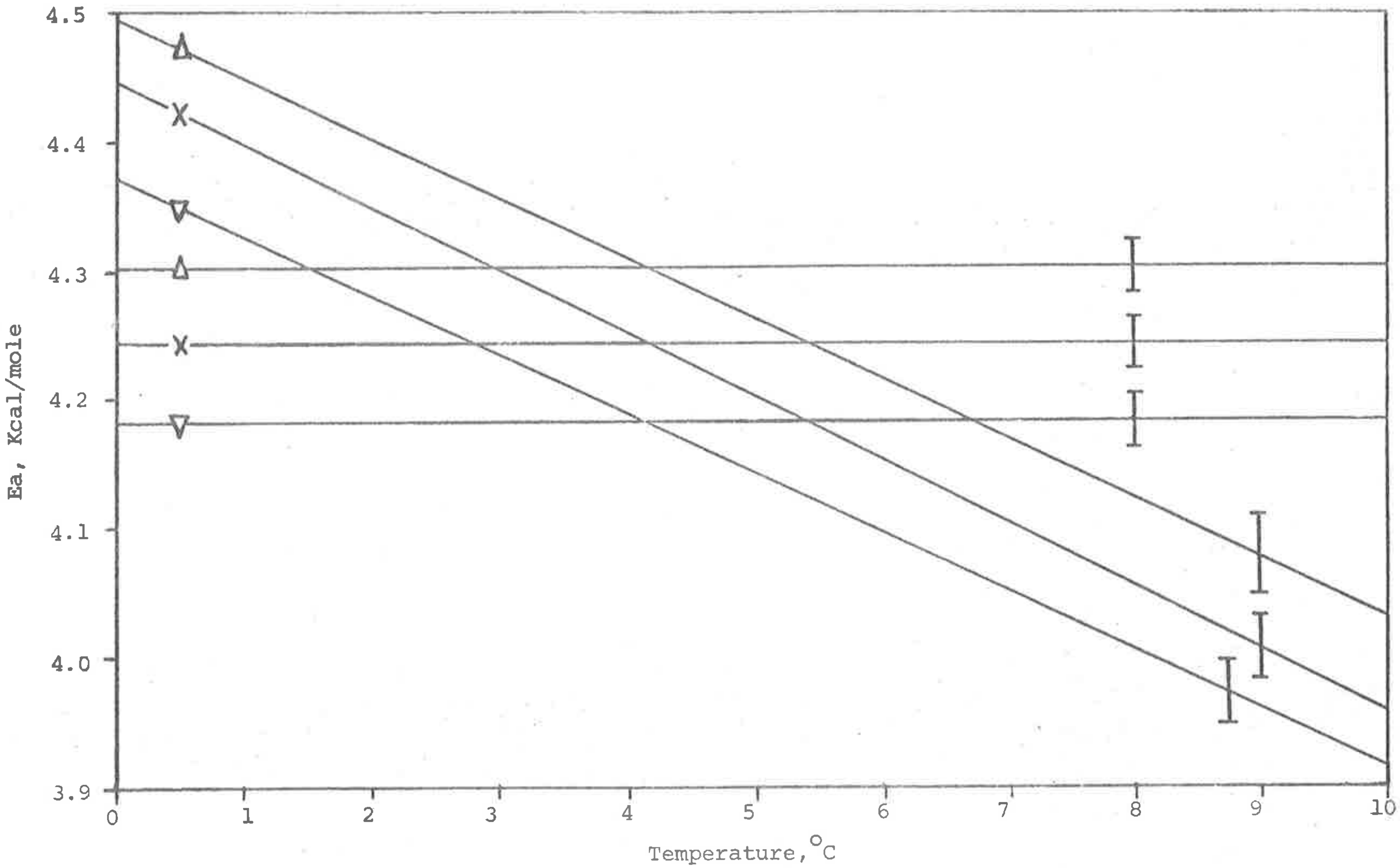

4.5
4.4
4.3
4.2
4.1
4.0
3.9
Ea, Kcal/mole
0
1
2
3
4
5
6
7
8
9
10
Temperature, °C

FIGURE 3.3

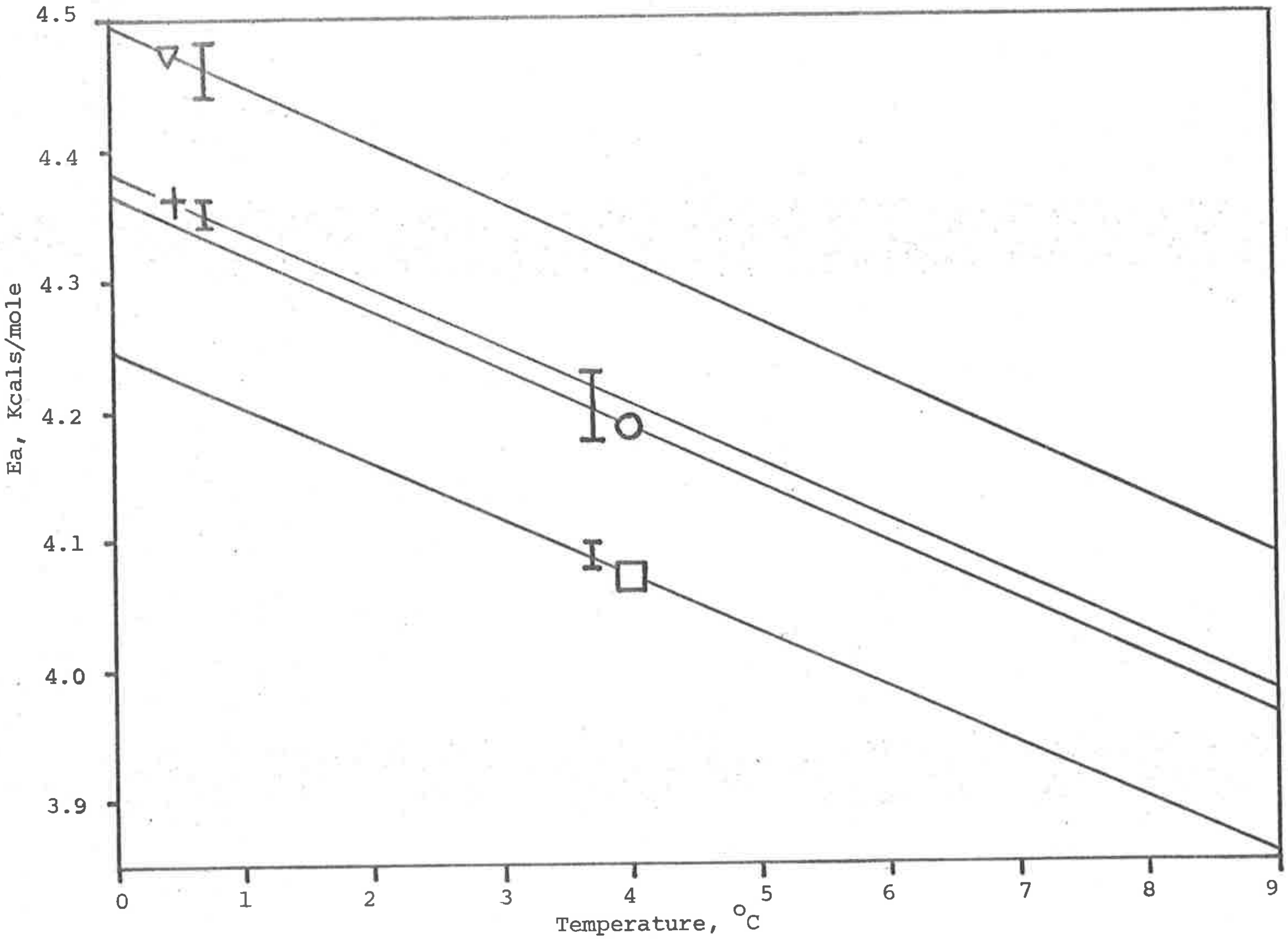
The temperature dependence of Ea for the K^+ and Cl^- ions at infinite dilution and at a finite concentration derived from equations 3.6 and 3.9.

▽ $Ea(\lambda^{o}_{Cl^-})$

\+ $Ea(\lambda_{Cl^-})$

○ $Ea(\lambda^{o}_{K^+})$

□ $Ea(\lambda_{K^+})$


4.5
4.4
4.3
4.2
4.1
4.0
3.9
Ea, Kcals/mole
0
1
2
3
4
5
6
7
8
9
Temperature, °C

One aspect of the present research is the re-examination of the basis upon which the uncertainties in Ea were evaluated, in conjunction with analytical expressions, to represent the temperature dependence of the conductance data. When the KCl work was first reported (1), it was concluded after considering the uncertainty in Ea at that time, that Ea between 0° and 9°C for these systems was independent of both temperature and concentration of the electrolyte. The uncertainty in Ea at this time was calculated in the following manner (27). An initial value for Ea was evaluated from two predicted values of conductance separated 0.5°C, obtained from the second order polynomial of, for example, Λ^{o} as $f(t)$. A second calculation of Ea followed, again using the Arrhenius equation, by adding the standard error of fit of the data to the second order polynomial as $f(t)$ to one of the values of Λ^{o}. The errors so obtained for Ea were as follows:- Ea (Λ^{o}) ± 0.14 and Ea (Λ) ± 0.12K cals/mole respectively.

In all systems described above, the only justifiable representation of Ea as $f(t)$ is Ea decreasing with increasing temperature, a finding which is at variance with some results previously reported by Horne and his co-workers.

Horne et al have reported a correlation between changes in the solution density and Ea for the conductance process, Ea passing through a maximum value near the region of the solutions maximum density. They have found maxima in Ea for the following systems:- KCl/water (28-30), KCl/D_2O (29) (30), CsCl and LiCl in water (31) and sea water (32). However, maxima were not detected for aqueous systems having HCl (33) and $MgCl_2$ (34) as electrolytes. Horne et al calculated Ea with the Arrhenius equation in conjunction with conductance data obtained from a graph of conductance against temperature (28) (32) (33). The most pronounced maxima in Ea as $f(t)$ were reported for the systems 0.1N KCl/water by Horne and Courant (28) and 0.001N CsCl/water by Horne and Johnson (31). However, in the case of the 0.1N KCl/water system, the earlier measurements of Horne and Courant (28) have been subsequently repeated by Horne and Johnson (29) (30), with the result that the temperature dependence of Ea below 2°C differs markedly, the maximum being far less pronounced in the latter case. Horne and Johnson write of the two studies that "The causes of this discrepancy are not clear, but we feel that the present curve is the more reliable" (35). The marked maximum in Ea for the 0.001N CsCl solution, reported by Horne and Johnson, initiated the measurements on the 0.0013088N CsCl solution reported in this thesis with the result that no maximum in Ea was found between 0° and 9°C, even if the experimental values of the equivalent conductance for this salt were used to calculate Ea from the Arrhenius relationship.

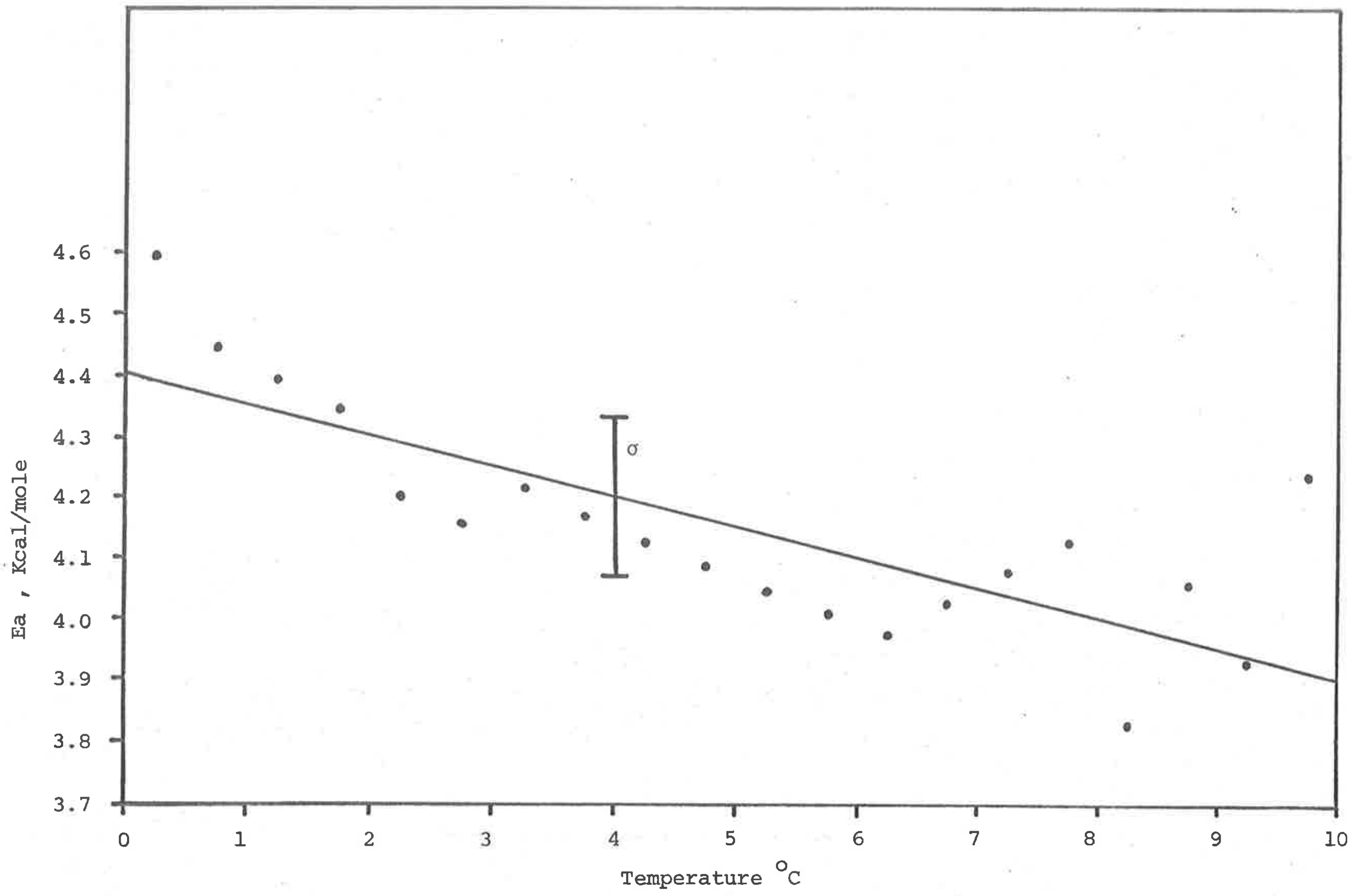
The maxima reported by Horne and Courant (32) for various chlorinity sea water solutions are based upon the data of Thomas, Thompson and Utterback (36). Horne and Courant graphically interpolated conductances followed by the computation of Ea with the Arrhenius equation.

Since no evidence has been found in this present research to support the assignment of a maximum value to Ea, it was considered desirable to re-examine another system in which Horne et al have reported a maximum in the plot of Ea against temperature, using the same data and calculation procedure as described by these authors. Consequently values of Ksp, for the 15% chlorinity sea water data of Thomas et al, were graphically interpolated at 0.5°C intervals between 0° and 10°C. Ea was subsequently calculated with the Arrhenius equation with Ksp-temperature values taken in sequence for the computation. The result is the subject of fig 3.4 on which is also recorded the least squares plot and the standard error of the fit of the data to the linear relationship between Ea and temperature. In contrast to the result reported by Horne and Courant, the assignment of a maximum value to Ea in the temperature region of 0° to 10°C is not justifiable.

The data of Thomas et al, which is the basis of Horne and Courant's findings, consists of measurements at 0°, 5° and 10°C in the temperature range of 0° to 10°C. In order to establish whether

FIGURE 3.4

The temperature dependence of Ea for a 15‰ chlorinity sea water solution derived from the integrated form of the Arrhenius equation, 3.7. The line of best fit of Ea to a linear function of temperature and the standard error of fit, σ, to this relationship is also denoted.


4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
Ea , Kcal/mole
σ
0
1
2
3
4
5
6
7
8
9
10
Temperature °C

a maximum in Ea in this temperature range does exist, a number of conductance measurements at sufficiently small intervals in temperature, in close proximity to the temperature of maximum density of the solution, are required, so that any influence density changes may have upon conductance would be recorded. Hence Horne and Courant's findings can also be discounted for the same reason, since they are based upon three experimental observations only within the temperature region under consideration.

In their respective studies of Ea for viscous flow of water Horne, Courant, Johnson and Morgosian (37) and Korson, Drost-Hansen and Millero (38) have reported no anomalies in the region of maximum density a result which is an accord with the findings of this research for ionic transport in this temperature region. These findings demonstrate that the transport processes are too complex to be rationalised in terms of a single macroscopic property of the solvent. This statement brings to mind the shortcomings of another relationship between conductance and a macroscopic property of the solvent, its viscosity - Walden's Rule.

Upon the basis of the evidence presented in this chapter, the maxima in the energy of activation for the conductance process are not corroborated, but rather Ea decreases linearly with increasing temperature within the temperature region of the maximum density of the solution.

CHAPTER 3

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CHAPTER 4

THE CALIBRATION OF KINEMATIC CAPILLARY VISCOMETERS AND THE VISCOSITY OF WATER BETWEEN 0° AND 60°C

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CHAPTER 4

VISCOMETRY

4.1 Viscometry - its Theoretical Basis

The fundamental equation describing the laminar flow of a Newtonian liquid through a cylindrical tube is that of Poiseuille and Hagenbach (1):

$$\eta = \frac{\pi R^4 t(p_o - p_1)}{8Vl} \qquad 4.1$$

where p_o and p_1 are the pressures at the ends of the tube of length l with a radius R. V is the efflux volume in a time t of a liquid with absolute viscosity η. For a discussion of the assumptions underlying equation 4.1, the reader is referred to reference (1). However, two correction terms, namely, the Hagenbach or Kinetic Energy correction and the Couette correction term, will be discussed here because of their importance in the evaluation of viscometric data.

The Kinetic Energy Correction

Near the entrance and efflux sectors of the tube, the liquid flow has not attained steady state: for example, at the entrance to the tube initial disturbances due to the acceleration of the liquid from rest have not been damped out. Consequently, a correction factor must be applied to account for the dissipation of some of the applied pressure when the liquid accelerates from rest upon entering the tube. Barr (2) expressed the pressure effective in overcoming the viscous forces as

$$p^{eff} = (p_0 - p_1) - \frac{mdV^2}{\pi^2 R^4 t^2} \qquad 4.2$$

d being the liquid density and m a constant whose value is related to the shape of the capillary ends. Replacement of

$(p_o - p_1)$ in 4.1 by this effective pressure p^{eff} yields :

$$\eta = \frac{\pi R^4 t(p_0 - p_1)}{8Vl} - \frac{mdV}{8\pi lt} \qquad 4.3$$

where $(mdV)/(8\pi lt)$ is the Kinetic Energy correction term

The Couette Correction Term

In the derivation of the Poiseuille-Hagenbach equation, it is assumed that the liquid flow is everywhere parallel to the axis of the tube. Related to this assumption is the Couette term (3), which is expressed in terms of a hypothetical increase, Δ, in the length of the capillary, to account for the viscous energy expanded in the formation of the streamlines at the entrance and efflux sectors of the tube.

Equation 4.3 becomes

$$\eta = \frac{\pi R^4 t(p_o - p_1)}{8V(l + \Delta)} - \frac{mdV}{8\pi t(l + \Delta)} \qquad 4.4$$

In the absence of external pressure, the hydrostatic head of liquid in the viscometer is the driving force for liquid flow through the capillary, the pressure term $(p_o - p_1)$ may be replaced by h d g thus:-

$$\eta = \frac{\pi R^4 tdhg}{8V(l+\Delta)} - \frac{mdV}{8\pi t(l+\Delta)} \qquad 4.5$$

h being the mean height of the liquid column and g the gravitational acceleration.

Evaluation of the Kinematic Viscosity

Equation 4.5 can be written in the form

$$\eta = Cdt - Bd/t$$

$$\eta/dt = C - B/t^2 \qquad 4.6$$

Where $C = (\pi R^4 hg)/(8V(1+\Delta))$ and
$B = (mV)/(8\pi(1+\Delta))$

The calibration of conventional (4) capillary viscometers can be achieved by measuring the flow times of a number of liquids of known viscosity and density, followed by a plot of η/dt against t^{-2} as suggested by equation 4.6. If the resulting graph is linear, the kinetic energy correction coefficient, B, which is the observed slope can be regarded as being a constant for the particular range of calibrating liquids used. If, however, the resultant graph of η/dt against t^{-2} is nonlinear, the kinematic viscosity of the test liquid can be evaluated from this plot. Other methods of evaluating B have been discussed by Stokes and Mills (5).

Evaluation of the Kinetic Energy Correction Term.

In principle, given the flow time, a liquid's viscosity can be evaluated from an expression such as equation 4.6, by evaluating the instrument constants B and C from the physical dimensions of the apparatus, and assumed values for m and Δ. Such a fundamental method has been extensively discussed by Swindells, Hardy and Cottington (6) and Swindells, Coe and Godfrey (7). The reader is therefore referred to their texts, in which these authors describe the elaborate procedures required for the determination of a liquid's viscosity by such a method. In practice, except for absolute determination, the Kinetic Energy Correction term is evaluated by the method described in the previous section.

Yet another approach to the problem has been suggested by Caw and Wylie (8), namely, to minimise the Kinetic Energy term by using long flared capillary viscometers. These authors proposed the following form for equation 4.6.

$$\eta/dt = C - K/t^{n+1} \qquad 4.7$$

Where $B = K/t^{n-1}$ 4.8

The value of n was found to depend upon the capillary design. For a conventional capillary, n was found to be unity, while for the longest flared capillary, n had a numerical value of four. Values for intermediate capillary designs ranged between these limits. Caw and Wylie used the function 4.11 to evaluate their experimental results obtained from four instruments, each having two timing bulbs above a common capillary, but a different relationship between the length of the flare and the overall length of the capillary. In the equations which follow a subscript of 1 and 2 denotes a property of the upper or lower timing bulb respectively. Equation 4.7 can be written for each timing bulb thus:-

$$\eta/d = C_1 t_1 - K/t_1^n \qquad 4.9$$

$$\eta/d = C_2 t_2 + K\alpha/t_2^n \qquad 4.10$$

Where α is the ratio defined by

$$\alpha = V_2^n h_1^{\sqrt{(n-1)}} / V_1^n h_2^{\sqrt{(n-1)}} \qquad 4.10b$$

Equations 4.9 and 4.10 can be combined for a given liquid to yield the following expression

$$\frac{C_1 t_1}{C_2 t_2} - 1 = K \left[\frac{(t_2^n / t_1^n) - \alpha}{C_2 t_2^{n+1}} \right] \qquad 4.11$$

Hence a plot of $(C_1 t_1 / C_2 t_2) - 1$ against $((t_2^n / t_1^n) - \alpha)/C_2 t_2^{n+1}$ will have a slope of K the Kinetic Energy correction coefficient.

Figures 3 and 4 of reference (8) are plots for equation 4.11, for which n=1 and 4 are substituted respectively. It can be seen from these graphs, that the slope K is a minimum for the longest flared capillary, independent of the value of n chosen for comparing the four cases on each graph. The final decision, as to whether K can be regarded as being negligible for the long-flared viscometer in question, must be made in conjunction with the comparison of the relative magnitudes of the K/t^n and Ct terms for the flow time t of interest. If the Kinetic energy term is negligible then equation 4.6 can be written as :-

$$\eta = C\,d\,t \qquad 4.12$$

In this eventuality the measurement of the flow time of one liquid, whose viscosity and density are accepted as standards, would evaluate the single instrument constant C, thus eliminating the limitations inherent in the evaluation of K from instrument dimensions including m and Δ required for the evaluation of the Kinetic energy term.

Such a possibility will be examined by evaluating K via Caw and Wylie's function, 4.11, and applying the results to the evaluation of the viscosity of water between 0° and 60°C, using the relationship 4.12.

4.2 Viscometry Experimental

The Photo-electric timing technique used to record the flow times of the test and calibrating liquids in this work has already been discussed in detail by Steel (9). Consequently, only departures from the apparatus recorded in his text are described here.

The Thermostat: a water bath, in which the viscometers were supported upon a levelled frame (9) using the three point locating technique, was regulated within the limits defined in appendix 4.1. The regulating devices used are also recorded. The cooling unit employed has been described in chapter 2.4(a).

Thermometers: these were bomb calorimeter instruments and have already been described in chapter 2.4(a). Prior to the commencement of the calibration of the viscometers, the thermometers used were calibrated against the platinum resistance thermometer.

The Viscometers

The Tilting Viscometer

Principal of Operation

Let us assume that the viscometer has been charged with the required amount of liquid, then, prior to the flow time determination, the viscometer is tilted about its axis from its operating position, fig 4.1, to that depicted in fig 4.2. When the bulbs A and B together with the capillary D, fig 4.3, are filled with liquid, it is returned to its upright position and the viscometric run has commenced.

Description of the Viscometer

This viscometer, of the suspended level type and depicted diagramatically in fig 4.3, was designed principally for non-aqueous solution work. Once filled, repeated flow times could be recorded without exposing the contents to potential water contamination during the flow time measurements. Bulb C had a volume such that, when the instrument was tilted about its axis with the aid of rod R, bulbs A, B and the capillary D were filled with liquid. Further, an air gap existed between bulb C and the remainder of the apparatus at the completion of the liquid's flow time.

FIGURE 4.1

The tilting viscometer depicted in the vertical operating position for the measurement of the flow time of a liquid.

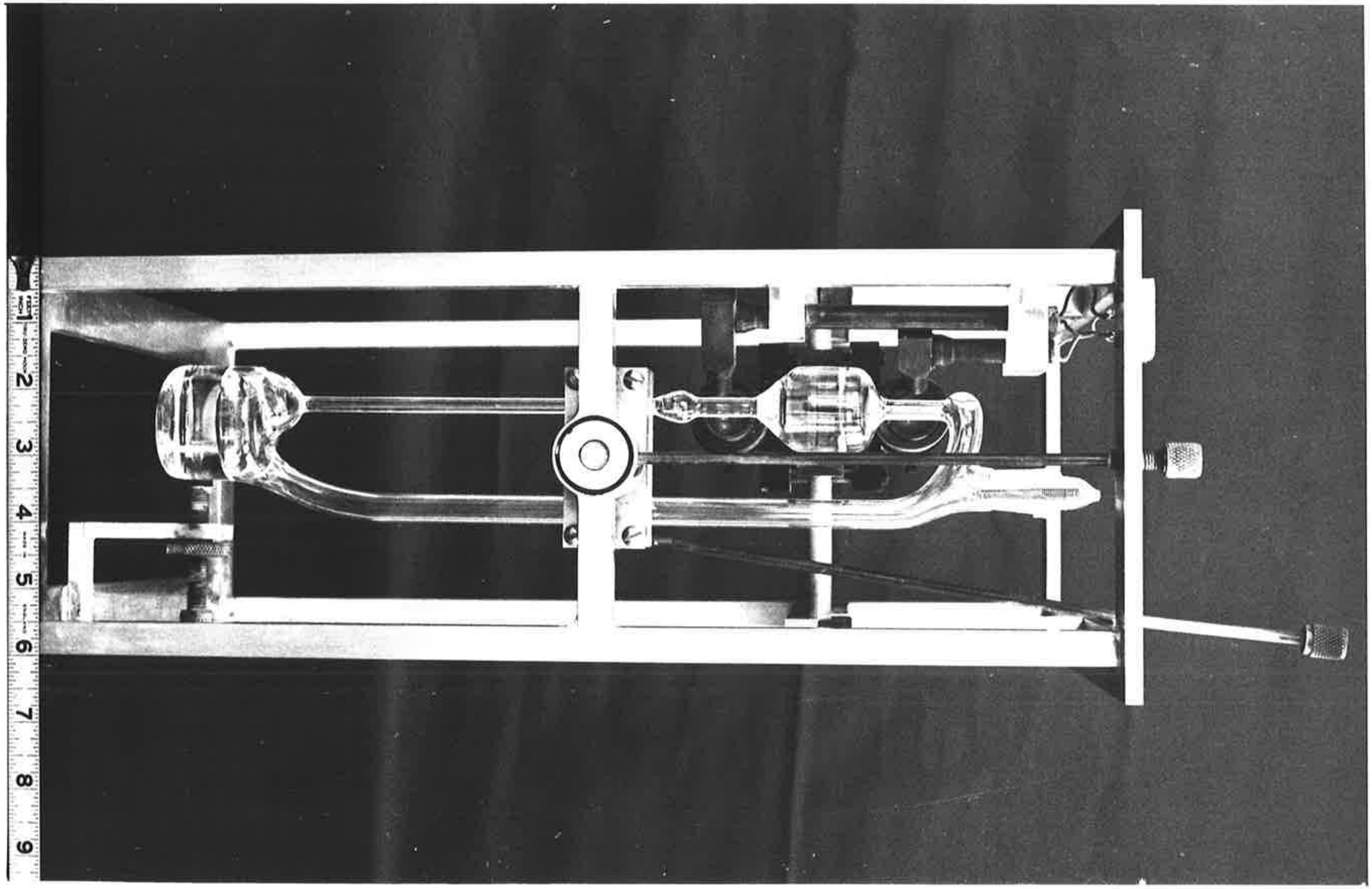


FIGURE 4.2

The tilting viscometer tilted about its axis to charge the viscometer with liquid prior to the measurement of the flow time. Also depicted is the locating stop, S, and the manipulating rod, R.

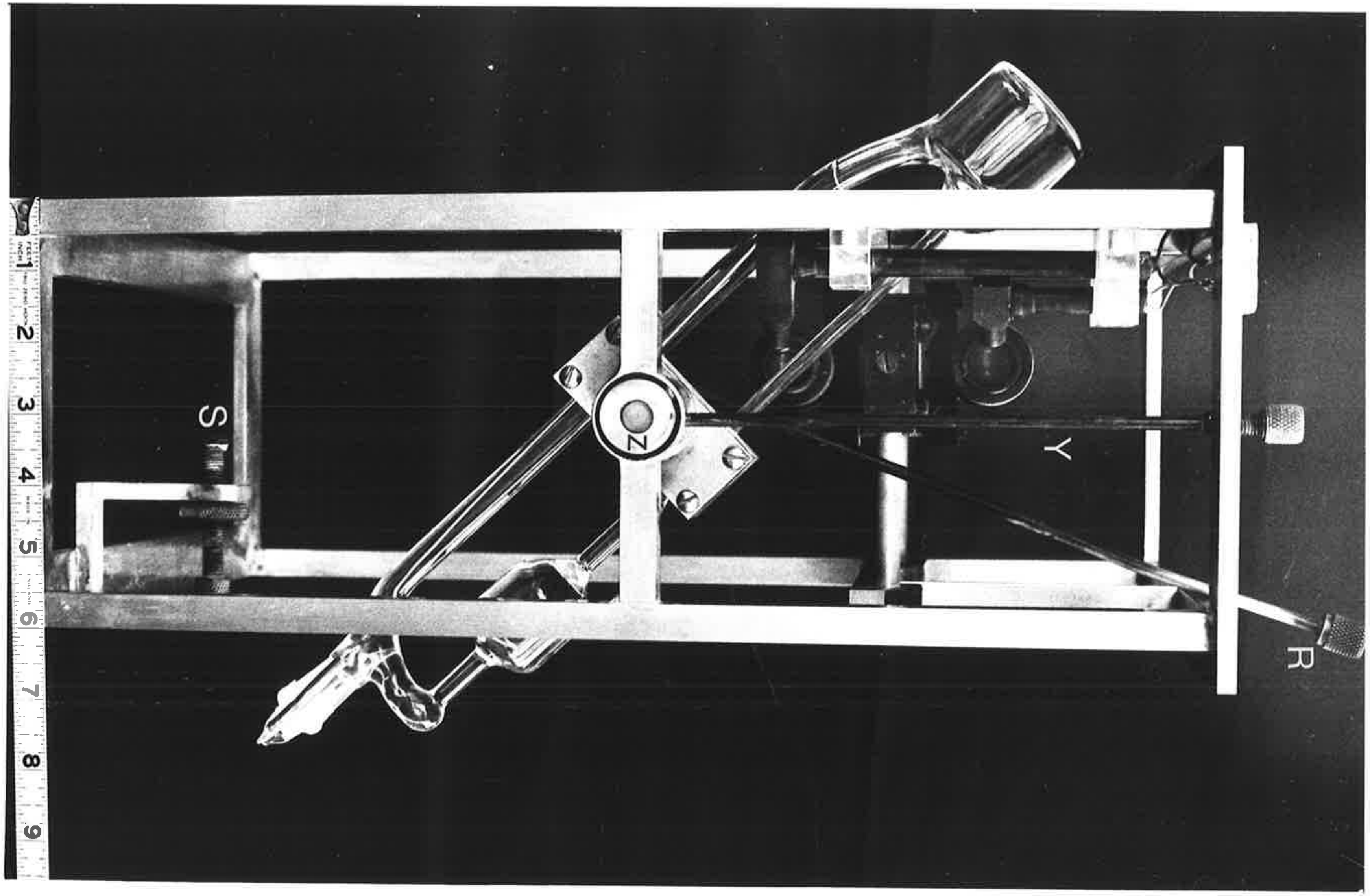
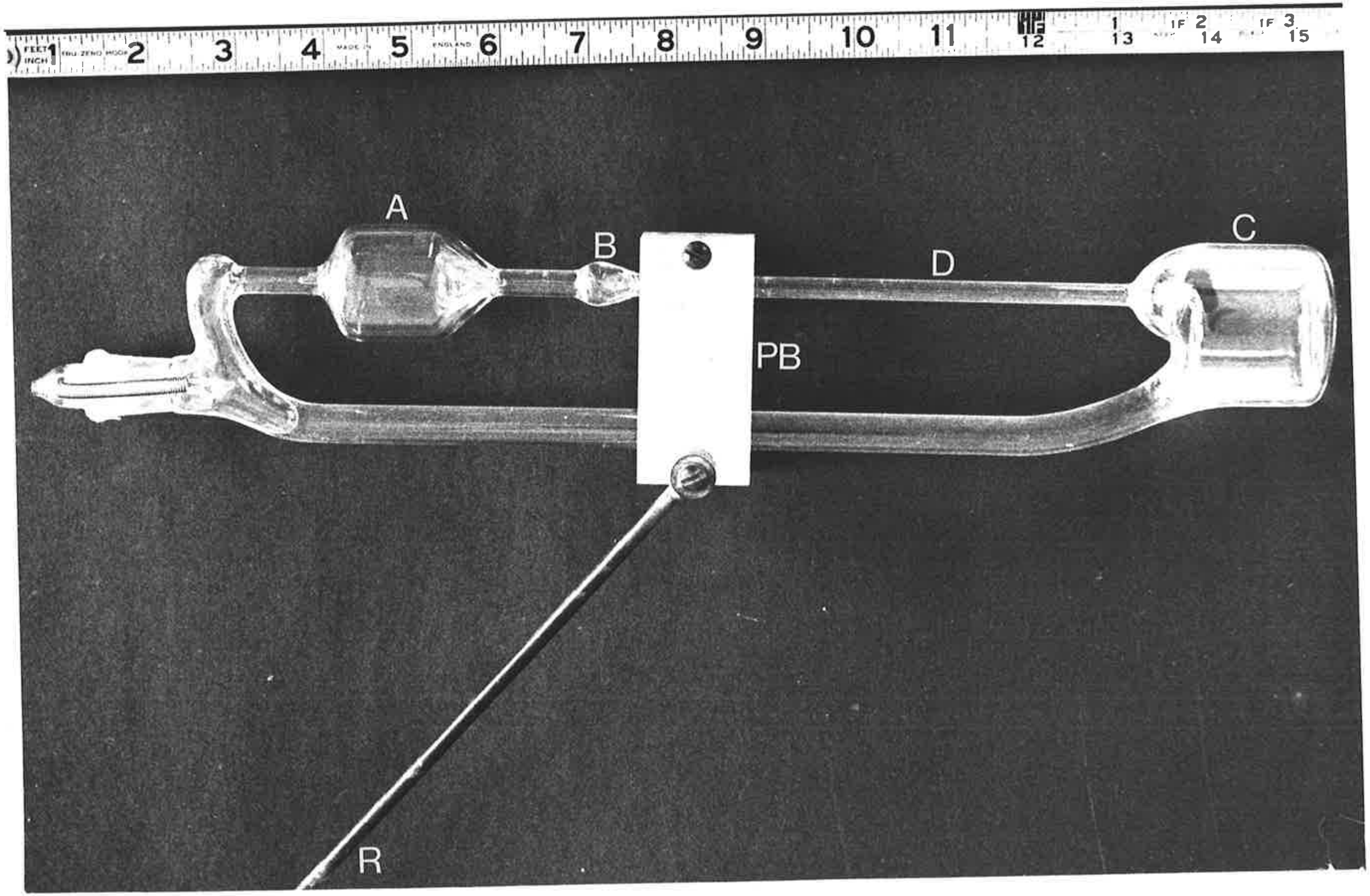

S
Z
Y
R

FIGURE 4.3

The tilting viscometer, removed from its supporting frame, depicting the bulbs A, B and C, the partially flared capillary, D, the split perspex mounting block, PB, and the rod, R, with which the instrument is manipulated between the vertical operating position, figure 4.1, and the filling mode depicted in figure 4.2.


A
B
C
D
PB
R

When the instrument was returned to the vertical operating position, bulb C rested against the stop S, see figs 4.1 and 4.2. Originally, rod Y was intended to lock the viscometer in a reproducible operating position. S, at this stage of development, was a coarse locating device. Once in position, Y was to be tightened, thus locking the viscometer in position by mating with a small hole drilled in the ring Z of fig 4.2. This procedure was abandoned in favour of utilizing the contact of S and bulb C to fix the operating position of the instrument, the two components being held in contact with a humble rubber band (threaded through the steel springs of the stopper assembly and attached to the viscometer supporting frame). The success of this location technique can be demonstrated by examining the flow times recorded for water at 25°C during a period of 18 months, appendix 4.5. The viscometer was supported in a split perspex block, PB, fig 4.3, which was in turn affixed to the axle assembly.

Another departure from (9) was the photo resistor mounting. Rubber "O" rings were used as seals between the resistor housing, CH of fig 4.4, and the resistor. The tops of the tubes T above their perspex block mounts were sealed with aquarium putty. With this arrangement, the system proved water-tight in the temperature range 5° to 60°C over a period of 18 months.

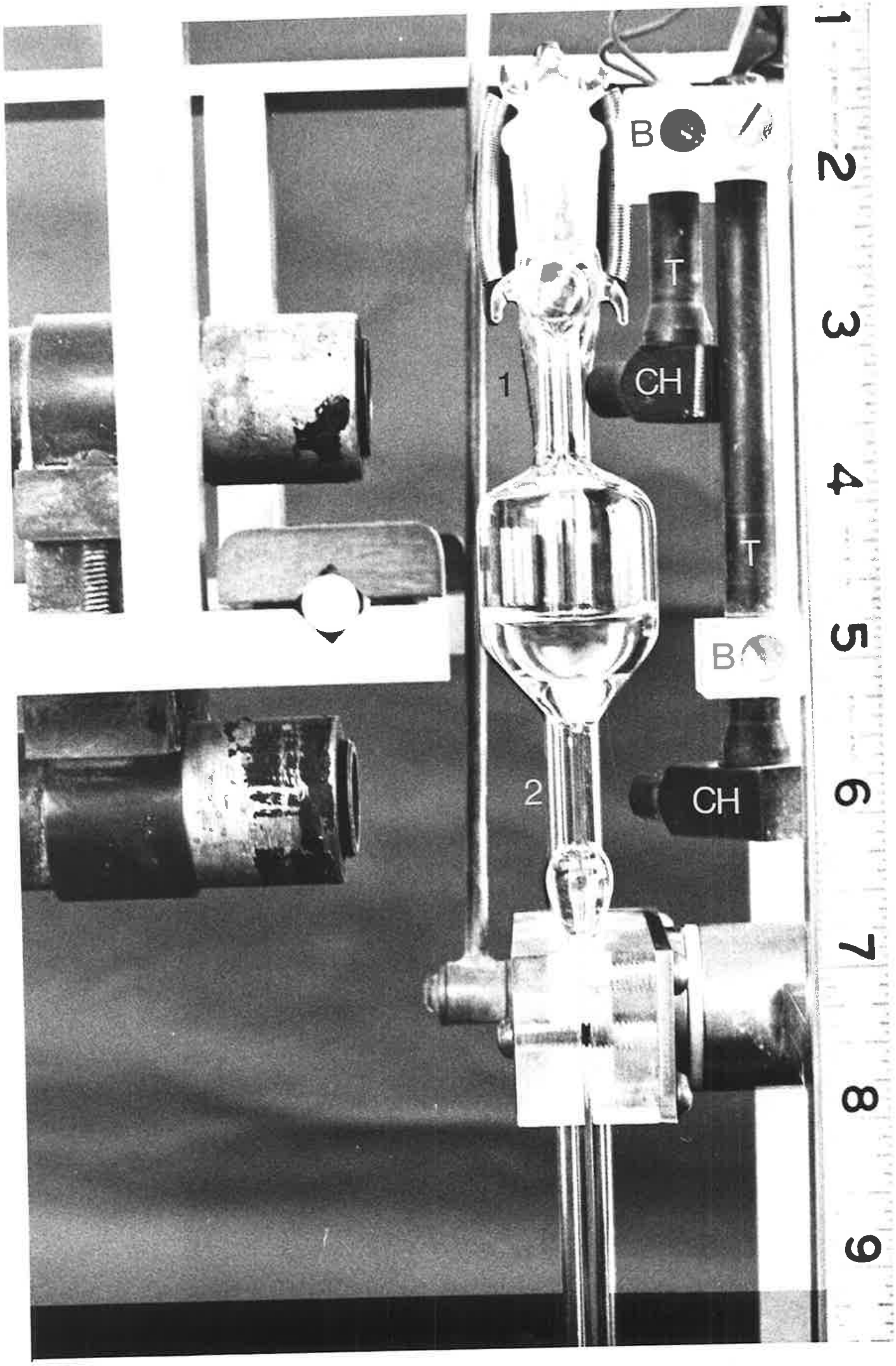
Once the light beams had been focused on the viscometer capillary at points 1 and 2 fig 4.4, the positioning of the photo resistors could be adjusted to intersect the light beams deflected from the capillary, with the aid of the screws mounted in the support blocks. A multimeter was particularly useful in finding the position of minimum resistance of the illuminated resistor.

A partially-flared capillary was incorporated into the instrument. (See fig 1(b) of reference (6).)

Water at various temperatures was chosen as the calibrating liquid for the evaluation of the instrument constants. Further reference will be made to this matter later in this chapter.

FIGURE 4.4

The tilting viscometer mounted in its supporting frame depicting the photo-resistor mounts, CH, their supporting tubes, T, and support blocks, B, together with the positions at which the capillary is illuminated for the upper and lower photo-resistors, points 1 and 2 respectively. The positioning of the photo-resistors, relative to the capillary, can be achieved with the aid of the screws mounted in the blocks, B.


1
2
3
4
5
6
7
8
9
B
T
CH
T
B
CH
1
2

The Double-bulb Ubbelohde Viscometer "PEI"

A second viscometer was employed in this research for the measurement of the flow time of water at 0°, 5°, 20°, 25°, 30°, 35°, 40°, 50° and 60°C. This instrument, which is the subject of fig 4.5, had been used extensively in viscometric studies of some of the alkali halides in 20% sucrose/water solutions by Mulcahy (10), and has been described in detail by this author. It is of the Ubbelohde design incorporating two timing bulbs mounted above a common long-flared capillary. For the mounting of this viscometer in its frame the reader is also referred to reference (9).

Mulcahy recorded flow times for the upper and lower timing bulbs for water, 10% and 20% aqueous sucrose solutions at 25°C. It was felt desirable to undertake a new set of double bulb measurements in order to increase the number of data points and also the range of test viscosities employed. This project required the incorporation of a timing mark to define the end of the liquid's flow time for the lower bulb since Mulcahy used strips of adhesive tape as temporary timing marks in his double bulb experiments. The light beam for the upper bulb's lower photo-resistor shone on the glass capillary which connected the two timing bulbs, marking the commencement of the flow time for the lower bulb. A second timer, of the same design as the one used for the automatic timing of the upper bulb, was manually operated to record the flow times for the lower bulb.

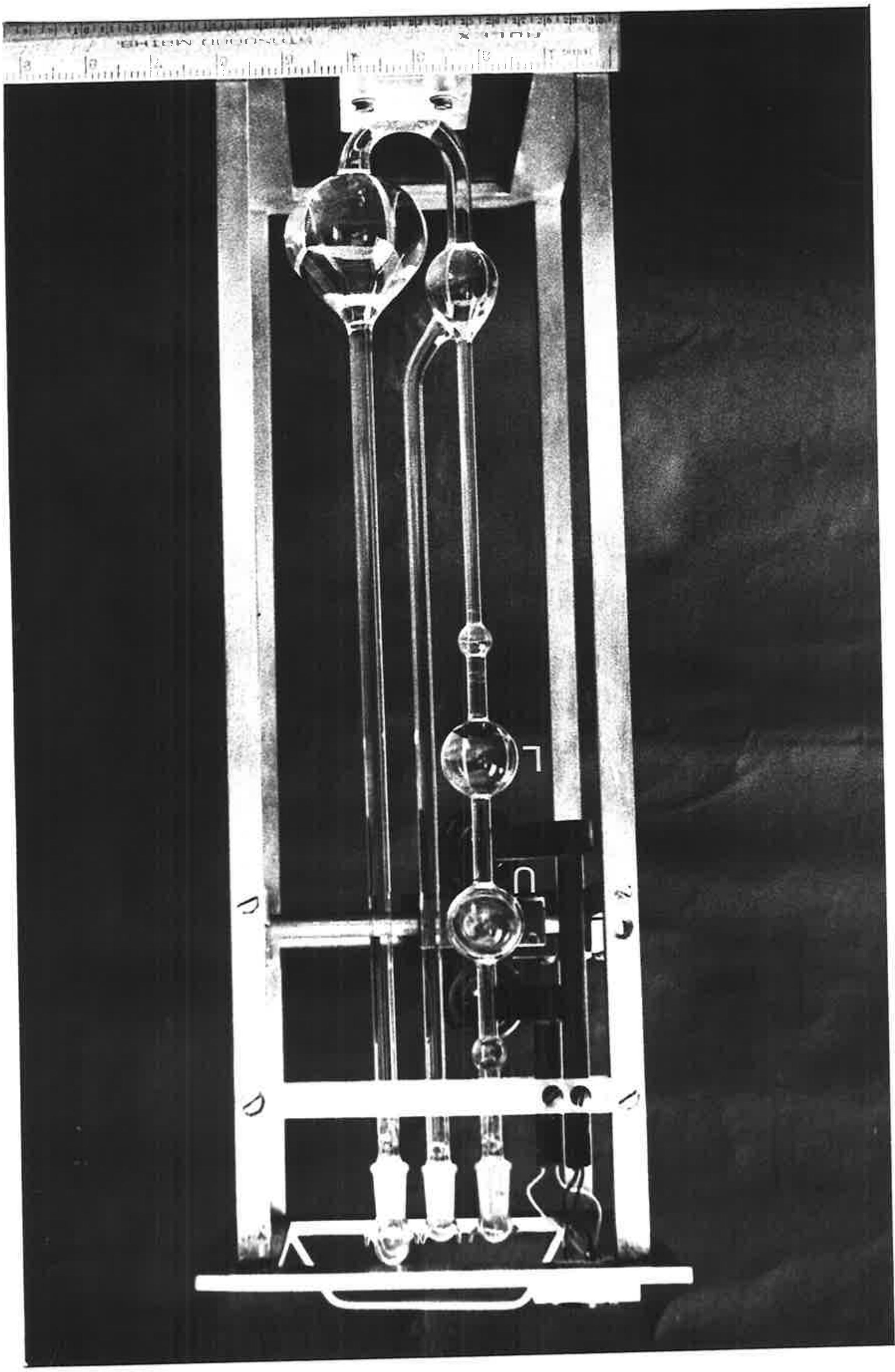
Placement of Liquids Into the Viscometers

All liquids were introduced into the viscometers through funnels incorporating a glass frit of porosity 2. The viscometers were cleaned with chromic acid, leached with deionized water, and finally soaked for several days, with a number of changes of conductance water. When not in use the instruments were filled with conductance water and left standing.

Except for the water calibration runs, the instrument was dried prior to charging by rinsing it several times with redistilled methanol, followed by repeated evacuations with a water aspirator.

FIGURE 4.5

The double-bulb Ubbelohde viscometer PEl depicting the upper and lower timing bulbs, U and L respectively.



Precautions were taken to shield pure DMF from atmospheric moisture while the viscometer was being filled. Once the liquid was in the filtering funnel on the viscometer, it was isolated from the atmosphere with guard tubes containing fused calcium chloride.

In the case of water and the water/DMF mixtures, the liquid was introduced into the viscometer through the filtering funnel without the attachment of the guard tubes to the funnel. At least three rinsings of the viscometer were undertaken before the sample to be investigated was sealed in the instrument. In many instances, the measurement was repeated on another sample of liquid.

Once the required volume of liquid was in the viscometer the stopper was sealed in place with Parafilm and a pair of steel springs. Contamination of the test liquid by the thermostat medium during the refilling cycle that followed the flow of the liquid through the capillary was thus prevented. For flow time measurements other than 25°C the viscometer was allowed to equilibrate with the bath, during which time the stopper was quickly removed and replaced several times. This procedure allowed the attainment of equilibrium between the liquid and its vapour at atmospheric pressure and at the temperature of the viscometric determination. The viscometer was removed from the bath, sealed and replaced in the thermostat.

The viscosity of DMF and its mixtures with water will be presented in chapter 5.

The Flow Time

The measurement of this quantity was repeated until at least four consecutive values were obtained which agreed within 0.01%. This usually involved disregarding the initial two readings recorded whilst equilibration was in progress. Later values during a run, with the rare exception, came well within the above tolerance.

4.3 Discussion

The kinetic energy correction coefficient, K, for capillary viscometers can be evaluated in several ways, from the slope of a calibration plot of η/dt against t^{-2} for example. However, of prime interest in this research is the use of the Caw and Wylie (8) function 4.11, a method which has yet to be employed in the evaluation of K with the aim of determining the viscosity of a test liquid to a precision comparable with that of the absolute viscosity of water at $20^{o}C$ (7). By conducting double-bulb flow time measurements over the range of test viscosities, K for the viscometer can be determined over this spectrum of flow times on the basis of the viscosity of one liquid which is required for the evaluation of the instrument constants C_1 and C_2.

Flow times for the two timing bulbs of PE1 were recorded at the temperatures indicated in table 4.1. The physical dimensions of PE1 required for the computation of K using 4.11 are: $V_1 =$ 10.496 cm^3, V_2 = 11.072 cm^3, h_1 = 23.0 cm, h_2 = 16.5 cm and l = 11.3 cm.

Table 4.2 summarizes the method used to compute the instrument constants C_1 and C_2 prior to the evaluation of K with $n = 1$ in 4.11. The value of K, its standard error σK and the standard error of the fit of the data to the linear plot, σ, are also recorded in this table. The functional data required for the evaluation of K for the last iteration are recorded in appendix 4.2. Appendix 4.3 is a graphical representation of these data which shows the least squares plot and σ.

Caw and Wylie found that the substitution of $n = 4$ in 4.11 provided a better representation of their data for long-flared capillary viscometers similar to PE1. This point can also be investigated using the double-bulb flow time data recorded in this research. With $n = 4$ in 4.11 $K = 7.94\text{x}10^4$, $\sigma K = 7.28\text{x}10^4$ and $\sigma =$ $1.078\text{x}10^{-4}$ computed via steps (a) to (d) of table 4.2. The data required for the evaluation of K has been recorded in appendix 4.4. σK is as large as K itself, a situation identical for the Caw and

TABLE 4.1

Temp. °C	Flow times, in seconds, for water in viscometer PE1		The kinetic energy correction term as a percentage of the C term* for viscometer PE1	
	Upper Bulb	Lower Bulb	Upper Bulb	Lower Bulb
0	1591.53 ± 0.04	2316.15 ± 0.06	0.011	0.007
5	1350.80 ± 0.03	1966.07 ± 0.05	0.014	0.011
20	892.85 ± 0.02	1299.37 ± 0.03	0.033	0.024
25	794.44 ± 0.02	1155.89 ± 0.06	0.042	0.031
30	712.74 ± 0.02	1037.16 ± 0.05	0.052	0.038
35	643.70 ± 0.03	936.79 ± 0.04	0.064	0.046
40	585.55 ± 0.02	852.09 ± 0.07	0.078	0.057
50	492.84 ± 0.02	717.13 ± 0.04	0.11	0.082
60	422.76 ± 0.01	-	0.15	-

* $C_1 = 1.1243\text{x}10^{-5}$, $C_2 = 7.725\text{x}10^{-6}$, $K = 0.003$ and

$\alpha = 1.05_5$

TABLE 4.2

Computation of the Kinetic Energy Correction Coefficient, K, for Viscometer PE1 According to Equation 4.11

(a) α is computed from equation 4.10b.

(b) Let $^{*}K = 0.0$

(c) C_1 and C_2 are computed from equation 4.12 given η, t_1, t_2 and d for water at 20°C.

$$C_1 = 1.1243\text{x}10^{-5} \quad \text{and} \quad C_2 = 7.725\text{x}10^{-6}$$

(d) Given t_1 and t_2, a value of x and y can be computed for each temperature according to:

$$y = (C_1t_1/C_2t_2)-1 \text{ and } x = (\{t_2^n/t_1^n\}-\alpha)/C_2t_2^{n+1}$$

From 4.11 K is the slope of the resultant linear plot of y against x. K was evaluated by the method of least squares and found to be for n = 1:

$$K = 1.834\text{x}10^{-3} \text{ with } \sigma K = 1.276\text{x}10^{-3} \text{ and } \sigma = 1.023\text{x}10^{-4}$$

(e) Re-arrange equations 4.9 and 4.10 and compute C_1 and C_2 using the value of K evaluated in part (d). Steps (d) and (e) repeated until K constant:final values

$$K = 1.836\text{x}10^{-3} \text{ with } \sigma K = 1.231\text{x}10^{-3} \text{ and } \sigma = 9.911\text{x}10^{-5}$$

---

* An alternative approach computes an initial value for K, when n = 1, from equations 4.6 and 4.8 setting $\Delta = 0.0$ and $m = 1.12$ (reference 6) C_1 and C_2 are computed from equations 4.9 and 4.10. Final values from steps (d) and (e) are:

$$K = 1.842\text{x}10^{-3} \text{ with } \sigma K = 1.279\text{x}10^{-3} \text{ and } \sigma = 1.029\text{x}10^{-4}$$

Wylie functional plot obtained with n = 1 in 4.11. Further, σ differs insignificantly for the two representations, i.e. n = 1 and n = 4. It appears from the above analysis that the use of n = 4 in equation 4.11 offers no advantage over n = 1 as a representation of the data. We shall return to this point at a later stage in this discussion.

A very important point can be made, however, upon the basis of n = 1 in equation 4.11. By accepting $3.0\text{x}10^{-3}$ as an estimate of the maximum value of K, i.e. $K+\sigma K$, values of the Kt_1^{-2} and αKt_2^{-2} terms for water at 20°C are obtained which are 0.033% and 0.023% of C_1 and C_2 respectively. The kinetic energy correction terms can be neglected since they are small relative to the respective C terms. Therefore, the instrument constants C_1 and C_2 of the two bulbs can be evaluated at 20°C from equation 4.12. Table 4.1 contains values of the Kt_1^{-2} and αKt_2^{-2} terms expressed as a percentage of the corresponding C terms for water between 0° and 60°C. The values of C_1, C_2 and K used in the construction of this table have been described in this paragraph and are summarized at its base, together with the value of α. From this table it is evident that given C_1 and C_2 the viscosity of a liquid can be evaluated to a precision of better than 0.1% by neglecting the kinetic energy correction term for flow times greater than t_1 for water at 50°C. Since $K+\sigma K$ was used to compute the magnitude of Kt^{-2} relative to the C terms, the contribution quoted in table 4.1 can be regarded as a maximum value. Consequently, the lower limit of the flow time for which the kinetic energy term can be neglected is probably more like t_1 for water at 60°C. It should be noted that the kinetic energy correction term when expressed as a percentage of the C terms for a given value of t, is smaller when n = 4 than when n = 1.

The negligibility of the kinetic energy correction term has some very interesting implications. The absolute determination of the viscosity of water at 20°C by Swindells, Coe and Godfrey (7) has been confirmed by an independent determination by Roscoe and Bainbridge (11). Acceptance of this standard yields, in conjunction with the flow times and the density of water at 20°C the instrument constants C_1 and C_2 of PE1 according to the relationship:

$$\eta/dt = C \qquad 4.12$$

Given, then, the flow time and the density of a test liquid, its viscosity can be evaluated from 4.12. It must be emphasised that this approach to the determination of liquid viscosities, based only upon the measurements of Swindells et al (7), is the soundest yet proposed. It does not require the estimation of values for the constants m and Δ that appear in equation 4.5 for the viscosity η. Ultimately, knowledge of these constants is essential for the evaluation of the kinetic energy correction term for conventional viscometers (6) (7). Acceptance of standards other than the 20°C value presupposes the correct estimation of m and Δ used in their derivation. Furthermore, this approach does not require the dimensions of the instrument to a precision comparable with that required for an absolute viscosity determination (7).

Presented in table 4.3 is the viscosity of water between 0° and 60° evaluated upon the basis described in the preceding paragraph using the double-bulb flow times recorded in table 4.1 and the density data for water given in table 4.4. Since the precision of the flow times is better than 0.01% and the density of water is even more accurately known, the factors limiting the precision of the measurements will be the viscosity of water at 20°C and the magnitude of the kinetic energy correction term. Also recorded in table 4.3 are values for the viscosity of water arising from studies by the National Bureau of Standards of the United States of America (7) (12) (13), Weber (14), Korson, Drost-Hansen and Millero (15) and values appearing in compilations by Cragoe (12) and Robinson and Stokes (16). It can be observed from table 4.3 that the agreement between the values obtained in this research and the remainder of these data is within 0.1% between 25° and 40°C. Having considered the magnitude of the correction term it was concluded that the viscosity of water between 0° and 50°, and probably 60°, evaluated in this research had a precision of better than 0.1%.

TABLE 4.3

THE VISCOSITY OF WATER, IN cP, AT VARIOUS TEMPERATURES

Temp. °C	Hardy and Cottington	Coe and Godfrey	Cragoe	Swindells	Weber **	Korson et al	Robinson and Stokes	This Research Viscometer PE1	
								Upper Bulb	Lower Bulb
0	-	-	1.7865	-	1.793	1.7916	1.787	1.789_3	1.788_9
5	1.5184	-	1.5170	-	1.521	1.5192	1.516	1.518_6	1.518_7
20	(1.002)	(1.002)	(1.002)	(1.002)	(1.002)	(1.002)	(1.002)	(1.002)	(1.002)
25	-	0.8903	0.8903	0.8903	0.8903	0.8903^*	0.8903	0.890_5	0.890_3
30	-	0.7976	0.7975	-	0.7975	0.7975^*	0.7975	0.797_8	0.797_7
35	-	-	-	-	0.7189	0.7195	0.7194	0.719_3	0.719_3
40	0.6531	0.6531	0.6531	0.6526	0.6530	0.6532^*	0.6531	0.653_1	0.653_1
50	-	-	0.5471	0.5467	-	0.5471^*	0.5467	0.547_5	0.547_4
60	0.4665	-	0.4668	0.4666	-	0.4666^*	0.4666	0.467_3	-

* Viscometer calibrated by using N.B.S. data at these temperatures.

** Experimental values, table 1 of reference (14).

Further evidence to support this conclusion will be presented later in this chapter.

The reliability of the 0° and 5° values of this research can be further demonstrated in conjunction with an investigation of the value of n to be used in equation 4.7 for PE1 and the tilting viscometer respectively. Tables 4.4 and 4.5 present the viscosity data required for the computation of values of η/dt required for the analysis to follow. Literature viscosity data were drawn from table 4.3, with the exception of the 0° and 5° values which are from this research. Viscosity data in table 4.5 are also from this research. Flow time data for the tilting viscometer are recorded in appendix 4.5.

Using the linear regression program PUTT values from table 4.4 of η/dt_1 corresponding to 20°C and higher were fitted to equation 4.7 with n = 1, 2, 3 and 4. This data for PE1 was re-submitted to PUTT with the inclusion of the 0° and 5° values derived from the viscosity of water at these temperatures evaluated in the present research. The values of C_1, σC_1, K, σK and σ for each value of n substituted into equation 4.7 are presented in table 4.6. From table 4.6 it can be seen that for each value of n C_1, K and σ are effectively unaltered by the inclusion of the additional 0° and 5° values. Since the standard error of fit, σ, is less than 0.1% of the η/dt_1 term in either case it is concluded that the viscosity of water at 0° and 5°C obtained in this research can, as proposed earlier, be considered accurate to within 0.1%, the quoted accuracy of one of the N.B.S. sets of data being 0.1% (13). By examining the value of σ for the fit of the data to equation 4.7 for different values of n it can also be concluded that the four representations of the data are equivalent within the quoted uncertainties of the tabulated viscosities of water. Hence, although such a step is unnecessary because the kinetic energy correction term has been shown to be negligible, the instrument constants for PE1 could be evaluated by using a value of n from 1 to 4 in equation 4.7.

The computations just described for PE1 were repeated for the

TABLES 4.4 AND 4.5

VALUES OF η/dt FOR THE TILTING VISCOMETER AND PE1 FOR WATER BETWEEN 0° AND 60°C

Temp. °C	TABLE 4.4					TABLE 4.5	
	Literature Values	Density≠	Viscometer PE1		Tilting Viscometer	This Work	Tilting Viscometer
	ηcP	g/cm³	η/dt_1	η/dt_2	η/dt	ηcP	η/dt
0	$(1.789_1)^*$	0.99984	(1.1243)	(7.725)	-	1.789_1	-
5	$(1.518_6)^*$	0.99996	(1.1243)	(7.725)	(1.4478)	1.518_4	1.4478
20	(1.002)	0.99820	1.1243	7.725	1.4471	$(1.002)^{**}$	1.4471
25	0.8903	0.997047	1.1240	7.725	1.4459	0.890_4	1.4461
30	0.7975	0.99565	1.1238	7.724	1.4453	0.797_8	1.4458
35	0.7195	0.99403	1.1242	7.724	1.4445	0.719_3	1.4445
40	0.6531	0.99221	1.1241	7.725	1.4442	0.653_1	1.4442
50	0.5467	0.98804	1.1227	7.716	1.4398	0.547_4	1.4417
60	0.4666	0.98321	1.1225	-	1.4353	0.467_3	1.4375

* This Research; ** Reference 7; ≠ Reference 16.

TABLE 4.6

VALUES OF THE COEFFICIENTS OF EQUATION 4.7 FOR n = 1, 2, 3 AND 4 FOR VISCOMETER PE1

n	Temperature Range °C	C_1	σC_1	K	σK	σ
1	20 - 60	1.1249 E - 5	2.95 E - 9	-4.336 E - 3	9.30 E - 4	3.51 E - 9
1	0 - 60	1.1247 E - 5	1.93 E - 9	-3.721 E - 3	6.87 E - 4	3.29 E - 9
2	20 - 60	1.1245 E - 5	2.13 E - 9	-1.593 E + 0	3.28 E - 1	3.39 E - 9
2	0 - 60	1.1244 E - 5	1.40 E - 9	-1.522 E + 0	2.43 E - 1	2.92 E - 9
3	20 - 60	1.1243 E - 5	1.86 E - 9	-6.278 E + 2	1.31 E + 2	3.44 E - 9
3	0 - 60	1.1243 E - 5	1.25 E - 9	-6.322 E + 2	1.01 E + 2	2.91 E - 9
4	20 - 60	1.1242 E - 5	1.78 E - 9	-2.539 E + 5	5.62 E + 4	3.60 E - 9
4	0 - 60	1.1242 E - 5	1.26 E - 9	-2.626 E + 5	4.50 E + 4	3.10 E - 9

tilting viscometer using the values of η/dt recorded in table 4.4. The values of C, K and σ, table 4.7, for a given value of n are unaltered by the addition of the 5° value computed from the viscosity of water at that temperature evaluated in this research. σ for the tilting viscometer data is in each case less than 0.1% of η/dt. Consequently, the viscosity of water at 5° must have a precision of better than 0.1%. It should be noted that no flow time measurement was made at 0° with the latter instrument. It is apparent from table 4.7 that the best representations of the data for this viscometer correspond to $n = 2$ and 3. However, for all representations, i.e. $n = 1$ to 4, the standard error of fit is less than 0.1% of η/dt. As a consequence the representations can not be distinguished within the error of the tabulated viscosities of water.

Caw and Wylie define the value of n as being that which linearises the plot of the L.H.S. of equation 4.11 against the R.H.S.. It will be recalled that, for PE1, σ for the Caw and Wylie plots for $n = 1$ and 4 were similar, being $9.911\text{x}10^{-5}$ and $1.078\text{x}10^{-4}$ respectively; consequently either value of n satisfies the definition of this quantity according to Caw and Wylie for the range of flow times studied with PE1. The same significance should be attached to n in the investigation of η/dt as a function of $1/t^{n+1}$. Since for both PE1 and the tilting viscometer σ for the fit of η/dt as a function of $1/t^{n+1}$, with $n = 1$ to 4, is less than the quoted error in the tabulated viscosities, it is concluded that the instrument constants C and K can be determined from equation 4.7 with $n = 1$, 2, 3 or 4 because each value of n is equally applicable according to the definition of n as proposed by Caw and Wylie.

In addition, values of η/dt for the tilting viscometer evaluated from the viscosity of water between 5° and 60°C obtained in the present research and recorded in table 4.5 were expressed as a function of $1/t^{n+1}$ according to equation 4.7. The results of this analysis are recorded in table 4.8. In other words the instrument constants of the tilting viscometer have now been evaluated to a

TABLE 4.7

VALUES OF COEFFICIENTS OF EQUATION 4.7 FOR n = 1, 2, 3 AND 4 FOR THE TILTING VISCOMETER

n	**Temperature** Range °C	C	σC	K	σK	σ
1	20 - 60	1.4508 E - 5	6.04 E - 9	-1.63 E - 2	1.16 E - 3	7.13 E - 9
1	5 - 60	1.4502 E - 5	5.69 E - 9	-1.53 E - 2	1.16 E - 3	8.24 E - 9
2	20 - 60	1.4483 E - 5	3.01 E - 9	-4.68 E + 0	2.20 E - 1	4.75 E - 9
2	5 - 60	1.4483 E - 5	2.37 E - 9	-4.66 E + 0	1.85 E - 1	4.36 E - 9
3	20 - 60	1.4471 E - 5	2.86 E - 9	-1.44 E + 3	7.54 E + 1	5.27 E - 9
3	5 - 60	1.4473 E - 5	2.68 E - 9	-1.48 E + 3	7.56 E + 1	5.61 E - 9
4	20 - 60	1.4464 E - 5	3.70 E - 9	-4.58 E + 5	3.41 E + 4	7.47 E - 9
4	5 - 60	1.4467 E - 5	3.82 E - 9	-4.75 E + 5	3.76 E + 4	8.59 E - 9

TABLE 4.8

VALUES OF COEFFICIENTS OF EQUATION 4.7 FOR n = 1, 2, 3 AND 4 FOR THE TILTING VISCOMETER, BASED ON THE VISCOSITY OF WATER - THIS RESEARCH.

n	Temperature Range °C	C	σC	K	σK	σ
1	5 - 60	1.4495 E - 5	3.69 E - 9	-1.237 E - 2	7.55 E - 4	5.35 E - 9
2	5 - 60	1.4480 E - 5	1.65 E - 9	-3.745 E + 0	1.29 E - 1	3.05 E - 9
3	5 - 60	1.4472 E - 5	2.42 E - 9	-1.184 E + 3	6.82 E + 1	5.06 E - 9
4	5 - 60	1.4467 E - 5	3.37 E - 9	-3.798 E + 5	3.32 E + 4	7.58 E - 9

precision which permits the evaluation of a test viscosity to better than 0.1%, for flow times corresponding to those for water between 5° and 60°, by utilizing the results of the viscometric investigation undertaken in the present research. By reference to table 4.8 support can be gained for the previous assertion of the precision of the viscosity data obtained in the present study. A comparison of the magnitude of σ for $n = 1$ to 4 with η/dt reveals that the internal consistency of the viscosity data obtained in the present research between 5° and 60°C is better than 0.1%. Since the 20°C value of Swindells et al is included in these data, the precision of the remaining data, including the 60° value, follows axiomatically.

CHAPTER 4

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CHAPTER 5

DMF - ITS PURIFICATION AND SOME PROPERTIES OF ITS MIXTURES WITH WATER

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CHAPTER 5

5.1 Introduction

A review of some of the chemical properties of DMF, that have been presented in the literature, should shed some light upon the possible impurities present in this compound and what is therefore required of a purification procedure. Further, an insight into some of the possible properties of DMF/water mixtures could also be gleaned from a survey of the relevant literature. A description of the two DMF purification procedures used in this research will be followed by a comparison of the DMF/water mixtures, subsequently prepared by each method, from the point of view of their viscosities, densities and as solvents for conductance studies. The experimental results of the density and viscometric studies of the DMF/water system will also be presented.

5.2 The Purification of DMF

5.2(a) Purification Methods - A Review

Perhaps the dominating chemical property of the amides, which is of significance in this research, is their susceptibility to hydrolysis. This reaction, while proceeding slowly in neutral solution, increases rapidly in acidic or alkaline media with the formation of a carboxylic acid and an amine (1). With regard to DMF, Philipp et al (2) and Tury'an et al (3) have suggested that, as a result of hydrolysis, formic acid and dimethylamine are present in solution; while Moskalyk et al (5) have only proposed that formic acid is an impurity in DMF. In addition DMF as received contains water as another impurity. Oehme (4) has proposed that photolytic decomposition is the source of impurities in DMF, dimethylamine and formaldehyde being the products. Deal et al (6) have further widened the scope of the source of impurities by suggesting that formamide and N-methylformamide are present in commercial grade DMF, together with their hydrolysis products. Presumably these amides are byproducts in the synthesis of DMF itself.

Ample evidence has been accumulated to show that DMF is unstable in the presence of acidic and basic materials. Thomas et al (7), Moskalyk et al (5) report its instability under both these conditions while the observations of Allen et al (8) and Deal et al (6) are restricted to the behaviour of DMF in basic media. Buncel et al (9) have recently reported that aqueous DMF solutions are unstable in the presence the hydroxyl ion, with formate ion and dimethylamine being the products of decomposition. The findings of these latter authors confirm the earlier suggestion of Deal et al, who proposed that formate ion was produced under alkaline conditions in DMF itself.

DMF decomposes slightly at its normal boiling point, resulting in the formation of carbon monoxide and dimethylamine (7) (5). Distillation, therefore, must be undertaken at reduced pressure. Butler (10) has cited the findings of others who recommend that distillation must be carried out at pressures less than 1 mm of Hg to avoid the thermal decomposition of the formamides.

Thomas et al (7) have studied a number of purification procedures and found that DMF placed over solid KOH and CaH_2 at room temperatures, even for a few hours, caused decomposition of DMF giving a "considerable amount" of dimethylamine as a product. However, we can conclude from the work of Zuagg et al (11) that the dimethylamine formed would be removed during the distillation procedure from the following evidence to be found in their paper. Their purification procedure consisted in shaking benzene dry DMF with P_2O_5, decanting the DMF and shaking with KOH pellets then distilling it under reduced pressure. Now, according to Thomas et als' findings, dimethylamine would be formed, yet from the analysis of the purified DMF Zuagg reports no titratable acidic impurities and $<7\times10^{-6}$M dimethylamine to be present. Thus, we can conclude that the latter compound is removed during the distillation procedure. Consequently CaH_2 and KOH could be used to remove formic acid and water from DMF. From the work of Ritchie et al (12) we can also conclude, as from the work of Zuagg et al, that the use of P_2O_5 as a purifying agent is not detrimental when the utilization of this reagent is examined from the point of view of the final DMF obtained. Ritchie et al dried DMF with molecular sieves and distilled the DMF at reduced pressure over P_2O_5. The product obtained was $<5\times10^{-6}$M in acidic or basic impurities. The conclusion to be drawn from the work of Thomas et al, Zuagg et al and Ritchie et al, is that although KOH or P_2O_5 may cause decomposition of the DMF, these impurities do not finally contaminate their purified product.

Thomas et al reasoned that simple vacuum distillation will not remove water from DMF. Their proposal has since been confirmed by the work of Susarev (13) and Ivanova et al (14) who found that for various DMF/water mixtures, distilled under varying pressures, the distillate was always both components. Hence, we can conclude that water must be removed prior to distillation.

From the above review we have seen that, in addition to water, the principal impurities in commercial grade DMF are formic acid and dimethylamine. Further it can be tentatively concluded that KOH and P_2O_5 can be used in the purification of DMF provided the concentration of water is reduced, prior to the use of these chemicals, to lessen the rate of hydrolysis which, in the presence of water, they would catalyse. Since Zuagg et al also report that purified DMF, which was allowed to stand under an atmosphere of dry nitrogen, gradually accumulated dimethylamine DMF should therefore be purified just prior to use.

It can also be concluded that the rate of hydrolysis of DMF in the presence of water and basic or acidic materials is increased. More relevant however, in this work would be the instability of DMF/water mixtures resulting from acidic or basic impurities that remain in the DMF after its purification.

Since there is a diversity of purification procedures reported in the literature, a review of some of them at this point is desirable; a few examples of each procedure will be cited.

In some instances DMF is used "as received" (15)(16); in others no details are reported (17) (18); while others again use a single or multistep purification procedure. The simplest method is distillation under reduced pressure (19-22). Other workers have relied upon a chemical reaction to remove some of the impurities from DMF followed by distillation at reduced pressure.

Some reagents that have been used are KOH (13)(23-25), CaO (26-28), CaH_2 (29), Na_2CO_3 (30), calcium carbide (31): yet others report a combination of chemicals, e.g. KOH and P_2O_5 (32) (33) and CaO and KOH (34).

Molecular sieves (35) have recently been preferred (10) to chemical treatment to remove impurities present in the formamides, due to their susceptibility to decomposition and hydrolysis in the presence of either acidic or basic compounds. In one instance, DMF was stood over sieves before use (36), and in others distillation followed this step (37) (38).

Ion exchange resins have been used with (39) or without (5) the use of molecular sieves in the purification procedure used.

Anhydrous $CuSO_4$ (10) has been reported to dehydrate amides with an added advantage of complexing with amines.

In the case of DMF, upon the basis of this review to date, there appears to be doubt as to which general purification procedure is the better one; whether, for example, to remove water and other impurities with acidic and/or basic reagents or to use molecular sieves and anhydrous $CuSO_4$ thus lessening the risk of decomposition of DMF since it will not then be subjected to compounds which are known to decompose it. Consequently, it was decided to use both types of purification procedure.

5.2(b) The Purification of DMF-Experimental

In the first method Unilab laboratory reagent DMF was stored over B.D.H. calcium hydride for several days with intermittent shaking, followed by fractional distillation under reduced pressure, <1.0 mm Hg, with dry nitrogen bubbling through the liquid. From an initial charge of 1 litre $\approx$ 100 mls was rejected before collecting the middle cut the final 200 mls also being rejected.

The second procedure adopted was to treat the DMF with anhydrous $CuSO_4$ prepared by heating B.D.H. A.R. grade $CuSO_4$ in an oven at 160^o (40). After standing, with intermittent shaking over the $CuSO_4$ for ≈1 week, the DMF was fractionally distilled under reduced pressure the initial 50 mls and the last 100 ml per litre treated being rejected. The middle cut was stored over B.D.H. 3A molecular sieves for 48 hours. A fresh batch of sieves was used for each distillation. The DMF was then distilled from a second still and the same amount of liquid was rejected as for the first stage in the preparation.

5.2 (c) Results

The DMF as supplied had a water content of ≃ 0.01M and a Ksp of ≈1 to $6x10^{-6}ohms^{-1}cm^{-1}$at 25^oC.

Water was estimated by Karl Fischer's method which has been used previously for water determination in DMF (29), (42) and (43). The experimental method used for this technique has been described in Chapter 2.

Both purification procedures resulted in a final product which on an average basis had the same conductance, viscosity and density at 25^0C. However, the sieve/$CuSO_4$ dehydrating technique was superior to CaH_2 treatment since the water concentration for the former ranged between 0.0003M to 0.001M whilst for the latter 0.001M to 0.002M. Table 5.1 reports the conductance, viscosity, density and water content for various samples of DMF purified in this work; also recorded are these properties, where reported, from the literature.

There is excellent agreement between the density recorded for DMF by Prue and Sherrington with the result obtained in this work which is an average of ten samples. The remaining values recorded in table 5.1 for this quantity could be explained by some water being present in the sample because the densities of DMF/H_2O mixtures are greater than pure DMF itself. The agreement between Prue and Sherrington's value for the viscosity of DMF and that

TABLE 5.1

SOME PROPERTIES OF DMF AT 25°C

Reference	Density g/cm^3	Viscosity cP	Ksp $x10^{-7}$	Water Content
This work	(0.943890) (±0.000005)	0.801_2	0.6-3.0	0.003M
Prue et al (33)	0.9439	(0.796) (±0.003)	0.4-2.7	0.007%
Ames et al (23)	0.9443	0.796	0.6-2.0	-
Chateau et al (44)	(0.9447) (±0.0002)	0.802	0.7-2.5	0.005%
French et al (32)	0.94415	0.76	0.6-2.6	-
Kittila (45)	0.9445	0.802	-	-
Paul et al (30)	-	-	3	-
Pistoia et al (19)	-	-	3	-
Geller (20)	0.9443	-	-	-
Held et al (29)	-	-	0.32-1.5	0.002%
Butler (36)	-	-	-	0.005%
Ruholf et al (41)	0.9445	-	-	-
Brummer (38)	-	-	0.2-0.5	-
Thomas et al (7)	-	-	0.3	(0.001) (-0.007M)

reported by Ames et al is excellent in contrast to the value found in this work. Since the viscometer used in this work was not charged with DMF under anhydrous conditions, trace of water absorbed by the DMF during this step could explain the higher value obtained for the viscosity of DMF since water in DMF increases the latter's viscosity.

Within experimental error the densities and viscosities of DMF/H_2O mixtures are independent of the purification procedure used for the preparation of the organic component.

5.3 DMF/Water Mixtures as a Conductometric Solvent

A solvent for conductance studies should conform to the following three criteria. Firstly, the solvent conductivity itself should be low to minimise errors due to the solvent correction. Secondly there should be a small or zero drift in conductance with time; lastly, and most important of all, the conductivity of the solute must be independent of the magnitude of the solvent's conductivity.

The last point will be discussed first. A limiting conductance run for KCl for each of the solvent systems containing 80% and 60% water was measured. The DMF used to prepare each solvent was purified by the CaH_2 method. A second series of conductance measurements at each solvent composition were subsequently made using solvent prepared with the $CuSO_4$/sieve purification method. The two sets of data for each system were combined and analysed with the Pitts and Fuoss-Hsia conductivity equations. The results of this analysis of the conductance data are presented in table 5.2.

TABLE 5.2

CONDUCTANCE OF KCl IN WATER/DMF MIXTURES - DMF BEING PREPARED BY THE TWO PURIFICATION PROCEDURES FOR EACH SOLVENT COMPOSITION

Conductivity Equation	% water	Λ^0	a	Ka	σ
Pitts	79.73_8	$96.98_5 \pm 0.008$	$3.0_0 \pm 0.01$	-	0.011
Fuoss-Hsia	79.73_8	$96.99_3 \pm 0.009$	$6.0_8 \pm 0.04$	$0.95_5 \pm 0.008$	0.006
Pitts	61.24_2	$65.89_5 \pm 0.008$	$2.5_4 \pm 0.01$	-	0.010
Fuoss-Hsia	61.24_2	$65.91_5 \pm 0.01$	$6.7_2 \pm 0.08$	$1.7_0 \pm 0.01$	0.014

Since σ is the fit of the data to the conductance equation, it can be regarded as being an estimate of the reproducibility of the equivalent conductance, Λ, for a given system for this reason it is concluded that Λ for each solvent system is independent of the purification procedure used for the preparation of the DMF. Further, for a given solvent composition, it is also concluded that Λ is independent of the magnitude of the solvent correction since the Ksp of the solvent, as a percentage of the Ksp of the solution, differs by at least 0.1% for the two sets of conductivity measurements.

Reported in table 5.3 are the DMF/H_2O mixtures for which Ksp data, as a function of time, were recorded. All solvents used in the conductometric and transport number studies associated with this work are included in this table. Solvents marked with an asterisk were not used for conductance or transport number work. It should be pointed out here that solvent numbers 21 and 22 were prepared from solvent 20 which was prepared several days before the others, a common sample of DMF being used in all cases.

It can be argued that the $CuSO_4$/sieve purification technique is the better one of the two investigated, by citing the solvents 19, 26, 27 and 28 which, as a function of water concentration, were the best prepared for this work. The only plausible explanation for the variability of the solvent Ksp, for a given water concentration, is the inconsistency between the samples of purified DMF. Since the distillation procedure is common to both methods this inconsistency could be related to the variability in the different samples of DMF prior to purification.

With further reference to table 5.3 it can be observed that in all cases the drift in Ksp of the solvent with time is small thus fulfilling one of the criteria of a solvent for conductometric studies. The more important requirement that the solvent correction be as small as possible, to lessen the uncertainty in the solute's conductance, was less satisfactorily attained. Associated with the last point, solvents 19, 26, 27, and 28 show that the Ksp of the

TABLE 5.3

SPECIFIC CONDUCTANCE OF DMF/WATER MIXTURES AT 25^{o}C

Solvent Number	Water %	Time Soln. Prepared (Days)	Period of Measurement (Days)	Purification Method	Range of Kspx10^{-6} ohms^{-1}cm^{-1}
9	79.73_7	2	1	CaH_2	1.39 -1.44
13	80.00_0	2	1	$CuSO_4$/S	4.83 -4.93
20	79.98_9	5	4	$CuSO_4$/S	4.02 -4.87
21	79.73_8	8	3	$CuSO_4$/S	6.46 -7.11
10	61.24_2	2	1	CaH_2	1.72 -1.78
15	61.24_1	3	2	$CuSO_4$/S	3.055-3.81
22	61.24_2	8	8	$CuSO_4$/S	5.38 -5.70
26*	59.82_2	7	7	$CuSO_4$/S	0.904-1.62
-*	50.0	7	7	$CuSO_4$/S	1.16 -2.25
14	40.06_8	2	1	$CuSO_4$/S	2.41 -2.55
16	40.00_1	2	1	$CuSO_4$/S	1.43 -1.44
17	40.02_7	3	2	$CuSO_4$/S	1.09 -1.37
18	40.07_0	4	3	$CuSO_4$/S	1.50 -1.53
27*	40.00_4	4	4	$CuSO_4$/S	0.497-0.872
11	31.34_6	2	1	CaH_2	4.22 -4.31
28*	31.29_9	5	5	$CuSO_4$/S	0.366-0.874
1	20.00_6	2	1	CaH_2	1.26 -1.26
19	20.00_8	7	6	$CuSO_4$/S	0.486-0.488

* Solvents not used for conductance or transport number work

majority of the solvents could be lower, together with the variability in the solvent Ksp for a given water concentration as an added criticism.

However, as already stressed the most important requirement of a conductance solvent has been fulfilled which is that for a given electrolyte concentration and solvent, Λ is independent of the magnitude of the solvent correction. Hence, it can be concluded that Λ is independent of the solvent impurities since it is highly unlikely that they would be of equal concentration for two independently prepared solvents. One further important piece of evidence can be reported here to support the preceding argument. The limiting ionic conductance for the K^+ ion will be shown to be, within 0.12%, independent of the anion i.e. Cl^- or Br^- in the 40% H_2O/DMF solvent system. This fact rests upon measurements made on electrolyte solutions prepared from four independently prepared DMF/water mixtures!

5.4 Density Studies in the DMF/Water System

5.4 (a) Introduction

The density measurements made in this research can be divided into two segments.

In conductance studies the equivalent conductivity of an electrolyte, which is defined as the conductance across parallel electrodes 1cm apart and having sufficient area to contain 1 gm equivalent of electrolyte, is a matter of prime interest. From this statement it follows that the concentration of the electrolyte must be expressed by volume. Since the electrolyte solutions were prepared gravimetrically, density measurements are therefore required to facilitate the expression of the concentration of the electrolyte in terms of equivalents per unit volume.

Since a discrepancy was noted between the densities of the DMF/H_2O solvents prepared in this research and the values quoted in the literature for comparable mixtures, it was thought that further investigation of the densities of DMF/H_2O mixtures was desirable.

5.4 (b) Experimental

The technique used in this research can be best described as "tared pycnometry". The tare is a sealed vessel having closely similar volume, form and mass to the pycnometer containing the solution and eliminates the need to apply buoyancy corrections to the balance readings.

The mass of the three single-stemmed pycnometers, when dry, were matched to within 0.002g and their volumes, being approximately 30 cm^{-3}, were within $0.02cm^{-3}$. The sealed tare had a dry weight close to that of the pycnometers and contained a weight of conductance water close to that of a pycnometer filled to the scratch mark with the same liquid. The pycnometers and tare are depicted in figure 5.1. The cross-sectional area of the precision bore tubing, 0.0111 cm^2, of which the stems were constructed was evaluated by Ellerton (46) who arrived at this conclusion by measuring the length of a known weight of mercury at various positions in the capillary. Hence the measurement of the distance between the meniscus and the scratch mark permits the calculation of the mass of liquid in the pycnometer filled to this mark.

The volumes of the pycnometers to the scratch mark were evaluated by using conductance water as the calibrating liquid; the density of water at $25^{o}C$ was taken to be 0.997044 g/cm^3 (48). Table 5.4 presents the results of the calibration made in duplicate, together with those reported by Mulcahy (47).

The pycnometers, rinsed with redistilled methanol and dried in a vacuum oven at 40^0 for twenty minutes, were filled with a 50 cm^3 syringe fitted with a stainless steel needle. A separate syringe and needle was used for each pycnometer. Once filled, the pycnometers were supported in a water bath maintained at $25^o \pm 0.002^o$ by means of a mercury-toluene regulator in conjunction with a thyratron relay unit. Having adjusted the menisci as close as possible to the respective scratch marks with the syringes, the equilibrated pycnometers were removed from the bath and the internal surfaces above the menisci

FIGURE 5.1

The pycnometers and the sealed tare.

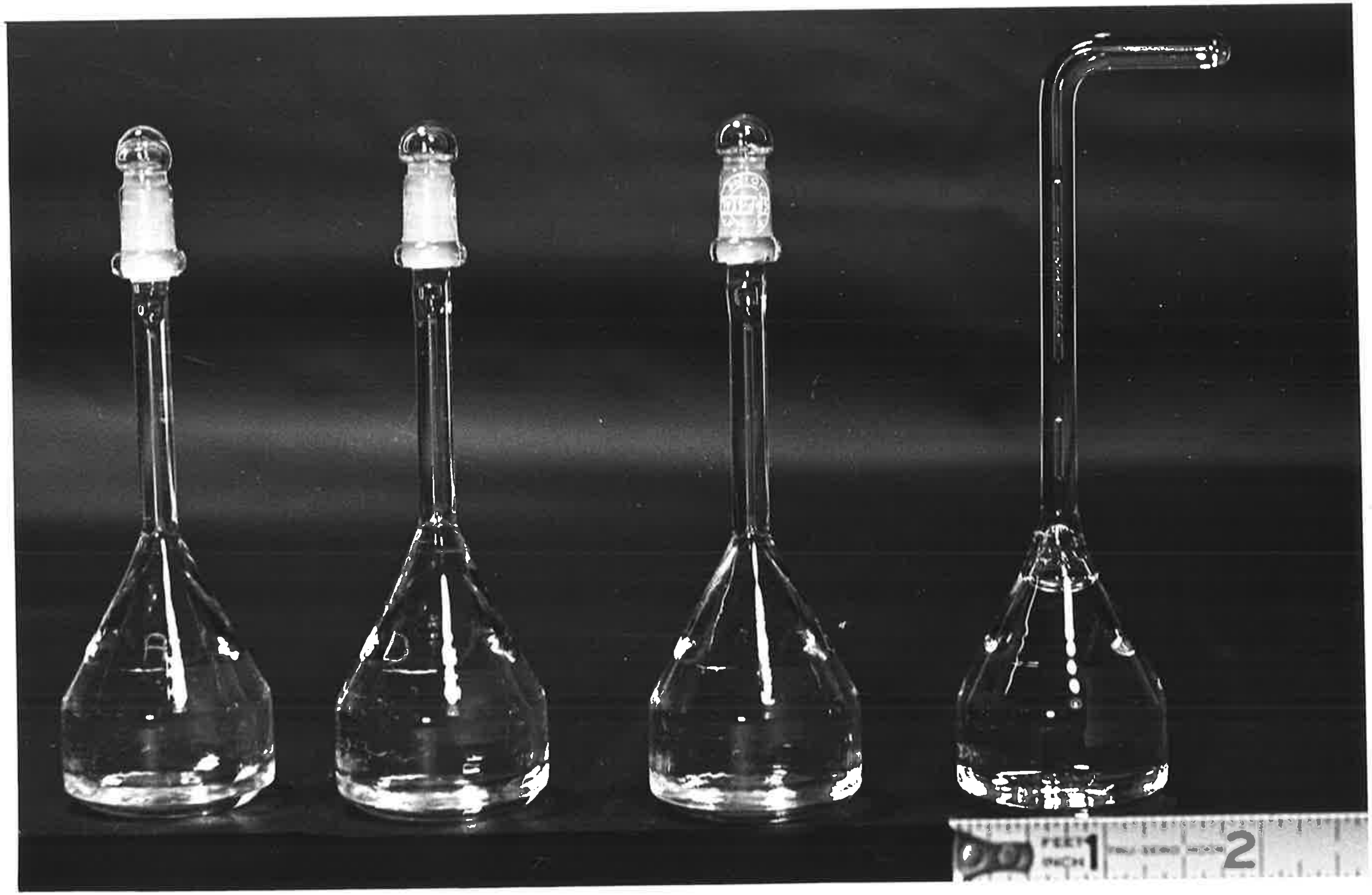

FEET
INCH
1
2

TABLE 5.4

PYCNOMETER CALIBRATIONS

Pycnometer	This Research		Mulcahy	
	m_1, g	V, cm^3	m_1, g	V, cm^3
A	0.03356	33.04445	0.03369	33.04450
	0.03369	33.04465	0.03372	33.04453
			0.03377	33.04463
B	0.02544	33.03810	0.02495	33.03767
	0.02550	33.03813	0.02537	33.03806
			0.02540	33.03806
D	0.04456	33.05585	0.04462	33.05586
	0.04459	33.05583	0.04455	33.05578
			0.04468	33.05589

were dried with extra-hard filter paper. This procedure allowed easier inspection of the bulbs for air bubbles and the capillaries for any droplets of remaining liquid. Following re-equilibration, the caps were removed prior to measurement, in triplicate, of the distances between the menisci and the scratch marks with a cathetometer. The pycnometers and tare were wiped with a moist cotton cloth, dried and finally wiped with chamois leather before placement in the Mettler B6C200 balance case for equilibration. The vessels were weighed to constant weight relative to the tare. During the weighing procedure the vessels were manipulated with a pair of forceps. The determination was completed by noting the wet and dry bulb temperatures and the barometric pressure in the balance room.

5.4 (c) Results and Discussion

The density of a liquid can be evaluated from the following relationship reported and discussed by Mulcahy (47).

$$\Delta d = \frac{m_2 - m_1}{V}\left[1 - \frac{d_a}{d_m}\right] + \Delta d' \qquad 5.1$$

A negligible correction term has been symbolically represented in equation 5.1 by Δd' to facilitate the discussion of the range of applicability of this equation in its absence.

d_m = the density of the balance masses,
d_a = the density of air in the balance room,
m_2 = difference in balance readings for tare and pycnometer + solution,
m_1 = difference in balance readings for tare and pycnometer + water
V = volume of the pycnometers and

Δd is the density increment between water, the calibrating liquids, and the solution being measured.

Δd' is composed of terms which are related to the dry weight of the pycnometer and tare, the weight of the pycnometer and the tare filled with water and the quantity m_2 and a term which allows for the measurements being performed in an atmosphere having a different density to that in which the calibrations were made.

For the pycnometer and tare set used in the present research Mulcahy (47) concluded, after considering the difference in mass between the dry pycnometers and the tare in conjunction with the difference in mass between the pycnometers and tare filled with water that the contributions of these two terms to $\Delta d'$ in equation 5.1 could be neglected. With regard to the two remaining terms of $\Delta d'$, if the density of air varies $\pm 1 \times 10^{-4}$ g/cm^3 then, for a pycnometer of 30cm^3, $\Delta d' = 3 \times 10^{-6}$ g/cm^3 (47). But as the density of the balance room air fluctuated only $\pm 1.2 \times 10^{-5}$ g/cm^3 during the course of this research, this term is also negligible. Assuming that a precision of 1×10^{-6} in Δd is sought, then m_2 must be <2g. Hence the maximum variation of Δd allowable, for this set of pycnometers, is ±0.07 either side of the density of water. The limits of solution density observed in this research were between 0.94389_0 and 1.0012_5 g/cm^3. Hence all of the conditions defined by Mulcahy which permit the neglect of the $\Delta d'$ term have been met in this research.

The reproducibility of the density measurements can be gauged from the results presented in table 5.5 of triplicate and duplicate determinations of the densities of single DMF/H_2O mixtures. Geller's (20) and Blankenship and Clampitt's (50) values are also included in this table where the concentrations of water are comparable with those of the mixtures prepared in this research. The last authors quote "a maximum deviation of 0.5%" in their density values while Geller reports an accuracy of ±0.0002 g cm^{-3}. The extent of the discrepancy, ≃ 0.5%, between Geller's values and those obtained in this research is comparable with the degree of precision of Blankenship et al. Consequently the last authors' values need not be considered further as they will not resolve the discrepancy between the remaining two sets of data. A comparison of the results obtained can be made for a 50% mixture in this research with that of

TABLE 5.5

THE DENSITY OF DMF/WATER MIXTURES AT 25^{o}C

		THIS RESEARCH				LITERATURE VALUES			
						Geller		Blankenship et al	
Water Mole %	Water % by Wt	Solvent Number	Averaged Density g/cm^3	Deviation from Meanx10^{-6}	Number Averaged	Water % by Wt	Density g/cm^3	Water Mole %	Density g/cm^3
0.0	0.0	-	0.94389_0	5	14	0.0	0.9943	0.0	0.9463
16.55	4.658	24	0.95289_6	-	1	5.0	0.9534	20.0	0.9588
35.33	11.869	6	0.96478_7	3	3	10.0	0.9637		
38.051	13.148	25	0.96681_6	-	1			40.0	0.9718
	19.391	23	0.97557_0	-	1				
50.369	20.008	19	0.97632_0	-	1	20.0	0.9784	50.0	0.9773
	20.006	1	0.97632_7	-	1				
64.944	31.346	11	0.98770_4	2	2	30.0	0.9911	60.0	0.9881
	40.070	18	0.99291_7	-	1	40.0	1.0017		
	40.027	17	0.99291_7	-	1				
	40.001	16	0.99291_5	-	1				
73.065	40.068	14	0.99291_9	3	2			70.0	0.9931
	41.175	7	0.99340_1	3	3				
	50.0*	-	0.9962	-	-	50.0	1.0023		
81.302	51.729	2	0.99630_0	8	3			80.0	0.9939
	60.036	8	0.99698_4	4	3				
86.888	60.000	12	0.99699_2	3	2	60.0	0.9982		
	61.241	15	0.99700_6	-	1				
	61.242	10	0.99701_2	4	2				

TABLE 5.5 (Continued)

		THIS RESEARCH				LITERATURE VALUES			
						Geller		Blankenship et al	
Water Mole %	Water % by Wt	Solvent Number	Averaged Density gcm^3	Deviation from Meanx10^{-6}	Number Averaged	Water % by Wt	Density gcm^3	Water Mole %	Density gcm^3
89.932	68.668	5	0.99690_6	3	3	70.0	0.9976	90.0	0.9957
	79.414	3	0.99639_2	3	3				
	79.737	9	0.99637_4	-	1				
94.196	80.00	13	0.99637_1	-	1	80.0	0.9927	95.0	0.9960
97.639	91.064	4	0.99622_3	0	2	90.0	0.9971		
100.0	100.0	-	0.997044	-	-	100.0	0.9971	100.0	0.9771

* Interpolated value - this research

Geller and the single point determination of Raridon and Kraus (49). The last authors report a value of 0.996 g/cm^3 in agreement with the value graphically interpolated from this research. Evidence to support the precision of the density measurements made in this research will be given later in this chapter.

The densities of KCl and KBr solutions in DMF/H_2O mixtures are presented in appendices 5.1 and 5.2.

The density, d, of an electrolyte solution of concentration C can be related to the density of the solvent, d_o, thus (51) ÷

$$d = d_o + A_1C - A_2C^{3/2} \qquad 5.2$$

where:

$$A_1 = \frac{M_2 - d_0\,\phi_2^0}{1000}$$

$$A_2 = \frac{S_v\,d_0}{1000}$$

The basis of equation 5.2, often termed the Root equation, is the work of Masson (52) and Root (53). M_2 is the molecular weight of the electrolyte, ϕ_2^0 is the limiting apparent molar volume of the electrolyte and S_v is defined by Masson's relationship thus ÷

$$\phi_2 = \phi_2^0 + S_v\sqrt{C}$$

ϕ_2 is the apparent molar volume.

It was found in this work that $(d-d_o)/m$ or $(d-d_o)/C$ could be regarded as sufficiently constant to allow precise conversion of the molality of a solution to a molarity. As a matter of interest the density data for KCl and KBr measured in this research were fitted to Root's equation with program ROOTEQ. The coefficients A_1 and A_2 so obtained are recorded in appendix 5.1, while the derived values of ϕ_2^0 are tabulated in table 5.6. The results obtained suggest that Root's equation is applicable to KBr and KCl in DMF/H_2O mixtures,

TABLE 5.6

VALUES OF THE LIMITING APPARENT MOLAR VOLUME, ϕ_2^o cm^3/Mole, FOR VARIOUS ELECTROLYTES IN WATER AND DMF/WATER MIXTURES AT 25^{o}C

Salt	Solvent	Tared Pycnometry This Research ϕ_2^o	 Mulcahy ϕ_2^o	Other Values ϕ_2^o
KCl	water	-		26.52^a, 26.81^a, 26.886^b
CsCl	water	-	40.0 ± 0.3	$39.15^{a,b}$
NaI	water	-	35.4 ± 0.1	35.10^a
KI	water	-	45.4 ± 0.1	45.36^a
CsI	water	-	58.0 ± 0.2	57.74^a
KBr	water	-	33.8 ± 0.1	33.73^a
KCl	80% H_2O/DMF	26.8 ± 0.3		
KBr	80% H_2O/DMF	33.7 ± 0.5		
KCl	60% H_2O/DMF	26.9 ± 0.4		
KBr	60% H_2O/DMF	34.0 ± 0.5		
KCl	40% H_2O/DMF	27.3 ± 0.3		
KBr	40% H_2O/DMF	35.2 ± 0.2		
KCl	31% H_2O/DMF	22.9 ± 0.9		

(a) Reference (51); (b) Reference (54)

hence Masson's relationship is also valid in these systems.

Mulcahy has reported values for ϕ_2^0 for a number of electrolytes in water and 20% aqueous sucrose solutions obtained from density measurements made with the same set of pycnometers and tare used in this research. His aqueous solution values together with the literature values cited by Harned and Owen (51), together with those of Vaslow (54) are reproduced in table 5.6. This agreement is good thus providing a firmer basis for estimating the precision of the technique used in this work by comparing previously reported values of ϕ_2^0 with those evaluated by the method of tared pycnometry. The standard error of ϕ_2^0, S.E., denoted in table 5.6 is clearly related to the fit of the data to Root's equation. The superficially large standard error of ϕ_2^0 recorded in the present research are explicable in terms of an uncertaintity of ≃ ± 0.0005% in $(d-d_o)$. Having established the precision of the density measurements obtained in this research it is hereby proposed that the densities of the DMF/H_2O mixtures obtained in this research are more reliable than those reported by Geller.

5.5 The Viscosity of DMF/Water Mixtures

Table 5.7 presents the flow times recorded with the tilting viscometer for various DMF/water mixtures, the composition of which is expressed as a percentage of water by weight. The experimental technique employed in recording the flow times set out in table 5.7 has been presented in chapter 4. The viscosity of each mixture, given its flow time and density, was evaluated from equation 4.7 with n set to unity. The instrument constants C and K for this viscometer are based upon the viscosity of water obtained in this research between 5^o and 60^o; the values of C, $1.4495 \times 10^{-5} \pm 4.0 \times 10^{-9}$, and K, $-1.1237 \times 10^{-2} \pm 7.6 \times 10^{-4}$, have been presented in table 4.8 . After considering the uncertainties in these coefficients, it should thereby, be possible to evaluate the viscosity of a test liquid with a precision of 0.1%. The internal consistency can be gauged by comparing multiple determinations of the viscosity of the mixtures

TABLE 5.7

VISCOSITY AND DENSITY OF DMF/WATER MIXTURES AT 25°C

Water % by Wt	Solvent Number	Density g/cm^3	Number of Flow Times Averaged	Average Flow Time-Seconds	Viscosity cP
11.86_9	6	0.96478_7	4	982.36±0.055	1.372_6
20.00_6	1	0.97632_7	8	1324.53±0.15	1.873_5
20.00_7	19	0.97632_0	7	1324.75±0.014	1.873_8
31.34_6	11	0.98770_4	12	1672.94±0.063	2.393_8
41.17_5	7	0.99340_1	6	1737.07±0.059	2.500_6
40.06_8	14	0.99291_9	7	1738.72±0.015	2.501_7
40.00_1	16	0.99291_5	6	1738.44±0.037	2.501_3
40.02_7	17	0.99291_7	5	1738.65±0.025	2.501_5
40.07_0	18	0.99291_7	5	1738.57±0.029	2.501_4
51.72_9	2	0.99630_0	8	1602.77±0.020	2.313_8
60.03_6	8	0.99698_4	7	1424.08±0.09	2.057_1
61.24_2	10	0.99701_2	10	1394.70±0.06	2.014_6
61.24_2*	10	0.99701_1	10	1394.70±0.08	2.014_6
61.24_1	15	0.99700_6	9	1394.71±0.02	2.014_7
68.66_8	5	0.99690_6	8	1222.10±0.08	1.764_9
79.41_4	3	0.99639_2	4	983.96±0.020	1.419_9
79.73_7	9	0.99637_4	7	978.89±0.088	1.412_5
80.00_0	13	0.99637_1	6	971.27±0.004	1.401_5
91.06_4	4	0.99622_3	5	961.89±0.19	1.098_7

* Measurement repeated after 1 week

containing 20%, 40% and 60% water, respectively; these values are reproducible, in each case, to within 0.1%, which is the expected precision of the measurements. In addition the value obtained for the viscosity of these mixtures is independent of the time lapse between preparation and measurement, since the 61.242% mixture number 11 was allowed to stand for a week before the measurement was repeated.

Viscosities of DMF/H_2O mixtures were also measured by Blankenship and Clampitt (50) and a single determination in a 50% mixture reported by Raridon and Kraus (49) who quote a precision of 0.2% for their result. Since the quoted precision of the former author's measurements is 8%, no further consideration of their results is required. When the results of Raridon and Kraus for the viscosity of a 50% mixture is compared with this research, the agreement appears to be reasonable. A satisfactory comparison is complicated by the lack of data in the region of the viscosity maximum. The viscosities measured in this work together with the value of 2.348cP recorded by Raridon and Kraus are graphically presented in fig 5.2.

Within the estimated uncertainties of the respective techniques, the densities and viscosities of DMF/H_2O mixtures measured in this research are independent of the method used for the purification of the organic component. This point is illustrated by citing the solvents containing 20% H_2O and 61.24% H_2O. The CaH_2 method was used to purify solvents 1 and 11 while the $CuSO_4$/sieve procedure was employed for solvents number 20 and 16, the densities and viscosities recorded for these solutions are recorded in table 5.7.

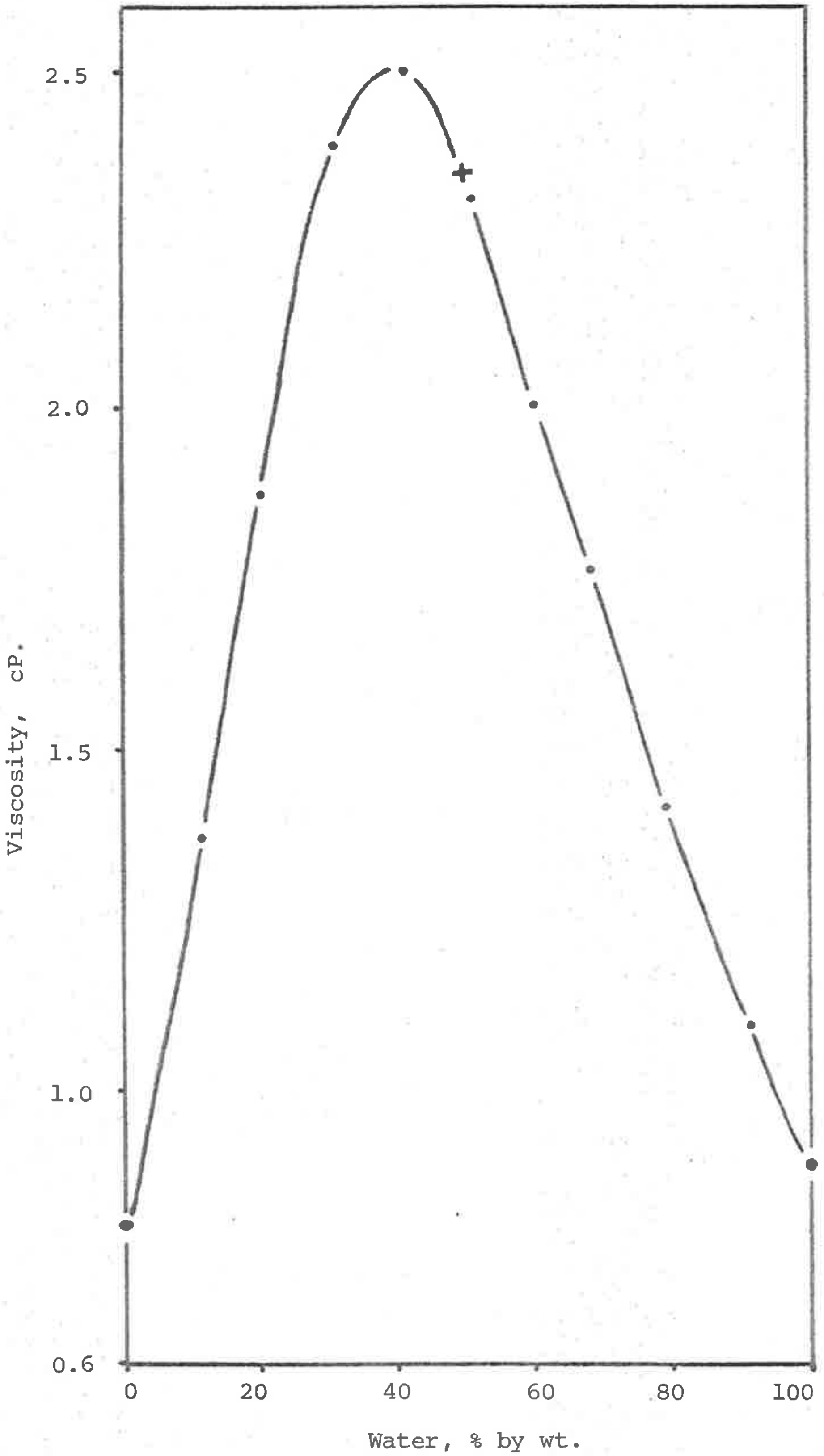
Discussion of the viscosities, densities of DMF/water mixtures and solutions of KBr and KCl in these solvents will be raised, where applicable, in the discussion of the results of the conductance studies made in this solvent system.

FIGURE 5.2

The dependence of the viscosity of DMF/water mixtures upon composition at 25°C.

● The Present Research

+ Raridon and Kraus (49)


Viscosity, cP.
2.5
2.0
1.5
1.0
0.6
0
20
40
60
80
100
Water, % by wt.

CHAPTER 5

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CHAPTER 6

TRANSPORT NUMBER MEASUREMENTS IN DMF/WATER MIXTURES AT 25°C

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CHAPTER 6

6.1 Introduction

The significance of the term transport or transference number has been discussed by Spiro (1) (2) and Robinson and Stokes (3). Bearing in mind their texts, only one point needs to be raised in this thesis. In the case of weak electrolytes or electrolytes in which complex ions can be formed between their anions and cations, Spiro (1) (2) has shown that caution must be used in the interpretation of the experimental results of transport number measurements. In such a context, what is relevant to this research is the possibility of charged silver halide complexes being formed by the dissolution of the silver halide that comprises the reversible electrodes in the transport number apparatus. If ionic species are formed by such a process, in fact what is measured is the nett contribution to the transport of electrical current by each of the cationic or anionic constituents of the solution.

The authors cited above (2) (4) and MacInnes (5) have discussed a number of experimental methods that can be employed for the measurement of transport numbers. The method of Steel and Stokes (6) (7) (8) used in this research is essentially a modification of the classical Hittorf procedure in which the tedious, error prone chemical analysis of concentration changes, due to the passage of the D.C. current through an electrolyte solution, has been replaced by the more rapid and precise technique of conductometric analysis. The measurements are made in a cell which has two functional parts, the first being a modified Hittorf cell from which the middle compartment(s) is omitted, while the second integral part consists of a conductance cell for the determination of the concentration change in one of the two compartments after the passage of the electrolysing current. The principal advantages of this technique over its predecessor are increased precision together with a simplified and more rapid experimental procedure. One disadvantage of the modified Hittorf is that it lacks the precision of the moving boundary method. In spite of this, the modified Hittorf is preferable to the latter technique due to its inherent simplicity in terms of apparatus and experimental procedure. An interesting comparison can be made between the method of Steel and Stokes, as described in their paper and in this thesis, with a precise classical Hittorf study by MacInnes and Dole (9) and the moving boundary method described in detail by Spiro (2).

The modified Hittorf has been employed previously in the measurement of transport numbers of various electrolytes in water (8) (10), methanol (8), glycerol/water (6) (8) (11), mannitol/water (8) (11), sucrose/water (6) (8) (11) and α-alanine/water (12). An aim of this research has been to examine the applicability of the technique of Steel and Stokes to a solvent system in which measurements may be restricted due to the solubility of the silver halide of the electrodes with the formation of ionic silver halide complexes.

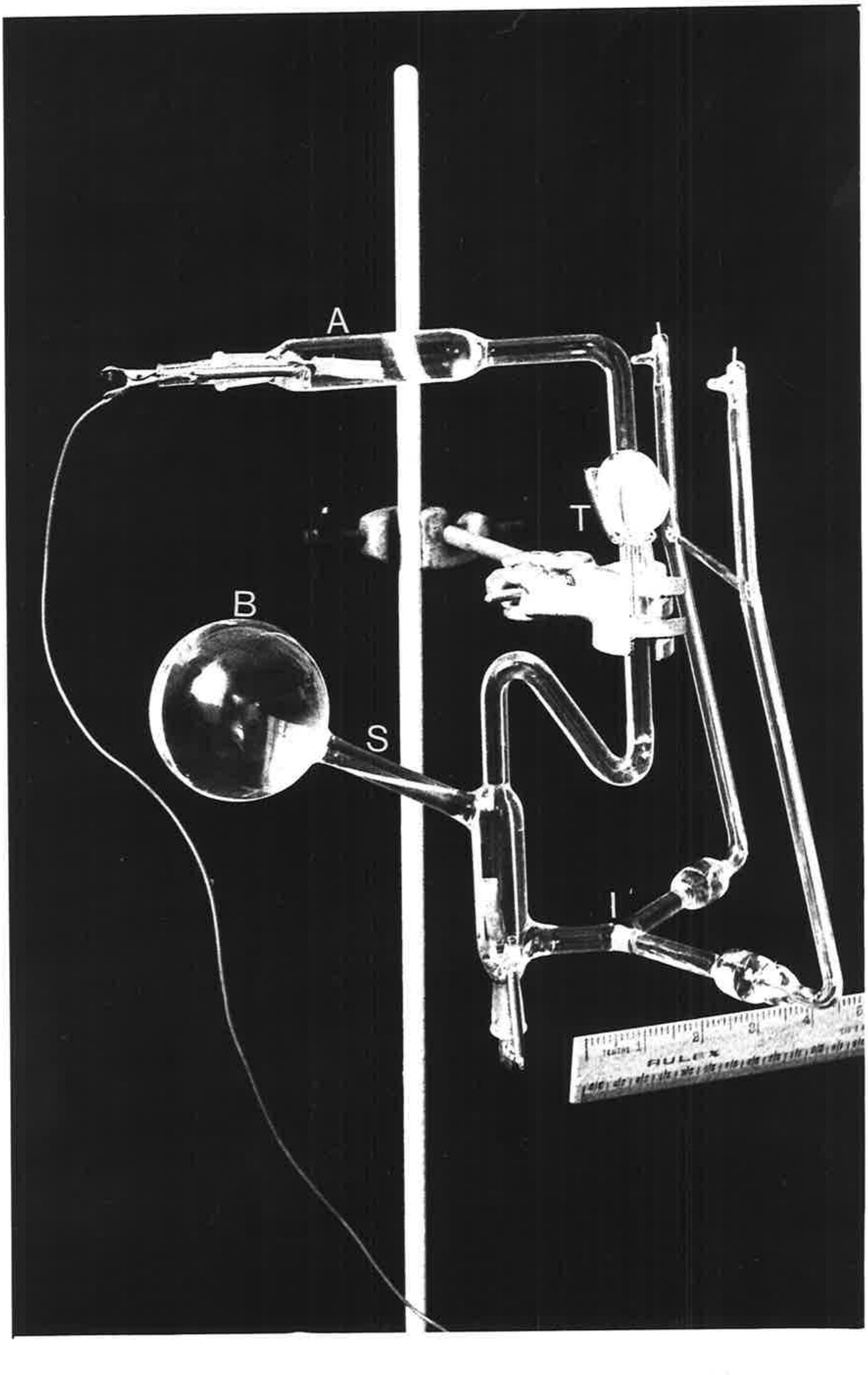
6.2 Experimental

The cell is supported in the oil bath in the position illustrated in figure 6.1. As the negative terminal of the D.C. power supply is connected to the compartment below the tap T, this can be conveniently termed the cathode compartment. The remaining elements of the apparatus are the mixing bulb B connected to the apparatus by the stem S and the conductance cell I whose electrodes were lightly platinized.

A similar resistance-frequency dependence to flask cell C at resistances > 10K Ω was exhibited by the transport number cells when they functioned as conductance cells. The effect was far more pronounced for the transport number cells and was exhibited at cell resistances > 3K Ω. However, by measuring the cell resistance at frequencies < 6Kc/s, a frequency independent resistance could be obtained as described for flask cell C in Chapter 2. The cell constants of the transport number cells, TA1 and TA2, were determined using the method of Chiu and Fuoss (13) and Lind et al (14); the values obtained are presented in table 6.1. The consistency of the

FIGURE 6.1

A transport number cell depicting the tap, T, intervening between the anode compartment, A, and the cathode compartment, the latter being the volume below T and consisting of the conductance cell I, the mixing bulb B and the stem S. The *S* shaped tube above the stem S and below the tap T minimizes the effect of intermixing between the two compartments due to convection currents caused by Joule heating.


A
T
B
S
I
RULEX

cell constant obtained for cell TA1 at widely differing resistance values confirms the correctness of the procedure used for the evaluation of the frequency independent resistance of conductance cells described and discussed in Chapter 2.

TABLE 6.1

THE CELL CONSTANT, cm^{-1}, OF THE TRANSPORT NUMBER CELLS TA1 AND TA2 AT 25°C

Cell	Calibrating Solution	Cell Constant cm^{-1}
TA1	0.031513 N	24.570 ± 0.002
TA1	0.0098649 N	24.571 ± 0.001
TA1*	0.033824 N	24.567 ± 0.001
TA2	0.033824 N	30.341 ± 0.001

* Cell coated with water repellant layer

The bulb and the stem of the mixing chamber were coated with a layer of silicone water repellant (6) to ensure that the contents of the bulb were quantitatively transferred to the remainder of the apparatus after the mixing period. The cell constant is independent of this layer (8), a point which can also be noted from table 6.1.

The volume of the cathode compartment, i.e. the volume below the tap T, excluding the volume of bulb B, to a reference scratch mark situated on the stem S of the mixing bulb was determined by the following method. Having weighed the dried siliconed cell containing the cathode (bare platinum) sufficient conductance water was placed in the cathode compartment for the meniscus to be situated in the stem S. The cell was then reweighed with the Stanton beam balance, the distance between the scratch mark and the meniscus measured to within 0.1 mm with a pair of vernier calipers and, finally, the temperature of the calibrating liquid was noted. Temperature-density data for water was obtained from reference (15). The volume measurements were repeated so as to include the length of the stem S to ascertain the uniformity of its cross sectional area. The volumes of both cells are presented in table 6.2.

TABLE 6.2

CALIBRATION OF THE VOLUME OF THE CATHODE COMPARTMENT OF THE TRANSPORT NUMBER CELLS

Cell	Number of Determinations	Volume of Cathode to Scratch Mark	Volume - Distance Relationship Between Meniscus and Scratch Mark on Stem
TA1	12	$41.435 \pm 0.003\text{cm}^3$	$1\text{mm} \equiv 0.0371 \pm 0.0003\text{cm}^3$
TA2	8	$37.944 \pm 0.003\text{cm}^3$	$1\text{mm} \equiv 0.0383 \pm 0.006\text{cm}^3$

The platinum gauze base of the D.C. electrodes (10) was cleaned with boiling conc. HNO_3 and thoroughly leached prior to the electrodeposition of silver onto its surface from a 0.1M K_2 $(Ag\{CN\}_2)$ solution, silver gauze acting as the anode. Both the time and the current (<7ma) of the electrolysis were noted. Some of the deposited silver was electrolytically converted into silver halide in a 0.1M aqueous solution of the appropriate potassium halide. The time and current (<4ma) were also noted. In all 6X coulombs of Ag and 3X coulombs of silver halide were placed on the cathode prior to the transport number run during which X coulombs of current were to be passed through the cell (8). From the current and the time of each preparative step, the mass of Ag and silver halide can be calculated and combined with density data for these substances (16). A volume correction to be applied to the volume of the cathode can be calculated. Fresh electrodes were prepared for each run. The silver halide remained firmly affixed to each electrode in all systems studied.

The cell was dried by rinsing it several times with redistilled methanol followed by repeated evacuations with a water aspirator. The electrodes were dried in an air oven. After placing the anode and tap in position the cell was rinsed four times with the test solution before charging it with enough solution to fill the apparatus so that the meniscus was close to the scratch mark on the stem. The mixing bulb was filled with air. The cathode was placed in the cell which was allowed to stand in the 25°C oil bath overnight. The electrodes and tap were sealed in position with a thin smear of silicone high vacuum grease situated at the extremities of the ground glass joints furthest away from the contents of the cell. Steel springs were employed to keep the electrodes and tap firmly in position.

Having measured the initial series of resistance-volume measurements (6) (8) to ascertain the concentration of the electrolyte prior to the commencement of the electrolysis, the leads from the stabilised D.C. current circuit were connected to the silver-silver halide electrodes. Electrical contacts on the exterior of the electrodes were covered with a plastic sheath. The leads were firmly affixed to the cell with cord to prevent movement during the electrolysis. While the cell was re-equilibrating, the D.C. circuit was "warming up" by passing the required amount of current for the run through a dummy load in the form of a 100 KΩ decade resistance box, the setting of which was obtained by measuring the resistance across the D.C. electrodes at a frequency of 10 Kc/s.

As the double pole-double throw mercury switch transferred the current to the cell the crystal timer, used for the viscometric measurements, was started. At 100 second intervals the voltage drop across a 500 Ω wire wound resistance was measured with a Doran (17) potentiometer. The resistor was calibrated with the Jones-Dike bridge at 15 frequencies between 0.5 and 20 Kc/s and its frequency independent resistance was found to be 500.11 Ω. The Doran was calibrated against a certified Cambridge (18) potentiometer at various settings of the Doran, the results being presented in table 6.3. The performance of the constant current supply constructed in the electronics workshop of this Department can be gauged from the voltage-time data recorded during a run presented

TABLE 6.3

CALIBRATION OF THE DORAN POTENTIOMETER AGAINST A CERTIFIED CAMBRIDGE POTENTIOMETER, TYPE 44248

Doran - volts	Cambridge - volts	Doran/Cambridge
1.7	1.69991	1.00005
1.6	1.59993	1.00004
1.5	1.49996	1.00002
1.4	1.39998	1.00001
1.3	1.30000	1.00000
1.2	1.20003	0.99998
1.1	1.10004	0.99996
1.0	1.00006	0.99994
0.9	0.90008	0.99991
0.8	0.80011	0.99986

in table 6.4.

The electrolysis was terminated by the transfer of the current to the dummy load resistor as the timer was stopped. The closure of the tap T followed as rapidly as possible. Conductometric analysis of the cathode compartment ensued, ultimately succeeded by the opening of tap T and the third and final series of resistance-volume measurements. The sequence of events described in this paragraph have been more extensively described by Steel and Stokes (6) and Steel (8).

6.3 Results and Discussion

It is assumed for the purposes of the immediate discussion that, if in a solution of KBr there are only K^+ and Br^- ions present, then the apparent transport number of the K^+ ion is given by (6).

$$q\, t_{K^+}\,(\text{app}) = (C_2 - C_1)\, V\, F \qquad 6.1$$

where C_1 = the concentration of electrolyte in the cell prior to the electrolysis - evaluated from the first set of resistance measurements.

C_2 = the concentration in the cathode compartment after the electrolysis - second set of resistance measurements.

F is the Faraday (19).

V is the volume of the solution in the cathode compartment evaluated by the meniscus to scratch mark measurements made during the run and the volume calibrations described in the previous section of this chapter. V was corrected for the volume occupied by the silver-silver halide of the cathode.

q is the number of coulombs passed during the electrolysis corrected for the solvent conductivity (6).

Let C_3 be the concentration of the electrolyte in the cell after the remixing of the two compartments, then the concentrations C_1, C_2 and C_3 are evaluated by the method of Steel and Stokes (6).

C_1 should equal C_3 since, in principle, the last quantity corresponds to the analysis of the middle compartment of the classical Hittorf experiment, that is, a check that the composition

TABLE 6.4

REGULATION OF THE VOLTAGE ACROSS THE SILVER/SILVER-HALIDE ELECTRODES OF THE TRANSPORT NUMBER APPARATUS DURING A RUN

Time secsx10^2	Volts	Time secsx10^2	Volts	Time secsx10^2	Volts
1	1.4986	27	1.5059	53	1.4988
2	1.5000	28	1.5060	54	1.4988
3	1.5009	29	1.5059	55	1.4992
4	1.4988	30	1.5064	56	1.4997
5	1.5005	31	1.5064	57	1.5002
6	1.5009	32	1.5064	58	1.5000
7	1.5009	33	1.5062	59	1.5007
8	1.5021	34	1.5070	60	1.5003
9	1.5020	35	1.5078	61	1.5007
10	1.5030	36	1.5073	62	1.5005
11	1.5038	37	1.5078	63	1.5007
12	1.5041	38	1.5073	64	1.5011
13	1.5039	39	1.5079	65	1.5011
14	1.5045	40	1.5073	66	1.5011
15	1.5041	41	1.5083	67	1.5011
16	1.5045	42	1.5073	68	1.5017
17	1.5047	43	1.5082	69	1.5018
18	1.5047	44	1.5080	70	1.5017
19	1.5050	45	1.5081	71	1.5015
20	1.5052	46	1.5080	72	1.5011
21	1.5055	47	1.5082	73	1.5011
22	1.5058	48	1.5076	74	1.5015
23	1.5060	49	1.5079	75	1.5015
24	1.5061	50	1.5081	76	1.5020
25	1.5061	51	1.5077	77	1.5015
26	1.5061	52	2.4990	OFF	7752.6 secs

of the solution remains unaltered due to the electrolysis. However, C_3 was always lower than C_1 by amounts ranging from 0.01% to 0.06%. This can be observed from table 6.5 in which Ksp_1 and Ksp_3 correspond to the Ksp measured in the transport number cell during the determination of C_1 and C_3 respectively. Similar observations have been reported by Steel (8) who attributed the effect to the adsorption of electrolyte by the freshly exposed silver halide surface that occurs during electrolysis. At each of the three sets of resistance-volume measurements, mixing of the cell contents was continued until a constant resistance reading, to within 1 in 50,000, was recorded indicating that the adsorption process was completed.

Since the concentration change is not $C_2 - C_1$, this term must be replaced by $C_2 - C_3$ to allow for the electrolyte adsorbed by the electrodes.

Expressing the transport number for the K^+ ion in the Hittorf frame of reference, i.e. relative to the solvent, equation 6.1 becomes:-

$$q\ t_{K^+}\ (\text{Hittorf}) = (m_2 - m_3)\ M\ F \qquad 6.2$$

where $(m_2 - m_3)$ gives the change in molality upon electrolysis and M is the mass of solvent in the cathode compartment. Conversion of molarities to molalities was achieved with density-concentration data reported in Chapter 5 for KCl and KBr in DMF/water mixtures. In water Scott's data (20) for KBr was used to compute the coefficients A_1 and A_2 of the Root equation 5.2.

The precision of the transport number measurements made in this research can be guaged by comparing the values of t_{K^+}, presented in table 6.6, obtained for aqueous KBr solutions of comparable concentrations in this research, with those of Steel (21) and Keenan and Gordon (22), the last authors using the moving boundary method. A comparison of values of t_{K^+} for aqueous KCl solutions evaluated with the method of Steel et al and the moving boundary results of Longsworth (26) for this salt, has been made by Steel (10). It can be noted from table 6.6 and reference (10) that

TABLE 6.5

THE Ksp OF KCl AND KBr SOLUTIONS IN WATER AND WATER/DMF MIXTURES AT 25°C MEASURED IN THE TRANSPORT NUMBER CELLS AND CONVENTIONAL CONDUCTANCE CELL A

Solute	Water % by Wt	Ksp1 x10^{-3}	Ksp3 x10^{-3}	Ksp1-Ksp3 %	Ksp of Solution Cell A x 10^{-3}	Ksp_1-Ksp (Cell A) %
KBr	100.00	4.45336	4.45222	0.03	-	-
KBr	79.99	1.89213	1.89127	0.045	1.89177	0.019
KBr	79.99	1.80865	1.80755	0.060	-	-
KBr	61.24	1.71753	1.71719	0.020	1.71759	0.027
KBr	40.00	1.22312	1.22276	0.029	1.22349	0.030
KCl	40.03	1.27730	1.27726	0.003	-	-
KCl	40.07	1.52410	1.52394	0.010	1.52390	0.014
KCl	40.07	1.52394	1.52363	0.020	1.52390	0.00
KBr	20.01	1.37992	1.37987	0.004	1.37022	0.70

TABLE 6.6

TRANSPORT NUMBERS OF KCl AND KBr IN WATER AND DMF/WATER MIXTURES AT 25°C MEASURED BY THE HITTORF AND THE MOVING BOUNDARY METHODS

C	Electrolyte	Water % by Wt	Time of Electrolysis (secs)	Coulomb	t_+
0.032959	KBr (a)	100.0	8011.25	26.410	0.4841
0.0287475	KBr (b)	100.0	7200	22.9825	0.4840
0.03	KBr (c)	100.0	-	-	0.4837
0.031242	KCl (b) (d)	100.0	3300	22.6888	0.4898
0.031242	KCl (e)	100.0	-	-	0.4900
0.0210633	KBr (a)	79.99	8013.4	25.3904	0.5111
0.0201006	KBr (a)	79.99	9033.8	24.4098	0.5115
0.0289589	KBr (a)	61.24	8158.3	25.1115	0.5244
0.0299175	KBr (a)	40.00	10019.3	23.6567	0.5245
0.0321876	KCl (a)	40.03	10013.8	24.1414	0.5260
0.0388960	KCl (a)	40.07	6559.7	19.6415	0.5265
0.0388919	KCl (a)	40.07	7752.6	23.2501	0.5267
0.0368795	KBr (a)	20.01	9019.92	23.2072	0.4882

(a) This Research; (b) Reference (21), Hittorf; (c) Reference (22), moving boundary; (d) Reference (10), Hittorf; (e) References (26), (10) moving boundary.

agreement between the two methods is 0.1%. The conductance data used in the evaluation of t_{K^+} (KBr) in this research was obtained from the literature (23-25).

The limiting cationic transport number was calculated from the following relationship (10) (11):-

$$t_+^{o'} = t_+ + \frac{(0.5 - t_+)\ B_2 \sqrt{C}}{(1 + B\, a \sqrt{C})\ \Lambda^o} \qquad 6.3$$

The values of Λ^o and a required for the computation of $t_{K^+}^{o'}$ are recorded in Chapter 7 tables 7.7 and 7.8. If $t_{K^+}^{o'}$ (KBr) for water is computed with equation 6.3 using t_{K^+} (KBr) of this research, the result obtained is 0.485_o which can be compared with the result of Keenan and Gordon, $t_{K^+}^{o} = 0.4847$, evaluated from more extensive data. The data upon which the values of t_{K^+} of this research are based are presented in appendix 6.1.

The system KBr in 20% water/DMF is excluded from the immediate discussion. After comparing the Ksp of the solution measured in the transport number cell prior to electrolysis, Ksp_1, with the Ksp of the solution measured in conductance cell A it is concluded from the data presented in table 6.5 that the conductance of the solution is altered to a negligible extent by being in contact with the silver-silver halide electrodes of the transport number apparatus. Hence, it is indeed reasonable to assert that the quantity measured is in fact the constituent ion transport number for the K^+ ion.

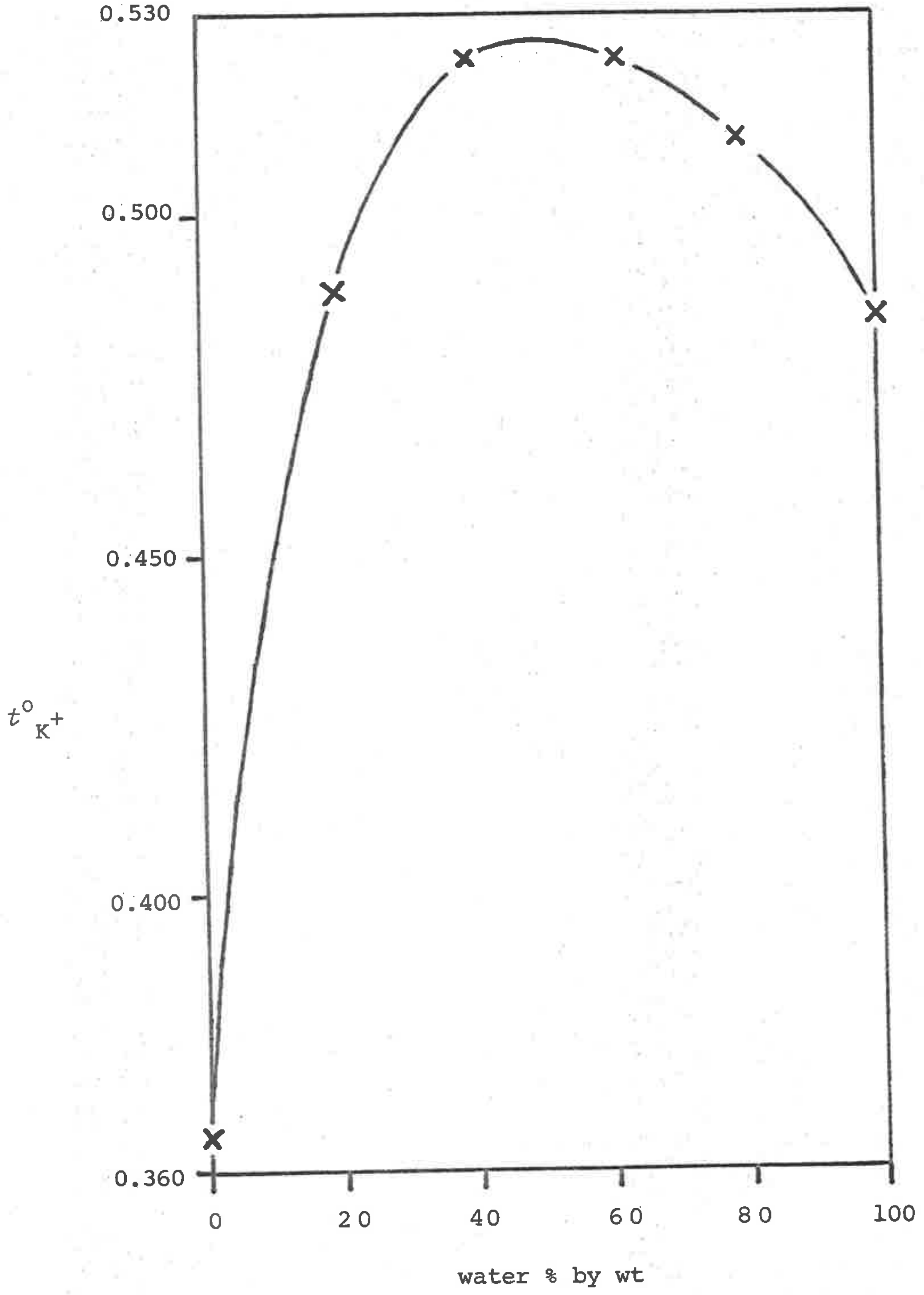
In the case of 40% and 80% water mixtures the respective values of $t_{K^+}^{o'}$ were averaged. The reproducibility of the measurements is illustrated by KCl in 40% water and KBr in 80% water. Two independently prepared stock solutions were used and for the last system two transport number cells were also employed. The results for the last two electrolyte-solvent mixtures also show that t_{K^+} is independent of the time and the current used for the electrolysis, hence mixing of the two compartments of the apparatus by convection currents resulting from Joule heating must be negligible. No gassing of the electrodes was observed as no bubbles were seen in the apparatus after the electrolysis was completed nor did the meniscus reading change from the value observed prior to electrolysis.

$\lambda^{o}_{K^+}$ can be computed from, first $t^{o}_{K^+}$ (KBr) and Λ^{o} (KBr), and, secondly, $t^{o}_{K^+}$ (KCl) and Λ^{o} (KCl) in 40% water/DMF mixtures, the values being 24.3_0 and 24.2_7 respectively. That is, within 0.12%, they are identical, a result which also supports the precision of the transport number measurements made in this research. The values of $t^{o}_{K^+}$ have been summarized in Chapter 7, table 7.10. The dependence of $t^{o}_{K^+}$ (KBr) upon solvent composition is graphically illustrated in figure 6.2. $t^{o}_{K^+}$ for KBr in DMF was computed from $\lambda^{o}_{K^+}$ and $\lambda^{o}_{Br^-}$ evaluated by Prue and Sherrington (27) based on transport number data in DMF.

Returning to KBr in 20% water/DMF mixture, the cell resistance drifted with time after thermal equilibration should have been completed. If the contents were mixed a sudden decrease in resistance with time was observed. This observation, supported by the appearance of bare silver metal of the silver-silver halide electrode, can be explained by the dissolution of solid AgBr with the subsequent formation of an ionic silver halide complex(s). The run was consequently abandoned and fresh electrodes were prepared. The electrolyte solution was saturated with AgBr and the transport number determination was repeated. No drift in resistance with time was noted. The preparation of the AgBr is given in appendix 6.2. Since the Ksp of the solution is 0.70% higher, table 6.5, due to the presence of the silver complexes each Ksp, corresponding to C_1, C_2 and C_3, were reduced by 0.70%, i.e. the Ksp values are effectively expressed in terms of the Ksp of KBr solutions in the absence of the silver halide ions. From the corrected Ksp values C_1, C_2 and C_3 were evaluated by the usual method (6). Further, the number of coulombs passed through the cell were reduced by the solvent correction and 0.70%, since current is also transported by the silver complex. A more detailed investigation, which would entail the more precise way of evaluating the constituent

FIGURE 6.2

The dependence of the cationic transport number of KBr in DMF/water mixtures upon composition at 25°C.


0.530
0.500
0.450
0.400
0.360
$t^o_{K^+}$
0
20
40
60
80
100
water % by wt

ionic transport number for K^+ in this system, would have been to conduct transport number measurements at a number of concentrations in conjunction with stability constant measurements similar to that described by Alexander et al (28) and Butler (29), so that the concentration of each ionic species could be evaluated. Then, using a procedure similar to that described by Spiro et al (30) for orthophosphoric acid solutions, the constituent ion transport number for K^+ could be evaluated. Due to the solubility of silver halides no further measurements were undertaken in solvents having less than 20% water.

Transport number studies in pure DMF have been reported by Prue and Sherrington (27) and Paul et al (31). Their respective results may be compared by citing the values of $\lambda^o_{Li^+}$ evaluated from their measurements which were 25.0 (27) and 23.62 (31). Scrutiny of the two experimental procedures reveals that the study of Prue et al is the more reliable. Unlike the last authors, the result of Paul et al is in doubt due to the solubility of AgCl in DMF in the presence of chloride ion (28) (29). The lower result of Paul et al is explicable in terms of the presence of ionic silver halide complexes, since in this research the resistance of KBr solution in 20% water/DMF is lower in the presence of the silver complex which suggests that this compound is more mobile than the bromide ion. Hence, more current would be carried by the anionic constituents of the solution in the cell of Paul et al due to this effect. Therefore their value of $\lambda^o_{Li^+}$ is lower than that reported by Prue and Sherrington.

Some preliminary investigations were carried out in order that the problem of the solubility of the silver halide could be overcome. Silver electrodes and silver nitrate solutions seemed at first to be a possibility, but Prue and Sherrington and Chateau and Moncet (32) have reported the instability of $AgNO_3$ and Butler (29) of $AgClO_4$ solutions in DMF. Similar results were obtained in this research for aqueous DMF solutions of $AgNO_3$. The solutions remained clear for about a day, became cloudy and finally a brown precipitate, probably silver, was observed. The solutions were prepared in subdued light and stored in darkness. As a result, silver nitrate solutions and Ag electrodes do not hold much promise for transport number studies. However, using a simple autogenic rising boundary apparatus, obtained from an undergraduate teaching laboratory, a sharp boundary was formed above the cadmium metal cathode for a KCl solution in 40% water/DMF mixture. This method holds more promise for further research in overcoming the problem of the solubility of the silver halide of the silver-silver halide electrodes.

CHAPTER 6

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CHAPTER 7

THE LIMITING EQUIVALENT CONDUCTANCES OF KCl AND KBr AND THE IONIC CONDUCTIVITIES OF THE K^+, Br^- AND Cl^- IONS IN WATER/DMF MIXTURES AT 25°C.

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CHAPTER 7

7.1 Experimental Measurements and Solvent Properties

Some points of interest have already been raised in Chapter 5 in which evidence was presented to support the proposal that Λ at a given concentration of KCl in 60% and 80% water solvent mixtures was independent of the purification method used to prepare the organic component of the solvent. It was also proposed that Λ was independent of the magnitude of the solvent correction.

In general the conductivity measurements made in this research for each electrolyte-solvent system were supplemented by making measurements in a second cell, usually upon an independently prepared electrolyte solution. The concentration dependence of Λ for each electrolyte-solvent system is presented in appendix 7.1. The cells and the solvent sample from which the stock was prepared are also recorded. The density measurements that were used to convert the molality of each electrolyte solution to a molarity have been described in Chapter 5.

The pertinent solvent properties required for the evaluation of Λ^o are presented in table 7.1. The dielectric constants of pure DMF and water are the result of the measurements of Leader and Gormley (1) and Wyman (2) respectively. There have been a number of reported values for the dielectric constants of various DMF/water mixtures. The dielectric constants presented in table 7.1 were interpolated from the measurements of Douheret and Morenas (3), Douheret (4) and Reynaud (5). Lanier (6), however, presents dielectric constant data in graphical form only. In addition, Badoz-Lambling and Demange-Guerin (7) have reported values at 22.4°C and Ghodstinat et al (8), the last authors, did not report the temperature at which the determination was carried out. The viscosity of pure DMF is that reported by Ames and Sears (9) and Prue and Sherrington (10), while the viscosity of DMF/water mixtures and pure water at 25°C have been presented and discussed in Chapters 4 and 5.

7.2 The Evaluation of Λ^o

TABLE 7.1

VISCOSITIES AND DIELECTRIC CONSTANTS OF DMF-WATER MIXTURES AT 25°C

Water % by Wt.	Viscosity cP.	Dielectric Constant
100.0	0.8903	78.54
80.00_0	1.401_5	$74._8$
79.41_4	1.419_9	$74._7$
61.24_1	2.014_6	$69._3$
40.02_7	2.501_6	$60._6$
31.34_6	2.393_8	$56._1$
20.00_6	1.873_5	$49._8$
0.0	0.796	36.71

7.2 (a) The Basis for the Computation of the Parameters of Pitts and Fuoss-Hsia Conductivity Equations

The values of the fundamental constants used in this research were those of Rossini, Gucker, Johnson, Pauling and Vinal (11) as cited by Robinson and Stokes (12) and Fuoss and Accascina (13).

The full Pitts (14) (15) and Fuoss-Hsia (16) conductivity equations were used in this research to evaluate Λ^o, a, and, where applicable, Ka in preference to approximated forms of these equations used previously by Fernandez-Prini and Prue (17), Fernandez-Prini (18) and Justice (19) who have expressed Pitts equation in the form of equation 7.1; Fernandez-Prini (20) has, in addition, similarly treated the Fuoss-Hsia conductivity equation.

$$\Lambda = \Lambda^o - S\sqrt{C} + EC\ln C + J_1 C - J_2 C^{3/2} \qquad 7.1$$

Evaluation of Λ^o with Pitts (P) and Fuoss-Hsia (F-H) equations requires initial estimates of Λ^o, and a. A value of Λ^o obtained from a plot of Λ against $\sqrt{C}$ proved satisfactory. For a an initial value of 3 or 5Å for (P) and (F-H) respectively were used. If the associated case for F-H was used, an initial value of Ka = 0.5 in most cases was employed.

The parameters of the conductivity equations were evaluated by using computer programs written in FORTRAN which are given as an appendix to this thesis. The principle of R.L. Kay's (21) program, to which a number of adaptations were made by the author of this thesis, used for the evaluation of the parameters of the conductivity equations is as follows. From the input values of Λ and C, together with the estimates of Λ^o, a and, where applicable, Ka a value of Λ is computed from the theoretical conductivity equation for each value of C. Hence a series of Λ (observed) - Λ (calculated) = $\delta\Lambda$ are obtained. Each unknown, Λ^o, a and Ka is increased in sequence by a factor of 1.005 and Λ (calculated) is computed for each value of C. Hence, by this process, the program has computed $\{(\partial\Lambda/\partial\Lambda^o), (\partial\Lambda/\partial a), (\partial\Lambda/\partial \mathrm{Ka})\}$ and $\delta\Lambda$. By solving equation 7.2 (21) by the method of least squares the increments of each unknown $\Delta\Lambda^o$, Δa and ΔKa are evaluated which will minimize equation 7.3.

$$\delta\Lambda = \frac{\partial\Lambda}{\partial\Lambda^o}\,\Delta\Lambda^o + \frac{\partial\Lambda}{\partial a}\,\Delta a + \frac{\partial\Lambda}{\partial Ka}\,\Delta Ka \qquad 7.2$$

$$(n-3)\sigma^2 = \Sigma(\delta\Lambda)^2 \qquad 7.3$$

n is the number of observations of Λ.
Adding the increments $\Delta\Lambda^o$, Δa and ΔKa onto the initial estimates, the second and subsequent cycles are undertaken, until convergence is attained which is considered to have occurred when $|\Delta a/a| < 1x10^{-3}$.

From equation 7.2 two types of calculation are possible depending upon whether the program iterates for Ka, the associated case, or Ka is assumed to be zero, the non-associated case.

7.2 (b) The Non-Associated Computation

Pitts

Instead of utilizing the tabulated values of S_1 and T_1 (14) these functions were computed from the original equations (14) at each value of κa with subroutines written for the two programs, PITTS and PITTSV2, which evaluated Λ^o and a from his conductivity equation. Program PITTS is based on equation 1.32 following the method of evaluating Λ^o and a as outlined by Pitts et al (22). PITTSV2 is based upon Kay's method of computation, equation 7.2, and a rearranged, but not approximated, form of equation 1.32 (23). Table 7.2 presents the parameters of the Pitts equation in the case of KCl in water at 25°C, using the combined data of Lind and Fuoss (25) and Chiu and Fuoss (24), as evaluated by programs PITTS and PITTSV2, together with the comparable results of Pitts et al (22) for this salt obtained by a similar procedure as program PITTS. Cm in table 7.2 denotes the maximum concentration of electrolyte in a given data set. It is interesting to note, after examining table 7.2, that Pitts et al (26) do not regard the Kay type calculation as being adaptable to the full Pitts equation.

Fuoss-Hsia

The basis of the non-associated computation for the Fuoss-Hsia equation is program UNASS for which the term $(\partial\Lambda/\partial Ka)\Delta Ka$ of equation 7.2 is equated to zero.

Table 7.3 presents Λ^o and a together with their uncertainties

TABLE 7.2

VALUES OF Λ^o AND a, FOR KCl-WATER AT 25°C, EVALUATED FROM PITTS CONDUCTIVITY EQUATION WITH PROGRAMS PITTS AND PITTSV2

Cm	Program	$\Lambda^o \pm \sigma\Lambda^o$	$a \pm \sigma a$	σ
0.0948	PITTS	149.86	3.04	0.016
0.0948	PITTSV2	149.86 ± 0.01	3.03 ± 0.01	0.015
0.0403	PITTS	149.86	3.03	0.012
0.0403	PITTSV2	149.85 ± 0.01	3.04 ± 0.01	0.011
0.0239	PITTS	149.86	3.04	0.020
0.0239	PITTSV2	149.85 ± 0.04	3.05 ± 0.04	0.018
≈0.02	Reference 22	149.89	3.00	0.018*
(0.0099)	Reference 22	149.87	3.02	0.011**

* Data of Chiu and Fuoss (24)

** Data of Lind and Fuoss (25)

and the standard error of fit of the data, σ, to the respective equation, for KCl in DMF/water mixtures, evaluated from the (P) and (F-H) theories on the assumption that Ka = 0. In general as Cm decreases, particularly in the case of (F-H), there is better agreement between experiment and theory as manifested by the decrease in σ with Cm. Also, with the exception of (F-H) at Cm = 0.0948 for water, Λ^o is constant, unlike a, with varying Cm. It can also be noted that (P) is more successful at higher values of Cm than (F-H). However, on the basis of Ka = 0 both theories have one point in common - a systematically decreasing with D in the case of (P) particularly, an observation which suggested that ionic association was responsible. Hence, the non-associated case was not considered further.

As recorded in Chapter 1, Pitts, in the formulation of his theory of conductivity, assumed that the electrolyte was completely dissociated. However, Justice (19) has employed an extension of Pitts theory to compute association constants from conductance data. Such a step was not undertaken in the present research, therefore (P) was not utilized further. The remaining computations were carried out with the Fuoss-Hsia theory by assuming Ka to be finite.

7.2 (c) The Associated Computation

The soundness of the calculation procedure can be demonstrated by data for the electrolytes KCl, NaCl and CsI in water using the conductivity data of Fuoss et al for these salts at 25°C (24) (25) (27). Two methods of evaluating the parameters Λ^o, a and Ka were used, both yielding, for a given salt, the same optimum values for these quantities. First, the three quantities were simultaneously iterated with program LOAOKA, the basis of the computation being equation 7.2. Second, a band of a values, encompassing the expected value by at least 5Å were used as input with estimates of Λ^o and Ka to program ITERA, which returned a pair of values of Λ^o and Ka which minimized equations 7.2 and 7.3 for each input value of a. The term $(\partial\Lambda/\partial a)\Delta a$ was dropped from equation 7.2. The method of evaluating the optimum values of Λ^o, a and Ka from such a procedure has already

TABLE 7.3

Λ^o AND a FOR KCl IN DMF/WATER MIXTURES, AT 25°C, AS COMPUTED FROM PITTS AND FUOSS-HSIA EQUATIONS ASSUMING THAT Ka = 0

Water % by Wt	Cm	Equation	Λ^o	± $\sigma\Lambda^o$	a	± σa	σ
100.0	0.0948	P	149.859	0.006	3.03	0.006	0.015
100.0	0.0948	F - H	150.000	0.020	3.303	0.020	0.071
100.0	0.0403	P	149.854	0.008	3.035	0.008	0.011
100.0	0.0403	F - H	149.927	0.016	3.424	0.016	0.026
100.0	0.0239	P	149.854	0.039	3.052	0.039	0.018
100.0	0.0239	F - H	149.874	0.057	3.480	0.030	0.024
79.4	0.019	P*	96.993	-	2.966	-	0.002
79.4	0.019	F - H	97.039	0.005	3.449	0.005	0.001
79.4	0.0847	P	96.985	0.008	2.995	0.008	0.011
79.4	0.0847	F - H	97.143	0.029	3.261	0.029	0.049
61.2	0.0876	P	65.895	0.008	2.535	0.008	0.010
61.2	0.0876	F - H	65.996	0.023	2.957	0.023	0.039
40.0	0.0454	P	46.191	0.009	1.924	0.009	0.009
40.0	0.0454	F - H	46.257	0.011	2.567	0.011	0.012
40.0	0.022	P	46.198	0.034	1.906	0.034	0.011
40.0	0.022	F - H	46.230	0.026	2.626	0.026	0.009
31.3	0.0141	P	42.943	0.040	1.845	0.040	0.014
31.3	0.0141	F - H	42.957	0.051	2.670	0.051	0.017
20.0	0.006	P	44.724	0.010	1.210	0.010	0.004
20.0	0.006	F - H	44.730	0.018	2.058	0.018	0.005

* PROGRAM PITTS : ERRORS OF COEFFICIENTS NOT COMPUTED

been described by Fuoss and co-workers (28) (29) (30). McKenzie and Fuoss (28) reported that this method of evaluating Λ^o and Ka from a band of a values was superior to the procedure used earlier by Chiu and Fuoss (24) and Hsia and Fuoss (27), who used a series of Ka values embracing the expected value of this quantity. Reported in table 7.4 are the values of Λ^o, a and Ka evaluated by program LOAOKA for KCl, NaCl and CsI, together with the results of Fuoss et al for these salts (24) (27). As it can be seen from table 7.4 the values of Λ^o, a and Ka, for a given salt are identical. The second entry in the σ column for this research was obtained by summing the individual values of $\delta\Lambda$ as reported by Fuoss et al for the data points used in the present research, since their complete set of data was not used for each salt. Having taken this latter step complete agreement is evident. The basis of the evaluation of Ka in this table is equation 1.36 in conjunction with the activity coefficient as predicted by the Debye-Hückel limiting law at each value of κ.

For the conductance runs measured in this research Λ^o, a and Ka were evaluated with programs LOAOKA and ITERA as described above for the alkali halides in water at 25°C. Fuoss (31) has already stated that, from experience, the upper limit of the range of applicability of the Fuoss-Hsia equation is $\kappa a \simeq 0.5$ or $f^2 \simeq 0.5$. In some systems measured in this research both these limits were exceeded. As a consequence two steps were taken. First Cm was decreased, the result being that the minimum in the σ-a plot became broader and finally disappeared. However, the position of the minimum did not alter appreciably as Cm decreased. An analogous broadening has been reported by Fuoss and co-workers (27) (24) in the case of σ-Ka plots as Cm decreases. The second observation was that in no system, up to the largest value of Cm measured, did $\delta\Lambda$ become large and systematic as Cm increased.

Reported in table 7.5 are Λ^o, a and Ka for KCl and KBr in DMF/water mixtures evaluated from program LOAOKA upon the basis of the activity coefficient, f, being computed from the limiting law.

TABLE 7.4

VALUES OF Λ^o, a, Ka FOR KCl, CsI AND NaCl IN WATER AT 25^o AS COMPUTED BY THE THREE PARAMETER ITERATIVE PROGRAM LOAOKA

Salt	Reference	Λ^o	a	Ka	σ
KCl[a]	This Research	149.89 ± 0.01	5.68 ± 0.05	0.79 ± 0.01	0.017
KCl	Reference 24	149.90	5.655	0.79	0.017
CsI[b]	This Research	154.17 ± 0.01	5.52 ± 0.05	0.94 ± 0.01	0.017 (0.015)
CsI	Reference 27	154.173± 0.015	5.504± 0.020	0.94	0.006
NaCl[c]	This Research	126.55 ± 0.01	6.14 ± 0.02	0.926± 0.002	0.005 (0.005)
NaCl	Reference 24	126.55	6.11	0.92	0.016

a. Data of Chiu and Fuoss (24) and Lind and Fuoss (25)

b. Data of Hsia and Fuoss (27)

c. Data of Chiu and Fuoss (24)

Excepting KCl in 61% and KBr in 20% water mixtures, it can be seen from table 7.5 that the condition that the minimum value of f^2, f^2_{min}, be ≃ 0.5 has been met. However, in the case of KCl in 61% water, if Cm is decreased so as to raise $f^2_{min} > 0.5$ the position of the minimum in the σ-a plot did not alter. The case of 20% water/ DMF system with KBr as solute will be raised later in this discussion.

All further data to be reported in this thesis are evaluated by iterating the three parameters simultaneously, since it has been shown that this method yields identical results for the optimum values of Λ^o, a and Ka, as compared with the method of Fuoss et al, in which bands of Ka and a values are submitted to programs similar to ITERA described in this discussion.

In Chapter 1 the attributes of the Debye-Hückel expression, 1.16, for the activity coefficient were discussed. Briefly its virtues are that its functional form is known (32) and it gives reasonable account of the dependence of experimental values of log f upon κ on the basis of a suitable choice for the a parameter (33). The limiting law has been used previously in conjunction with the Fuoss-Onsager equations by Fuoss and co-workers (25) (34) (35) (36). Justice and Fuoss (35) examined three expressions for computing the activity coefficient, the limiting law, the Debye-Hückel expression and the latter function with the distance parameter set to, q, the critical distance of Bjerrum (37).

$$q = \frac{|z_1 z_2| e^2}{2DkT}$$

Justice and Fuoss reported that the fit of the data to the Fuoss-Onsager equation was superior when the limiting law was used to compute values of f. These last authors justified the use of the limiting law by the following rationale - "this procedure can be justified on the argument that equ. 5 allows for long range interionic effects (which are clearly independent of the shape or size of the ions), while short range effects are all subsumed in the Ka term which explicitly and sensitively depends on the contact

TABLE 7.5

VALUES OF Λ^o, a AND Ka FOR KCl AND KBr IN DMF/WATER MIXTURES AT 25°C. Ka EVALUATED ON THE BASIS OF THE ACTIVITY COEFFICIENTS AS COMPUTED FROM THE DEBYE-HÜCKEL LIMITING LAW.

Water Wt. %	Salt	Cm	f^2_{min}	$\Lambda^o \pm \sigma\Lambda^o$	$a \pm \sigma a$	Ka ± σKa	σ
100.0	KCl	0.095	0.49	149.888 ± 0.011	5.677 ± 0.052	0.792 ± 0.008	0.017
79.4	KCl	0.085	0.49	96.993 ± 0.009	6.075 ± 0.040	1.001 ± 0.004	0.006
80.0	KBr	0.050	0.57	97.259 ± 0.006	6.432 ± 0.048	0.721 ± 0.006	0.005
61.2	KCl	0.088	0.44	65.915 ± 0.014	6.724 ± 0.078	1.696 ± 0.008	0.014
61.2	KBr	0.038	0.58	65.507 ± 0.014	6.405 ± 0.217	0.959 ± 0.046	0.007
40.0	KCl	0.045	0.49	46.242 ± 0.013	8.246 ± 0.082	3.748 ± 0.016	0.006
40.0	KBr	0.039	0.52	46.443 ± 0.006	7.914 ± 0.051	2.324 ± 0.004	0.002
31.3	KCl	0.014	0.64	42.898 ± 0.013	11.074 ± 0.250	5.002 ± 0.072	0.007
20.0	KCl	0.006	0.70	44.719 ± 0.005	12.838 ± 0.223	9.583 ± 0.047	0.004
20.0	KBr	0.044	0.40	46.378 ± 0.011	10.061 ± 0.039	6.732 ± 0.031	0.004

distance a" (35). However, such an argument neglects one very important point. Short range interactions are accounted for in the conductance equation by terms involving Ka and a, but, by using the limiting law no account is being taken of these interactions in the activity coefficient expression.

It is of interest, therefore, to examine the effect of neglecting the short range interionic interaction term $(1 + \kappa a)$ in the activity coefficient expression, and the effect that the neglect of this term might have upon the values of Ka and a computed from the Fuoss-Hsia equation on the basis of the limiting law. Such an examination is important for three reasons. Firstly, the observed systematic dependence of a for KCl and KBr in DMF/water mixtures upon D, table 7.5, might be related to the neglect of the $(1 + \kappa a)$ term in the activity coefficient expression. Secondly, for KBr in 20% water-DMF mixture, even though $f^2 < 0.5$, σ is of the order of ± 0.01% in Λ which is a reasonable estimate of the error in the experimental values of Λ. Thirdly, Ka not only depends upon the computed value of f^2 but the theoretical expression of Fuoss (28) links Ka and a thus:

$$\mathrm{Ka} = \frac{(4\ \pi\ Na^3)}{(\ 3000\ )}\ \mathrm{EXP}\ (e^2/a\mathrm{DkT})$$

The effect of neglecting the $(1 + \kappa a)$ term in the activity coefficient expression can be guaged by comparing values of log f computed from various expressions, including the limiting law and the Debye-Hückel equation, with experimental values of log f from data presented by Robinson and Stokes (33). One conclusion to be drawn from their tabulation is that, on the basis of comparing experimental and predicted values of log f, the use of the limiting law to predict reasonable values for f^2 of NaCl in water, to be utilized in the computation of Ka in the realm of applicability of the Fuoss-Hsia equation, is unjustifiable. Table 7.6 presents values of f^2 computed from the following sources. For the limiting law and the Debye-Hückel expression, with $a = 5.0$Å, the values of f^2 were computed from the respective expressions during the analysis of the conductance data for NaCl presented in tables 7.4 and 7.8. Comparison has been made with the experimental value of f^2 computed from reference (33). From the data presented in table 7.6 the Debye-Hückel expression gives the more reasonable value of f^2 and is to be preferred to the limiting law.

TABLE 7.6

VALUES OF f^2 COMPUTED FROM THE DEBYE-HÜCKEL LIMITING LAW AND THE DEBYE-HÜCKEL EQUATION WITH a = 5.0Å, COMPARED WITH AN EXPERIMENTAL VALUE OF f^2, FOR NaCl IN WATER AT 25°C

Source	C	$C\gamma$	f^2
Limiting Law	0.047244	0.046056	0.604
Debye-Hückel	0.047244	0.046361	0.690
Experimental Value	0.04981	-	0.673

Since the discrepancy between experimental and calculated value in the case of the limiting law must be attributed to the neglect of the $(1 + \kappa a)$ term, then the computation of a value for the activity coefficient must include this term.

Justice (38) has recently expressed the view that the use of the limiting law is unjustifiable; he accounts for the short range interionic interactions in the activity coefficient expression by setting a equal to q (19) (38) in the Debye-Hückel expression.

It is of interest to note also at this point that if $a = q$ was used in the activity coefficient expression, Justice (19) and co-workers (39) found that a evaluated from J_1 and J_2 of equation 7.1 were close to q even though the terms of J_2 were functionally incomplete (38) (40).

Lanier (6) has graphically reported activity coefficient data for NaCl in various organic-water mixtures including DMF-water. In the last system, in the realm of applicability of the Fuoss-Hsia equation, it appears from his graphical representation of his activity coefficient data that there is good agreement between experimental and the values predicted by the Debye-Hückel expression on the basis of $a \simeq 4.6\mathring{A}$ over the entire dielectric constant range studied.

In this research account was made of short range inter-ionic interactions in the activity coefficient expression by the following procedures - a fixed to an arbitrary value, $5.0\mathring{A}$ - iterating the distance parameter in the conductivity equation and the activity coefficient expression and by equating $a = q$ the Bjerrum critical distance. The values of Λ^o, Ka, a and the ion size term of the activity coefficient expression, termed a_f in tables 7.7 and 7.8, for KBr and KCl in DMF/water mixtures are presented in these tables. In addition, the value of f^2 corresponding to Cm in both tables 7.7 and 7.8, the last mentioned also containing the results obtained for NaCl and CsI in water.

A number of observations from these tables can be made. Firstly, with the exception of NaCl, Λ^o and σ are independent of the method used for computing f. In the case of NaCl no reasonable explanation for this observation can be given. Secondly, the dependence of a upon D is reduced, but not eliminated, by setting $a>0$ in the Debye-Hückel expression.

From the data for the potassium halides in DMF/water mixtures for optimum agreement between experimentally determined and the theoretical concentration dependence of Λ requires that the a parameter, as determined by the F-H equation, be dependent upon D. This is contrary to the F-H model for the ions which are regarded as being rigid charged spheres and their collision diameter, a, as a consequence should be constant. If a is fixed as required by the model, for example to the value of a found for the electrolytes in aqueous solution (28), then the uncertainties of the parameters Λ^o and Ka as well as σ are greater than if a is permitted to vary. This situation can be illustrated with the data for KCl presented in table 7.9. The biggest objection to fixing a, supported by the data in table 7.9 is that σ, for the solvents containing 61% water

TABLE 7.7

Λ^o, α AND Ka FOR KBr IN WATER AND WATER/DMF MIXTURES AT 25°C.

Ka EVALUATED ON DIFFERENT BASIS FOR COMPUTING THE ACTIVITY COEFFICIENT

Salt	Cm	f^2_{min}	a_f	Water Wt. %	$\Lambda^o \pm \sigma\Lambda^o$		$\alpha \pm \sigma\alpha$		Ka ± σKa		σ
KBr	0.10	0.49	0.0	100.0	151.71	0.011	5.774	0.093	0.708	0.013	0.036
	0.10	0.62	5.0	100.0	151.71	0.012	4.914	0.114	0.432	0.025	0.038
KBr	0.050	0.57	0.0	80.0	97.259	0.006	6.423	0.048	0.721	0.006	0.005
	0.050	0.67	5.0	80.0	97.260	0.007	5.736	0.058	0.526	0.011	0.005
	0.050	0.67	5.7	80.0	97.260	0.007	5.686	0.058	0.509	0.011	0.005
	0.050	0.65	q=3.7	80.0	97.259	0.007	5.846	0.058	0.564	0.010	0.005
KBr	0.038	0.58	0.0	61.2	65.507	0.014	6.405	0.217	0.959	0.046	0.007
	0.038	0.66	5.0	61.2	65.512	0.014	5.518	0.246	0.602	0.074	0.008
	0.038	0.67	5.4	61.2	65.512	0.014	5.475	0.244	0.583	0.074	0.008
	0.038	0.65	q=4.0	61.2	65.512	0.014	5.621	0.248	0.648	0.073	0.008
KBr	0.039	0.52	0.0	40.0	46.443	0.006	7.914	0.051	2.324	0.004	0.002
	0.039	0.61	5.0	40.0	46.456	0.007	6.424	0.095	1.619	0.029	0.003
	0.039	0.63	6.2	40.0	46.455	0.006	6.218	0.093	1.495	0.031	0.002
	0.039	0.61	q=4.62	40.0	46.456	0.007	6.499	0.094	1.662	0.028	0.003
KBr	0.044	0.40	0.0	20.0	46.378	0.011	10.061	0.039	6.732	0.031	0.004
	0.044	0.52	5.0	20.0	46.393	0.011	7.490	0.085	4.850	0.032	0.004
	0.044	0.55	6.8	20.0	46.386	0.010	6.848	0.091	4.190	0.049	0.004
	0.044	0.53	q=5.6	20.0	46.391	0.011	7.254	0.088	4.615	0.038	0.004
	0.034	0.44	0.0	20.0	46.369	0.006	10.104	0.030	6.708	0.018	0.002
	0.034	0.54	5.0	20.0	46.386	0.006	7.571	0.065	4.884	0.028	0.002

TABLE 7.8

Λ^o, a AND Ka FOR CsI, NaCl AND KCl IN WATER AND KCl IN DMF/WATER MIXTURES AT 25°C. Ka EVALUATED ON DIFFERENT BASIS FOR COMPUTING THE ACTIVITY COEFFICIENT

Salt	Cm	f^2_{min}	a_f	Water Wt. %	$\Lambda^o \pm \sigma\Lambda^o$		$a \pm \sigma a$		Ka ± σKa		σ
NaCl	0.088	0.51	0.0	100.0	126.546	0.006	6.143	0.023	0.926	0.002	0.005
	0.088	0.63	5.0	100.0	126.564	0.005	5.097	0.027	0.597	0.006	0.005
	0.088	0.63	5.09	100.0	126.564	0.005	5.087	0.027	0.593	0.006	0.005
	0.088	0.60	q=3.6	100.0	126.563	0.005	5.288	0.026	0.666	0.005	0.005
CsI	0.095	0.49	0.0	100.0	154.170	0.012	5.516	0.052	0.936	0.009	0.017
	0.095	0.62	5.0	100.0	154.175	0.010	4.118	0.072	0.433	0.022	0.017
	0.095	0.60	4.2	100.0	154.176	0.010	4.227	0.073	0.478	0.022	0.017
KCl	0.095	0.49	0.0	100.0	149.888	0.011	5.677	0.052	0.792	0.008	0.017
	0.095	0.61	5.0	100.0	149.899	0.010	4.635	0.060	0.444	0.017	0.017
	0.095	0.59	q=3.6	100.0	149.899	0.010	4.808	0.067	0.509	0.016	0.019
KCl	0.085	0.49	0.0	79.4	96.993	0.009	6.075	0.040	1.001	0.004	0.006
	0.085	0.61	4.9	79.4	97.007	0.008	4.915	0.049	0.594	0.012	0.006
	0.085	0.61	5.0	79.4	97.007	0.008	4.905	0.049	0.590	0.012	0.006
	0.085	0.59	q=3.7	79.4	97.007	0.008	5.077	0.049	0.660	0.011	0.006
KCl	0.088	0.44	0.0	61.2	65.915	0.014	6.724	0.078	1.696	0.008	0.014
	0.088	0.58	5.0	61.2	65.936	0.014	4.800	0.154	0.921	0.053	0.015
	0.088	0.58	4.8	61.2	65.936	0.014	4.833	0.154	0.938	0.052	0.015
	0.088	0.56	q=4.0	61.2	65.938	0.014	5.009	0.153	1.029	0.049	0.015
KCl	0.045	0.49	0.0	40.0	46.242	0.013	8.246	0.082	3.748	0.016	0.006
	0.045	0.59	q=4.6	40.0	46.254	0.012	5.915	0.176	2.583	0.017	0.006
KCl	0.014	0.64	0.0	31.3	42.898	0.013	11.074	0.250	5.006	0.072	0.007
	0.014	0.73	9.2	31.3	42.907	0.014	9.186	0.431	4.354	0.067	0.007
	0.014	0.69	q=5.0	31.3	42.907	0.014	9.909	0.364	4.668	0.030	0.007
KCl	0.006	0.70	0.0	20.0	44.719	0.005	12.838	0.223	9.583	0.047	0.004
	0.006	0.76	10.4	20.0	44.725	0.006	10.436	0.434	8.432	0.144	0.004
	0.006	0.73	q=5.6	20.0	44.723	0.006	11.572	0.332	9.085	0.049	0.004

and less, far exceeds what is regarded as being a reasonable estimate of the experimental error in the conductivity measurements. Hence a fixed value for a is unacceptable. A preferable explanation for the variation of a with D is that it is an artifact of the model rather than an effect of the ions being separated by solvent molecules which is contrary to the definition of a. There also appears from the data presented in tables 7.7 and 7.8 to be little correlation in the range of dielectric constant studied between a and q although as D decreases q increases.

It is concluded that the only reasonable interpretation that can be given to a is that it is a quantity that permits, in conjunction with Ka, optimum agreement between the experimental and theoretical concentration dependences of Λ thereby allowing the evaluation of Λ^o. Confidence can be expressed in the values of Λ^o obtained, for a given system, as they are independent of the value of a and Ka.

For the Ka parameter, upon the basis of the (F-H) model, both electrolytes are slightly associated in DMF/water mixtures. Since from the theoretical expression for Ka of Fuoss a and Ka are interdependent and the significance that can be attached to a is in doubt, no further comments need be expressed about the Ka parameter.

Returning to KBr in the 20% water mixture Cm was decreased as much as possible leaving 5 points to be re-submitted to program LOAOKA. If the limiting law is used to compute f, then Λ^o does vary slightly outside the limits defined by the error of this quantity which contrasts with the result obtained by using the Debye-Hückel expression. Further, the use of the limiting law has been shown to give inferior estimates of f, hence little confidence can be expressed in the variation of Λ^o with Cm if the limiting law is employed.

Fuoss and Hsia (16) have already noted that terms higher than $O(C^{3/2})$ are significant in the description of the concentration dependence of Λ when $\delta\Lambda$ begins to increase systematically with increasing Cm and the values of Λ^o, a and Ka are also dependent upon

TABLE 7.9

THE VALUES OF Λ^o, a AND Ka FOR KCl IN WATER/DMF MIXTURES AT 25°C WHEN a IS TREATED AS A VARIABLE OR IS FIXED TO ITS APPROXIMATE VALUE FOR KCl IN WATER

Water % by Wt	Λ^o	$\sigma\Lambda^o$	a	σa	Ka	σKa	σ
100.0	149.888	0.011	5.677	0.052	0.792	0.008	0.017
79.4	96.993	0.009	6.075	0.040	1.001	0.004	0.006
79.4	97.058	0.013	5.700	0.00	0.955	0.008	0.020
61.2	65.915	0.014	6.724	0.078	1.696	0.008	0.014
61.2	66.032	0.028	5.60	0.00	1.515	0.026	0.045
40.0	46.242	0.013	8.246	0.082	3.748	0.016	0.006
40.0	46.455	0.032	5.60	0.00	3.138	0.051	0.033
31.3	42.898	0.013	11.074	0.250	5.002	0.072	0.007
31.3	42.003	0.032	5.60	0.00	3.228	0.146	0.033
20.0	44.719	0.005	12.838	0.223	9.583	0.047	0.004
20.0	44.768	0.015	5.60	0.00	5.465	0.160	0.021

Cm. In the case of KBr in 20% water/DMF mixture although σ has decreased with Cm either value of σ, i.e. with Cm = 0.044 or 0.034, suggest that the agreement between experimentally and theoretically determined Λ is within the experimental error of the conductance measurements. Hence it is concluded from this research that the upper limit of the realm of applicability of the Fuoss-Hsia equation in DMF/water mixtures is greater than that corresponding to $f^2 \simeq 0.5$ as described by Fuoss (31) upon the basis of electrolytes in dioxane/water mixtures.

Presented in table 7.10 are the values of Λ^o, $t^o_{K^+}$, $\lambda^o_{K^+}$, $\lambda^o_{Br^-}$ and $\lambda^o_{Cl^-}$ evaluated from the conductance and transport number data for KCl and KBr in water, DMF and DMF-water mixtures. In the case of KBr in DMF Prue and Sherrington (10), Ames and Sears (9) and French and Glover (41) have reported 84.3_8, 84.1 and 85.0 cm^2 Int. Ω^{-1} equivalents^{-1} respectively as being the value of Λ^o at 25°C for this salt. Prue and Sherrington's values of 84.3_8, 30.8, 55.1 and 53.6 for Λ^o, $\lambda^o_{K^+}$, $\lambda^o_{Cl^-}$ and $\lambda^o_{Br^-}$ in DMF respectively were accepted. These last authors have already discussed the conductivity data for KBr in DMF cited above. For KBr in water at 25°C the data of Jones and Bickford (42), Owen and Zeldes (43) and Benson and Gordon (44) were combined and the results obtained for this system have been included in table 7.7. KBr in water has not been included in the previous analysis of conductance data since of the three sets of conductivity data cited above for this salt only Owen and Zeldes (43) report original Λ, C values; the other authors' data are quoted only at rounded concentrations, $\lambda^o_{K^+}$ from Λ^o (KCl) and Λ^o (KBr) using Longsworth's (45) value for $t^o_{K^+}$ (KCl) and Gordon et al's (46) value for $t^o_{K^+}$ (KBr) are in agreement. The reader's attention has already been drawn to the fact that $\lambda^o_{K^+}$ (KBr) and $\lambda^o_{K^+}$ (KCl) in a 40% water/DMF mixture are identical to within 0.12%.

TABLE 7.10

VALUES OF Λ^o, $t^o_{K^+}$, $\lambda^o_{K^+}$, $\lambda^o_{Br^-}$, $\lambda^o_{Cl^-}$ DERIVED FROM LIMITING CONDUCTANCE AND TRANSPORT NUMBER DATA OF KCl AND KBr IN WATER AND WATER/DMF MIXTURES AT 25°C

Water Wt %	Salt	Λ^o	$t^o_{K^+}$	$\lambda^o_{K^+}$	$\lambda^o_{Br^-}$	$\lambda^o_{Cl^-}$
100.0	KCl	149.90	0.4905	73.5_3	-	76.3_7
100.0	KBr	151.71	0.4847	73.5_3	78.1_8	-
79.4	KCl	97.00	-	-	-	47.3_3
80.0	KBr	97.26	0.510_8	49.6_8	47.5_8	-
61.2	KCl	65.94	-	-	-	31.6_7
61.2	KBr	65.51	0.523_1	34.2_7	31.2_4	-
40.0	KCl	46.25	0.524_6	24.2_7	-	21.9_6
40.0	KBr	46.46	0.523_0	24.3_0	22.1_6	-
31.3	KCl	42.91	(0.513)*	$22._0$	-	$20._9$
20.0	KCl	44.72	-	-	-	22.0_3
20.0	KBr	46.39	0.489_2	22.6_9	23.7_0	-
0.0	KCl†	-	-	-	-	55.1
	KBr†	84.3_8	-	30.8	53.6	-

* Interpolated value; † Reference (10)

CHAPTER 7

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CHAPTER 8

THE DEPENDENCE OF THE STOKES RADIUS AND THE LIMITING EQUIVALENT CONDUCTANCE OF THE K^+ ION UPON THE COMPOSITION OF SOME AQUEOUS SOLVENT MIXTURES AT 25°C

CHAPTER 8

The terminal velocity, ν, under the influence of a force, Ξ, a macroscopic particle of radius R, attains as it moves through an idealized medium a continuum of viscosity, η, is given by Stokes' law thus (1):

$$\nu = \Xi/(6\pi\eta R)$$

By treating an ion, such as a cation, as being a rigid charged sphere immersed in such an idealized solvent, Stokes' law can be rewritten in terms of the limiting ionic conductivity because this quantity is related to the limiting ionic mobility which can, in turn, be expressed in terms of the ionic velocity attained under the influence of a unit force (1).

$$\lambda^{o}_{+} = |z+|F^{2}/(6\pi\eta R^{+}N) \qquad 8.1$$

The Stokes radius, R^{+}, of a univalent cation can thus be calculated from the following expression:

$$R^{+} = 0.8194/(\lambda^{o}_{+}\eta) \qquad 8.2$$

Since the Stokes radius in this model is constant the difference between the viscosity of one medium and another must alone account for any change in conductivity of a given ion in the two solvents. In other words, a change in conductivity has a simple interpretation which is that an ion encounters a different hydrodynamic resistance to its motion in each solvent. In the application of Stokes law to formulate the retarding influence that an ion experiences as it moves through the solvent an important point is being neglected, namely that, contrary to the classical derivation of this law, the solvent cannot be regarded as being continuous (2) (3) since its molecules are of comparable dimensions to the ions themselves.

Another point that will be raised later in this discussion is that solvent properties other than its macroscopic viscosity influence ionic motion. To propose that viscosity is the sole source of retardation of ionic motion is, in itself, a gross simplification which neglects more important effects on the molecular level. Several such considerations will be introduced at this point, but which will be discussed more fully later in this chapter. One solvent property, the dipole of the solvent molecules and their proposed effect upon conductivity, has been examined by Fuoss (4). Since the ion is of comparable dimensions to the solvent molecules, one would intuitively expect that the structure of the solvent, i.e. the deviation from the ideal of the continuum model, would also be an important influence.

Equation 8.1 relating conductivity and the macroscopic viscosity of the solvent is known as Walden's Rule, a relationship which, when tested experimentally with a variety of ionic solutes in numerous solvents, can be best described, except in a few exceptional instances, as an approximation (3) (4) (5). This result leads to the obvious conclusion that other influences besides viscosity determine the mobility of an ion and hence its conductivity. It can be noted that large ions in aprotic solvents (3) and the larger homologues of the tetraalkylammonium ions in water (6) are among the few examples that can be quoted in which the behaviour, as demanded by Stokes' law, is approximated to a reasonable degree. Even this situation is complicated, however, as deviations are observed in systems in which specific solvent-solvent interactions occur, notably hydrogen bonding which seems to play a role in the local hydrodynamics of ionic motion (3). The failure of Walden's Rule is sometimes attributed to the variation of the size of the hydrodynamic entity, i.e. in this case the ion and its co-sphere, from solvent to solvent as a result of differing solvent molecules being attached to the ion in a permanent solvation sheaf (7) contrary to the model itself in which R^+ by definition is a constant. In the formulation of equation 8.1, it has been assumed that the solvent adheres perfectly to the surface of the ion with the result that the viscous frictional coefficient was equated to $6\pi\eta R^+$ (2) (8). However, Robinson and Stokes (6) have suggested that the numerical constant may not be 6π and proposed a correction procedure that can be applied to the Stokes radii of small ions in water upon the basis that the larger homologues of the tetra-alkylammonium cations in water closely approximate equation 8.1. Nightingale (9) has applied the suggestion of Robinson and Stokes to ions in aqueous solution. It can be noted here that Zwanzig (8), on the basis of the Fuoss-Boyd-Zwanzig model, obtained closer agreement between experimentally observed values of λ and that calculated from their model when the viscous frictional coefficient was equated to $4\pi\eta R^{+}$, i.e. to the condition in which the solvent slips over the surface of the ion. Other suggestions have centred upon the viscosity term itself, arguing that this quantity should be raised to a power, i.e. $\Lambda^{o}\eta^{\chi}$ = constant. For the aqueous non-electrolyte solvent systems studied by Steel, Stokes and Stokes (10), Accascina and Petrucci (11) (12) and Steel (14) and for the cyanoethylsucrose/acetonitrile system studied by Treiner and Fuoss (13) a value of $\chi<1.0$ is required since the decrease in conductance is less than that demanded by Stokes' law. Robinson and Stokes (15) have already stated that for some aqueous non-electrolyte systems the 'constant' χ depends upon the nature of the non-electrolyte and the ion, χ being closer to unity for large ions. In aqueous mixtures of DMF, MeOH, dioxane and EtOH, for example, in which $\Lambda^{o}\eta$ decreases with increasing added component concentration, a value of $\chi>1.0$ is required because a simple first order viscosity term is insufficient to account for the observed decrease in conductivity.

In departing from the model discussed up to this point, Fuoss (4) has attributed the observed dependence of the Walden product upon the dielectric constant of the solvent to electrostatic interactions between the ion and the dipoles of the solvent molecules, resulting in a nett increase in the local viscosity of the solvent in the vicinity of the ion. Hence the ionic velocity is subjected to an additional retardation, of electrostatic origin, resulting from ion-solvent-dipole interactions. Fuoss, as a result of "heuristic arguments" (4), expressed equation 8.1 in the following form:

$$\lambda_{+}^{o} = |z+|F^{2}/(6\pi\eta N(R_{\infty}^{+} + {}^{S}/D)) \qquad 8.3$$

The dependence of the Stokes radius R^{+} upon the dielectric constant of the medium can be written from equations 8.1 and 8.3 as:

$$R^{+} = R^{+}_{\infty} + {}^{S}/_{D} \qquad 8.4$$

R^{+}_{∞} in equations 8.3 and 8.4 is the hydrodynamic radius of the cation in a hypothetical solvent of infinite dielectric constant in which all electrostatic forces are zero (4). According to equation 8.4 R^{+} should vary linearly with D^{-1}, S being in Fuoss's model an empirical constant.

The linear plots, for R^{+} or R^{-} as a function of dielectric constant, obtained by Fuoss were presented as evidence to support the correctness of the arguments that lead to the formulation of his empirical relationships - 8.3 and 8.4. Some sections of these plots for polar-polar mixed solvent systems, however, were non-linear. Fuoss (4) explained this by suggesting that hydrogen bonding played an important role in the local hydrodynamics of a moving ion. It is also interesting to note, at this point, a suggestion by Accascina and Petrucci (11) (16) that the reason for the increase of $\Lambda^{o}\eta$ with increasing non-electrolyte concentration for KCl in ethylene glycol/water and glycerol/water mixtures respectively, as opposed to its decrease in MeOH/water mixtures, might be related to the number of hydrogen bonds that could be formed between the components of the solvent.

Boyd (17) (18) and Zwanzig (8) (19) later evaluated S theoretically and found that it was related to the relaxation time of the solvent, Γ, and the viscosity of the solvent.

Boyd's (17) (18) and Zwanzig's (1963) (19) result, for the sticking boundary condition, may be written as:

$$S = \frac{\Gamma e^{2}}{9\pi\eta (R^{+}_{\infty})^{3}} \left[\frac{D - D\infty}{D}\right] \qquad 8.5$$

while Zwanzig's latter results (1970) (8), for the sticking boundary condition -

$$S = \frac{\Gamma e^{2}}{16\pi\eta (R^{+}_{\infty})^{3}} \left[\frac{D - D\infty}{2D + 1}\right] \qquad 8.6$$

- for the slipping boundary condition -

$$S = \frac{\Gamma e^2}{8\pi\eta(R_\infty^+)^3}\left[\frac{D - D^\infty}{2D + 1}\right] \qquad 8.7$$

where D and D^∞ are the static and high frequency dielectric constants respectively.

In the Fuoss-Boyd-Zwanzig model, FBZ, the frictional force the ion experiences as it moves through the solvent, is comprised of the classical Stokes term, $6\pi\eta R^+$ for stick or $4\pi\eta R^+$ for slip (8), and the solvent relaxation effect induced by the motion of the ions through the medium. It is interesting to compare the result of Boyd and Zwanzig with a theoretical equation derived by Debye (20)

$$\Gamma = (4\pi\eta r^3)/kT \qquad 8.8$$

in which r is the radius of the orientable particle. Hence from Debye's, Boyd's and Zwanzig's respective models Γ should vary proportionally with η. Dannhauser and Johari (52) have noted that, although the Debye equation, 8.8, should be inapplicable for strongly associated liquids, $\Gamma \propto \eta$ is often observed, water at various temperatures is a good example (20).

If in the Zwanzig formulae, D^∞ is neglected with respect to D (21) (22) and in addition for the 1970 results, 8.6 and 8.7, the approximation is made that $2D + 1 \simeq 2D$, then S from the FBZ model can be written as -

$$S = (\text{constant } \Gamma)/\eta(R_\infty^+)^3$$

The fact that these approximations are reasonable will be demonstrated later in this discussion. Since by definition R_∞^+ is a constant for a given ion, it follows that S must be related to Γ the ion induced dipole relaxation effect. Consequently the relative magnitudes of the values of S obtained for an ion in a number of mixed solvents must be related and therefore in turn relatable to the relative strengths of ion-solvent interactions in the solvent mixtures.

It is also evident from the FBZ equation, 8.4, that two estimates of the quantity R_∞^+ can be evaluated, one from the coefficient S and the other from the intercept of a plot of R^+ against D^{-1}. The latter method has been used extensively by Fuoss and co-workers (23-26) in studies of alkali halide ions, including K^+ (23), in dioxane/water mixtures. Later, using the Zwanzig expression 8.5 Justice and Fuoss (21) evaluated $R_\infty^+(K^+)$ for dioxane/water mixtures. Atkinson and Mori (27) evaluated R_∞^+ for alkali metal ions, including K^+, in dioxane/water mixtures and glycerol/water mixtures using an equation analogous to 8.3 and the Boyd and Zwanzig expression for S, 8.5, retaining the term $(D - D\infty)/D$.

In addition to those conducted by the authors cited above, studies of the dependence of the Stokes radius for the K^+ ion upon composition on the basis of the FBZ hypothesis have been made by Justice and Fuoss (21), (glycine/water and dioxane/water) Treiner and Justice (28), (β-alanine/water) and Mewett (29) (α-alanine/water). The work of Accascina and Petrucci (11) (16), glycerol/water, ethylene glycol/water and methanol/water, was restricted to the application of Fuoss' empirical equation prior to the detailed formulation of S by Boyd and Zwanzig.

One aim of the present research has been to extend the studies cited above by examining the dependence of R^+ for the K^+ ion on solvent composition in aqueous mixtures of tetrahydrofuran (THF), EtOH, acetone, MeOH, DMF and iso-propanol (i-PrOH). A deficiency of previous studies (21-23) (28) (30), with the exception of those of Atkinson and Mori (27) and Mewett (29) has been the assumption of the independence of the transport number upon the composition of a mixed solvent. Thus in the present research for each of the DMF/water mixtures in which the limiting conductance of a salt was determined ionic conductivities were evaluated by the measurement of the cationic transport number. For KCl in EtOH/water and MeOH/water mixtures advantage was taken of the availability in the literature of transport number data for this salt in these solvent systems. However, for aqueous mixtures of acetone, THF and i-PrOH respectively, no such data were available and consequently the above mentioned assumption of the constancy of the transport number was applied at each solvent composition.

The Stokes radius of K^+ in the mixed solvents cited below were calculated from equation 8.2. The absolute viscosity of each solvent quoted is based upon that of water at 20°C as determined by Swindells, Coe and Godfrey (31). Ionic conductivities and hence the Stokes radius of the potassium ion, $R^+(K^+)$, are based upon the values of Λ^o recorded in the original papers. Conductivities of KCl in the various solvents were obtained from the following references: MeOH/water (32) (33); MeOH (34); EtOH/water (35); EtOH (36); dioxane/water (23); acetone/water and (i-PrOH)/water (37); acetone $\lambda^o_{Cl^-}$ (38), $\lambda^o_{Br^-}$ (39); THF/water (40); glycine/water (21); β-alanine/water (28) and α-alanine/water (29).

Transport number data for KCl was obtained from the following references: α-alanine/water (29); MeOH (41); MeOH/water (42) (43); EtOH/water (44); ethylene glycol/water (45); glycerol/water (46); dioxane/water (47) and glycine/water (48) (49).

The computed values of $R^+(K^+)$ are recorded in appendix 8.1.

Although values of $R^+(K^+)$ were not computed from them, values of $\lambda^o_{K^+}$ in these solvents are utilized in the discussion to follow: $\lambda^o_{K^+}$, based on transport number data in 10 and 20% sucrose/water, glycerol/water, 10% mannitol/water (10) (50); glycerol/water (12) (46) and ethylene glycol/water (11) (45) are recorded in appendix 8.2.

The values of S presented in table 8.1 were evaluated from plots of $R^+(K^+)$ against 100/D for the aqueous solvent mixtures denoted in this table. Where in the construction of these graphs, the values of R^+ were evaluated upon the assumption that $t^o_{K^+}$ (KCl) was independent of composition and equal to 0.4905 (51), this is indicated in the table. Transport number data for KCl in aqueous mixtures of acetone, i-PrOH and THF have yet to be reported. As two distinct slopes can be assigned to a plot of $R^+(K^+)$ against 100/D for THF/water mixtures, figure 8.1, two entries have been made in table 8.1. No value of S has been assigned to i-PrOH, for in the range of dielectric constant over which conductance measurements were made, the plot of $R^+(K^+)$ against 100/D is distinctly non-linear.

From table 8.1 it can be observed that there is no correlation between the value of S and the magnitude or the position, expressed

TABLE 8.1

VALUES OF THE COEFFICIENT S OF THE FUOSS-BOYD-ZWANZIG THEORY FOR THE K^+ ION IN SOME AQUEOUS SOLVENT MIXTURES AT 25°C

Added Component	Dependence of $t^o_{K^+}$ upon solvent composition	Maximum in Solvent Viscosity		S Seconds/ Poise
		Value cP	Position X_2	
DMF	This Research	2.5	0.27^a	189
MeOH	(41) (42) (43)	1.6	$0.27^{b,e}$	98
EtOH	(44)	2.4	0.24^b	89
THF	constant = 0.4905	1.8	0.14^c	73
acetone	constant = 0.4905*	1.4	0.15^b	64
THF	constant = 0.4905	1.8	0.14^c	37
dioxane	constant = 0.4905	2.0	0.24^d	20
dioxane	(47)	2.0	0.24^d	18
i-PrOH	constant = 0.4905	3.1	0.31^f	-
α-alanine	constant = 0.4905	-	-	22
α-alanine	(29)	-	-	26
β-alanine	constant = 0.4905	-	-	21
glycine	constant = 0.4905	-	-	19
glycine	(48) (49)	-	-	13

* $\lambda^o_{K^+}$ in acetone based on $\lambda^o_- = \lambda^o_+$ for tetrabutylammonium and triphenylboroflouride ions in acetone (39)

(a) This Research

(b) Reference (69)

(c) Reference (40)

(d) References (23), (26) and (88)

(e) Reference (32)

(f) Reference (92)

FIGURE 8.1

The dependence of the Stokes radius of the potassium ion, R^{+} (K^{+}) in Å, upon the dielectric constant of the solvent, 100/D, at 25°C, in aqueous mixtures of:

▲ α-alanine, based on transport number data for KCl in α-alanine/water mixtures.

△ α-alanine, transport numbers assumed to be independent of solvent composition.

⊡ β-alanine, transport numbers assumed to be independent of solvent composition.

◒ glycine, based on transport number data of KCl in glycine/water mixtures.

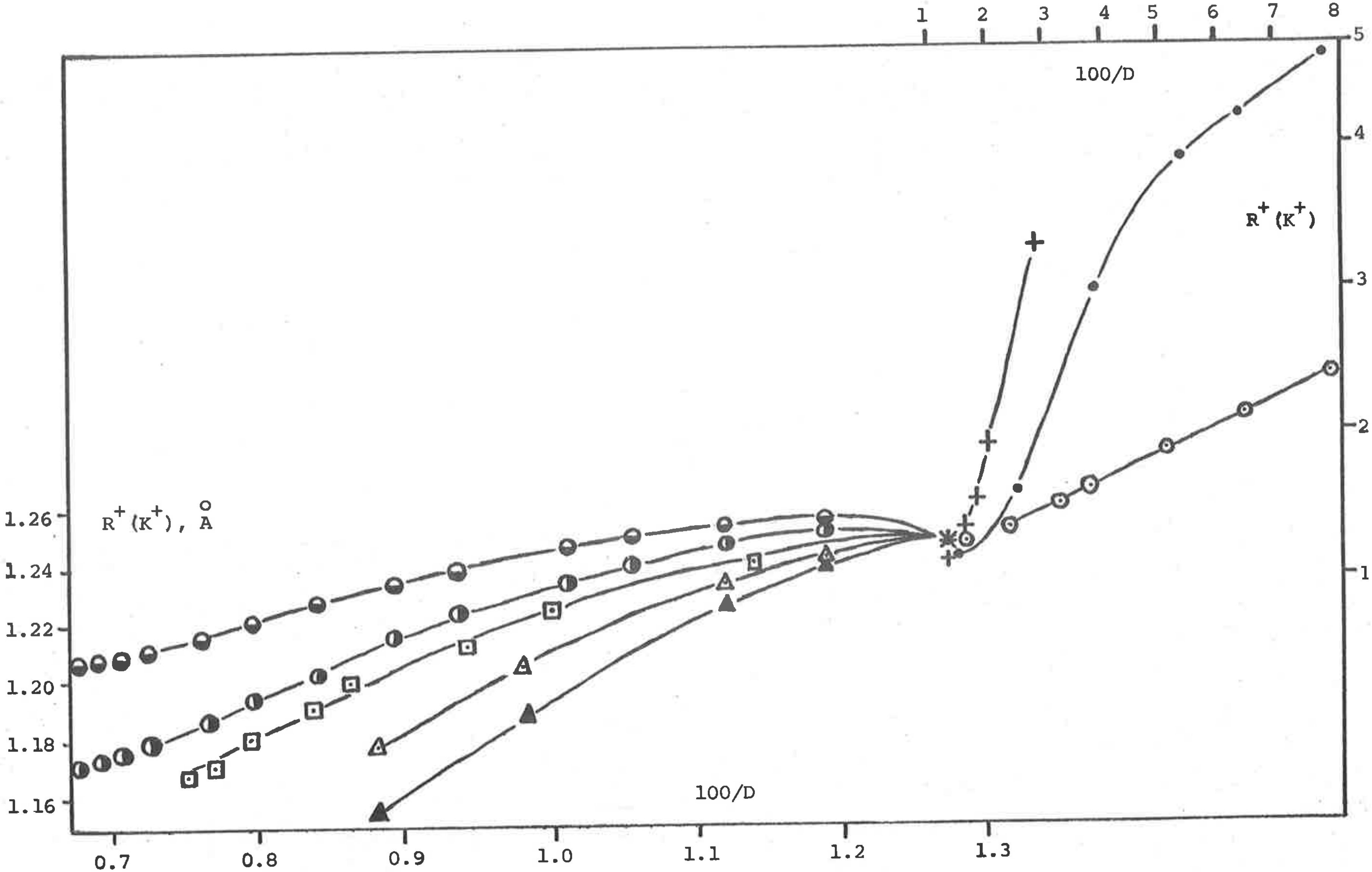
◑ glycine, transport numbers assumed to be independent of solvent composition.

+ DMF, based on transport number data for KCl in this solvent system.

⊙ dioxane, transport numbers assumed to be independent of solvent composition.

● THF, transport numbers assumed to be independent of solvent composition.

(✱ Pure water)


1
2
3
4
5
6
7
8
100/D
5
4
$R^+(K^+)$
3
2
1
1.26
$R^+(K^+)$, Å
1.24
1.22
1.20
1.18
1.16
100/D
0.7
0.8
0.9
1.0
1.1
1.2
1.3

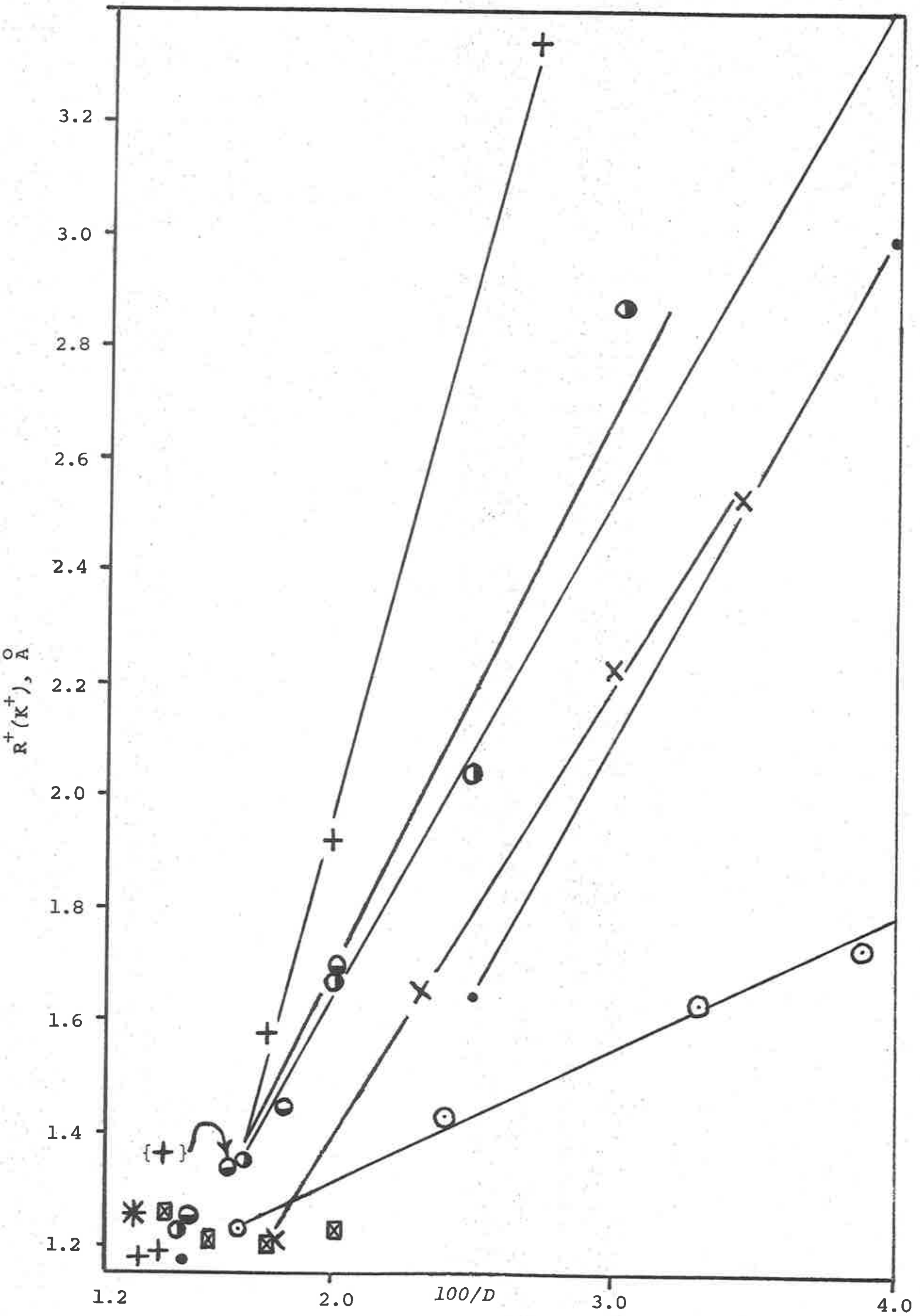
as mole fraction, X_2, of added component, of the maximum in the solvent viscosity. Hence it is concluded that the sequence of the values of S must be related to the strength of the K^+ ion-solvent interactions. At constant temperature a longer relaxation time for a liquid is interpreted as indicating that the strength of intermolecular interactions are stronger than in a liquid with a shorter relaxation time (52-57). Therefore it is proposed, on the basis of the FBZ model, that the strength of K^+ ion-solvent interactions decreases as the value of the coefficient S decreases.

The effect of assuming that transport numbers are independent of solvent composition can be examined by instancing the aqueous α-alanine, β-alanine, glycine and dioxane solvent systems for which the values of S are approximately constant, once this assumption is made. From such a constancy in S Justice and Fuoss (21), and later, Treiner and Justice (28), concluded that a single K^+ induced solvent relaxation time was present in aqueous mixtures of glycine, β-alanine and dioxane - that of water molecules. This was interpreted as indicating that the added component did not participate in the relaxation process (21). However, if S is evaluated upon the basis of the solvent dependence of the transport number, then the non-constancy of S becomes evident from table 8.1. The data presented in this table supports an earlier conclusion of Mewett (29) who proposed that the added component was participating in the ion induced dipole relaxation process. His conclusions were based upon the glycine/water, α-alanine/water and dioxane/water systems having computed the value of S from transport number data for KCl in these amino-acid/water mixtures. From the values of S presented in table 8.1, when evaluated upon the basis of transport number data, the non-constancy in this coefficient suggests that it is a unique property of the K^+ ion-solvent system under consideration. The dependence of $R^+(K^+)$ in the solvent systems cited in table 8.1 upon the dielectric constant of the solvent is graphically represented in figures 8.1 and 8.2. The curved region of each plot in the vicinity of pure water will be discussed later, since initial interest centres upon the

FIGURE 8.2

The dependence of the Stokes radius of the potassium ion, R^+ (K^+) in Å, upon the dielectric constant of the solvent, 100/D, at 25°C, in aqueous mixtures of:

+ DMF
◑ MeOH
× EtOH
◒ acetone
● THF
○ dioxane
☒ i-PrOH
(✱ Pure water)


3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
R+(K+), Å
{+}
1.2
2.0
100/D
3.0
4.0

sections of figures 8.2 and 8.3 within which $R^+(K^+)$ varies linearly with D^{-1} in accordance with the theoretical predictions of the FBZ hypothesis. Figure 8.3 presents the results obtained for the Stokes radii of K^+, Cl^- and Br^- ions in DMF/water mixtures. For each system cited, with the exception of K^+ in water/i-PrOH, linear segments are obtained in figures 8.2 and 8.3.

Earlier it was proposed that, as the value of S decreased, so did the strength of K^+ ion-solvent interactions. Evidence to support this proposal is provided by the N.M.R. studies of Fratiello and his co-workers who have investigated cation-solvent interactions in aqueous mixtures of varying concentrations of added component - DMF, N-methylformamide (NMF), dimethylsulphoxide (DMSO), THF, dioxane, acetone, EtOH and MeOH. These authors could find no evidence to suggest that cations were interacting with dioxane (58) (60) (61), THF (61) (62) or acetone (58) (61), even for such ions as Al^{+++} and Co^{++} which were found to interact strongly with DMF, DMSO and NMF in their aqueous mixtures. On this basis it might be reasonable to conclude that the only ion-dipole interaction occurring between acetone/water, dioxane/water and THF/water mixtures respectively is that with water molecules. Although this conclusion does not explain the different values of S observed for these respective solvent systems, it does support the view of Justice et al (21) that in the dioxane/water system the sole interaction is between the ion and water molecules. In an earlier study Fratiello and Miller (58) investigated the interaction between a number of univalent, divalent and trivalent cations and aqueous mixtures, 10:1 mole ratio of water, of DMSO, DMF, EtOH, MeOH, dioxane and acetone. The univalent cations were Li^+, Na^+ and K^+. The strength of the cation-organic component interactions was observed to vary as follows with the latter:

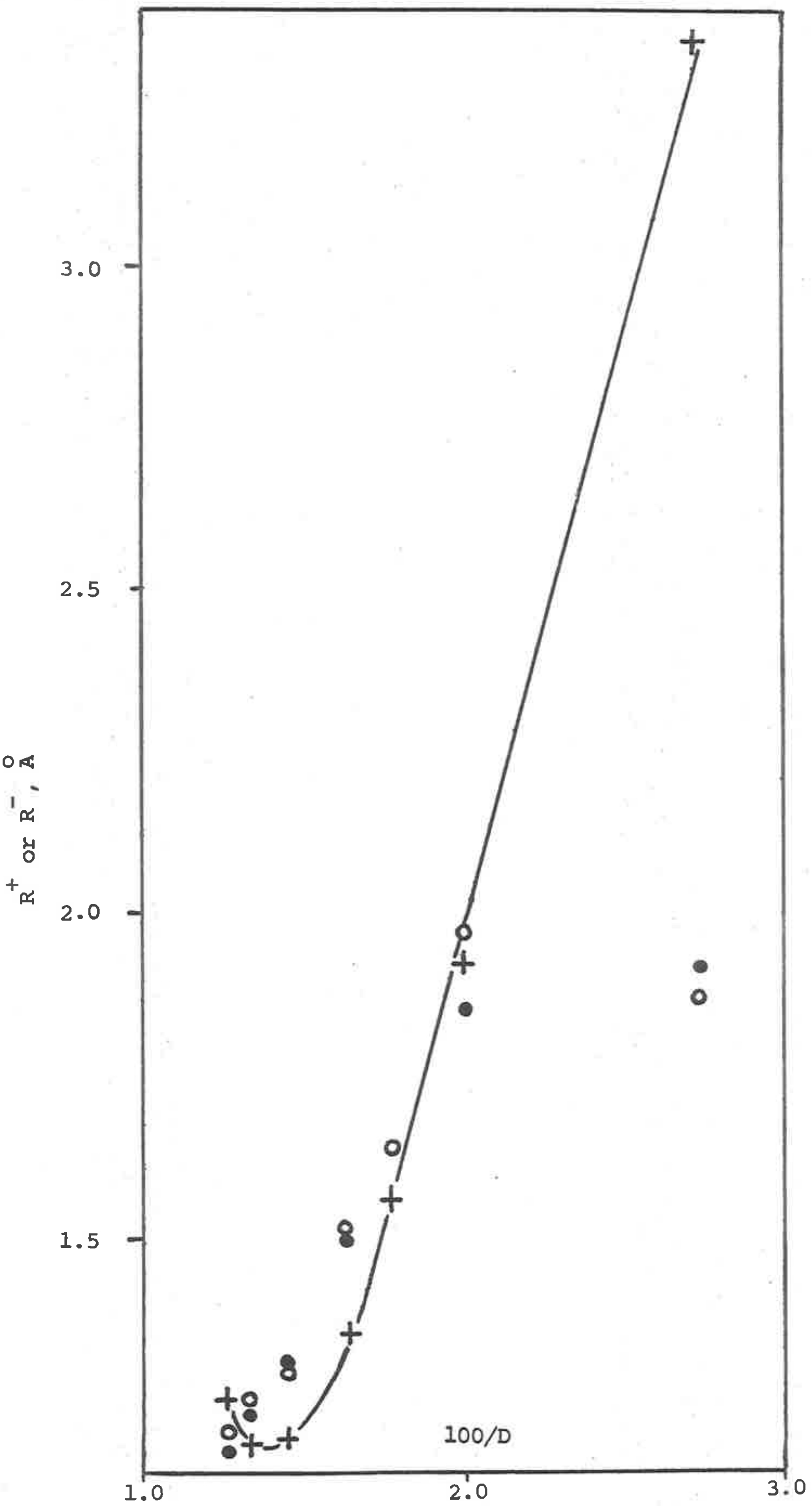
NMF>DMSO, DMF>alcohols (MeOH>EtOH)>acetone, dioxane.

Evidence of strong interaction between cations and some of the aprotic molecular components of the solvent mixtures studied is provided by the case of Al^{+++} (58) (61) in which separate resonance signals were noted for coordinated and bulk component in the cases

FIGURE 8.3

The dependence of the Stokes radius of the K^+, Cl^- and Br^- ions upon the dielectric constant of DMF/water mixtures, expressed as 100/D, at 25°C.

+ R^+ (K^+)
○ R^- (Cl^-)
● R^- (Br^-)


R^+ or R^-, Å
3.0
2.5
2.0
1.5
100/D
1.0
2.0
3.0

of dimethylacetamide (DMA), NMF, DMSO and DMF. The coordination number of Al^{+++}, with respect to the organic component, increased as the concentration of DMSO and DMF increased (61). However, in aqueous acetone, dioxane and THF mixtures respectively Al^{+++} ions appeared to be exclusively coordinated by water molecules, reinforcing once again the weak interaction between these molecules and cations in comparison to that of DMF and DMSO. This result is in agreement with the findings of the present research for S (DMF/water)> S (THF/water), S (acetone/water) and S (dioxane/water). Cation-solvent component interactions were investigated for $AlCl_3$, $TiCl_4$ and $CoCl_2$ in aqueous mixtures of acetone, acetonitrile (ACN), DMA, DMF, DMSO, dioxane, EtOH, MeOH, NMF, THF and tetramethyl urea (TMU) were the subject of a further study by Fratiello and co-workers (59). This last study should provide a better basis for comparison between cation-organic component interactions, as established by N.M.R. and the values of S rather than an earlier study (58) because the concentration of the non-aqueous component was varied over a wider range extending into the organic rich region, i.e. where the plots of R^+ are linear, and the study of Fratiello and Miller (58) is restricted to one water concentration, 10:1 mole ratio of water at which point the plots of R^+ are curved.

The complexing facility of acetone, diethyl ether (EE), DMF, DMSO, THF and TMU with boron trifluoride (BF_3) has been established by Fratiello and Schuster (63) by means of P.M.R. The sequence obtained can be taken as a measure of the electron donating ability of the molecules towards BF_3 and may therefore serve as an indication of the possible strength of the interaction between these molecules and water, when they comprise the added component of the solvent systems being considered in this discussion. The results obtained for BF_3 in MeOH and EtOH were not considered to be reliable due to possible chemical reactions (63).

Table 8.2 presents the strength of cation - added component interactions as determined by N.M.R., cation-solvent interactions as established by the sequence of the values of S obtained from the FBZ hypothesis and, finally, the electron donating ability of the added component towards BF_3 as determined by P.M.R.

TABLE 8.2

(a) Relative strengths of cation-added component interactions, as determined by N.M.R. (59), in aqueous mixtures of DMSO, MeOH, EtOH, TMU, THF, acetone, ACN and dioxane.

DMSO > amides, alcohols (MeOH>EtOH) > TMU > THF > acetone, ACN, dioxane.

(b) Relative strengths of K^+ ion-solvent interactions determined by the magnitude of the coefficient S of the Fuoss-Boyd-Zwanzig theory.

DMF/water >> MeOH/water > EtOH/water > THF/water > acetone/water > THF/water > dioxane/water.

(c) Relative electron donating facility of some liquids to BF_3 as determined by P.M.R. (63).

DMF, DMSO > TMU >> THF >> diethyl ether > acetone.

It can be seen from this table that there is general agreement between the sequences, suggesting that the magnitude of cation-solvent interactions as determined either by N.M.R. or from conductance, upon the basis of the FBZ hypothesis, depends upon the electron donating facility of the added component. Such a proposal requires that the added component have an influence upon the ion induced relaxation process from the added component. The sequence DMSO > DMF > THF > ACN is supported by the dielectric and emf study of Douheret (64), who reports that the magnitude of ion-solvent interactions, in aqueous mixtures of these dipolar aprotic liquids, lies in this sequence which differs slightly from his order for the magnitude of water-added component interactions - DMSO > ACN, DMF > THF.

Generally the interactions between cations and dipolar aprotic liquids are greater than those of anions with the same liquid, particularly when the negative sector of the solvent dipole is localized on a bare oxygen atom, for example, in the cases of DMSO, DMF and DMA (65). Several spectroscopic studies have established that the site of cation-DMF interactions is the carbonyl group (58) (66), while another report (67) indicates that this grouping is the site of electron donation for hydrogen bond formation.

The increase in cation-solvent interactions compared to anion-solvent interactions, i.e. $\lambda^o_{K^+}$ decreases relative to $\lambda^o_{Cl^-}$ and $\lambda^o_{Br^-}$ as the concentration of DMF is increased, is illustrated by the change in the Stokes radii for the K^+, Cl^- and Br^- ions in DMF/water mixtures presented in figure 8.3. As cation-solvent interactions increase, relative to anion-solvent interactions, so the Stokes radius of the cation increases relative to that of the anions. By comparison with values of the limiting ionic conductivities of the K^+, Br^- and Cl^- ions in water (89) and MeOH (90) respectively and K^+ and Cl^- ions in EtOH (90) it is evident that for DMF/water mixtures for which $100/D<2.0$ are more "protic" in character than "aprotic". In water, MeOH and EtOH the respective limiting conductances of these ions are similar in each of these solvents.

Relaxation time data for aqueous mixtures of the solvents studied in this research, with the exception of dioxane, EtOH and MeOH, are not available. Consequently, most values of Γ/η recorded in table 8.3* are based upon Γ and η for the pure liquids. Sarojini (68) has reported, in graphical form, relaxation time data for aqueous solutions of EtOH and MeOH containing up to 5% water, the measurements being conducted at 30°C. Since the FBZ plots for K^+ are closely linear in all cases and the point corresponding to the pure liquid is situated on, or close to, the line of best fit, it is reasonable to assert that the value of Γ/η for the pure liquid is applicable to the remainder of the FBZ plot.

* See Page 197

Table 8.3 presents the values of S and Γ/η, the latter values being based upon relaxation times and viscosity values measured at $25^{o}C$ unless otherwise indicated. The most disturbing feature of table 8.3 is the lack of correlation between the magnitude of K^+ solvent interactions as determined by the sequence of the values of S and Γ/η since from the FBZ theory $S \propto \Gamma/\eta$

The order of decreasing K^+ ion-solvent interactions as determined by the coefficient S are:
DMF/water >> MeOH/water > EtOH/water > THF/water > acetone/water > THF/water > dioxane/water.

A sequence which can be compared with that defined by the values of Γ/η is:
EtOH/water > MeOH/water >> DMF/water > dioxane/water > acetone/water.

The lack of correlation between these sequences raises questions regarding the legitimacy of using a solvent property, namely its relaxation time, to characterise the strength of ion-solvent interactions. Further, since the values of Γ/η were determined from data for the pure liquids in the cases of MeOH, EtOH, DMF and acetone, their order of magnitude can be compared with the corresponding order of the relative strength of cation-solvent interactions as indicated by the values of $\lambda^{o}_{K^+}$ in these pure liquids.

Γ/η : EtOH > MeOH >> DMF > acetone 8.9

Relative strength of cation-solvent interactions as defined by the relative values of $\lambda^{o}_{K^+}$
: EtOH > DMF >> MeOH >> acetone 8.10

The lack of agreement is apparent, from which it is concluded that the quantity Γ/η and hence S is not related to K^+ ion-solvent interactions in any way.

The last point suggests that dielectric relaxation and electrolytic conductance are not related in the manner suggested by the FBZ model. This point can be examined further by applying a suggestion of Dannhauser and Johari (52) to the K^+ ion-solvent systems being discussed in the present research. 'The viscous-damped sphere model of Debye predicts that $\Gamma/\eta \simeq$ constant' (52) and since Walden's rule, also based on this model, predicts that conductance $\propto 1/\eta$ Dannhauser and Johari reasoned that the relaxation time of a pure liquid should be inversely proportional to its conductivity. It seems reasonable to extend Dannhauser and Johari's reasoning to include a comparison between the relaxation times of a number of solvent systems and the corresponding conductivity of an ion in these solvents. Thus the following sequence of solvent relaxation times can be predicted as defined by the values of $(1/\lambda^o_{K^+})$ in the respective solvents (appendix 8.1).

$$\text{EtOH} > \text{DMF} >> \text{MeOH} >> \text{acetone} \qquad 8.11$$

On the basis of table 8.3 the actual sequence of relaxation times for the pure liquids is seen to be:

$$\text{EtOH} > \text{MeOH} >> \text{DMF} > \text{acetone} \qquad 8.12$$

The last comparison, 8.11 and 8.12, reinforces the conclusion already drawn from sequences 8.9 and 8.10. A conclusion drawn by Dannhauser and Johari as a consequence for their search for a possible relationship between viscous flow, dielectric relaxation and conductivity of the pure liquid amides which they studied was that the representation of these highly structured liquids according to the sphere-in-continuum model was too gross a simplification. Their conclusion may well be pertinent to the present research, for in the FBZ model the sphere-in-continuum view is invoked to represent the electrolyte solution. The lack of correlation between ion-solvent interactions as defined by the relative values of $\lambda^o_{K^+}$ in the solvent systems and the values of the coefficient S, through Γ/η, may then be attributable to the fact that the sphere-in-continuum model is too gross a simplification of the electrolyte-solvent system.

It will be recalled that from the data presented in table 8.2 there seemed to be a correlation between the magnitude of K^+ ion-solvent interactions, as suggested by the coefficient S and cation-added component interactions reported by Fratiello and his co-workers. However, the extent of interactions as determined by N.M.R. is based upon the composition of the solvent expressed in terms of mole fraction, in contrast to the sequence of S values which are based on composition determined by the dielectric constant of the solvent. These two dependences in the case of the K^+ ion can be observed by referring to figures 8.4 for $\lambda^o_{K^+}$ as a function of dielectric constant and 8.5 for $\lambda^o_{K^+}$ in terms of the mole fraction of added components. By comparing figures 8.4 and 8.5 it can be seen that the dependence of $\lambda^o_{K^+}$ upon solvent composition expressed in the two ways differs. It will be recalled that the decrease in cation-added component interactions, as determined by N.M.R., was -

DMSO > alcohols (MeOH>EtOH), amides > THF > acetone, dioxane.

This sequence can be compared with the order of K^+ ion-solvent interactions at mole fraction of 0.4 from figure 8.5 as defined by the values of $\lambda^o_{K^+}$ in each solvent system -

dioxane/water > EtOH/water ≃ DMF/water ≃
THF/water >> MeOH/water, (≃ acetone/water?)

Having compared these last sequences, it is concluded that there is no evidence to support the earlier suggestion that the magnitude of K^+ ion-solvent interactions decreases with decreasing S. Once again there appears to be no relationship between the magnitude of S and K^+ ion-solvent interaction.

On the basis of equation 8.4 $R^+_\infty(K^+)$ may be evaluated from the

FIGURE 8.4

Plots of $\lambda^{o}_{K^+}$ against solvent composition expressed as the dielectric constant, at 25°C, of aqueous mixtures of:

+	DMF
●	THF
○	dioxane
◑	MeOH
✕	EtOH
◒	acetone
⊗	i-PrOH
▽	ethylene glycol
△	glycerol
(✳	Pure water)

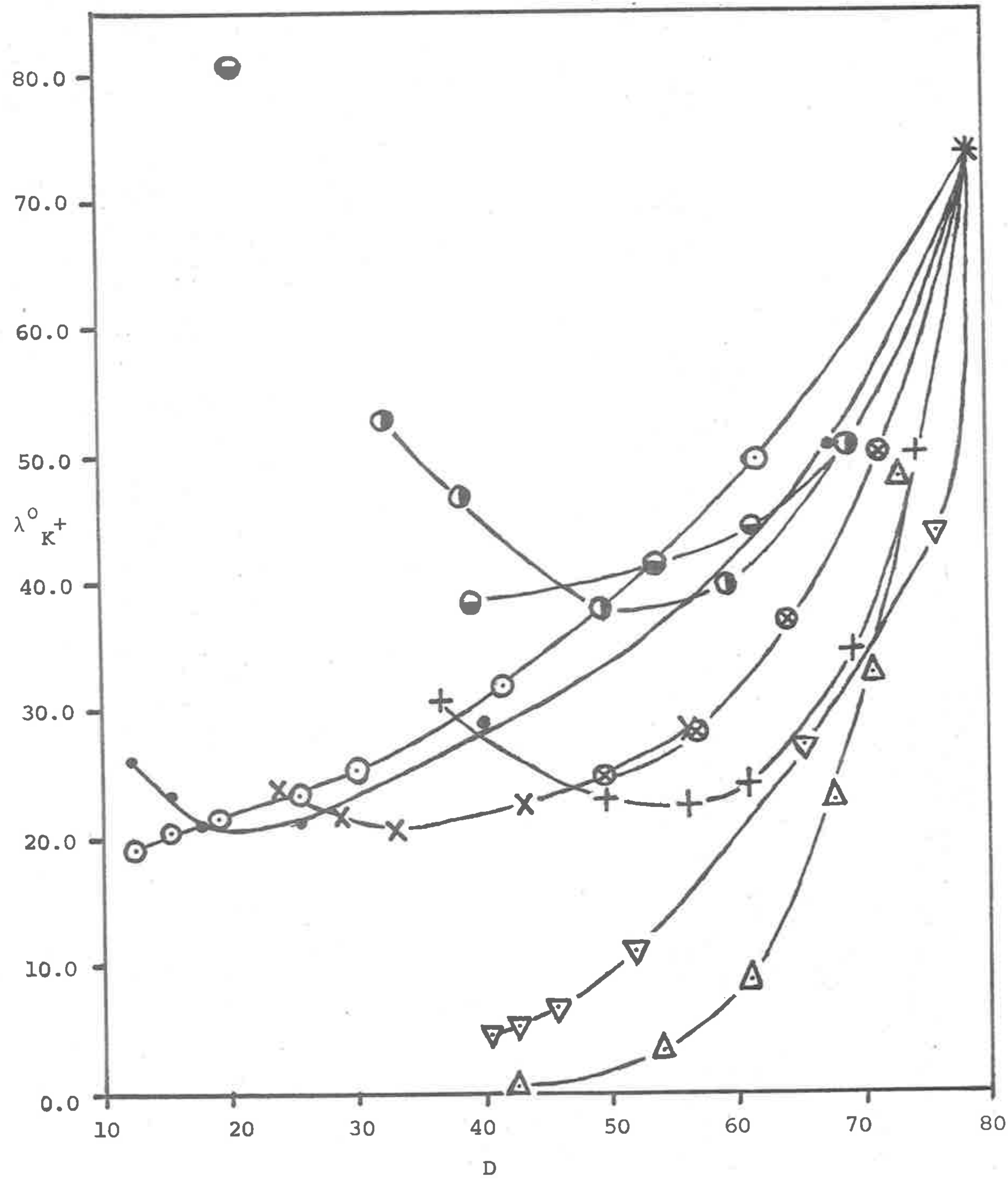

80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
$\lambda^o_{K^+}$
10
20
30
40
50
60
70
80
D

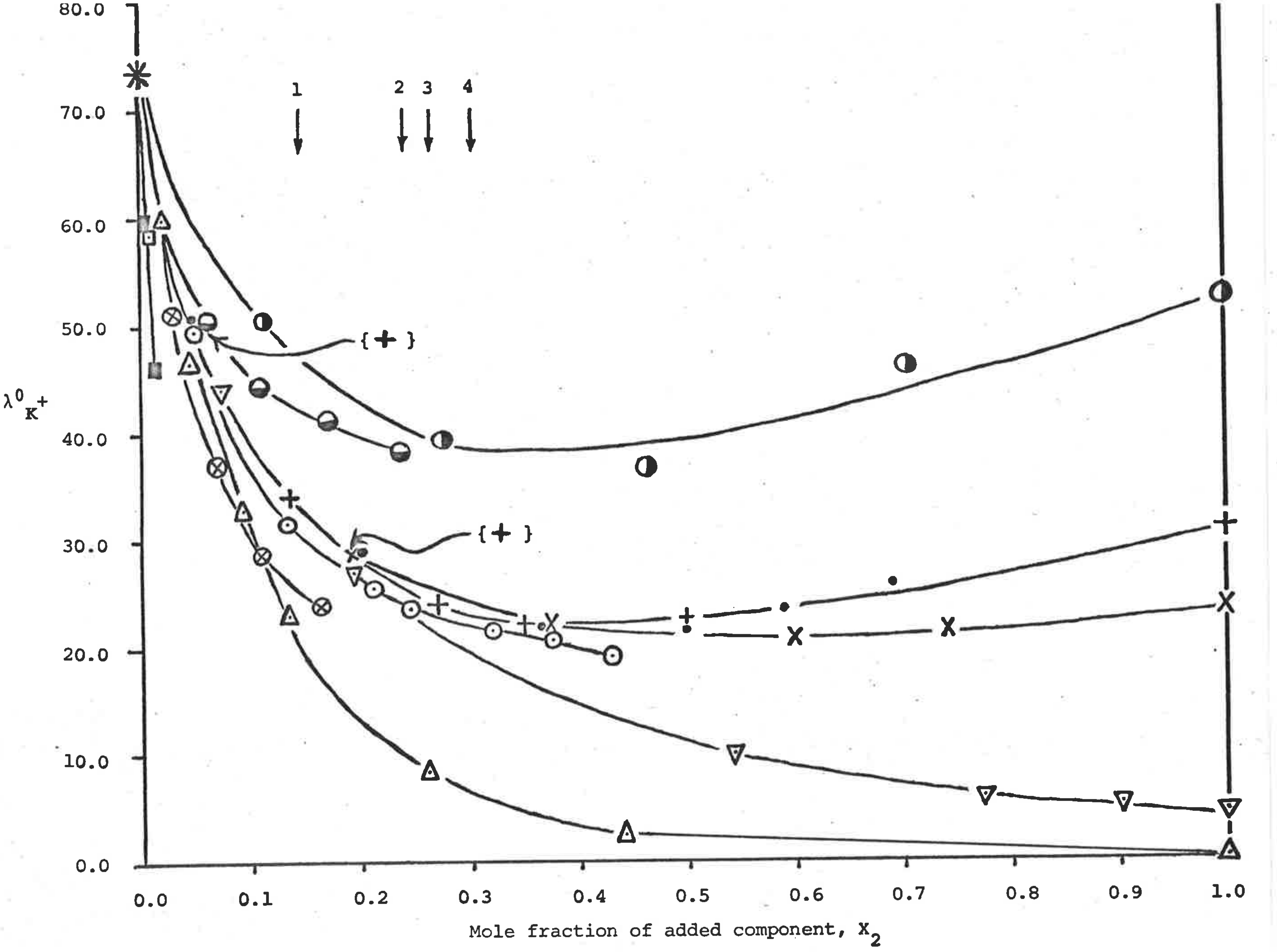
FIGURE 8.5

Plots of $\lambda^{o}_{K^+}$ against the solvent composition, expressed as mole fraction of added component X_2, in aqueous mixtures of:

◑	MeOH	○	dioxane
+	DMF	■	sucrose
◒	acetone	□	mannitol
●	THF	▽	ethylene glycol
⊗	i-PrOH	△	glycerol
✕	EtOH	(✳	Pure water)

The position of the viscosity maximum for the aqueous mixtures denoted below are indicated by the arrows situated in the upper left hand corner of fig 8.5.

1 : THF and acetone
2 : EtOH and dioxane
3 : DMF and MeOH
4 : i-PrOH


80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
$\lambda^0_{K^+}$
1
2
3
4
{+}
{+}
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Mole fraction of added component, X_2

intercept obtained from the FBZ plots by extrapolating their linear section to $D^{-1} = 0$. Alternatively it may be computed from the slope, S, of this linear section formulated according to the Boyd and Zwanzig expression, 8.5, and the appropriate value of Γ/η recorded in table 8.3. This latter method of computation has been described by Justice and Fuoss (21) and following these authors the term $(D - D\infty)/D$ was equated to unity for the evaluation of $R^{+}_{\infty}(K^{+})$ (slope) for the systems studied in the present research. The resultant values of $R^{+}_{\infty}(K^{+})$ (slope) and (intercept) are recorded and compared with literature values in table 8.4.

It is obvious from the values of $R^{+}_{\infty}(K^{+})$ presented in table 8.4 that this quantity, whether evaluated from the intercept or the slope is not a constant as proposed in the FBZ model. For dioxane/water in case (a) S was evaluated, following Justice and Fuoss (21) and Lind and Fuoss (23), by assuming that $t^{o}_{K^{+}}$ was independent of solvent composition and equal to 0.4905. The values of $R^{+}_{\infty}(K^{+})$ evaluated for the dioxane/water system in case (b) in the present research and by Atkinson and Mori (27) respectively are based on limiting ionic conductances for the K^{+} ion computed using transport number data for the dioxane/water system. However, from their paper it is not clear how Atkinson and Mori achieved this, for the paper they cite as their source of transport number data of HCl in dioxane/water mixtures is in fact the conductance study of Owen and Waters (70) for HCl in this solvent system. No transport number data or an empirical equivalent method of evaluating ionic conductances is to be found (70). Later Harned and Dreby (71) did report transport numbers for HCl in dioxane/water mixtures. On the basis of a rearranged form of equation 8.3 and Boyd and Zwanzig's expression for the electrostatic frictional coefficient, from which S is derived, Atkinson and Mori plotted $F^{2}/(N\eta\lambda^{o}_{K^{+}})$ against $(\Gamma(D-D\infty))/\eta D^{2}$ and evaluated $R^{+}_{\infty}(K^{+})$ from the intercept, $6\pi R^{+}_{\infty}(K^{+})$, and the slope, $2e^{2}/3R^{+}_{\infty}(K^{+})$, of the resultant plot.

The discrepancy between the literature values of $R^{+}_{\infty}(K^{+})$ (slope) and the comparable values obtained in the present research for the

TABLE 8.3

VALUES FOR THE SOLVENT RELAXATION TIME Γ, SOLVENT VISCOSITY η, Γ/η AND THE COEFFICIENT S FOR THE K^+ ION

Solvent	Water % by Wt	Solvent Relaxation Time, Γx10" Seconds	Solvent Viscosity η cP	Γ/ηx10^9 Seconds/ poise	S Seconds/ poise
DMF	0	1.5^a	0.796^b	1.9	189
MeOH	0	6.9^c	0.552^c	12.5	98
MeOH	0	4, $(30^\circ C)^d$	0.55, $(25^\circ C)^c$	7.3	98
MeOH	3	6, $(30^\circ C)^d$	0.62, $(25^\circ C)^e$	9.7	98
EtOH	0	14.4^c	1.084^c	13.3	89
EtOH	0	11, $(30^\circ C)^d$	1.1, $(25^\circ C)^c$	10	89
EtOH	3	15, $(30^\circ C)^d$	1.2, $(25^\circ C)^e$	13	89
THF	-	-	-	-	73
acetone	0	0.33 $(20^\circ C)^f$	0.323, $(20^\circ C)^f$	1.0	64
THF	-	-	-	-	37
dioxane	23.47	2.35^c	1.508^c	1.56	18

(a) Reference (54), (b) Reference (87), (c) Reference (27),

(d) Reference (68), (e) Reference (69), (f) Reference (17).

dioxane/water system in cases (a) and (b) is apparent from table 8.4. For dioxane/water, case (a) in the present research, a value of Γ/η at a different solvent composition from that used by Justice and Fuoss (21) was employed to evaluate $R_{\infty}^{+}(K^{+})$ (slope). Examination of the values of Γ and the corresponding values of η for the dioxane/water system cited by Atkinson and Mori reveals that the Debye equation 8.8, i.e. Γ/η = constant, is not obeyed over the whole composition range for there is a two-fold variation in the values of Γ/η for solvent mixtures having a composition between pure water and 95.15% dioxane. In order that $R_{\infty}^{+}(K^{+})$ be a constant it is evident from the Boyd and Zwanzig expression for S, 8.5, that Γ/η must be independent of solvent composition. Hence the differing results for $R_{\infty}^{+}(K^{+})$ (slope) for dioxane/water in case (a) may be explained in terms of the variation with composition of Γ/η. The discrepancy between the values of $R_{\infty}^{+}(K^{+})$ (slope) and (intercept) for dioxane/water case (b) are also explicable in the same terms. Analytically the methods of evaluating $R_{\infty}^{+}(K^{+})$ (intercept) and (slope) employed by Atkinson and Mori and in the present research are identical for they are based upon the same model in conjunction with an identical expression for the electrostatic frictional coefficient. Hence the non-constancy of R_{∞}^{+} must be attributable to the method used for its evaluation and in particular the non-constancy of Γ/η with solvent composition. The failure of the FBZ model to return constant values for $R_{\infty}^{+}(K^{+})$ (intercept) and/or (slope) must be attributed to the fact that the sphere-in-continuum model is an inadequate representation not only of the K^{+} ion-dioxane/water system but also the remaining systems studied in the present research. Therefore ion-solvent interaction effects are being grossly oversimplified by representing them in terms simply of addition of the FBZ electrostatic frictional term, containing the solvent properties - its dielectric relaxation time, viscosity and dielectric constant, to the classical Stokes frictional term. In other words, the failing of the FBZ model to qualitatively describe the relative magnitude of K^{+} ion-solvent interactions in the systems studied in

TABLE 8.4

VALUES OF $R_\infty^+(K^+)$, IN Å, EVALUATED FROM THE COEFFICIENT S AND THE INTERCEPT FROM THE FUOSS-BOYD-ZWANZIG EQUATION 8.4

Aqueous Solvent System	$R_\infty^+(K^+)$ (slope)			R_∞^+ (intercept)	
	Zwanzig (1963)		Zwanzig (1970)		
	This research	Literature	This research	This research	Literature
DMF	2.0	-	1.3	-1.80	-
MeOH	4.7	-	3.1	-0.30	-
EtOH	5.0	-	3.3	-0.44	-
THF	-	-	-	0.1	-
acetone	2.4	-	1.5	0.33	-
THF	-	-	-	1.8	-
dioxane case (a)	4.0	3.2[a]	2.6	0.86	0.84[c]
dioxane case (b)	4.1	5.2[b]	2.7	1.02	0.60[b]

(a) Reference (21), (b) Reference (27), (c) Reference (23) the present research is the description of these interactions in terms of macroscopic solvent properties together with an inadequate model for the electrolyte solution. At this point another pertinent short-coming of the sphere-in-continuum model should be recalled. It was concluded after comparing the sequences 8.11 and 8.12 that there was no correlation between the dielectric relaxation time of a solvent and the conductivity of the K^+ ion in the same solvent as predicted by the continuum model. It was thus concluded that the sphere-in-continuum model as a description of an electrolyte solution was too gross a simplification.

The equation of the term $(D - D\infty)/D$ to unity has a negligible effect upon the value of $R_\infty^+(K^+)$ obtained for if this latter quantity is recomputed for dioxane/water in case (a) by retaining this term in the expression for S, then $R_\infty^+(K^+)$ (slope) becomes 3.7Å as compared with the original 4.0Å. From table 8.4 it can be observed that agreement between R_∞^+ (intercept) and R_∞^+ (slope), for a given solvent system, is improved if Zwanzig's latest expression for S (for the sticking boundary condition) is used to compute R_∞^+ (slope) These values are based on equating $(D - D\infty)/(2D + 1) \simeq 1/2$ by assuming that $D\infty$ is negligible with respect to D. If the full term is retained, then R_∞^+ for dioxane/water for case (b) is reduced from 2.7Å to 2.5Å.

The significance of the relaxation time of a liquid in relation to conductivity is more doubtful following a more recent investigation of the dioxane/water system by Garg and Smyth (55). These last authors report two distinct series of relaxation times in contrast to the earlier measurement of Hasted et al (72). The longer series of times (55), which corresponds to that of Hasted et al, was dependent upon the composition of the mixture and passed through a maximum near the position of the viscosity maximum. As a result of dioxane/water interactions the relaxation process associated with the decay and reformation of the clusters took longer to occur (55), probably due to the structure-making, or stabilizing, influence dioxane could have in the water rich region upon the flickering clusters as a result of intercomponent hydrogen bonding. Therefore the single relaxation process characteristic of pure water is lengthened as a result of water-dioxane interactions and is dependent upon the dioxane concentration (55). The shorter relaxation time, ≃ 10 times faster, that occurs when dioxane is introduced into pure water, can be attributed to the rotation of singly bound water molecules of a cluster about the hydrogen bond (55) and is relatively independent of dioxane concentration. It is noteworthy that, if the shorter relaxation time has any significance in the FBZ model, it would reduce the value of $R_\infty^+(K^+)$ (slope) from 4.0Å to 1.8Å. The longer series of relaxation times being characteristic of hydrogen bonded aggregates (55) is contrary to the proposal of Justice and Fuoss (21) that the ion-induced dipole relaxation phenomenon and the dielectric relaxation process of the solvent itself was due to the relaxation of lone interstitially sited water molecules and not water molecules participating in cluster formation.

By far the most unsatisfactory feature of table 8.4 is the negative values obtained for $R_\infty^+(K^+)$ from the intercepts of the FBZ plots. A qualitative correlation may be drawn between the magnitude of $R_\infty^+(K^+)$ (intercept), and one added solvent property, namely the extent of intercomponent hydrogen bonding, for as this increases $R_\infty^+(K^+)$ decreases. In the region of excess added component, i.e. where the FBZ theory leads to a linear plot, the mixing of water with methanol (73), ethanol (73) and DMF (74) respectively is exothermic, in contrast to the solution of dioxane, for which the mixing process is endothermic (73) (75). These observations can be explained simply as the resultant of the simultaneous endothermic destruction of water structure in the presence of the organic component and exothermic interaction between the components: hydrogen bonding in the case of the alcohols (73). Evidence for the formation of intercomponent associations, in the instance of EtOH and water, is furnished by the X-ray diffraction study of Cennamo and Tartaglione (76). These last authors proposed that little dioxane-water association occurs in mixtures of these solvents. In comparison to water-DMF interactions, Douheret (64) classed those between water and THF as being weak, which also supports the proposal that, as $R_{\infty}^{+}(K^{+})$ evaluated from the intercept decreases, the extent of water added component hydrogen bonding increases.

It will be recalled that according to the FBZ model the frictional force experienced by the ion as it moves through the solvent is the sum of the electrostatic frictional term of Boyd and Zwanzig and the classical Stokes frictional term. The non-constancy in the values obtained for $R_{\infty}^{+}(K^{+})$ (slope), evaluated from the Boyd and Zwanzig electrostatic frictional term, were attributed to the inadequacy of the sphere-in-continuum model as a representation of the electrolyte solution. The Stokes frictional term is also, of course, based on the same model. It is of interest to pursue this matter further.

Interpretation of the dependence of conductance upon solvent composition in terms of Stokes law attributes this dependence to variation in solvent viscosity alone. The inadequacy of this interpretation as applied to the case of the K^{+} ion in the aqueous solvents studied in the present research may be illustrated by reference to figure 8.5. Most of these systems exhibit a viscosity maximum the position of which is indicated in the figure by means of a numbered vertical arrow. No correlation is evident between these positions and those corresponding to limiting conductance minima. However, in the ethylene glycol/water and glycerol/water solvent systems $\lambda^{0}_{K^{+}}$ does not exhibit a minimum and the solvent viscosity does not exhibit a maximum (77). Aqueous mixtures of sucrose likewise do not exhibit a viscosity maximum (91). However, as insufficient limiting conductance data for the K^{+} ion are available either for aqueous sucrose mixtures or for aqueous mixtures of mannitol and i-PrOH these respective systems must be excluded from consideration. From the data presented in figure 8.5 it is concluded that changes in the solvent viscosity for the systems studied in the present research bear no direct relationship to changes in conductivity with solvent composition.

Samoilov and co-workers have expressed the view that by adding MeOH to water (78) and to aqueous solutions of LiCl, NaCl and KCl (79) the structural temperature is increased. Methanol has therefore a structure making influence upon liquid water. These authors propose that MeOH molecules occupy the structural cavities in the open water structure, its interstitial sites; a clathrate compound is assumed to be formed. These views are similar to those of Franks and Ives (73) who, unlike Samoilov et al, propose that MeOH is accommodated into the lattice sites in contrast to EtOH, n-PrOH, i-PrOH and t-BuOH, which would occupy interstitial sites. Other authors have proposed that glycols (80), amides (53) and DMF, DMSO, THF and ACN (64) also occupy interstitial sites in the water structure at low concentrations of added component, with a subsequent stabilizing effect on the water structure (53) (73) (80).

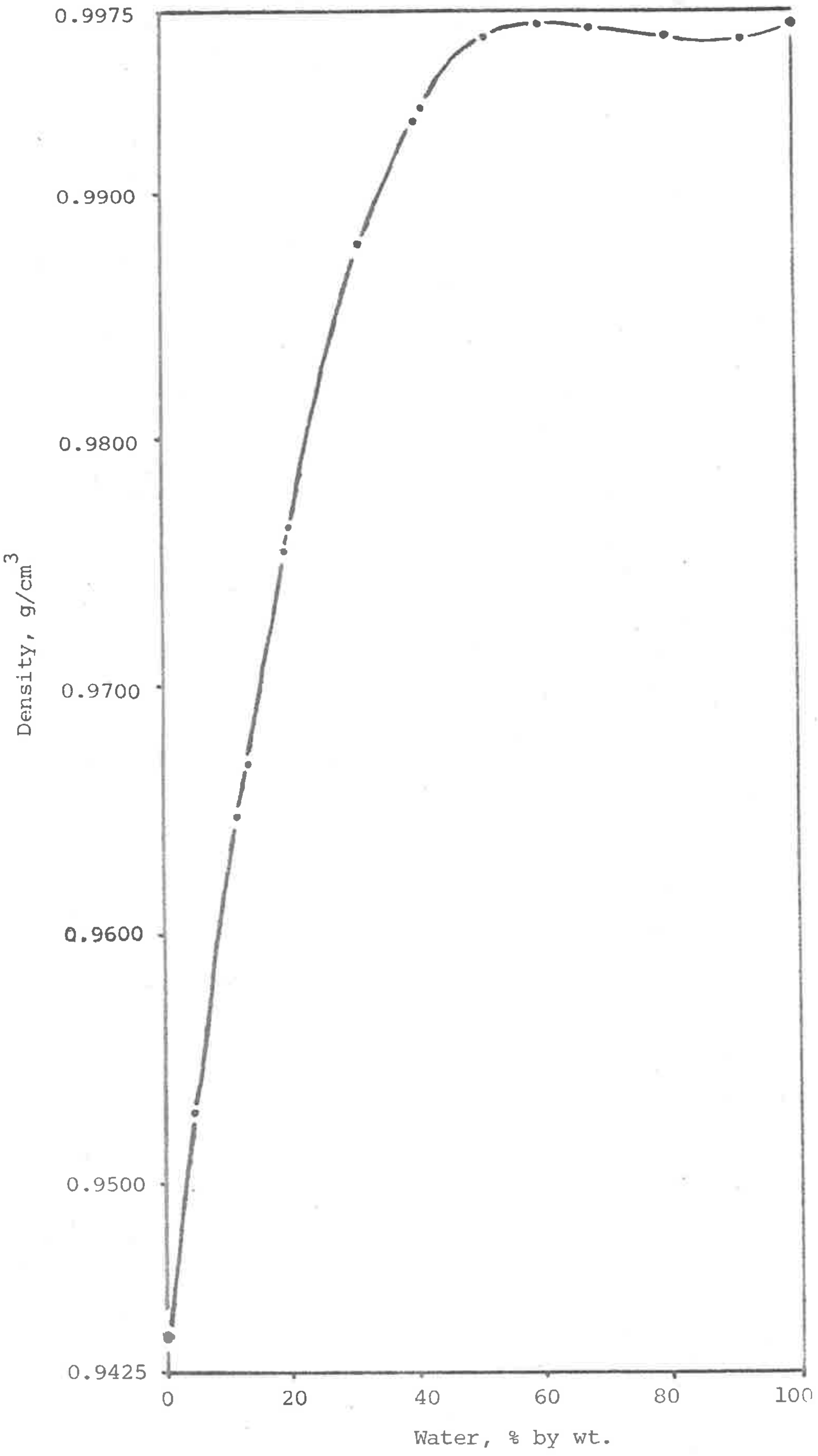
The proposition by Franks and Ives that MeOH occupies lattice sites is in keeping with the observation that it dissolves in water with little volume loss (73) in contrast to EtOH, n-PrOH, i-PrOH and t-BuOH which dissolve with increasing volume loss from EtOH to t-BuOH (73) (80) (86). This volume loss is expressed in terms of the change in the partial molar volume of the alcohol with composition.

From the density measurements made in this research on the DMF/water system, it can be proposed that a volume conservation phenomenon similar to the alcohols is occurring between 100 and 50% water. It can be observed from the graphical representation of density changes in DMF/water mixtures, figure 8.6, that for mixtures above about 50% water the dependence of density changes upon composition is small compared with that occurring in the remaining composition range. In explanation of the relative independence of composition of mixtures above 50% water it may be proposed that DMF molecules occupy interstitial sites in the water structure, thus conserving the volume of the system. Further, the limiting apparent molar volumes of KCl and KBr in DMF/water mixtures between 100% and 40% water, recorded in table 5.6, are only slightly dependent upon the DMF concentration.

Of the alcohols studied in this research only glycerol (86) does

FIGURE 8.6

The dependence of the density of DMF/water mixtures, at 25°C, upon composition.


0.9975
0.9900
0.9800
0.9700
0.9600
0.9500
0.9425
Density, g/cm3
0
20
40
60
80
100
Water, % by wt.

not exhibit a minimum in the partial molar volume of the alcohol in aqueous mixtures. In the sequence MeOH, EtOH, i-PrOH and ethylene glycol the minimum in the partial molar volume tends to lower alcohol concentrations. It can be noted from figure 8.5 that the plots of $\lambda^o_{K^+}$ in these alcohol/water mixtures follow the same sequence. It is of interest, therefore, to examine the relationship existing between volume changes in the solvent systems cited in this present research and the conductivity of the K^+ ion as the composition of the solvent is varied. A comparison of the variation with solvent composition of these on the basis of conductivity, $\lambda^o_{K^+}$, and the excess volumes of mixing, ΔV^E, has been made - figures 8.7 to 8.15. The method of computing the last quantity from density-concentration data has already been described by Nakanishi et al (80). Density data for this purpose were obtained from the respective sources for the systems listed: EtOH/water (81); pure EtOH (82); acetone/water (83); THF/water (40); pure THF (84); glycerol/water (85); iso-propanol/water (85) 20°C and ethylene glycol/water (86) 20°C. These data pertain to 25°C unless otherwise indicated.

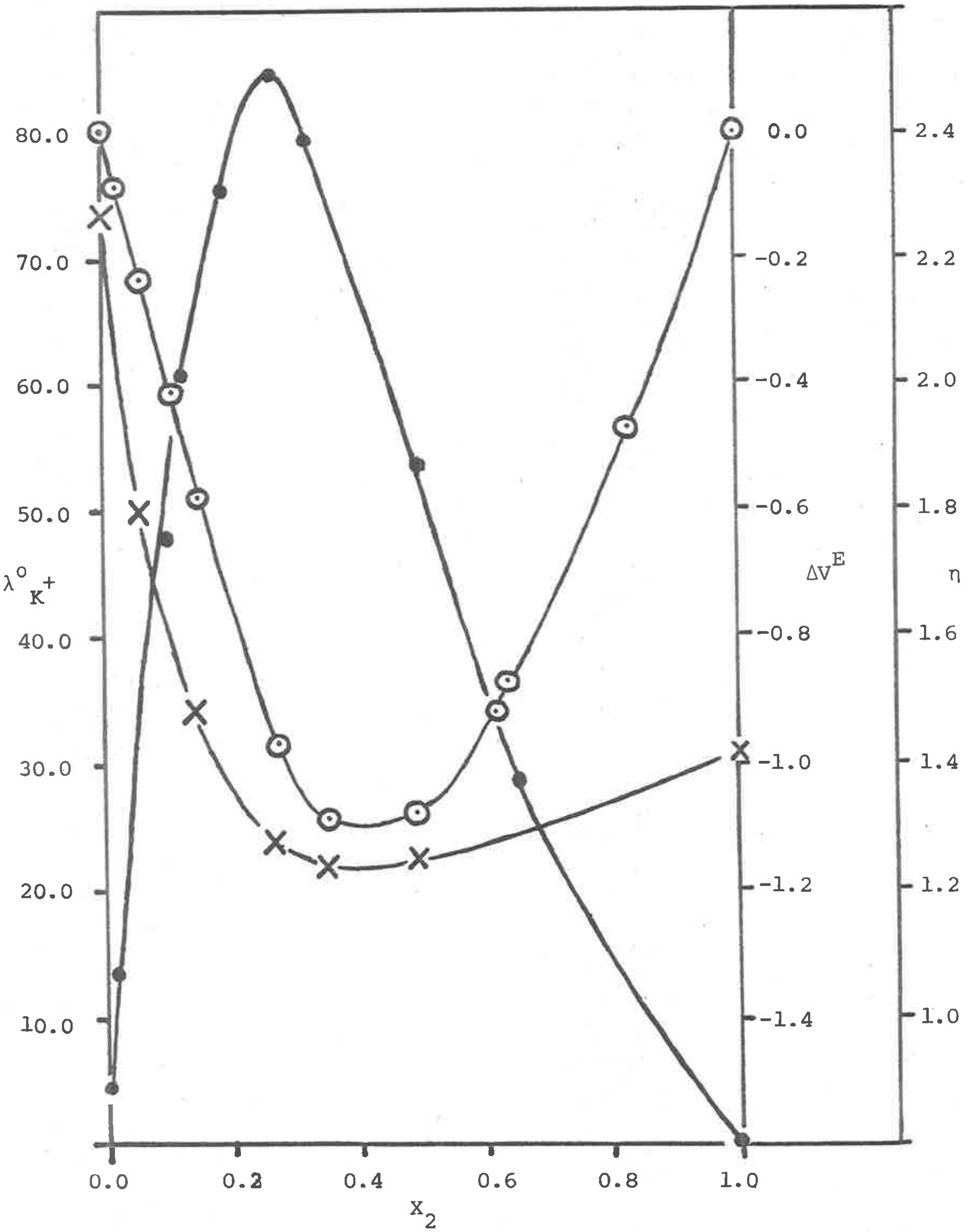
Each of the figures 8.7 to 8.15 comprises three plots, the first representing the dependence of $\lambda^o_{K^+}$, the second that of the solvent viscosity (η) and the third that of ΔV^E, upon solvent composition expressed as mole fraction of added component. Figures 8.7, 8.8, 8.11 and 8.12 display some interesting features, the most striking of which is the close correlation between the forms of the $\lambda^o_{K^+}$ and ΔV^E plots over a wide range of solvent composition of the systems DMF/water, MeOH/water, THF/water and EtOH/water respectively. For these four systems it can also be noted that there is a better correlation between the solvent composition dependences of $\lambda^o_{K^+}$ and ΔV^E than between those of $\lambda^o_{K^+}$ and the viscosity. In the case of the ethylene glycol/water and glycerol/water systems, figures 8.14 and 8.15 respectively, the correlation between the forms of the $\lambda^o_{K^+}$ and ΔV^E curves is restricted to the water-rich region of the composition range. It can be seen from figures 8.10 and 8.13, for the acetone/water and i-PrOH/water systems respectively, that insufficient conductance data

FIGURES 8.7 TO 8.15

On each graph is plotted the dependence of $\lambda^{o}_{K^{+}}$, the excess volume of mixing (ΔV^{E}) and the viscosity (η) upon the composition, expressed as the mole fraction of the added component (X_2), of the denoted aqueous mixture.

LEGEND

X : $\lambda^{o}_{K^{+}}$, cm^{2} ohm^{-1} equiv.$^{-1}$
⊙ : ΔV^{E}, cm^{3} mole^{-1}
● : η, cP



<u>FIGURE 8.7</u>: DMF/water

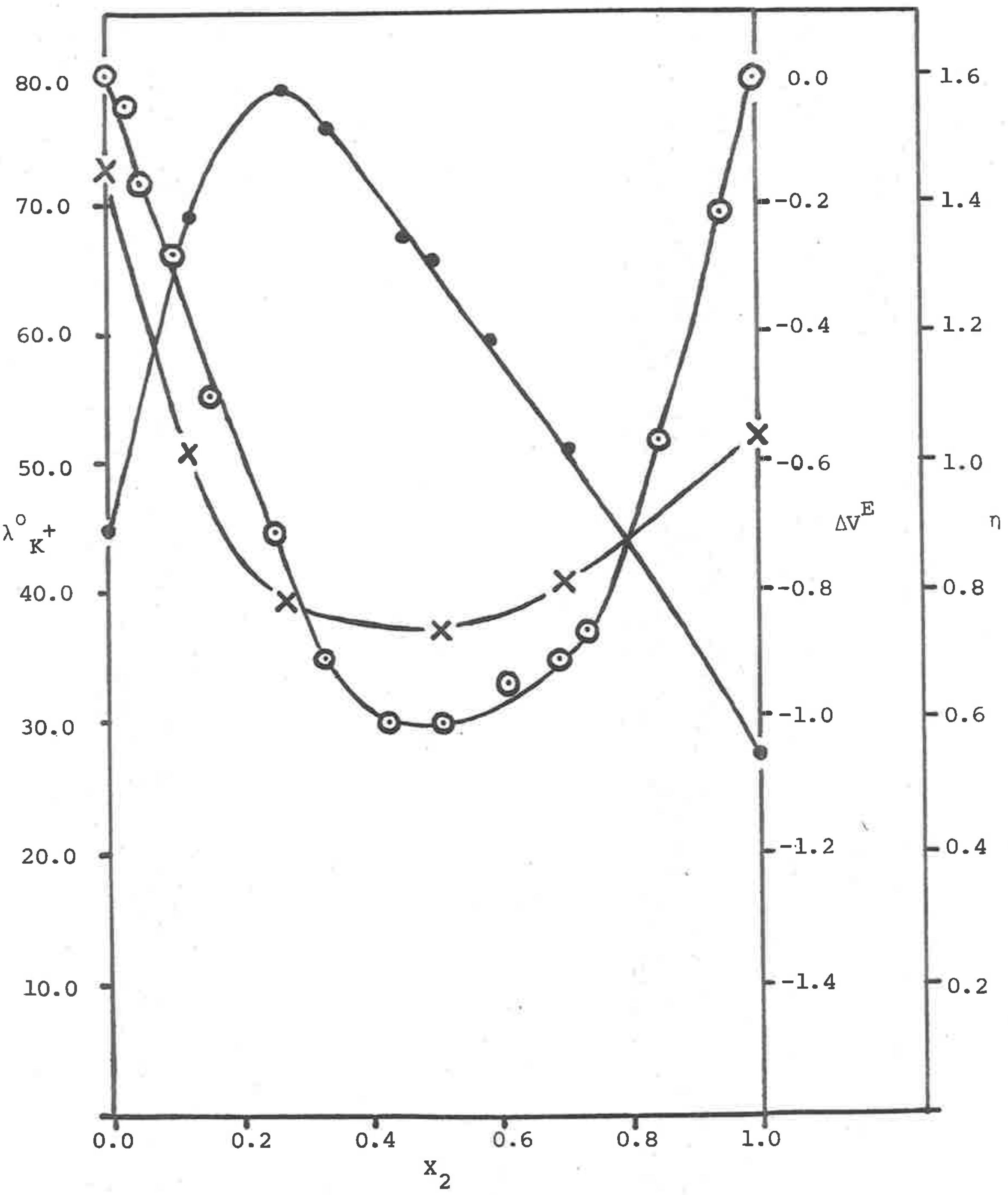


FIGURE 8.8: MeOH/water

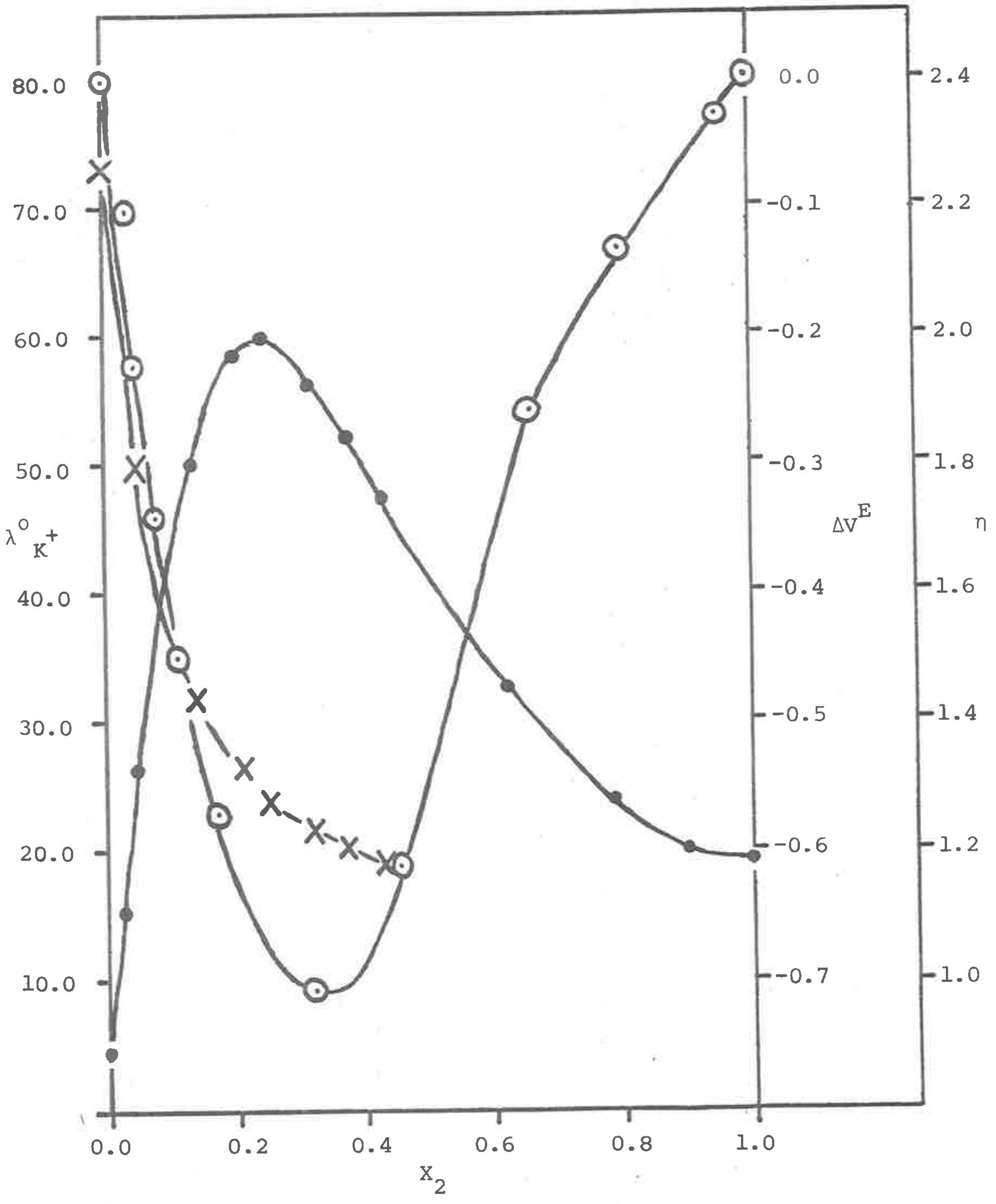


FIGURE 8.9: dioxane/water

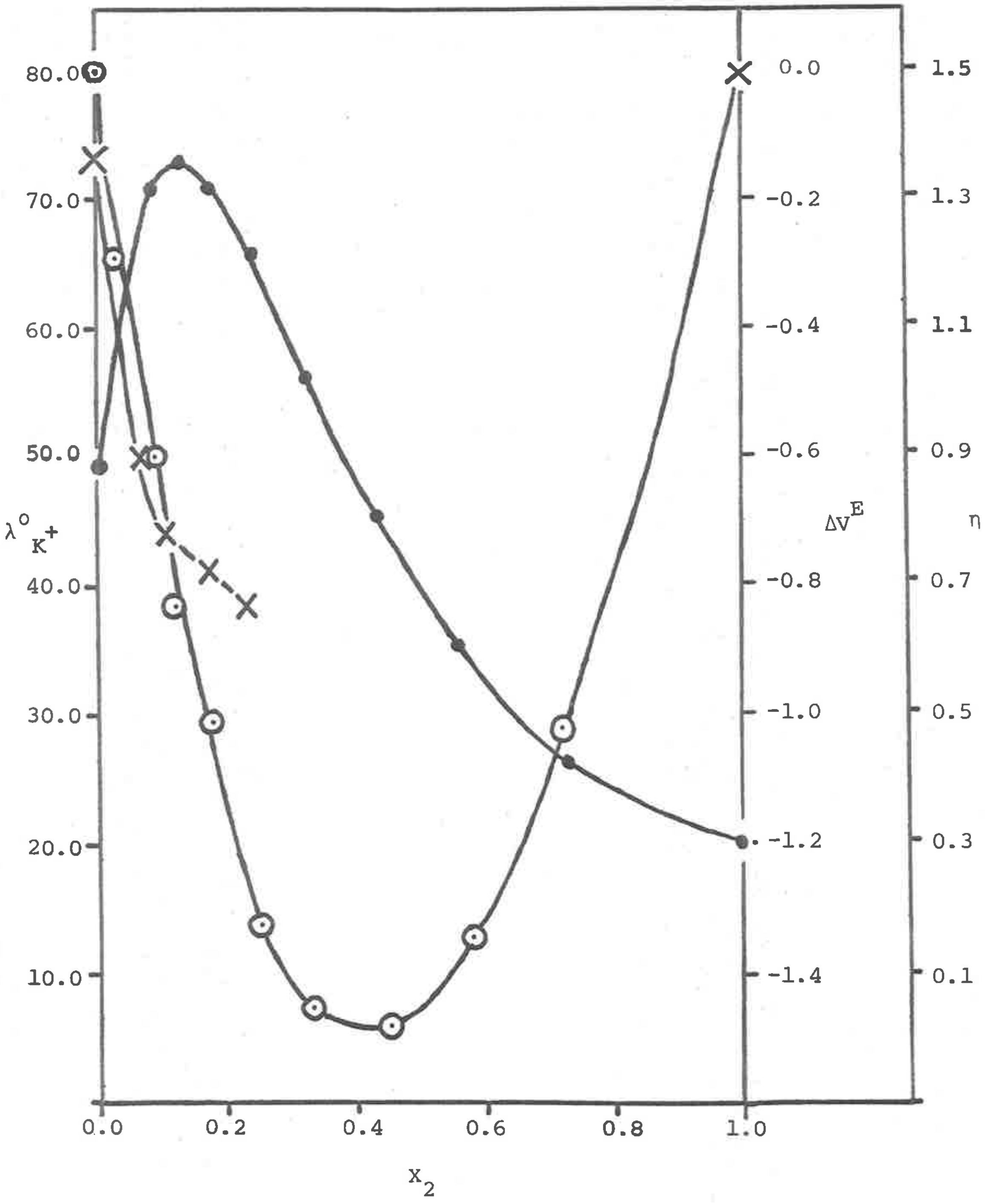


FIGURE 8.10: acetone/water

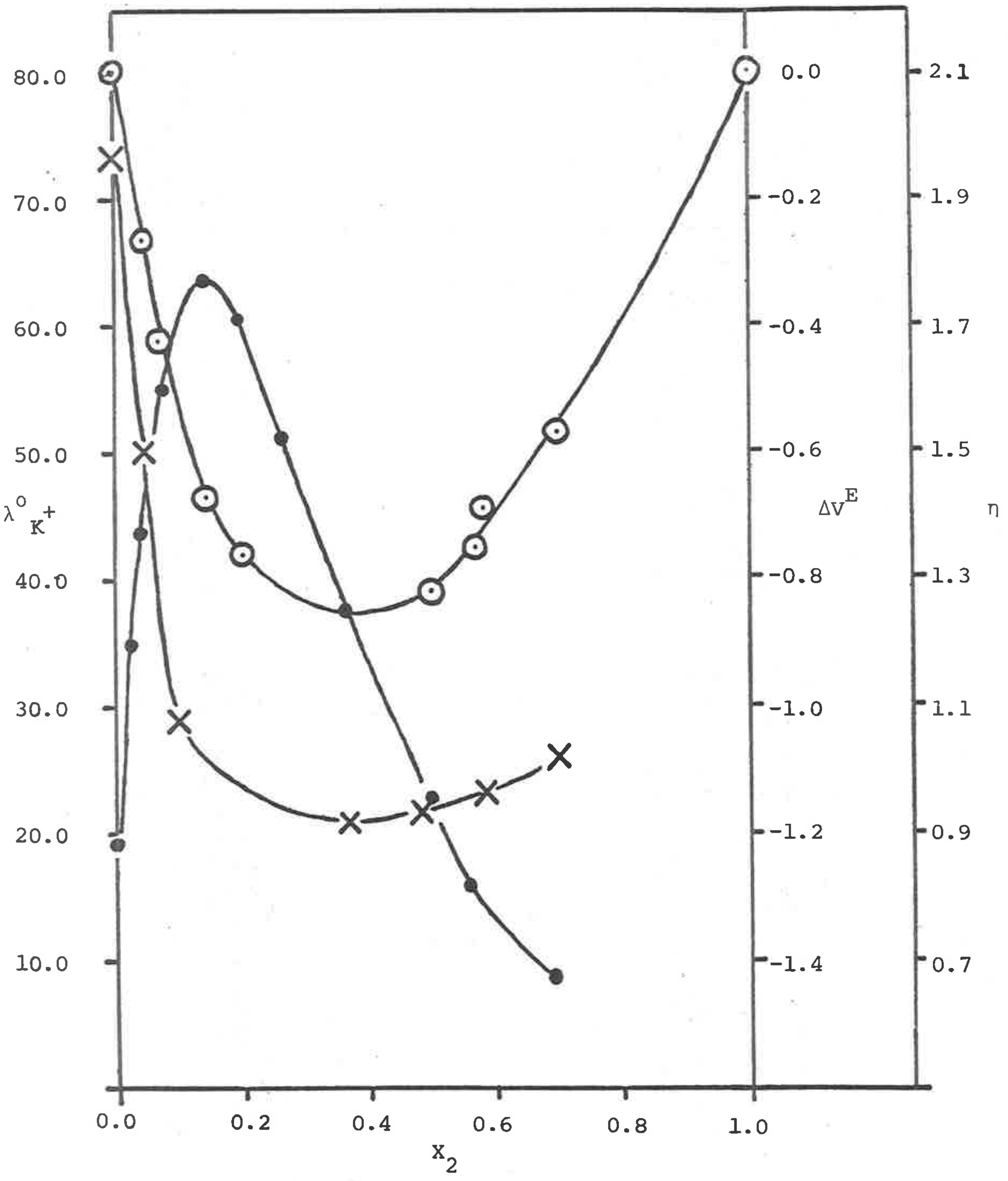


FIGURE 8.11: THF/water

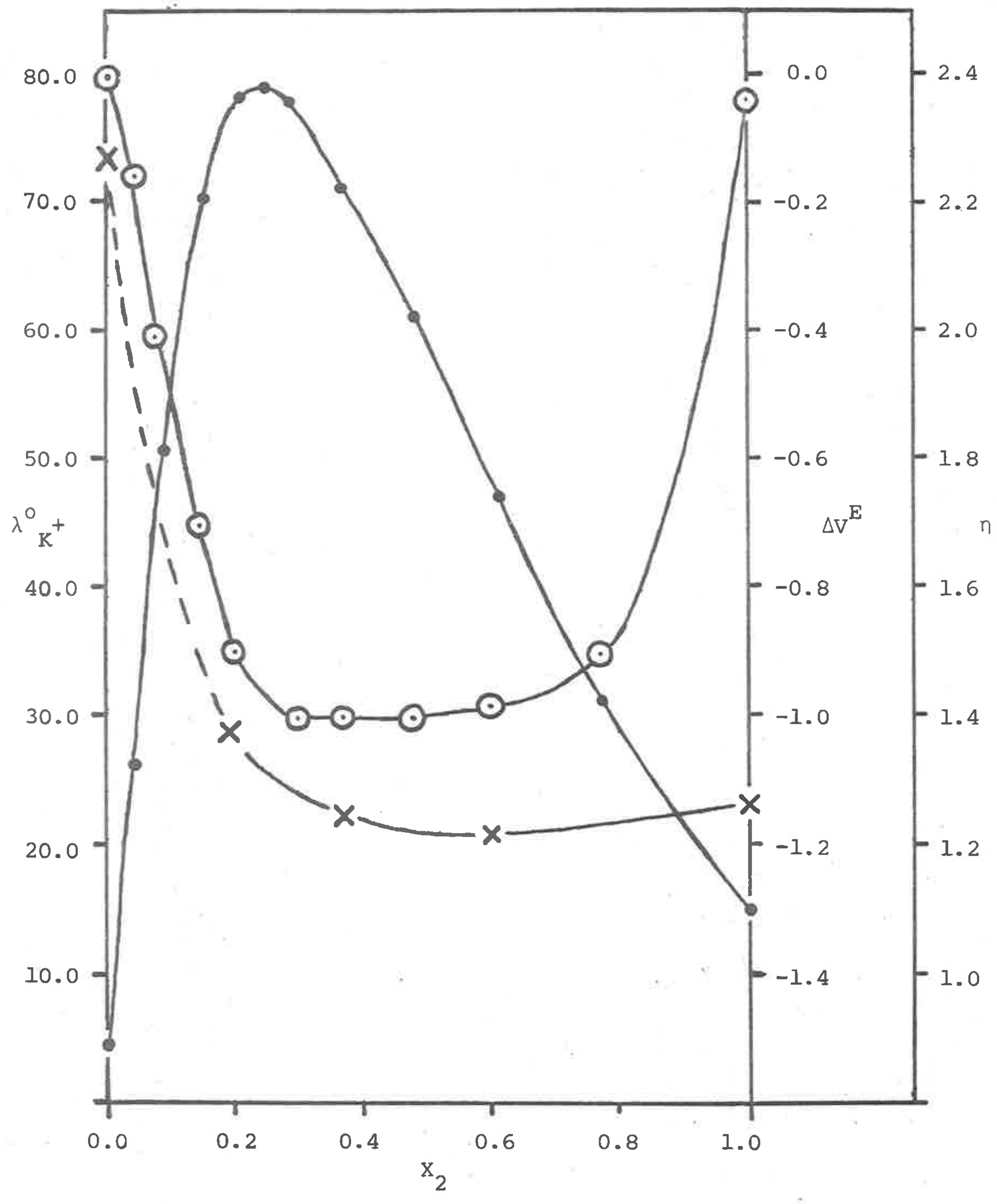


FIGURE 8.12: EtOH/water

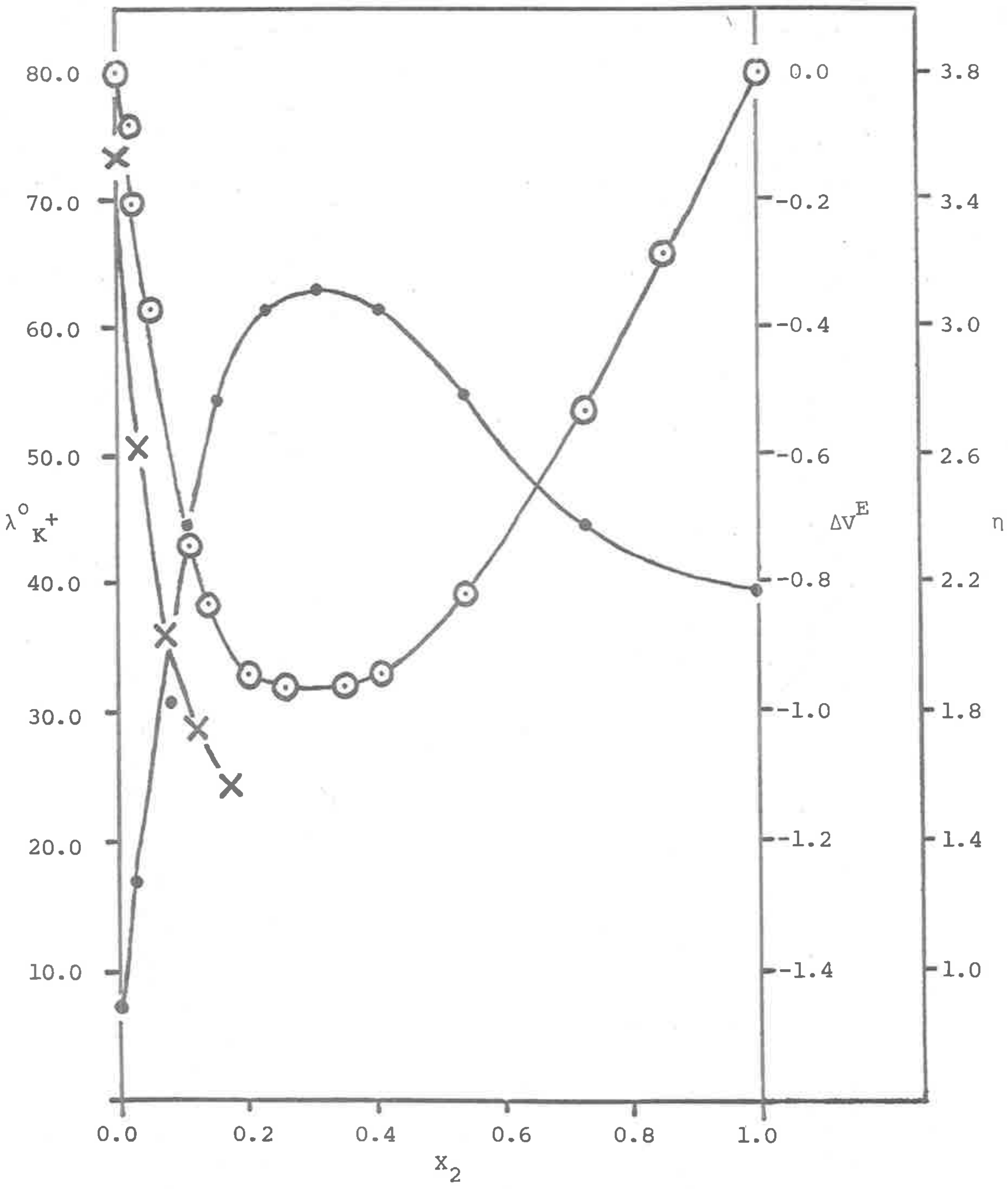


FIGURE 8.13: i-PrOH/water

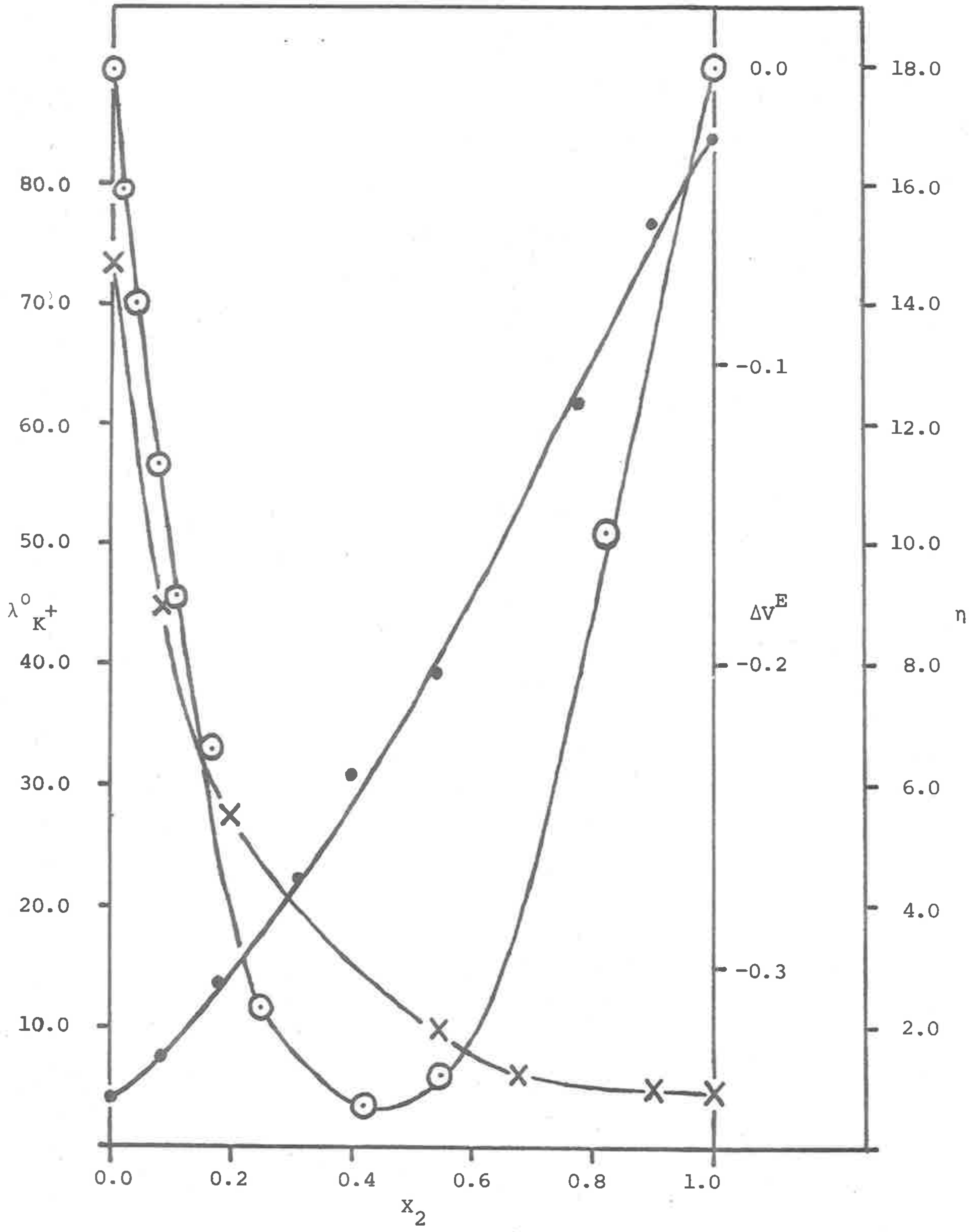


FIGURE 8.14: ethylene glycol/water

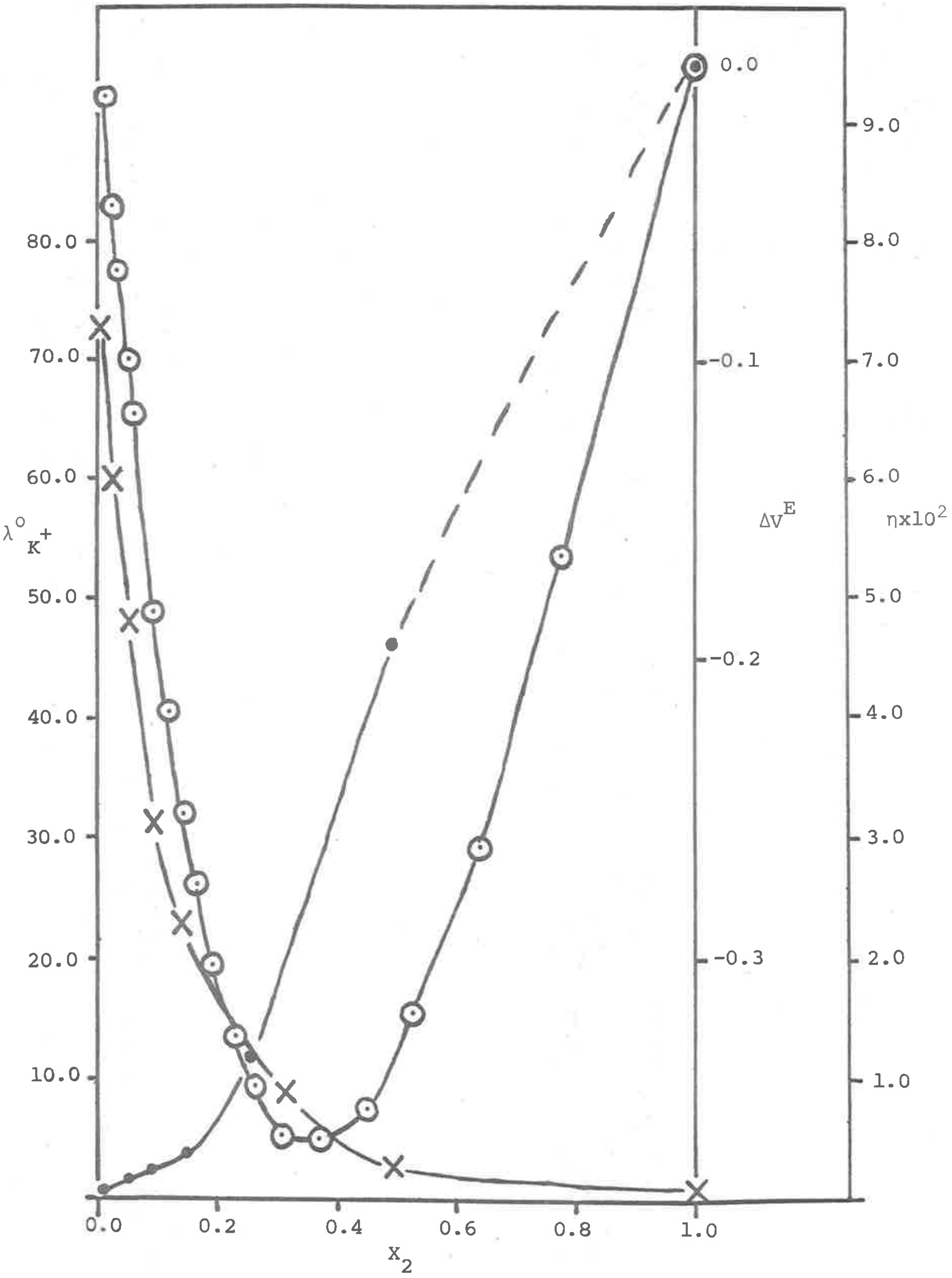


FIGURE 8.15: glycerol/water

are available for a conclusion to be drawn from the respective dependence of $\lambda^{o}_{K^+}$ and ΔV^E upon solvent composition. Although the available data for $\lambda^{o}_{K^+}$ in dioxane/water mixtures are restricted in solvent composition range, an aqueous rich region correlation between the forms of the $\lambda^{o}_{K^+}$ and ΔV^E curves is apparent from figure 8.9. On the basis of the above observations it is concluded as a general rule, particularly in the aqueous rich region, that there is a common effect in these systems which relates conductivity and volume changes in the solvent system resulting from the addition of the organic component to water.

The marked decrease in electrical conductivity in the water rich region can be explained qualitatively on the basis of Samoilov's model for liquid water (93) (94) and his proposals relating to the transport processes of conductance, self diffusion and diffusion in aqueous solution (95). Samoilov proposes that each of these processes takes place by a series of activated jumps of the reference particle from one equilibrium position to the next via the interstitial sites of the open water structure. In the case of conductance, the energy of activation is the height of the potential barrier separating the reference ion and the adjacent equilibrium site into which an ion can migrate. The height of this barrier reflects the magnitude of the interaction between the ion and its nearest neighbour water molecules (96). It will be recalled that the effect of small additions of the non-electrolytes considered in the present research to water was one of structure making. The height of the potential barrier separating the adjacent equilibrium sites in the water structure would thereby be increased. Therefore, the addition of any of these non-electrolytes to water would result in the observed decrease in the ionic conductance of the K^+ ion relative to its value in pure water. The second effect that would also contribute to a decrease in electrical conductivity by the added component is the occupation of the interstitial sites in the aqueous structure. If, as according to Samoilov's model, electrical transport takes place via the interstitial sites, then the occupation of these by added non-electrolyte would also inhibit electrical transport leading to a decrease in conductivity. According to Franks and Ives (73), for a given mole fraction, the larger the molecular size of the added component the larger would be the volume occupied by this species. Therefore, the depression in conductivity should be greatest for larger molecules. Such a trend can be observed from figure 8.5 for the largest non-electrolytes, sucrose and mannitol, depress the conductivity of the K^+ ion the most and the smallest molecule, MeOH, produces the least effect. This trend is evident in spite of the limited data available for the aqueous sucrose and mannitol systems. The composition dependence of $\lambda^o_{K^+}$ in acetone/water mixtures is anomalous when compared with that of i-PrOH/water mixtures since the molecular sizes of the added components are similar. By extending the volume effect already mentioned for MeOH (73) to include acetone it can be proposed that the molecules of the latter occupy lattice sites of the water structure so that their presence influences the interstitial ionic transport mechanism through the aqueous structure to a lesser degree than the other components considered. This applies particularly to i-PrOH. However, acetone and MeOH would nevertheless lower the conductivity of the K^+ ion by exerting a structure-making influence upon water thus increasing the height of the potential barrier separating the equilibrium sites.

The filling of the voids of the water structure can also explain the initial increase in solvent viscosity that occurs when the organic component is added to water. Since by this process the structure of water is stabilized, the viscosity of the system is thus increased. Although it has already been emphasised that there is a lack of a direct relationship between the solvent viscosity and $\lambda^o_{K^+}$, their initial dependence upon solvent composition can possibly be attributed therefore to a common phenomenon - viz the structure of water.

The point that should be emphasised is that the correlation drawn above is one between the respective forms of the composition dependences of $\lambda^o_{K^+}$ and ΔV^E. There is no correlation between the sequence of the maximum volume losses, in terms of ΔV^E, for the systems and the corresponding sequence defined by the values of $\lambda^o_{K^+}$. For example, the maximum volume loss for EtOH and MeOH are approximately equal yet the values of $\lambda^o_{K^+}$ in these aqueous solvent systems are vastly different. It is therefore concluded that the observed correlation is due to a property of the system that is dependent qualitatively but not quantitatively upon volume changes, ΔV^E. In conclusion it is proposed that the dependence of the limiting conductivity of the K^+ ion upon solvent composition correlates better with volume changes in the solvent system than with changes in solvent viscosity.

CHAPTER 8

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APPENDIX 2.1

THE MEASUREMENTS MADE WITH EACH DMF/WATER MIXTURE PREPARED IN THIS RESEARCH

Solvent Number	Water % by wt.	Balance (a)	Salt	Conductance	Transport	Viscosity	Density Solvent	Density Solution
1	20.006	S	KCl	X		X	X	X
2	51.729	M				X	X	
3	79.414	M				X	X	
4	91.064	M				X	X	
5	68.668	M				X	X	
6	11.869	M				X	X	
7	41.175	M				X	X	
8	60.036	M				X	X	
9	79.737	S	KCl	X		X	X	X
10	61.242	S	KCl	X		X	X	X
11	31.346	S	KCl	X		X	X	X
12	60.000	S	KBr				X	X
13	80.000	S	KBr	X		X	X	X
14	40.068	S	KBr	X		X	X	X
15	61.241	S	KBr	X	X	X	X	X
16	40.001	S	KBr	X	X	X	X	X
17	40.027	S	KCl	X	X	X	X	X
18	40.070	S	KCl	X	X	X	X	X
19	20.008	S	KBr	X	X	X	X	X
20	79.989	S	KBr	X	X		X	
21	79.938	M	KCl	X				
22	61.242	M	KCl	X				
23	19.391	M	KBr				X	X
24	4.658	M	KBr				X	X
25	13.148	M	KBr				X	X
26	59.822	M	Used as solvents for silver nitrate - Chapter 6					
27	40.004	M						
28	31.299	M						

(a) M = Mettler B5C1000, S = Stanton HD2 beam balance

APPENDIX 3.1

The concentration dependence of the equivalent conductance for KCl at various temperatures between 0° and 10°C

$C \times 10^4$	Λ	$\delta\Lambda$	Temp. °C
17.965	81.09	-0.02	0.54_6
33.177	80.38	0.01	0.53_8
48.855	79.85	0.01	0.54_2
62.128	79.45	0.03	0.53_5
80.469	79.03	0.00	0.53_9
99.242	78.65	0.02	0.53_7
27.693	83.09	-0.01	1.58_0
43.302	82.47	-0.01	1.56_9
59.962	81.94	0.02	1.56_6
76.261	81.57	-0.02	1.57_5
95.522	81.12	0.00	1.56_5
15.277	85.14	-0.04	2.14_8
20.886	84.75	0.04	2.13_0
34.893	84.18	0.01	2.15_5
46.690	83.80	0.01	2.16_5
58.813	83.47	-0.03	2.18_1
71.315	83.13	0.02	2.18_0
18.996	86.67	0.00	2.88_6
31.237	86.07	0.00	2.90_1
43.110	85.59	0.01	2.89_1
58.137	85.11	0.01	2.88_9
72.855	84.71	-0.02	2.89_6
88.606	84.28	0.02	2.89_0

APPENDIX 3.1 - Continued

$Cx10^4$	Λ	$\delta\Lambda$	Temp. °C
12.646	88.56	0.00	3.47_5
23.681	87.88	0.03	3.48_3
34.876	87.39	-0.01	3.48_7
47.922	86.90	0.02	3.48_1
57.476	86.61	0.00	3.49_1
71.312	86.23	0.00	3.49_1
14.264	90.04	-0.03	4.09_5
25.158	89.37	0.01	4.09_3
37.281	88.82	0.02	4.09_6
48.358	88.41	0.02	4.10_6
62.209	88.00	-0.01	4.11_8
78.664	87.54	0.00	4.10_9
112.220	86.77	0.00	4.10_6
9.8680	91.81	-0.03	4.66_0
35.625	90.35	-0.02	4.68_6
48.151	89.79	0.06	4.65_7
64.596	89.30	0.03	4.67_1
82.150	88.88	-0.02	4.68_6
98.171	88.50	-0.02	4.68_8
29.921	97.60	-0.03	7.47_3
61.569	96.28	0.02	7.47_6
98.472	95.21	0.05	7.47_8
149.29	94.20	-0.04	7.47_9

APPENDIX 3.1 - Continued

$C \times 10^4$	Λ	$\delta\Lambda$	Temp. °C
14.093	100.39	-0.04	8.21_3
28.094	99.46	0.02	8.20_9
48.216	98.55	0.03	8.20_0
74.918	97.68	0.01	8.21_0
106.618	96.87	0.00	8.20_9
150.041	95.95	-0.01	8.20_5

APPENDIX 3.2

Λ, λ_{K^+} and λ_{Cl^-} for a 0.078323N KCl solution

Temperature °C	Λ	λ_{K^+}	λ_{Cl^-}
-0.84_3	70.35_5	34.8_4	35.5_2
-0.69_2	70.67_6	35.0_0	35.6_8
-0.60_3	70.88_3	35.1_0	35.7_8
-0.51_6	71.04_3	35.1_8	35.8_6
-0.43_3	71.21_4	35.2_6	35.5_9
-0.34_6	71.39_6	35.3_6	36.0_4
-0.25_8	71.60_2	35.4_6	36.1_4
-0.17_3	71.74_9	35.5_3	36.2_2
-0.15_8	71.77_6	35.5_5	36.2_3
-0.13_8	71.81_9	35.5_7	36.2_5
-0.10_8	71.88_5	35.6_0	36.2_9
-0.07_4	71.97_2	35.6_4	36.3_3
-0.03_5	72.06_0	35.6_8	36.3_8
-0.01_0	72.07_6	35.6_9	36.3_9
$+0.00_8$	72.14_8	35.7_3	36.4_2
$+0.05_2$	72.20_1	35.7_5	36.4_5
0.16_1	72.44_9	35.8_8	36.5_7
0.60_5	73.37_5	36.3_3	37.0_5
0.91_2	74.04_9	36.6_6	37.3_9
0.91_8	74.10_8	36.6_8	37.4_3
1.13_7	74.51_5	36.8_8	37.6_4
1.50_8	75.29_9	37.2_7	38.0_3
1.75_7	75.88_3	37.7_5	38.3_3
2.02_0	76.38_6	37.7_9	38.6_0
2.50_2	77.41_0	38.2_9	39.1_2
3.09_6	78.67_9	38.9_1	39.7_7

APPENDIX 3.2 - Continued

3.52_2	79.59_8	39.3_6	40.2_4
4.08_7	80.82_8	39.9_6	40.8_7
4.64_7	82.09_7	40.5_8	41.5_2
6.40_7	86.03_0	42.4_7	43.5_6
8.32_1	90.35_4	44.5_7	45.7_8
9.11_0	92.14_7	45.4_4	46.7_1

APPENDIX 3.3

Λ for a 0.0013088N CsCl solution

Temp °C	Λ	Temp °C	Λ
0.11_4	83.35_9	5.02_2	95.51_6
0.60_0	84.60_0	5.58_4	96.95_3
1.55_7	86.89_9	5.58_7	96.97_0
1.82_7	87.55_5	6.02_7	98.08_2
1.91_2	87.75_7	6.66_0	99.70_4
2.55_1	89.29_7	7.43_7	101.71_1
2.92_7	92.21_2	8.43_7	104.43_1
3.46_0	91.54_1	9.20_7	106.30_0
3.95_7	92.76_9	9.76_9	107.78_2
4.65_7	94.58_0	9.78_7	107.83_7

APPENDIX 3.4

The coefficients, their standard errors and the standard error of the fit of the conductance data to polynomials of the form:

$$\ln\Lambda^0 = P' + \frac{Q'}{T} + \frac{R'}{T} + \frac{S'}{T}$$

APPENDIX 3.4 - Continued

Λ^0, KCl*, evaluated with the Robinson and Stokes equation

Order	Coefficients	S.E. of Coefficients	S.E. of Fit
1	P' = 1.2228 E+1	3.80 E-2	1.13 E-3
	Q' =-2.1369 E+3	1.05 E+1	
2	P' = 9.7913 E-1	1.65 E+0	4.61 E-4
	Q' = 4.0999 E+3	9.15 E+2	
	R' =-8.6443 E+5	1.27 E+5	
2	P' = 0.0000 E+0	0.00 E+0	4.44 E-4
	Q' = 4.6428 E+3	4.13 E+0	
	R' =-9.3967 E+5	1.14 E+3	

* Λ^0, KCl, evaluated with the Pitts equation is the subject of tables 3.4 and 3.5.

$\lambda^0_{Cl^-}$, derived from the Robinson and Stokes' equation and Steel's temperature dependence for the limiting transport number data for KCl

Order	Coefficients	S.E. of Coefficients	S.E. of Fit
1	P' = 1.1653 E+1	4.13 E-2	1.23 E-3
	Q' =-2.1668 E+3	1.14 E+1	
2	P' =-3.4494 E-1	1.98 E+0	5.54 E-4
	Q' = 4.4856 E+3	1.10 E+3	
	R' =-9.2203 E+5	1.52 E+5	
2	P' = 0.0000 E+0	0.00 E+0	5.23 E-4
	Q' = 4.2943 E+3	4.87 E+0	
	R' =-8.9553 E+5	1.35 E+3	

APPENDIX 3.4 - Continued

$\lambda^0_{Cl^-}$, derived from the Robinson and Stokes' equation and Kay et al's temperature dependence for the limiting transport number data for KCl

Order	Coefficients	S.E. of Coefficients	S.E. of Fit
	P' = 1.1707 E+1	3.99 E-2	
1	Q' =-2.1821 E+3	1.10 E+1	1.19 E-3
	P' =-1.9473 E-1	1.65 E+0	
2	Q' = 4.4165 E+3	9.17 E+2	4.62 E-4
	R' =-9.1458 E+5	1.27 E+5	
	P' = 0.0000 E+0	0.00 E+0	
2	Q' = 4.3086 E+3	4.06 E+0	4.36 E-4
	R' =-8.9962 E+5	1.12 E+3	

$\lambda^0_{K^+}$, derived from the Robinson and Stokes' equation and Steel's temperature dependence for the limiting transport number data for KCl

Order	Coefficients	S.E. of Coefficents	S.E. of Fit
	P' = 1.1409 E+1	3.49 E-2	
1	Q' =-2.1051 E+3	9.66 E+0	1.04 E-3
	P' = 1.1878 E+0	1.61 E+0	
2	Q' = 3.5622 E+3	8.93 E+2	4.50 E-4
	R' =-7.8548 E+5	1.24 E+5	
	P' = 0.0000 E+0	0.00 E+0	
2	Q' = 4.2207 E+3	4.08 E+0	4.38 E-4
	R' =-8.7675 E+5	1.13 E+3	

APPENDIX 3.4 - Continued

$\underline{\lambda}^{0}_{K^+}$, derived from the Robinson and Stokes' equation and Kay et al's temperature dependence for the limiting transport number data for KCl

Order	Coefficients	S.E. of Coefficients		S.E. of Fit	
1	P' = 1.1361 E+1	3.71	E-2	1.11	E-3
	Q' = -2.0911 E+3	1.03	E+1		
2	P' = 6.1932 E-1	1.79	E+0	5.01	E-4
	Q' = 3.8646 E+3	9.95	E+2		
	R' = -8.2547 E+5	1.38	E+5		
2	P' = 0.0000 E+0	0.00	E+0	4.76	E-4
	Q' = 4.2079 E+3	4.43	E+0		
	R' = -8.7305 E+5	1.23	E+3		

Λ for the 0.078323 N KCl solution

1	P' = 1.1943 E+1	1.77	E-2	9.20	E-4
	Q' = -2.0936 E+3	4.86	E+0		
2	P' = 2.6291 E+0	5.53	E-1	2.89	E-4
	Q' = 3.0598 E+3	3.06	E+2		
	R' = -7.1275 E+5	4.23	E+4		
2	P' = 0.0000 E+0	0.00	E+0	2.61	E-4
	Q' = 4.5145 E+3	2.02	E+0		
	R' = -9.1392 E+5	5.55	E+2		

APPENDIX 3.4 - Continued

λ_{Cl^-} for the 0.078323N KCl solution

Order	Coefficients	S.E. of Coefficients	S.E. of Fit
1	P' = 1.1379 E+1	1.64 E-2	
	Q' = -2.1262 E+3	4.51 E+0	8.50 E-4
	P' = 3.1032 E+0	6.09 E-1	
2	Q' = 2.4528 E+3	3.37 E+2	3.18 E-4
	R' = -6.3332 E+5	4.66 E+4	
	P' = 0.0000 E+0	0.00 E+0	
2	Q' = 4.1698 E+3	2.32 E+0	2.93 E-4
	R' = -8.7078 E+5	6.38 E+0	

λ_{K^+} for the 0.078323N KCl solution

Order	Coefficients	S.E. of Coefficients	S.E. of Fit
	P' = 1.1116 E+1	2.02 E-2	1.04 E-3
1	Q' = -2.0598 E+3	5.54 E+0	
	P' = 6.3884 E-1	5.81 E-1	
2	Q' = 3.7377 E+3	3.22 E+2	3.04 E-4
	R' = -8.0184 E+5	4.45 E+4	
	P' = 0.0000 E+0	0.00 E+0	
2	Q' = 4.0911 E+3	1.64 E+0	2.83 E-4
	R' = -8.5072 E+5	4.51 E+2	

APPENDIX 3.4 - Continued

Λ for the 0.0013088N CsCl solution

Order	Coefficients	S.E. of Coefficients	S.E. of Fit
1	P' = 1.1943 E+1	2.44 E-2	1.15 E-3
	Q' = -2.0542 E+3	6.77 E+0	
2	P' = 2.3004 E+0	8.78 E-1	4.17 E-4
	Q' = 3.3116 E+3	4.89 E+2	
	R' = -7.4642 E+5	6.80 E+4	
2	P' = 0.0000 E+0	0.00 E+0	4.80 E-4
	Q' = 4.5917 E+3	2.83 E+0	
	R' = -9.2448 E+5	7.86 E+2	

APPENDIX 4.1

Temperature Regulation of Viscometric Bath

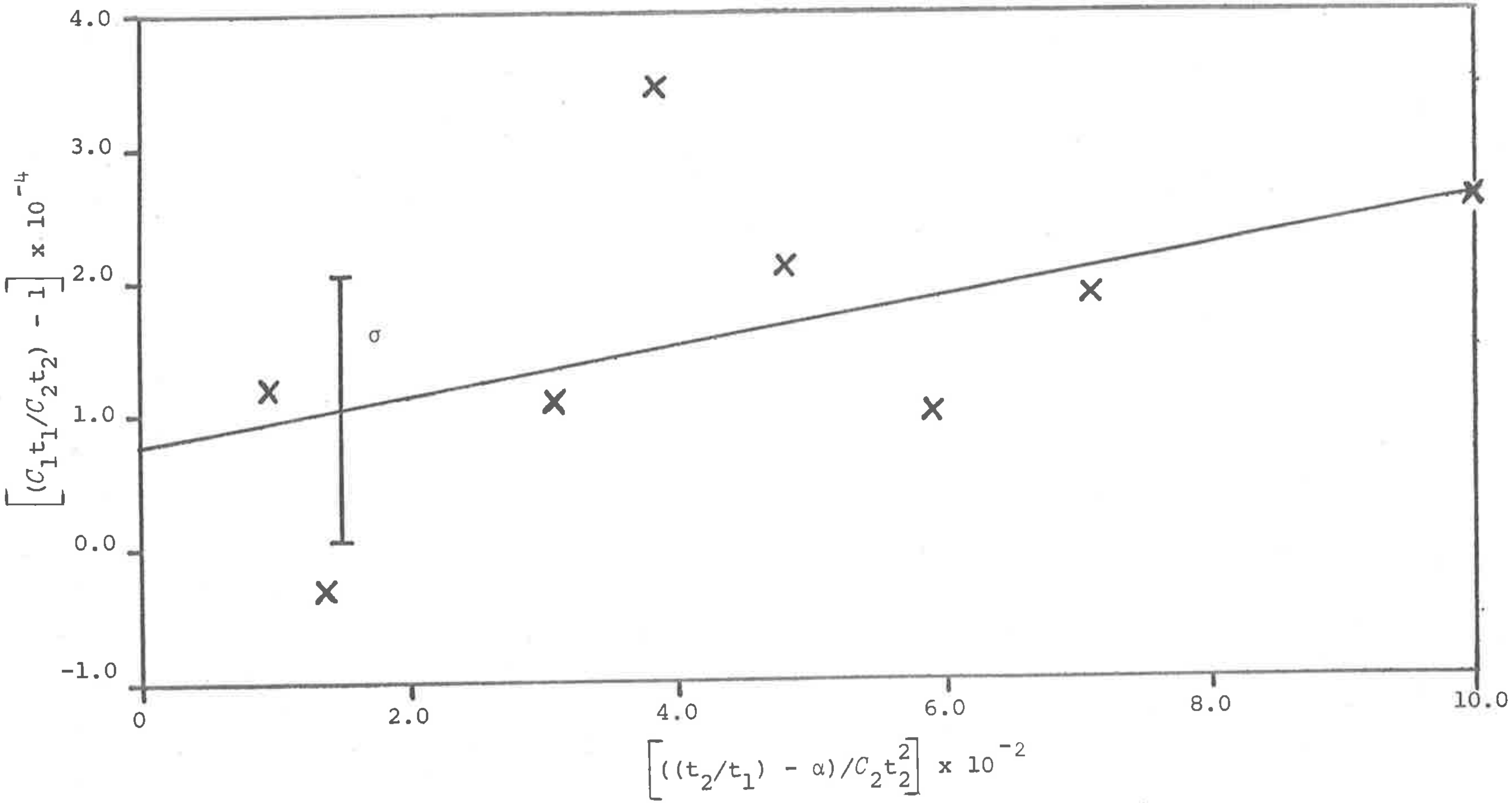
Temp. °C	Temperature Fluctuations	Regulatory Equipment Used
0°, 5° and 20°	±0.005°	Stirrer, refrigeration unit, solid state proportional controller, thermistor sensor and base heater.
25°, 30° and 35°	±0.002°	Stirrer, mercury toluene regulator, thyratron relay unit.
40°, 50° and 60°	±0.002°	Stirrer, solid state proportional controller, thermistor sensor and base heater.

APPENDIX 4.2

Values of (C_1t_1/C_2t_2) and $((t_2/t_1)-\alpha)/(C_2t_2^2)$ from equation 4.11 with n = 1

Temp. °C	C_1t_1/C_2t_2	$(t_2/t_1)-\alpha$	$C_2t_2^2$	$(t_2/t_1)-\alpha/C_2t_2^2$
0	1.00012	0.4004	41.449	0.0096601
5	0.99997	0.4006	29.866	0.013413
20	1.00011	0.4004	13.045	0.030694
25	1.00035	0.4001	10.323	0.038758
30	1.00021	0.4003	8.3113	0.048163
35	1.00011	0.4004	6.7805	0.059052
40	1.00019	0.4003	5.6100	0.071357
50	1.00026	0.4002	3.9734	0.100717

$C_1 = 1.1246\text{x}10^{-5}$
$C_2 = 7.726\text{x}10^{-6}$
$\alpha = 1.05_5$



Appendix 4.3: The evaluation of the kinetic energy correction coefficient, *K*, for viscometer PE1 from equation 4.11 with n = 1. Also denoted is the line of best fit and the standard error of the fit of the data, σ, to the linear relationship.

APPENDIX 4.4

Values of (C_1t_1/C_2t_2) and $((t_2^4/t_1^4)-\alpha)/(C_2t_2^5)$ from equation 4.11 with n = 4

Temp. °C	C_1t_1/C_2t_2	$(t_2^4/t_1^4)-\alpha$	$C_2t_2^5$	$(t_2^4/t_1^4)-\alpha/C_2t_2^5$
0	1.00007	2.4471	5.1491 E* + 11	4.7531 E - 12
5	0.99994	2.4508	2.2693 E + 11	1.0799 E - 11
20	1.00007	2.4478	2.8613 E + 10	8.5549 E - 11
25	1.00030	2.4439	1.5941 E + 10	1.5331 E - 10
30	1.00016	2.4461	9.2710 E + 9	2.6385 E - 10
35	1.00006	2.4480	5.5730 E + 9	4.3923 E - 10
40	1.00014	2.4464	3.4699 E + 9	7.0502 E - 10
50	1.00021	2.4452	1.4652 E + 9	1.6688 E - 9

* FORTRAN Notation used to denote exponent in this table.

$C_1 = 1.1243\text{x}10^{-5}$
$C_2 = 7.725\text{x}10^{-6}$
$\alpha = 2.03_8$

APPENDIX 4.5

Flow Time Data for Tilting Viscometer

Temp. °C	Number of Runs	Average Flow Times in Seconds	Deviation from Average Flow Times in Seconds	Number of Flow Time Measurements Averaged
5	1	1048.83	±0.020	6
20	2	693.662	±0.023	12
25	8	617.563	±0.067	40
30	2	554.211	±0.046	15
35	3	500.952	±0.051	24
40	3	455.761	±0.031	19
50	2	384.297	±0.020	10
60	2	330.637	±0.020	14

APPENDICES 5.1 AND 5.2

Density Data for KCl and KBr in DMF/Water Mixtures at 25°C

(a) Appendix 5.1 Density data fitted to the Root equation, 5.2, with program ROOTEQ.

(b) Symbols for Appendices 5.1 and 5.2

d(exp) = measured density
d(calc) = density calculated from Root equation
d_o = solvent density
σ = standard error of fit of the data to the Root equation
C = molarity
m = molality
A_1 & A_2 = coefficients of the Root equation

APPENDIX 5.1

KCl in 79.737% Water/DMF Mixture

$C \times 10^4$	$m \times 10^4$	d(exp)	d(calc)	$\delta d \times 10^6$
55.518	55.729	0.996634	0.996638	4
120.79	121.27	0.996951	0.996948	-3
204.38	205.24	0.997340	0.997344	4
258.95	260.07	0.997609	0.997602	-7
502.58	589.84	0.998756	0.998749	-7
753.79	758.11	0.999914	0.999927	13
1139.4	1147.1	1.001730	1.001726	-4

Solvent Number, 9; $d_o = 0.996374$

$A_1 = 4.781 \times 10^{-2} \pm 3.0 \times 10^{-4}$; $A_2 = -2.48 \times 10^{-3} \pm 9.8 \times 10^{-4}$; $\sigma = 9 \times 10^{-6}$

APPENDIX 5.1 (Continued)

KCl in 61.242% Water/DMF Mixture

$Cx10^4$	$mx10^4$	d(exp)	d(calc)	$\delta dx10^6$
28.976	29.065	0.997148	0.997150	2
70.246	70.470	0.997345	0.997345	0
155.02	155.55	0.997747	0.997744	-3
173.70	174.31	0.997830	0.997832	2
269.02	270.03	0.998279	0.998279	0

Solvent Number, 10; $d_o = 0.997012$

$A_1 = 4.769x10^{-2} \pm 3.9x10^{-4}$; $A_2 = -3.63x10^{-3} \pm 2.7x10^{-3}$; $\sigma = 3x10^{-6}$

KCl in 40.070 and 40.027% Water/DMF Mixtures

$Cx10^4$	$mx10^4$	d(exp)	d(calc)	$\delta dx10^6$
129.68	130.65	0.993520	0.993524	5
185.62	187.04	0.993780	0.993784	4
249.15	251.11	0.994078	0.994078	0
321.86	324.44	0.994414	0.994413	-1
353.51	356.40	0.994551	0.994559	8
434.21	437.85	0.994940	0.994929	-11
477.81	481.86	0.995131	0.995128	-3
757.23	764.30	0.996394	0.996397	4

Solvent Numbers, 17, 18; $d_o = 0.992917$

$A_1 = 4.747x10^{-2} \pm 2.9x10^{-4}$; $A_2 = -5.45x10^{-3} \pm 1.3x10^{-3}$; $\sigma = 7x10^{-6}$

APPENDIX 5.1 (Continued)

KCl in 31.346% Water/DMF Mixture

$Cx10^4$	$mx10^4$	d(exp)	d(calc)	$\delta dx10^6$
13.564	13.733	0.987772	0.987772	0
26.995	27.333	0.987836	0.987839	3
62.393	62.422	0.988005	0.988008	3
108.68	110.06	0.988223	0.988222	-1
140.64	142.44	0.988372	0.988367	-5
197.63	200.21	0.988615	0.988618	3

Solvent Number, 11; $d_o = 0.987704$

$A_1 = 5.194x10^{-2} \pm 8.4x10^{-4}$; $A_2 = -4.06x10^{-2} \pm 6.6x10^{-3}$; $\sigma = 4x10^{-6}$

KBr in 80.000% Water/DMF Mixture

$Cx10^4$	$mx10^4$	d(exp)	d(calc)	$\delta dx10^6$
101.16	101.52	0.997212	0.997215	3
148.29	148.90	0.997613	0.997613	0
225.44	226.45	0.998258	0.998264	6
272.77	274.03	0.998671	0.998663	-8
415.45	417.56	0.999866	0.999867	1
580.49	583.78	1.001259	1.001259	0

Solvent Number, 13; $d_o = 0.996371$

$A_1 = 8.540x10^{-2} \pm 4.3x10^{-4}$; $A_2 = -3.45x10^{-3} \pm 2.0x10^{-3}$; $\sigma = 7x10^{-6}$

APPENDIX 5.1 (Continued)

KBr in 60.000% Water/DMF Mixture

$Cx10^4$	$mx10^4$	d(exp)	d(calc)	$\delta dx10^6$
81.175	81.443	0.997680	0.997678	-2
83.138	83.414	0.997691	0.997695	4
125.86	126.30	0.998053	0.998054	1
134.02	134.49	0.998126	0.998122	-4
147.93	148.45	0.998238	0.998239	1
242.17	243.11	0.999028	0.999028	0

Solvent Number, 12; $d_o = 0.996992$

$A_1 = 8.510x10^{-2} \pm 4.5x10^{-4}$; $A_2 = -6.56x10^{-3} \pm 3.4x10^{-3}$; $\sigma = 3x10^{-6}$

KBr in 40.068% and 40.001 Water/DMF Mixtures

$Cx10^4$	$mx10^4$	d(exp)	d(calc)	$\delta dx10^6$
177.13	178.51	0.994404	0.994403	-1
211.28	212.95	0.994684	0.994688	4
331.33	334.08	0.995689	0.995690	1
370.79	373.92	0.996022	0.996019	-3
385.21	388.49	0.996142	0.996139	-3
443.14	447.01	0.996620	0.996622	2
643.12	649.20	0.998286	0.998286	0

Solvent Number, 14, 16; $d_o = 0.992919$

$A_1 = 8.408x10^{-2} \pm 1.7x10^{-4}$; $A_2 = -2.47x10^{-3} \pm 7.7x10^{-4}$; $\sigma = 3x10^{-6}$

APPENDIX 5.2

Densities of KCl and KBr in DMF/Water Mixtures

Electrolyte	Solvent Number	%H_2O	d_o	$C\times10^4$	$m\times10^4$	d(exp)
KCl	1	20.006	0.976327	63.948	65.573	0.976589
KBr	15	61.241	0.997006	384.69	386.36	1.000237
KBr	15	61.241	0.997006	289.69	290.86	0.999474
KBr	19	20.008	0.976320	366.05	375.37	0.979535
KBr	19	20.008	0.976320	442.35	453.72	0.980209
KBr	23	19.391	0.975570	-	368.21	0.978740
KBr	25	13.418	0.966816	-	385.34	0.970237
KBr	24	4.658	0.952896	-	362.65	0.956278

APPENDIX 6.1

Cation transport numbers of KBr in water and DMF/water mixtures together with KCl in the same mixed solvent at 25°C. The only symbol not defined in Chapter 6 is i which is the electrolysis current. Values of q quoted are corrected for the solvent conductance.

KBr in Water, Cell TA1

C_1	C_2	m_2	C_3	m_3
0.0323044	0.0354778	0.0356269	0.0322959	0.0324278

M = 41.578 g

V = 41.587 cm^3

i = 3.2955 milliamps

t = 8016.41 seconds

q = 26.410 coulomb

t_{K^+} (apparent) = 0.4834

t_{K^+} (Hittorf) = 0.4841

KBr in 79.989% Water, Solvent Number 20, Cell TA1

C_1	C_2	m_2	C_3	m_3
0.0210731	0.0242856	0.0243951	0.0210633	0.0211562

M = 41.526 g

V = 41.709 cm^3

i = 3.1737 milliamps

t = 8013.4 seconds

q = 25.390 coulomb

t_{K^+} (apparent) = 0.5107

t_{K^+} (Hittorf) = 0.5111

KBr in 79.989% Water, Solvent Number 20, Cell TA2

C_1	C_2	m_2	C_3	m_3
0.0201131	0.0234664	0.0235713	0.0201006	0.0201883

M = 38.253 g

V = 38.420 cm^3

i = 2.7110 milliamps

t = 9033.8 seconds

q = 24.410 coulomb

t_{K^+} (apparent) = 0.5112

t_{K^+} (Hittorf) = 0.5115

APPENDIX 6.1 (Cont'd)

KBr in 61.241% Water, Solvent Number 15, Cell TA1

C_1	C_2	m_2	C_3	m_3
0.0289649	0.0322320	0.0323657	0.0289589	0.0290755

M = 41.479 g   V = 41.646 cm^3 i = 3.0846 milliamps

t = 8158.3 seconds   q = 25.112 coulomb t_{K^+} (apparent) = 0.5238

t_{K^+} (Hittorf) = 0.5244

KCl in 40.027% Water, Solvent Number 17, Cell TA1

C_1	C_2	m_2	C_3	m_3
0.0321876	0.0353346	0.0356221	0.0321858	0.0324446

M = 41.420 g   V = 41.753 cm^3 i = 2.41239 milliamps

t = 10013.8 seconds   q = 24.1414 coulomb t_{K^+} (apparent) = 0.5255

t_{K^+} (Hittorf) = 0.5260

KCl in 40.070% Water, Solvent Number 18, Cell TA1

C_1	C_2	m_2	C_3	m_3
0.0388960	0.0414606	0.0418058	0.0388919	0.0392127

M = 41.336 g   V = 41.677 cm^3 i = 2.9977 milliamps

t = 6559.7 seconds   q = 19.642 coulomb t_{K^+} (apparent) = 0.5259

t_{K^+} (Hittorf) = 0.5265

KCl in 40.070% Water, Solvent Number 18, Cell TA1

C_1	C_2	m_2	C_3	m_3
0.0388919	0.0419239	0.0422738	0.0388830	0.0392036

M = 41.336 g   V = 41.677 cm^3 i = 3.00676 milliamps

t = 7752.6 seconds   q = 23.250 coulomb t_{K^+} (apparent) = 0.5260

t_{K^+} (Hittorf) = 0.5267

APPENDIX 6.1 (Cont'd)

KBr in 40.001% Water, Solvent Number 16, Cell TA1

C_1	C_2	m_2	C_3	m_3
0.0299271	0.0329814	0.0332558	0.0299175	0.0301629

M = 41.579 g
V = 41.920 cm^3
i = 2.3637 milliamps
t = 10019.3 seconds
q = 23.657 coulomb
t_{K^+} (apparent) = 0.5239
t_{K^+} (Hittorf) = 0.5245

KBr* in 20.008% Water, Solvent Number 19, Cell TA1

C_1	C_2	m_2	C_3	m_3
0.0368795	0.0397382	0.0407536	0.0368782	0.0378206

M = 40.472 g
V = 41.502 cm^3
i = 2.5916 milliamps
t = 9019.92 seconds
q = 23.368 coulomb
t_{K^+} (apparent) = 0.4901
t_{K^+} (Hittorf) = 0.4908

* Not corrected for presence of silver halide.

KBr** in 20.008% Water, Solvent Number 19, Cell TA1

C_1	C_2	m_2	C_3	m_3
0.0366088	0.0394325	0.0404401	0.0366075	0.0375392

M = 40.472 g
V = 41.502 cm^3
i = 2.5916 milliamps
t = 9019.92 seconds
q = 23.207 coulomb
t_{K^+} (apparent) = 0.4875
t_{K^+} (Hittorf) = 0.4882

** Corrected for presence of silver halide.

APPENDIX 6.2

Preparation of Silver Bromide

Silver Bromide was prepared from Unilab AR silver nitrate and Unilab AR potassium bromide. Repeated washings of the solid followed until the specific conductance of the supernatant liquor was constant. This solid was later dried in darkness to constant weight in a vacuum oven at 50°C, and stored in a dark cupboard in an evacuated dessicator over phosphorus pentoxide.

APPENDIX 7.1

The Concentration Dependence of Λ for KCl and KBr in DMF/Water Mixtures at 25°C

Solvent Number	Cell	$Cx10^4$	Λ	$\delta\Lambda x10^3$
KCl in solvents 9 and 21, 79.74 and 79.94% water respectively				
9	C	85.3200	91.626	-7
9	C	109.159	91.011	-2
9	C	129.702	90.546	4
9	C	149.621	90.146	3
9	C	170.550	89.761	5
9	C	192.733	89.390	3
21	A	331.511	87.585	-11
21	A	394.967	86.927	3
21	A	598.664	85.290	2
21	A	847.640	83.807	0
KCl in solvents 10 and 22, 61.24% and 61.24% water respectively				
10	C	45.6730	62.829	20
10	C	76.7667	62.019	2
10	C	103.455	61.467	-2
10	C	119.124	61.188	-9
10	C	138.825	60.867	-14
10	C	174.031	60.358	-17
22	A	286.899	59.058	11
22	A	371.855	58.328	9
22	A	492.553	57.486	4
22	A	637.324	56.667	0
22	A	876.072	55.596	-4

APPENDIX 7.1 (Continued)

Solvent Number	Cell	$C\times10^4$	Λ	$\delta\Lambda\times10^3$
KCl in solvents 17 and 18, 40.03% and 40.07% water respectively				
17	D	67.2991	42.954	-7
18	D	95.8807	42.352	10
17	D	161.672	41.349	-5
18	D	182.084	41.079	6
17	D	228.560	40.567	-6
18	D	258.673	40.254	7
17	D	287.064	40.002	-4
17	D	312.893	39.779	-4
18	D	329.757	39.631	6
17	D	338.620	39.570	-4
17	D	384.574	39.223	-4
18	D	385.088	39.213	2
18	D	432.292	38.885	4
17	D	434.212	38.882	6
18	D	454.050	38.742	5
KCl in solvent 11, 31.35% water				
11	C	15.7555	41.188	5
11	C	38.6133	40.273	-9
11	C	58.8221	39.680	-3
11	C	82.1911	39.121	3
11	C	100.408	38.746	5
11	C	117.101	38.437	4
11	C	140.638	38.047	-6

APPENDIX 7.1 (Continued)

Solvent Number	Cell	$C \times 10^4$	Λ	$\delta\Lambda \times 10^3$
KCl in solvent 1, 20.01% water				
11	C	5.15569	43.390	4
11	C	8.83366	42.979	-1
11	C	14.4124	42.494	-4
11	C	22.4007	41.939	-2
11	C	31.3608	41.427	2
11	C	47.5965	40.670	4
11	C	63.9483	40.045	-2
KBr in solvents 13 and 20, 80.00 and 79.99% water respectively				
13	D	46.1108	93.298	8
13	D	73.670	92.410	-6
13	D	107.240	91.570	-3
13	D	136.892	90.969	-4
13	D	171.685	90.370	-3
20	A	210.700	89.785	6
13	D	223.489	89.617	2
13	D	272.771	89.015	2
20	A	331.986	88.393	0
20	A	497.131	87.010	-1
KBr in solvent 15, 61.24% water				
15	D	44.4097	62.622	4
15	D	94.0779	61.521	-4
15	D	174.825	60.383	-6
15	D	239.540	59.721	0
15	D	287.718	59.313	3
15	A	289.693	59.304	-3
15	D	310.958	59.133	7
15	D	333.720	58.968	9
15	D	384.685	58,651	-10

APPENDIX 7.1 (Continued)

Solvent Number	Cell	$Cx10^4$	Λ	$\delta\Lambda x10^3$
KBr in solvent 14, 40.67% water				
14	D	64.8374	43.456	2
14	D	108.781	42.719	-3
14	D	153.097	42.153	-1
14	D	207.934	41.596	0
14	D	277.647	41.025	1
14	A	299.380	40.867	3
14	D	342.363	40.584	0
14	D	385.211	40.326	-2
KBr in solvent 19, 20.01% water				
19	D	64.1828	41.974	2
19	D	149.243	40.069	-3
19	D	215.469	39.069	-1
19	D	293.259	38.149	1
19	D	349.242	37.595	-1
19	A	366.051	37.432	8
19	D	374.836	37.363	-1
19	D	399.740	37.149	-2
19	D	442.346	36.804	-3

APPENDIX 8.1

KCl and KBr in DMF/water mixtures at 25°C [(a)]

Water % by wt.	D	η	$\lambda^0_{K^+}$	R^+	$\lambda^0_{Cl^-}$	$R^-_{Cl^-}$	$\lambda^0_{Br^-}$	$R^-_{Br^-}$	$^{100}/_D$
100.0	78.54	0.8903	73.5_3	1.252	76.3_7	1.205	78.1_8	1.177	1.273
80.0	$74._8$	1.40_2	49.6_8	1.176	-	-	47.5_8	1.228	1.337
79.4	$74._7$	1.42_0	-	-	47.3_3	1.219	-	-	1.339
61.2	$69._3$	2.01_5	34.2_7	1.187	31.6_7	1.284	31.2_4	1.302	1.443
40.0	$60._6$	2.50_2	24.3_0	1.348	21.9_6	1.491	22.1_6	1.478	1.650
31.3	$56._1$	2.39_4	$22._0$	1.56	$20._9$	1.638	-	-	1.783
20.0	$49._8$	1.87_4	22.6_9	1.927	22.0_3	1.984	23.7_0	1.845	2.008
0.0	36.71	0.796	30.8	3.35	55.1	1.87	53.6	1.92	2.724

(a) This Research - Values of $\lambda^0_{K^+}$, $\lambda^0_{Br^-}$, $\lambda^0_{Cl^-}$, D and η have been presented in Chapter 7 of this thesis.

APPENDIX 8.1

KCl in methanol/water mixtures at 25°C

methanol % by wt.	Λ^0 (a)	D (a)	η (a)	t_{K^+} (b)	$\lambda^0_{K^+}$	R^+	$100/D$
20.2	99.2	69.2	1.378	0.508	50.4	1.180	1.445
40.2	78.2	59.6	1.58	0.509	39.8	1.303	1.678
60.7	74.2	49.8	1.34	0.507	37.6	1.622	2.008
(50.0)*	75.10(c)	49.85(c)	1.319(c)	0.5068(d)	38.06	1.632	2.006
80.7	91.5	39.1	1.02	0.506	40.8	1.960	2.557
100.0	100.78(e)	32.63(g)	0.5445(g)	0.5001(f)	52.40	2.872	3.065

*50 mole %, (a) Reference (32), (b) Reference (43), (c) Reference (33)
(d) Reference (42), (e) Reference (34), (f) Reference (41), (g) Reference 1 page 458

APPENDIX 8.1

KCl in ethanol/water mixtures at 25°C

ethanol % by wt.	Λ^0 (a)	D (a)	η (a)	t_{K^+} (b)	$\lambda^0_{K^+}$	R^+	$^{100}/_D$
38.37	57.822	55.5	2.348	0.494	28.7	1.222	1.802
39.91	56.645	55.1	2.363	0.493	27.9	1.242	1.815
60.25	46.768	43.3	2.213	0.478	22.4	1.656	2.309
79.29	44.05	33.1	1.753	0.474	20.9	2.239	3.021
87.92	44.59	29.0	1.480	-	-	(2.531) (e)	3.448
100.0	45.40 (c)	24.3	1.078 (d)	-	23.55 (c)	3.228	4.115

(a) Reference (35), (b) Reference (44), (c) Reference (36),

(d) Reference (1) page 458, (e) $t^0_{K^+}$ = 0.4905

APPENDIX 8.1

KCl in iso-propanol/water mixtures at 25°C

iso-propanol % by wt.	Λ^0 (a)	D (a)	η (a)	$\lambda^0_{K^+}$ (b)	R^+ (b)	$^{100}/D$
10	103.81	71.4	1.277	50.92	1.260	1.400
20	75.22	64.1	1.838	36.90	1.208	1.560
30	59.00	56.9	2.359	28.94	1.200	1.757
40	48.91	49.7	2.781	24.00	1.228	2.012

(a) Reference (37), (b) $t^o_{K^+}$ (KCl) = 0.4905

APPENDIX 8.1

KCl in α-alanine/water mixtures at 25°C(a)

Molarity α-alanine	Λ^0	D	η	$\lambda^0_{K^+}$ (b)	R^+ (b)	$\lambda^0_{K^+}$ (c)	R^+ (c)	$^{100}/D$
0.2500	141.61	84.1	0.948	69.46	1.244	69.75	1.239	1.189
0.5000	133.77	89.9	1.0117	65.61	1.234	66.07	1.226	1.112
1.0000	119.56	101.5	1.1587	58.64	1.206	59.46	1.189	0.985
1.5000	106.00	113.1	1.3376	51.99	1.178	53.07	1.154	0.884

(a) Reference (29)

(b) $t^o_{K^+}$ (KCl) = 0.4905

(a), (c) $t^o_{K^+}$ (KCl/α-alanine/water) = $t^o_{K^+}$ (KCl/water) + 0.0068 (molarity α-alanine)

APPENDIX 8.1

KCl in β-alanine/water mixtures at 25°C (a)

Molarity β-alanine	Λ^0	D	η	$\lambda^0_{K^+}$ (b)	R^+ (b)	$^{100}/_D$
0.2619	142.42	87.6	0.9453	69.86	1.241	1.142
0.6192	132.59	100.0	1.029	65.04	1.224	1.000
1.1821	118.51	119.4	1.1832	58.13	1.191	0.8375
0.8000	128.19	106.2	1.0754	62.88	1.212	0.9416
1.0625	121.39	115.3	1.1481	59.54	1.199	0.8673
1.2119	118.14	120.5	1.1922	57.95	1.186	0.8299
1.3176	115.64	124.1	1.2248	56.72	1.180	0.8058
1.4531	112.48	128.8	1.2683	55.17	1.171	0.7764
1.4956	111.45	130.3	1.2819	54.67	1.169	0.7675

(a) References (28), (b) $t^0_{K^+}$ (KCl) = 0.4905

APPENDIX 8.1

KCl in glycine/water mixtures at 25°C

glycine molarity	Λ^0(a)	D(a)	η (a)	$\lambda^0_{K^+}$ (b)	R^+ (b)	$\lambda^0_{K^+}$(c)	R^+(c)	$^{100}/_D$
0.258	144.7	84.0	0.922	70.98	1.252	70.79	1.255	1.191
0.475	140.8	88.8	0.951	69.06	1.248	68.73	1.254	1.126
0.731	136.3	94.5	0.988	66.86	1.241	66.36	1.250	1.053
0.918	133.0	98.8	1.017	65.24	1.235	64.62	1.247	1.012
1.223	127.8	106.0	1.068	62.69	1.224	61.90	1.239	0.943
1.477	123.4	112.2	1.113	60.53	1.216	59.62	1.235	0.891
1.730	119.2	118.5	1.116	58.47	1.205	57.44	1.227	0.844
2.009	114.5	125.6	1.220	56.16	1.196	55.01	1.221	0.796
2.242	110.6	131.7	1.271	54.25	1.188	53.01	1.216	0.759
2.513	106.1	139.0	1.334	52.04	1.180	50.71	1.211	0.719
2.626	104.2	142.1	1.361	51.11	1.178	49.74	1.210	0.703
2.748	102.2	145.5	1.391	50.13	1.175	48.72	1.209	0.687
2.833	100.8	147.9	1.413	49.44	1.173	48.01	1.208	0.676

(a) Reference (21), (b) $t^o_{K^+}$(KCl) = 0.4905, (c) Reference (29) based on $t^o_{K^+}$(KCl/glycine/water) = $t^o_{K^+}$(KCl/water) - (0.005 glycine molality) Reference (14)

APPENDIX 8.1

KCl in tetrahydrofuran/water mixtures at 25°C (a)

tetrahydrofuran % by wt.	Λ^0	D	η	$\lambda^0_{K^+}$ (b)	R^+ (b)	$^{100}/_D$
15.00	102.69	68.0	1.381	50.37	1.178	1.471
49.95	59.23	40.0	1.718	29.05	1.642	2.500
70.00	44.30	25.6	1.259	21.73	2.995	3.906
80.05	44.60	18.3	0.959	21.88	3.906	5.464
85.00	47.75	15.6	0.824	23.42	4.246	6.410
90.00	53.03	12.6	0.678	26.01	4.646	7.937

(a) Reference (40)

(b) $t^o_{K^+} = 0.4905$

APPENDIX 8.1

KCl in acetone/water mixtures at 25°C

acetone % by wt.	Λ^0 (a)	D (a)	η (a)	$\lambda^0_{K^+}$ (b)	R^+	$^{100}/_D$
20	102.14	66.98	1.308	50.10	1.250	1.493
30	90.0	61.04	1.353	44.15	1.372	1.638
40	84.32	54.6	1.327	41.36	1.493	1.832
50	78.90	48.2	1.224	38.70	1.730	2.075
100	-	20.47 (c)	0.3040 (c)	80.5 (c) (d)	3.348	4.831

(a) Reference (37), (b) $t^o_{K^+}$ (KCl) = 0.4905, (c) Reference (39)

(d) $\lambda^0_{K^+}$ based on $\lambda^0_- = \lambda^0_+$ for tetrabutylammonium triphenyl-boroflouride in acetone (39)

APPENDIX 8.1

KCl in dioxane/water mixtures at 25°C

dioxane % by wt.	Λ^0 (a)	D (a)	η (a)	$\lambda^0_{K^+}$ (c)	R^+ (c)	t_{K^+} (b)	$\lambda^0_{K^+}$	R^+	100/D
22.2	100.74	60.16	1.330	49.41	1.247	0.495	49.87	1.235	1.662
43.6	69.13	41.46	1.803	33.91	1.340	0.459	31.73	1.432	2.412
56.7	56.45	30.26	1.977	27.69	1.497	0.450	25.40	1.632	3.305
61.7	52.32	25.85	1.991	25.66	1.604	0.454	23.75	1.733	3.870
69.9	46.26	19.32	1.928	22.69	1.873	0.466	21.56	1.972	5.176
75.0	42.34	15.37	1.844	20.77	2.140	0.480	20.32	2.186	6.506
78.8	39.45	12.74	1.755	19.35	2.413	0.490	19.33	2.415	7.849

(a) Reference (23), (b) Reference (47)

(c) $t^0_{K^+}$(KCl) = 0.4905

APPENDIX 8.2

Values of $\lambda^0_{K^+}$ in glycerol/water mixtures at 25°C

glycerol % by wt.	Λ^0 (a)	D (a)	η (a)	t_{K^+}(KCl) (b)	$\lambda^0_{K^+}$
10.0	-	75.6 (d)	1.150 (d)	-	60.0 (c)
20.0	-	72.9 (d)	1.537 (d)	-	47.6 (c)
20.37	95.62	73.80	1.561	0.502	48.0
34.26	64.60	70.45	2.520	0.509	32.9
44.45	45.26	67.55	3.879	0.512	23.2
64.67	17.33	60.75	11.90	0.514	8.91
80.46	5.144	53.80	46.0	0.510	2.62
100.0	0.2750	42.48	945.0	0.476	0.131

(a) Reference (12), (b) Reference (46), (c) Reference (10),
(d) Reference (14)

APPENDIX 8.2

Values of $\lambda^0_{K^+}$ in ethylene glycol/water mixtures at 25°C

ethylene glycol % by wt.	Λ^0 (a)	D (a)	η (a)	t_{K^+} (b)	$\lambda^0_{K^+}$
23.34	89.05	71.60	1.630	0.496	44.2
45.91	55.13	65.60	2.799	0.501	27.6
80.09	20.50	51.85	7.962	0.498	10.21
92.26	13.145	45.65	12.43	0.480	6.31
96.95	10.939	42.90	151.4	0.468	5.12
100.0	9.693	40.75	168.4	0.458	4.44

(a) Reference (11), (b) Reference (45)

APPENDIX 8.2

Values of $\lambda^0_{K^+}$ in 20 and 10% sucrose and 10% mannitol-water mixtures at 25°C

added component	% by wt.	D (a)	η (a)	$\lambda^0_{K^+}$ (b)
sucrose	20	73.66	1.699	46.1
sucrose	10	76.20	1.179	59.7
mannitol	10	77.12	1.192	58.6

(a) Reference (14), (b) Reference (10) and (50)

CONDUCTIVITY PROGRAMS

PROGRAMS LOAOKA, ITERA, UNASS, PITTSV2 AND PITTS

The procedure used in these programs for the computation of Λ^o, a and where applicable Ka from the input values of Λ and C has either been outlined in Chapter 7 or reference to the literature has been made therein.

As many systems as desired may be processed per run but after the last card of the final system a blank card precedes the EOF card.

Input Data

(A) PROGRAM LOAOKA

Computes Λ^o, a and Ka with the Fuoss-Hsia equation.

Card 1

FORMAT 102 - System identification - any combination of alphabetic or numeric characters up to 78 columns may be used.

Card 2

FORMAT 104 - the symbols have the following meanings:

N = Number of data points.
D = Solvent dielectric constant.
ETA = Solvent viscosity in poise.
T = Absolute temperature.
QK = Approximate Λ^o.
AR = Approximate ion size in Å.
PKV = Approximate association constant.

Cards 3 → N + 3

FORMAT 106 - A value of C, expressed as $C\times10^4$, and its corresponding Λ value per data card.

PROGRAM LOAOKA to be used in conjunction with SUBROUTINES SUBQC, SUBENE and SUBG2.

(B) PROGRAM ITERA

For each input value of a from a band of values of a a value of

Λ^{o} and Ka is computed from the Fuoss-Hsia equation.

Card 1

As PROGRAM LOAOKA.

Card 2

As PROGRAM LOAOKA - quantity AR of this card is ignored in PROGRAM ITERA.

Card 3

FORMAT 710 wherein:

A1 = The initial value of a.

DA = The increment in a.

A2 = The final value of a in the series of the input values of this quantity.

Cards 4 → N + 4

As PROGRAM LOAOKA for cards 3 → N + 3.

SUBROUTINES - as LOAOKA.

(C) PROGRAM UNASS

Program computes Λ^{o} and a with the Fuoss-Hsia conductivity equation for the non-associated case, i.e. Ka assumed to be zero.

Input Data

As PROGRAM LOAOKA - PKV of card 2 is ignored.

SUBROUTINES - SUBQC and SUBENE.

(D) PROGRAM PITTSV2

Program computes Λ^{o} and a with the Pitts conductivity equation.

Input Data

As PROGRAM UNASS.

SUBROUTINES - LAMCAL, S1T1 and SUBENE.

(E) PROGRAM PITTS

Program computes Λ^{o} and a with the Pitts conductivity equation.

Input Data

Card 1

As PROGRAM LOAOKA.

Card 2

FORMAT 4 : N, D, ETA, T and ECO (ECO ≡ QK) defined as card 2 of PROGRAM LOAOKA.

A1 and A2 are estimated bounds within which the ion size should lie.

Cards 3 → N + 3

FORMAT 5 - As FORMAT 106 of PROGRAM LOAOKA.

SUBROUTINES - DELTA, S1T1 and SUBENE.

OUTPUT

The principal output of each program is as follows:

LOAOKA

Λ^o, its standard error $\sigma\Lambda^o$, a, its standard error σa, Ka, σKa and the standard error of the fit of the experimental Λ-C values to the Fuoss-Hsia equation - σ. Also the deviation, $\delta\Lambda$, between experimental Λ and that computed from the theoretical equation is also given for each Λ-C point.

ITERA

For each input value of a output consists of Λ^o, $\sigma\Lambda^o$, Ka, σKa and σ.

UNASS

Λ^o, $\sigma\Lambda^o$, a, σa $\delta\Lambda$ and σ.

PITTSV2

As UNASS.

PITTS

Λ^o, a, σ and $\delta\Lambda$. $\sigma\Lambda^o$ and σa are not computed by this program.

```
      PROGRAM LOA0KA(INPUT,OUTPUT)
C
C.... PROGRAM ADAPTED FROM R.L.KAY≠S FUOSS HSIA  PROGRAM
C..... PROGRAM ITERATES FOR LAMDA 0 , A ZERO , $ ASSOCIATION CONST.
C.... PROGRAM TREATES DATA FOR ASSOCIATED CASE ONLY******************
C
      COMMON C(30),Q(30),G2(30),CG(30),F2(30),VF(30),FM(30),BCFM(30),
     1QC(30),QL(30),FMI(30),BCFMI(30),QCI(30),QCP(30),TDT(30),DQ(30),
     2DLQ(30),SQDL(30),SG(30),PKN(30),DQQ(30),WT(30),R(30),BARM(30),
     3DEN(30),QP(30),DK(30),
     4D,AA,QZ,FKAP,ALPHA,BETA,E1,E2,J
C
C
  100 PRINT 10
   10 FORMAT (1H1)
C
C     FIRST DATA CARD GIVES SYSTEM IDENTIFICATION
      READ 102
  102 FORMAT (78H
     1                                           )
C
C
      READ104,N,D,ETA,T,QK,AR,PKV
  104 FORMAT(I5,F11.0,5F10.0)
      IF(N.EQ.0) GO TO 700
C
  210 PRINT 211
  211 FORMAT(1H0,*ASSOCIATED ELECTROLYTE*)
      PRINT124
  124 FORMAT(1H0)
C
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM LOAOKA CONTINUED   $$$$$$$$$$$$$$$$
C
      PRINT 102
      PRINT124
      PRINT112,D,ETA,QK,PKV,T,AR
  112 FORMAT(22H  DIELECTRIC CONSTANT=F8.2,11H VISCOSITY=F10.6,12H INITI
     1AL QZ=F8.3,/,22H INITIAL ASSOCN CONST=F8.3,13H TEMPERATURE=F8.2,12
     2H INITIAL AA=F8.3/)
   85 READ106,(C(J),Q(J),J=1,N)
  106 FORMAT (2F10.0)
      PRINT719
  719 FORMAT(1H0,* INPUT   DATA*)
      PRINT717
  717 FORMAT(1H 3X,7H10000 C,6X,1HQ,/)
      PRINT718,(C(J),Q(J),J=1,N)
  718 FORMAT(F11.4,F10.3)
      PRINT124
C
C
      QO=280.195/D
C  BEGIN COMPUTATION HERE
  640 FLON=N
      DT=D*T
      SQRDT= SQRTF(DT)
      ALPHA=820400./(SQRDT*DT)
      BETA=82.501/(ETA*SQRDT)
      E1=2.9422E12/(DT**3)
      E2=0.43329E8/((DT*DT)*ETA)
      TA=SQRTF(6.0*E1)
      FKAP=50.294/SQRDT
  641 QZI=QK
```

```
      NX=0
      M1=0
      AA=AR
  650 NX=NX+1
      IF(PKV)652,649,651
  652 DO 653 J=1,N
      G2(J)=1.0
      CG(J)=C(J)*1.0E-4
  653 CONTINUE
      GO TO 610
  649 PKV=0.1
  651 DO 200 J=1.N
  200 CALL SUBG2 (TA,PKV,M1,SQRDT,QQ)
      IF(M1-10)610,610,196
  196 PRINT 197
  197 FORMAT(36HNO CONVERGENCE IN G1 AFTER 10 CYCLES)
      GO TO 100
C
C
  610 M=0
      M2=0
      QZ=QK
  504 AI=AA
      AP=1.005*AA
      M=M+1
      CYC=M
      IF(M-10) 520,513,513
  513 PRINT111
  111 FORMAT(1H0,*NO CONVERGENCE AFTER 10 CYCLES*)
      GO TO 100
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM LOAOKA CONTINUED   $$$$$$$$$$$$$$$$
C
  520 DO 33 J=1,N
      CALL SUBQC
      FMI(J)=FM(J)
      BCFMI(J)=BCFM(J)
      QCI(J)=QC(J)
      AA=AP
      CALL SUBQC
      QCP(J)=QC(J)
      TDT(J)=Q(J)+G2(J)*BCFMI(J)-G2(J)*FMI(J)*QZ
      DQ(J)=(200.0/AI)*(QCP(J)-QCI(J))
      AA=AI
      QZ=1.005*QZ
      CALL SUBQC
      QL(J)=QC(J)
      QZ=QZ/1.005
      DQQ(J)=(200.0/QZ)*(QL(J)-QCI(J))
      PKV=1.005*PKV
      CALL SUBG2 (TA,PKV,M1,SQRDT,QQ)
      IF(M1-10)32,32,196
   32 CALL SUBQC
      QP(J)=QC(J)
      PKV=PKV/1.005
   33 DK(J)=(200.0/PKV)*(QP(J)-QCI(J))
    3 SUM11=0.0
      SUM12=0.0
      SUM13=0.0
      SUM14=0.0
      SUM22=0.0
      SUM23=0.0
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM LOAOKA CONTINUED   $$$$$$$$$$$$$$$$

      SUM24=0.0
      SUM33=0.0
      SUM34=0.0
      DO 50 J=1,N
      SUM11=SUM11+DQQ(J)*DQQ(J)
      SUM12=SUM12+DQQ(J)*DQ(J)
      SUM13=SUM13+DQQ(J)*DK(J)
      SUM14=SUM14+DQQ(J)*TDT(J)
      SUM22=SUM22+DQ(J)*DQ(J)
      SUM23=SUM23+DQ(J)*DK(J)
      SUM24=SUM24+DQ(J)*TDT(J)
      SUM33=SUM33+DK(J)*DK(J)
   50 SUM34=SUM34+DK(J)*TDT(J)
      DET=SUM11*(SUM22*SUM33-SUM23*SUM23)-SUM12*(SUM12*SUM33-SUM13*SUM23
     1)+SUM13*(SUM12*SUM23-SUM13*SUM22)
      DETQ=SUM14*(SUM22*SUM33-SUM23*SUM23)-SUM12*(SUM24*SUM33-SUM23*SUM3
     14)+SUM13*(SUM23*SUM24-SUM22*SUM34)
      DETA=SUM11*(SUM24*SUM33-SUM23*SUM34)-SUM14*(SUM12*SUM33-SUM13*SUM2
     13)+SUM13*(SUM12*SUM34-SUM13*SUM24)
      DETK=SUM11*(SUM22*SUM34-SUM23*SUM24)-SUM12*(SUM12*SUM34-SUM13*SUM2
     14)+SUM14*(SUM12*SUM23-SUM13*SUM22)
      DQZ=DETQ/DET
      QZ=QZ+DQZ
      DLA=DETA/DET
      AA=AA+DLA
      DLK=DETK/DET
      PKV=PKV+DLK
      PRINT118,CYC,DLA,DQZ,DLK
  118 FORMAT(10H AT CYCLE F2.0,12H  DELTA AA =F7.4,12H  DELTA QZ =F7.4,1
     13H  DELTA PKV =F10.4)
```

```
      IF(PKV)320,320,321
  320 PKV=(PKV-DLK)/2.0
      PRINT119
  119 FORMAT(10X,23HPKV NEGATIVE  TRY PKV/2)
  321 DO 702 J=1,N
  702 CALL SUBG2 (TA,PKV,M1,SQRDT,QQ)
      IF(M1-10)703,703,196
  703 IF(AA)329,329,330
  329 AA=(AA-DLA)/2.0
      PRINT120
  120 FORMAT(20X,21HAA NEGATIVE  TRY AA/2)
      GO TO 504
  330 TSA=ABSF(DLA/AA)
      IF(TSA-0.0001)331,331,332
  332 GO TO 504
C
C
C
  331 B=560.37/(D*AA)
      FBJ=EXPF(B)/(B**3)
      PKCON=(2.523E-3)*(AA**3)*EXPF(B)
      SMSQ = 0.
      SMDL=0.0
      DO 701 J=1,N
      CALL SUBQC
      DLQ(J)=QC(J)-Q(J)
      SMDL=SMDL+DLQ(J)
      SQDL (J) = DLQ(J)**2
  701 SMSQ = SMSQ + SQDL(J)
      REAL = N
```

```
      QUOT=SMSQ/(REAL-3.0)
      SIGMA = SQRTF(QUOT)
      SG(NX)=SIGMA
      A11=ABSF(SUM11)
      A12=ABSF(SUM12)
      A13=ABSF(SUM13)
      A22=ABSF(SUM22)
      A23=ABSF(SUM23)
      A33=ABSF(SUM33)
      SGQ=SIGMA*SQRTF((A22*A33-A23*A23)/DET)
      SGA=SIGMA*SQRTF((A11*A33-A13*A13)/DET)
      SGK=SIGMA*SQRTF((A11*A22-A12*A12)/DET)
      S=ALPHA*QZ+BETA
      E=E1*QZ-E2
      PRINT124
  581 PRINT116,B,FBJ,PKCON
  116 FORMAT(11H BJERRUM-B=F10.3,10H WITH FBJ=F12.3,11H AND PKCON=F12.3)
      PRINT117,ALPHA,BETA,S,E1,E2,E
  117 FORMAT(8H  ALPHA=F7.4,5HBETA=F7.2,3H S=F7.2,4H E1=F6.3,4H E2=F6.2,
     13H E=F7.2)
      PRINT124
      PRINT126
  126 FORMAT(1H0,6X,*C*,12X,*CG*,11X,*GAMMA*,4X,*ACT SQU*,5X,*Q EXPT*,6X
     2,*Q CALC*,6X,*Q DASH*)
      PRINT127,(C(J),CG(J),G2(J),F2(J),Q(J),QC(J),DLQ(J),J=1,N)
  127 FORMAT(1X,F11.6,4X,F11.9,4X,F7.5,4X,F7.5,4X,F8.4,4X,F8.4,4X,F8.4)
      PRINT124
      PRINT114,QZ,SGQ,AA,SGA,PKV,SGK
  114 FORMAT(27H MINIMIZING VALUES ARE QZ =F10.3,4H PM F5.3,9H AND AA =F
     17.3,4H PM F5.3,/,/,17X,10H AND PKV =F10.3,4H PM F8.3)
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM LOAOKA CONTINUED   $$$$$$$$$$$$$$$$

      PRINT124
      PRINT123,SIGMA,SMDL
  123 FORMAT(25H     STANDARD DEVIATION =F6.3,18H WITH SUM-DELTAS =F6.3)
      PRINT124
      PRINT5000,QQ
 5000 FORMAT(1H0(*BJERRUM CRIT DIST=*,E14.7)
      PRINT124
      PRINT125
  125 FORMAT(55H*******************************************************)
C
      GO TO 100
C
  700 CONTINUE
C
      END
```

```
      PROGRAM ITER A(INPUT,OUTPUT)
C
C.... R.L.KAYS FUOSS-HSIA PROGRAM ADAPTED TO CALCULATE LAMBDA ZERO $
C..... KA GIVEN FIXED VALUES OF A ZERO
C
      COMMON C(30),Q(30),G2(30),CG(30),F2(30),VF(30),FM(30),BCFM(30),
     1QC(30),QL(30),FMI(30),BCFMI(30),QCI(30),QCP(30),TDT(30),DQ(30),
     2DLQ(30),SQDL(30),SG(30),PKN(30),DQQ(30),WT(30),R(30),BARM(30),
     3DEN(30),QP(30),DK(30),
     4D,AA,QZ,FKAP,ALPHA,BETA,E1,E2,J
C
C
  100 PRINT 10
   10 FORMAT (1H1)
C
C     FIRST DATA CARD GIVES SYSTEM IDENTIFICATION
      READ 102
  102 FORMAT (78H
     1                                    )
C
C
      READ104,N,D,ETA,T,QK,AR,PKV
  104 FORMAT(I5,F11.0,5F10.0)
      IF(N.EQ.0) GO TO 700
C
  210 PRINT 211
  211 FORMAT(1H0,*ASSOCIATED ELECTROLYTE*)
      PRINT124
  124 FORMAT(1H0)
C
C.... A1 INITIAL VALUE OF AZERO , DA INCRIMENT IN A , A2 FINAL VALUE OF
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM ITER A CONTINUED   $$$$$$$$$$$$$$$$

      READ710,A1,DA,A2
  710 FORMAT(3F5.0)
C
      PRINT 102
      PRINT124
      PRINT112,A1,DA,A2
  112 FORMAT(1H0,*INITIAL A*,2X,F10.4,2X,*INCRIMENT IN  A*,2X,F10.4,2X,*
     2FINAL VALUE OF A*,2X,F10.4)
      PRINT110,D,ETA,QK,PKV,T,AR
  110 FORMAT(22H  DIELECTRIC CONSTANT=F8.2,11H VISCOSITY=F10.6,12H INITI
     1AL QZ=F8.3,/,22H INITIAL ASSOCN CONST=F8.3,13H TEMPERATURE=F8.2,12
     2H INITIAL AA=F8.3/)
   85 READ106,(C(J),Q(J),J=1,N)
  106 FORMAT (2F10.0)
      PRINT719
  719 FORMAT(1H0,* INPUT   DATA*)
      PRINT717
  717 FORMAT(1H 3X,7H10000 C,6X,1HQ,/)
      PRINT718,(C(J),Q(J),J=1,N)
  718 FORMAT(F11.4,F10.3)
      PRINT124
C
      QQ=1.0
C
C  BEGIN COMPUTATION HERE
  640 FLON=N
      DT=D*T
      SQRDT= SQRTF(DT)
      ALPHA=820400./(SQRDT*DT)
      BETA=82.501/(ETA*SQRDT)
```

```
      E1=2.9422E12/(DT**3)
      E2=0.43329E8/((DT*DT)*ETA)
      TA=SQRTF(6.0*E1)
      FKAP=50.294/SQRDT
      PRK=PKV
      AA=A1
  641 QZI=QK
C.... AFTER EACH ITERATION WITH A VALUE OF A ZERO RESET ASS. CONST. TO
C..... THE INPUT VALUE FOR NEXT ITERATION
      PKV=PRK
      NX=0
      M1=0
  650 NX=NX+1
      IF(PKV)652,649,651
  652 DO 653 J=1,N
      G2(J)=1.0
      CG(J)=C(J)*1.0E-4
  653 CONTINUE
      GO TO 610
  649 PKV=0.1
  651 DO 200 J=1,N
  200 CALL SUBG2 (TA,PKV,M1,SQRDT,QQ)
      IF(M1-10)610,610,196
  196 PRINT 197
  197 FORMAT(36HNO CONVERGENCE IN G1 AFTER 10 CYCLES)
      GO TO 1
C
C
  610 M=0
      M2=0
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM ITER A CONTINUED   $$$$$$$$$$$$$$$$

      QZ=QK
  504 AI=AA
      M=M+1
      CYC=M
      IF(M-9)520,513,513
  513 PRINT111
  111 FORMAT(1H0,*NO CONVERGENCE AFTER 5 CYCLES*)
      GO TO 1
C
  520 DO 33 J=1,N
      CALL SUBQC
      FMI(J)=FM(J)
      BCFMI(J)=BCFM(J)
      QCI(J)=QC(J)
      TDT(J)=Q(J)+G2(J)*BCFMI(J)-G2(J)*FMI(J)*QZ
      AA=AI
      QZ=1.005*QZ
      CALL SUBQC
      QL(J)=QC(J)
      QZ=QZ/1.005
      DQQ(J)=(200.0/QZ)*(QL(J)-QCI(J))
      PKV=1.005*PKV
      CALL SUBG2 (TA,PKV,M1,SQRDT,QQ)
      IF(M1-1)32,32,196
   32 CALL SUBQC
      QP(J)=QC(J)
      PKV=PKV/1.005
   33 DK(J)=(200.0/PKV)*(QP(J)-QCI(J))
    3 SUM11=0.0
      SUM12=0.0
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM ITER A CONTINUED   $$$$$$$$$$$$$$$$

      SUM13=0.0
      SUM22=0.0
      SUM23=0.0
      DO 50 J=1,N
      SUM11=SUM11+DQQ(J)*DQQ(J)
      SUM12=SUM12+DQQ(J)*DK(J)
      SUM13=SUM13+DQQ(J)*TDT(J)
      SUM22=SUM22+DK(J)*DK(J)
   50 SUM23=SUM23+TDT(J)*DK(J)
      DET=SUM11*SUM22-SUM12*SUM12
      DETQ=SUM13*SUM22-SUM12*SUM23
      DETK=SUM11*SUM23-SUM12*SUM13
      DQZ=DETQ/DET
      QZ=QZ+DQZ
      DLK=DETK/DET
      PKV=PKV+DLK
      PRINT118,CYC,DLK,DQZ
  118 FORMAT(10H AT CYCLE F2.0,12H  DELTA PKV=F7.4,12H  DELTA QZ =F7.4,1
     2)
      IF(PKV)320.320,321
  320 PKV=(PKV-DLK)/2.0
      PRINT119
  119 FORMAT(10X.23HPKV NEGATIVE  TRY PKV/2)
  321 DO 702 J=1.N
  702 CALL SUBG2 (TA,PKV,M1.SQRDT,QO)
      IF(M1-10)703,703.196
  703 CONTINUE
  330 TSA=ABSF(DQZ/QZ)
      IF(TSA-0.00005)331.331,332
  332 GO TO 504
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM ITER A CONTINUED   $$$$$$$$$$$$$$$$
C
C
C
 331 B=560.37/(D*AA)
     FBJ=EXPF(B)/(B**3)
     PKCON=(2.523E-3)*(AA**3)*EXPF(B)
     SMSQ = 0.
     SMDL=0.0
     DO 701 J=1.N
     CALL SUBQC
     DLQ(J)=QC(J)-Q(J)
     SMDL=SMDL+DLQ(J)
     SQDL (J) = DLQ(J)**2
 701 SMSQ = SMSQ + SQDL(J)
     REAL = N
     QUOT=SMSQ/(REAL-3.0)
     SIGMA = SQRTF(QUOT)
     SG(NX)=SIGMA
     A11=ABSF(SUM11)
     A22=ABSF(SUM22)
     SGQ=SIGMA*SQRTF(A22/DET)
     SGK=SIGMA*SQRT(A11/DET)
     PRINT128.QZ.SGQ.PKV.SGK
 128 FORMAT(1H0.*LAMBDA 0 *,2X,F10.3,2X,F5.3.4X.*ASSN. CONST.*,2X,F10.3
    2,2X.F5.3)
     SGA=0.0
     S=ALPHA*QZ+BETA
     E=F1*QZ-E2
     PRINT124
 581 PRINT116.B.FBJ.PKCON
```

```
$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM ITER A CONTINUED   $$$$$$$$$$$$$$$

  116 FORMAT(11H BJERRUM-B=F10.3,10H WITH FBJ=F12.3,11H AND PKCON=F12.3)
      PRINT117,ALPHA,BETA,S,E1,E2,E
  117 FORMAT(8H  ALPHA=F7.4,5HBETA=F7.2,3H S=F7.2,4H E1=F6.3,4H E2=F6.2,
     13H E=F7.2)
      PRINT124
      PRINT124
      PRINT114,QZ,SGQ,AA,SGA,PKV,SGK
  114 FORMAT(27H MINIMIZING VALUES ARE QZ =F10.3,4H PM F5.3,9H AND AA =F
     17.3,4H PM F5.3,/,/,17X,10H AND PKV =F10.3,4H PM F9.3)
      PRINT124
      PRINT123,SIGMA,SMDL
  123 FORMAT(25H     STANDARD DEVIATION =F6.3,18H WITH SUM-DELTAS =F6.3)
      PRINT125
  125 FORMAT(55H*******************************************************)
C
      PRINT124
      PRINT124
    1 AA=AA+DA
      IF(AA.LE.A2) GO TO 641
      PRINT126
  126 FORMAT(1H0,6X,*C*,12X,*CG*,11X,*GAMMA*,4X,*ACT SQU*,5X,*Q EXPT*,6X
     2,*Q CALC*,6X,*Q DASH*)
      PRINT124
      PRINT127,(C(J),CG(J),G2(J),F2(J),Q(J),QC(J),DLQ(J),J=1,N)
  127 FORMAT(1X,F11.6,4X,F11.9,4X,F7.5,4X,F7.5,4X,F8.4,4X,F8.4,4X,F8.4)
      GO TO 100
  700 CONTINUE
      END
```

```
      PROGRAM UNASS(INPUT,OUTPUT)
C.... FUOSS HSIA EQUATION R.L. KAYS PROGRAM FOR THE NON ASSOCIATED CASE
     1QC(30),QL(30),FMI(30),PCFMI(30),QCI(30),QCP(30),TDT(30),DQ(30),
     2DLQ(30),SQDL(30),SG(30),PKN(30),DQQ(30),WT(30),P(30),BARM(30),
     3DEN(30),QP(30),DK(30),FM(30),BCFM(30),TDT(30),DQ(30),
     4D,AA,QZ,FKAP,ALPHA,BETA,E1,E2,J
      COMMON C(30),Q(30),G2(30),CG(30),F2(30),VF(30),FM(30),BCFM(30),
  100 PRINT10
   10 FORMAT(1H1)
      PRINT 213
  213 FORMAT(1H0,*NONASSOCIATED ELECTROLYTE*)
      READ 102
      PRINT 102
  102 FORMAT (78H
     1                                )
      PRINT124
  124 FORMAT(1H0)
      READ104,N,D,ETA,T,QK,AR,PKV
  104 FORMAT(I5,F11.0,5F10.0)
      IF(N.EQ.0) GO TO 700
      PKV=0.0
      PRINT719
  719 FORMAT(1H0,* INPUT   DATA*)
      PRINT124
      PRINT112,D,ETA,QK,PKV,T,AR
  112 FORMAT(22H  DIELECTRIC CONSTANT=F8.2,11H VISCOSITY=F10.6,12H INITI
     1AL QZ=F8.3,/,22H INITIAL ASSOCN CONST=F8.3,13H TEMPERATURE=F8.2,12
     2H INITIAL AA=F8.3/)
   85 READ106,(C(J),Q(J),J=1,N)
  106 FORMAT (2F10.0)
      PRINT717
  717 FORMAT(1H 3X,7H10000 C,6X,1HQ,/)
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM UNASS CONTINUED   $$$$$$$$$$$$$$$$$
      PRINT718,(C(J),Q(J),J=1,N)
  718 FORMAT(F11.4,F10.3)
C
  640 FLON=N
      DT=D*T
      SQRDT= SQRTF(DT)
      ALPHA=820400./(SQRDT*DT)
      BETA=82.501/(ETA*SQRDT)
      E1=2.9422E12/(DT**3)
      E2=0.43329E8/((DT*DT)*ETA)
      TA=SQRTF(6.0*E1)
      FKAP=50.294/SQRDT
 1000 QZI=QK
      NX=0
      DO 1653 J=1,N
      G2(J)=1.0
 1653 CG(J)=C(J)*1.0E-4
      AA=AR
 1650 NX=NX+1
      M=0
      QZ=QK
 1504 AI=AA
      AP=1.005*AA
      M=M+1
      CYC=M
      IF(M-10)1520,1520,1513
 1513 PRINT111
  111 FORMAT(1H0,*NO CONVERGENCE AFTER TEN CYCLES*)
      GO TO 100
C
```

```
$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM UNASS CONTINUED   $$$$$$$$$$$$$$$$

 1520 DO 1033 J=1,N
      CALL SUBQC
      FMI(J)=FM(J)
      BCFMI(J)=BCFM(J)
      QCI(J)=QC(J)
      AA=AP
      CALL SUBQC
      QCP(J)=QC(J)
      TDT(J)=Q(J)+G2(J)*BCFMI(J)-G2(J)*FMI(J)*QZ
      DQ(J)=(200.0/AI)*(QCP(J)-QCI(J))
      AA=AI
      QZ=1.005*QZ
      CALL SUBQC
      QL(J)=QC(J)
      QZ=QZ/1.005
 1033 DQQ(J)=(200.0/QZ)*(QL(J)-QCI(J))
 1003 SUM11=0.0
      SUM12=0.0
      SUM13=0.0
      SUM22=0.0
      SUM23=0.0
      DO 1050 J=1,N
      SUM11=SUM11+DQQ(J)*DQQ(J)
      SUM12=SUM12+DQQ(J)*DQ(J)
      SUM13=SUM13+DQQ(J)*TDT(J)
      SUM22=SUM22+DQ(J)*DQ(J)
 1050 SUM23=SUM23+DQ(J)*TDT(J)
      DET=SUM11*SUM22-SUM12*SUM12
      DETQ=SUM13*SUM22-SUM12*SUM23
      DETA=SUM11*SUM23-SUM12*SUM13
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM UNASS CONTINUED   $$$$$$$$$$$$$$$$$

      DQZ=DETQ/DET
      QZ=QZ+DQZ
      DLA=DETA/DET
      AA=AA+DLA
      PRINT121,CYC,DLA,DQZ
  121 FORMAT(10H AT CYCLE F2.0,12H  DELTA AA =F7.4,12H  DELTA QZ =F7.4)
      IF(AA)1329,1329,1330
 1329 AA=(AA-DLA)/2.0
      PRINT120
  120 FORMAT(1H0,*    AA NEGITIVE TRY AA/2*)
      GO TO 1504
 1330 TSA=ABSF(DLA/AA)
      IF(TSA-0.0001)1331,1331,1332
 1332 GO TO 1504
C
C
 1331 B=560.37/(D*AA)
      FBJ=EXPF(B)/(B**3)
      PKCON=(2.523E-3)*(AA**3)*EXPF(B)
      SMSQ=0.0
      SMDL=0.0
      DO 1701 J=1,N
      CALL SUBQC
      DLQ(J)=QC(J)-Q(J)
      SMDL=SMDL+DLQ(J)
      SQDL(J)=DLQ(J)**2
 1701 SMSQ=SMSQ+SQDL(J)
      REAL=N
      QUOT=SMSQ/(REAL-2.0)
      SIGMA=SQRTF(QUOT)
      SG(NX)=SIGMA
```

```
$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM UNASS CONTINUED   $$$$$$$$$$$$$$$$$

      A11=ABSF(SUM11)
      A22=ABSF(SUM22)
      SGQ=SIGMA*SQRT(A11/DET)
      SGA=SIGMA*SQRTF(A11/DET)
      S=ALPHA*QZ+BETA
      E=E1*QZ-E2
      PRINT124
      PRINT116,B,FBJ,PKCON
  116 FORMAT(11H BJERRUM-B=F10.6,10H WITH FBJ=F12.5,11H AND PKCON=F12.5)
      PRINT117,ALPHA,BETA,S,E1,E2,E
  117 FORMAT(7H ALPHA F9.5,5HBETA F9.5.3H S F9.4,4H E1 F9.4,4H E2 F9.4,
     13H E=F9.4)
      PRINT124
      PRINT129
  129 FORMAT(1H0,4X,*C*.6X,*EXP. LAMBDA*,6X,*LAMBDA CALC*,6X,*LAMBDA DAS
     1H*)
      PRINT130,(C(J),Q(J).QC(J),DLQ(J),J=1,N)
  130 FORMAT(1X.F10.4.4X,F10.4,4X.F10.4.4X,F10.4)
      PRINT128,QZ.SGQ,AA,SGA
  128 FORMAT(1H0,*MINIMIZING VALUES ARE QZ *,F10.3,2X,*PM*,F5.3,2X.*AND
     1A*,F7.3,2X,*PM*,F5.3)
      PRINT123.SIGMA.SMDL
  123 FORMAT(1H0.*STANDARD DEVIATION  *.F6.3,2X,*WITH SUM OF DELTAS  *,F
     16.3)
      PRINT125
  125 FORMAT(1H0(* CHOCKS AWAY CHAPS ALL OVER RED ROVER*)
C
C
      GO TO 100
  700 CONTINUE
      END
```

```
      PROGRAM PITTSV2(INPUT,OUTPUT)
      COMMON Q(30),QC(30),QCI(30),QCP(30),QL(30),DQ(30),DQQ(30),DLQ(30),
     2SQDL(30),TDT(30),C(30),RC(30),KAPPA(30),TERM1(30),TERM2(30),TERM3(
     330),SG(30),
     4J,AA,QZ,R2,TERM4
      REAL KAPPA
C..... FUNDAMENTAL CONSTANTS SEE FUOSS$ACCASCINA ELECTROLYTIC
C....  CONDUCTANCE PAGE 195
C.... REFERENCE E.PITTS ET Al TRANS. FAR. SOC.65,849,(1969)
  100 PRINT10
   10 FORMAT(1H1)
      PRINT 213
  213 FORMAT(1H0,*NONASSOCIATED ELECTROLYTE..PITTS EQN. VERSION2*)
      READ 102
      PRINT 102
  102 FORMAT (78H
     1                        )
      PRINT124
  124 FORMAT(1H0)
      READ104,N,D,ETA,T,QK,AR,PKV
  104 FORMAT(I5,F11.0,5F10.0)
      IF(N.EQ.0) GO TO 700
      PKV=0.0
      PRINT719
  719 FORMAT(1H0,* INPUT   DATA*)
      PRINT124
      PRINT112,D,ETA,QK,PKV,T,AR
  112 FORMAT(22H  DIELECTRIC CONSTANT=F8.2,11H VISCOSITY=F10.6,12H INITI
     1AL QZ=F8.3,/,22H INITIAL ASSOCN CONST=F8.3,13H TEMPERATURE=F8.2,12
     2H INITIAL AA=F8.3/)
      READ106,(C(J),Q(J),J=1,N)
  106 FORMAT (2F10.0)
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM PITTSV2 CONTINUED   $$$$$$$$$$$$$$$

      PRINT717
  717 FORMAT(1H 3X,7H10000 C,6X,1HQ,/)
      PRINT718,(C(J),Q(J),J=1,N)
  718 FORMAT(F11.4,F10.3)
C
  640 FLON=N
      AR=AR*1.0E-8
      DT=D*T
C..... R2=ROOT 2
C.... CALCULATE TERMS OF PITTS EQUATION INDEPENDENT OF LAMBDA0 AND A
      R2=1.4142136
      DO7I=1,N
      C(I)=C(I)*1.0E-04
      RC(I)=SQRT(C(I))
      KAPPA(I)=(5.029422E9*RC(I))/SQRT(DT)
      TERM1(I)=1.640024E-8*KAPPA(I)/ETA
      TERM2(I)=5.569352E-4*KAPPA(I)/DT
    7 TERM3(I)=3.0*TERM2(I)*TERM2(I)
      TERM4=(9.815772E-6*DT)/ETA
      PRINT3
    3 FORMAT(1H0.*.$.$.$.$.$.$.$.$.$.$.$.$.$.$.$.$.$.$.$.$.$.$.$.$.$.$$.
     2.$.$.$.$.$.$.$..$.$*)
      QZI=QK
      NX=0
      AA=AR
 1650 NX=NX+1
      M=0
      QZ=QK
 1504 AI=AA
      AP=1.005*AA
```

```
      M=M+1
      CYC=M
      IF(M-10)1520,1520,1513
 1513 PRINT111
  111 FORMAT(1H0,*NO CONVERGENCE AFTER TEN CYCLES*)
      GO TO 100
C
 1520 DO 1033 J=1,N
      CALL LAMCAL
      QCI(J)=QC(J)
      AA=AP
      CALL LAMCAL
      QCP(J)=QC(J)
      TDT(J)=Q(J)-QCI(J)
      AI=AI*1.0E8
      DQ(J)=(200.0/AI)*(QCP(J)-QCI(J))
      AI=AI*1.0E-8
      AA=AI
      QZ=1.005*QZ
      CALL LAMCAL
      QL(J)=QC(J)
      QZ=QZ/1.005
 1033 DQQ(J)=(200.0/QZ)*(QL(J)-QCI(J))
 1003 SUM11=0.0
      SUM12=0.0
      SUM13=0.0
      SUM22=0.0
      SUM23=0.0
      DO 1050 J=1,N
      SUM11=SUM11+DQQ(J)*DQQ(J)
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM PITTSV2 CONTINUED   $$$$$$$$$$$$$$$$
      SUM12=SUM12+DQQ(J)*DQ(J)
      SUM13=SUM13+DQQ(J)*TDT(J)
      SUM22=SUM22+DQ(J)*DQ(J)
 1050 SUM23=SUM23+DQ(J)*TDT(J)
      DET=SUM11*SUM22-SUM12*SUM12
      DETQ=SUM13*SUM22-SUM12*SUM23
      DETA=SUM11*SUM23-SUM12*SUM13
      DQZ=DETQ/DET
      QZ=QZ+DQZ
      DLA=DETA/DET
      DLA=DLA*1.0E-8
      AA=AA+DLA
      PRINT121.CYC.DLA ,DQZ
  121 FORMAT(1H0.*AT CYCLE*,F2.0.2X,*DELTA AA*,E14.7,2X.*DELTA QZ*,E14.7
     2)
      PRINT2004,AA,QZ
 2004 FORMAT(1H0.*AA*,E14.7,2X,*QZ*,E14.7)
      PRINT3
      IF(AA)1329.1329.1330
 1329 AA=(AA-DLA)/2.0
      PRINT120
  120 FORMAT(1H0.*     AA NEGITIVE TRY AA/2*)
      GO TO 1504
 1330 TSA=ABSF(DLA/AA)
      IF(TSA-0.0001)1331.1331.1332
 1332 GO TO 1504
C
C
 1331 AA=AA*1.0E8
      B=560.37/(D*AA)
```

```
      FBJ=EXPF(B)/(B**3)
      PKCON=(2.523E-3)*(AA**3)*EXPF(B)
      AA=AA*1.0E-8
      SMSQ=0.0
      SMDL=0.0
      DO 1701 J=1,N
      CALL LAMCAL
      DLQ(J)=QC(J)-Q(J)
      SMDL=SMDL+DLQ(J)
      SQDL(J)=DLQ(J)**2
 1701 SMSQ=SMSQ+SQDL(J)
      REAL=N
      QUOT=SMSQ/(REAL-2.0)
      SIGMA=SQRTF(QUOT)
      SG(NX)=SIGMA
      A11=ABSF(SUM11)
      A22=ABSF(SUM22)
      SGQ=SIGMA*SQRT(A11/DET)
      SGA=SIGMA*SQRTF(A11/DET)
      AA=AA*1.0E8
      PRINT124
      PRINT116.B,FBJ,PKCON
  116 FORMAT(11H BJERRUM-B=F10.6,10H WITH FBJ=F12.5,11H AND PKCON=F12.5)
      PRINT124
      PRINT129
  129 FORMAT(1H0,4X,*C*,9X,*EXP. LAMBDA*,2X,*LAMBDA CALC*,6X,*LAMBDA DAS
     1H*,9X,*KAPPA*)
      PRINT130,(C(J).Q(J),QC(J).DLQ(J),KAPPA(J),J=1,N)
  130 FORMAT(1X,F10.4,3X,F10.4,5X,F10.4,4X,F10.4,8X,E14.7)
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM PITTSV2 CONTINUED   $$$$$$$$$$$$$$$

      PRINT128,QZ,SGQ,AA,SGA
  128 FORMAT(1H0,*MINIMIZING VALUES ARE QZ *,F10.3,2X,*PM*,F5.3,2X,*AND
     1A*,F7.3,2X,*PM*,F5.3)
      PRINT123,SIGMA,SMDL
  123 FORMAT(1H0.*STANDARD DEVIATION  *,F6.3,2X,*WITH SUM OF DELTAS  *,F
     16.3)
C
C
      GO TO 100
  700 CONTINUE
      END
```

```
      PROGRAM PITTS(INPUT,OUTPUT)
      COMMONC(50),RC(50),EC(50),K(50),H(50),AA(50),G(50),B(50),DELCALC(5
     20),DCALCA1(50),DCALCA2(50),DELEXPT(50),DC(50),DCC(50),DEV(50),ECC(
     350),DIV(50),
     2 A,N,ECO,R2
C.... DATA PROCESSED WITH PITTS EQUN  EVALUATION OF LAMBDA 0 AND ION
C.....  SIZE PARAMETER ..... REFERENCE TRANS. FAR. SOC.66,693,(1970)
C.....  VALENCE OF IONS TAKEN AS UNITY IE CASE OF 1,1 ELECTROLYTE
C.....  FUNDAMENTAL CONSTANTS SEE FUOSS $ ACCASCINA MONOGRAPH
      REAL K
  100 PRINT1
    1 FORMAT(1H1)
C.... N= NO. DATA PTS. , ECO=EST. LAMBDA 0 A1*A2=INITIAL ION SIZE VALUES
C.....  ETA = SOLV. VISCOSITY  D= SOLVENT DIELECT. CONST.
      PRINT40
   40 FORMAT(1H0.*UNASSOCIATED ELECTROLYTE............PITTS EQUATION*)
      READ4,N,D,ETA,T,ECO,A1.A2
    4 FORMAT(I5,F11.0,5F10.0)
      IF(N.EQ.0) GO TO 700
      PRINT20,ETA,D
   20 FORMAT(1H0,*SOLVENT VISCOSITY *,F9.7,2X,*DIELECT. CONST. *,F6.3)
      PRINT21,ECO.A1,A2
   21 FORMAT(1H0.*INITIAL LAMBDA 0  *,F7.3,2X,*LOWER LIM A  *,F5.2,2X,*
     1UPPER LIMIT OF INPUT A *,F5.2)
      READ5,(C(I).EC(I),I=1,N)
    5 FORMAT(2F10.0)
      PRINT24
   24 FORMAT(1H0,* 10000 C *,4X,*LAMBDA*)
      PRINT23,(C(I).EC(I),I=1,N)
   23 FORMAT(1X,F9.4,2X,F8.4)
      A1=A1*1.0E-8
      A2=A2*1.0E-8
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM PITTS CONTINUED   $$$$$$$$$$$$$$$$$

      AOLD=(A1+A2)/2.
C.... IDENTIFIERS K,H,AA,G,B AS USED IN ABOVE REFERENCE
C.... CALCULATE FACTORS INDEPENDENT OF ECO $ A
      DT=D*T
C.... R2= ROOT2
      R2=1.4142136
C.... CALCULATE KAPPA K
      DO7I=1,N
      C(I)=C(I)*1.0E-04
      RC(I)=SQRT(C(I))
      K(I)=(5.029422E9*RC(I))/SQRT(DT)
      H(I)=(5.569352E-4*K(I))/(DT*RC(I))
C...... CALCULATE PITTS A ....IE AA
      AA(I)=H(I)*(R2-1.)
      G(I)=(2.944732E-5*DT*H(I))/ETA
    7 B(I)=3.*H(I)*H(I)
C.... ITERATE FOR ECO $ A
C..... M IS ITERATION COUNTER
      M=0
      OSTDEV=0.0
   15 A=A1
C.... DCALCA1,GIVEN A1$ECO..CALC DIFFERENCE BETWEEN LAMBDA 0 $ LAMBDA
C.....  FOR EACH VALUE OF THE LATTER
      CALL DELTA
C.... DCALCA2,GIVEN A2$ECO..CALC DIFFERENCE BETWEEN LAMBDA 0 $ LAMBDA
C..... DELEXPT....DIFFERENCE BETWEEN ESTIMATED LAMBDA 0 AND EXPERIMENTAL
C....2 OF LAMBDA
      DO8I=1,N
    8 DCALCA1(I)=DELCALC(I)
      A=A2
```

```
$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM PITTS CONTINUED   $$$$$$$$$$$$$$$$$
      CALL DELTA
      DO9I=1,N
      DELEXPT(I)=ECO-EC(I)
    9 DCALCA2(I)=DELCALC(I)
C.....SOLVE FOR DELTA$F CALCULATE NEW VALUE FOR LAMBDA 0 $ A
      R=S=T=U=0.0
      DO 10I=1,N
      TOP=DCALCA2(I)-DELEXPT(I)
      BOT=DCALCA2(I)-DCALCA1(I)
      R=R+(TOP/BOT)
      T=T+(TOP/(BOT*BOT))
      S=S+(1.0/BOT)
   10 U=U+(1./(BOT*BOT))
      RN=N
      BOTT=RN*U-S*S
      DEL=(RN*T-R*S)/BOTT
      F=(R*U-S*T)/BOTT
      ANEW=A2+(A1-A2)*F
      ECO=ECO+DEL
C.... TEST FOR CONVERGENCE
      A=ANEW
      CALL DELTA
      SDEV=SDEL=0.0
      DO11I=1,N
      DC(I)=DELCALC(I)
      DCC(I)=ECO-EC(I)
      DEV(I)=DCC(I)-DC(I)
      DIV(I)=DEV(I)
      SDEV=SDEV+DEV(I)
      DEV(I)=ABS(DEV(I))
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM PITTS CONTINUED   $$$$$$$$$$$$$$$$$
   11 SDEL=SDEL+(DEV(I)*DEV(I))
      AMEAN=SDEV/RN
      STDEV=SQRT(SDEL/(RN-2.))
C....   FOR FIRST ITERATION MEAN OF INPUT VALUES OF A PARAMETERS
C....  USED FOR ESTIMATING DELTA A
      DELA  =ANEW-AOLD
      PRINT52,M,ECO,DEL
   52 FORMAT (1H0,*ITERATION *,I2,2X,*LAMBDA 0 *,F8.4,2X,*DELTA LAMBDA 0
     2*,2X,F8.4)
      PRINT26,ANEW,DELA,STDEV
   26 FORMAT(1X,*A*,E14.7,2X,*DELTA A*,E14.7,2X,*ST. DEV. OF FIT*,F10.5)
      PRINT 27
   27 FORMAT(1H0,*END OF RECORD FROM ITERATION END OF RECORD FROM ITERAT
     1ATION END OF RECORD...*)
      TEST=ABS(OSTDEV-STDEV)
      IF(TEST.LT.0.001) GO TO 12
      A1=ANEW+1.0E-9
      A2=ANEW-1.0E-9
      AOLD=ANEW
      IF(M.GT.10) GO TO 100
      M=M+1
      OSTDEV=STDEV
      GO TO 15
   12 PRINT 28
   28 FORMAT(1H0,4X,*C*,9X,*ROOT C*,4X,*LAMBDA*,4X,*CALC*,4X,*DIFF*)
      DO 25 I=1,N
      ECC(I)=ECO-DELCALC(I)
   25 PRINT48,C(I),RC(I),EC(I),ECC(I),DIV(I)
   48 FORMAT(1X,F10.8,2X,F10.8,2X,F7.3,2X,F7.3,2X,F6.4)
      ANEW=ANEW*1.0E8
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM PITTS CONTINUED   $$$$$$$$$$$$$$$$$

      DECO=DANEW=0.0
      PRINT30,ECO,DECO,ANEW,DANEW
   30 FORMAT(1H0,*LAMBDA 0 *,F7.3,*  STANDARD ERROR  *,F6.4,*+++++ION SI
     2ZE  *,F7.4,*  STANDARD ERROR  *,F6.4)
      PRINT31,STDEV,AMEAN
   31 FORMAT(1H0,*STANDARD DEVIATION  *,F6.4,*   SUM OF DELTAS  *,F6.4)
      MEANS=S/RN
      RNN=SQRT(RN)
      SES=(STDEV*RNN)/SQRT(BOTT)
      SEI=(1.0/RN)+(RN*MEANS*MEANS)/(BOTT)
      SEI=STDEV*(SQRT(SEI))
      PRINT900,SES,SEI
  900 FORMAT(1H0,*SES*,E14.7,2X,*SEI*,E14.7)
      PRINT32
   32 FORMAT(1H0,* $$$$$ HERE ENDETH THE (6400+1).TH LESSON FROM ORACLE P
     2ER SYBIL $$$$$*)
      GO TO 100
  700 CONTINUE
      END
```

```
      SUBROUTINE SUBQC
C
C    SUBROUTINE TO CALC. EQUIV. COND.
C
      COMMON C(30),Q(30),G2(30),CG(30),F2(30),VF(30),FM(30),BCFM(30),
     1QC(30),QL(30),FMI(30),BCFMI(30),QCI(30),QCP(30),TDT(30),DQ(30),
     2DLQ(30),SQDL(30),SG(30),PKN(30),DQQ(30),WT(30),R(30),BARM(30),
     3DEN(30),QP(30),DK(30),
     4D,AA,QZ,FKAP,ALPHA,BETA,E1,E2,J
C
C
      B=560.37/(D*AA)
      CR=CG(J)
      SQRC=SQRTF(CR)
      Y=FKAP*AA*SQRC
      SVF=0.000473*CR*(AA**3)
      VF(J)=1.0+SVF
      W=0.7071
      X=Y
      CALL SUBENE(X,ENE)
      TZ=ENE
      P1=1.0+X+0.5*X*X
      P2=1.0+W*X+0.25*X*X
      P3=1.0+W*X+0.1667*X*X
      P4=2.0*P2*(1.0+X)*(1.0+X)
      P5=2.0*P3*P4
      P6=0.4576/(P4*P3)
      X=(1.0+W)*Y
      CALL SUBENE(X,ENE)
      T1=ENE
      X=(2.0+W)*Y
      CALL SUBENE(X,ENE)
```

```
$$$$$$$$$$$$$$$$$$$$$$$$   SUBROUTINE SUBQC CONTINUED   $$$$$$$$$$$$$$$$$$

      T2=ENE
      X=X/2.7071
      TR1=(7.0*T2+P1*T1-4.0*P1*P2*TZ)/(4.0*P4)
      XSQ=X*X
      PM2=-9.0/4.0+9.0*W/2.0+(-7.0/12.0+7.0*W/3.0)*X+(1.0/24.0+7.0*W/12.
     10)*XSQ
      BF23=PM2/P5
      AL8=8.0*BF23+2.0/P4+P6
      TOP=1.0+(9.0*W/8.0+0.5)*X+(W+1.0/24.0)*XSQ
      BOT=P2*P3*(1.0+X)
      RATIO=TOP/BOT
      BM1=4.0*RATIO
      BM2= (4.0*(1.0+0.75*X))/(P3*(1.0+X))
      ALGV=(16.0+6.0*W+(7.0+10.0*W)*X+(3.0+4.0*W)*XSQ)/(48.0*P2*(1.0+X)*
     1(1.0+X))
      TF2=-8.0*ALGV-4.0*TR1+4.0/(3.0*B*P2*(1.0+X))
      TF1=-4.0*TR1-AL8+BM1/B+BM2/(B*B)-2.0/(B**3)
      FNEG=-ALPHA*SQRC+E1*CR*TF1-E2*CR*TF2/QZ
      FM(J)=(1.0+FNEG)/VF(J)
      BCFM(J)=BETA*SQRC*FM(J)/(1.0+Y)
      QC(J)=(G2(J))*(QZ*FM(J)-BCFM(J))
      RETURN
      END
```

```
      SUBROUTINE SUBENE(X,ENE)
C
C   SUBROUTINE FOR CALCN OF NEG.EXPONENTIAL INTEGRALS
C
C..... FUOSS$ACCASCINA,ELECTROLYTIC CONDUCTANCE,INTERSCIENCE,1959
C.....                  PAGES 150 TO 153
      CON = -LOGF(X)-0.57722
      FN= 0.0
      FAC = 1.0
      TOT =0.0
      QNP = -1.0
   30 FN=FN+1.0
      FAC = FAC*FN
      QNP = -1.0*X*QNP
      FNTH = QNP/(FN*FAC)
      TOT=TOT+FNTH
      TRM=ABSF((1.0E4)*FNTH)
      ABT=ABSF(TOT)
      IF (ABT-TRM) 30,30,40
   40 ENG=CON+TOT
C***********************************************************************
C..... WHEN USED WITH PROGRAM PITTSV2 THE CARD IMMEDIATELY  BELOW
      ENE=ENG*EXPF(X)
C..... MUST BE REMOVED FROM THIS ROUTINE
C***********************************************************************
      RETURN
      END
```

```
      SUBROUTINE SUBG2 (TA,PKV,M1,SQRDT,QQ)
C
C   SUBROUTINE TO COMPUTE GAMMA,GIVEN ASSOCN CONST
C..... FUOSS$ACCASCINA,ELECTROLYTIC CONDUCTANCE,INTERSCIENCE,1959 P.92-3
C
      COMMON C(30),Q(30),G2(30),CG(30),F2(30),VF(30),FM(30),BCFM(30),
     1QC(30),QL(30),FMI(30),BCFMI(30),QCI(30),QCP(30),TDT(30),DQ(30),
     2DLQ(30),SQDL(30),SG(30),PKN(30),DQQ(30),WT(30),R(30),BARM(30),
     3DEN(30),QP(30),DK(30),
     4D,AA,QZ,FKAP,ALPHA,BETA,E1,E2,J
C
      CK=C(J)*1.0E-4
      TAU=TA*SQRTF(CK)
      G1=1.0
      M1=0
  198 M1=M1+1
      IF(M1-10)203,203,199
  199 RETURN
  203 SRG=SQRTF(G1)
      TOP=(4.20132E6)/(SQRDT**3)
      BOT=(50.294)/(SQRDT)
      SRC=SQRT(CK)
C                                                                       ********
      F2(J)=(TOP*SRC*SRG)/(1.0+(BOT*5.0*SRC*SRG))
C
      F2(J)=EXP(-2.0*F2(J))
      VAR=PKV*CK*F2(J)
      IF(VAR-0.03) 204,205,205
  204 G2(J)=1.0-VAR+2.0*(VAR**2)-5.0*(VAR**3)
      GO TO 206
  205 G2(J)=(SQRTF(1.0+4.0*VAR)-1.0)/(2.0*VAR)
  206 TESTG=ABSF(G1-G2(J))
```

```
$$$$$$$$$$$$$$$$$$$$$$$   SUBROUTINE SUBG2 CONTINUED   $$$$$$$$$$$$$$$$$

      IF(TESTG-0.00005) 201,202,202
  202 G1=G2(J)
      GO TO 198
  201 CG(J)=CK*G2(J)
      RETURN
      END
================================================================================
```

THE ACTIVITY COEFFICIENT IS COMPUTED IN ROUTINE SUBG2 LISTED ABOVE WITH THE DEBYE-HUCKEL EQUATION WITH THE ION SIZE TERM , A , SET TO 5.0

IF COMPUTATION WITH THE DEBYE-HUCKEL LIMITING LAW IS DESIRED THE ASTERISKED CARD IS EXCHANGED FOR-

```
      F2(J)=(-2.0*TAU*SRG)
```

FOR COMPUTATION WITH THE DEBYE-HUCKEL EQUATION WITH A SET TO THE BJERRIUM CRITICAL DISTANCE,QQ, -

```
      F2(J)=(TOP*SRC*SRG)/(1.0+(BOT*QQ*SRC*SRG))
```

FOR ITERATED A I.E. A OF THE ACTIVITY COEFFICIENT EQUATED TO AND ITERATED WITH A OF THE FUOSS-HSIA EQUATION THE FOLLOWING CARD IS USED IN SUBG2

```
      F2(J)=(TOP*SRC*SRG)/(1.0+(BOT*AA*SRC*SRG))
--------------------------------------------------------------------------------
```

```
      SUBROUTINE LAMCAL
      COMMON Q(30),QC(30),QCI(30),QCP(30),QL(30),DQ(30),DQQ(30),DLQ(30),
     2SQDL(30),TDT(30),C(30),RC(30),KAPPA(30),TERM1(30),TERM2(30),TERM3(
     330),SG(30),
     4I,AA,QZ,R2,TERM4
C......   BASED ON EQUATION 16 OF PITTS,E. TABOR,B.E. AND DALY,J.,
C.....    TRANS. FAR. SOC.,65, 849 , (1969 )
      REAL KAPPA
      Y=KAPPA(I)*AA
      Y1=Y+1.0
      YR2=Y+R2
C.... CALCULATE VALUES OF S1 $ Y1/(1+Y)
      CALL S1T1(Y,S1,T1)
      F1=QZ-(TERM1(I)/Y1)
      F2=YR2*2.4142136*Y1
      F2=1.0-(TERM2(I)/F2)
      F3=QZ*S1-T1*TERM4
      F3=TERM3(I)*F3
      QC(I)=F1*F2-F3
      RETURN
      END
```

```
      SUBROUTINE DELTA
      COMMONC(50),RC(50),EC(50),K(50),H(50),AA(50),G(50),B(50),DELCALC(5
     20),DCALCA1(50),DCALCA2(50),DELEXPT(50),DC(50),DCC(50),DEV(50),ECC(
     350),DIV(50),
     2 A,N,ECO,R2
C..... SUBPROGRAM CALCULATES DIFFERENCE (LAMBDA 0 - LAMBDA(I) FOR EACH
C..... VALUE OF I GIVEN AN ESTIMATE OF ION SIZE AND LAMBDA 0
      REAL K
      DO1I=1,N
      Y=K(I)*A
      Y1=Y+1.0
      YR2=Y+R2
C..... CALCULATE VALUES OF S1 $ T1/(Y+1)
      CALL S1T1(Y,S1,T1)
C..... CALC LAMBDA 0 COEFF.....,F3
      F1=(AA(I)*RC(I))/(Y1*YR2)
      F2=B(I)*C(I)*S1
      F3=ECO*(F1+F2)
C..... CALC G COEFF....F4
      F4=(1./Y1)-(F1/Y1)-(H(I)*RC(I)*T1)
      F4=G(I)*RC(I)*F4
      DELCALC(I)=F3+F4
    1 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE S1 T1(Y,S1,T1Y1)
C.... SUBPROGRAM CALCULATES S1 $ T1/(1+Y)  SEE PITTS PROC. ROY. SOC.
C..... A217,43,1953.   FOR S1 ...EQN. 3.99  FOR T1  EQN. 3.58
      R2=1.4142137
      YB1=Y*1.7071067
      YB2=Y*2.7071067
      YR2=R2+Y
      YR22=YR2*YR2
      Y1= 1.0+Y
      Y1S=Y1*Y1
      EY=EXP(Y)
      Y2=Y*Y
      EYB1=EXP(YB1)
      EYB2=EXP(YB2)
      TOP=2.7279224+(Y*5.242641)+2*Y2
      TERM1=TOP/(8.0*Y1S*YR22)
      X=Y
      CALL SUBENE(X.ENE)
      EIY=ENE
      TERM2=EY/(4.0*Y1)
      TERM2=TERM2*EIY
      TERM3=(9.8994956*EYB2)/(16.0*Y1S*YR2)
```

```
$$$$$$$$$$$$$$$$$$$$$$$   SUBROUTINE S1 T1 CONTINUED   $$$$$$$$$$$$$$$$$

      X=YB2
      CALL SUBENE(X,ENE)
      EIBETA2=ENE
      TERM3=TERM3*EIBETA2
      TERM4=(R2*EYB1)/(16.0*Y1*YR2)
      X=YB1
      CALL SUBENE(X,ENE)
      EIBETA1=ENE
      TERM4 = TERM4*EIBETA1
      S1=TERM1-TERM2+TERM3+TERM4
C.... CALCULATE PITTS T1/(1+Y)
      TERM1=3.0/(4.0*YR2)
      AX=(4.2426411*EYB1)/YR2
      AX=AX*EIBETA1
      AY=2.0*EY*EIY
      AZ=3.0/8.0
      TERM2=AX-AY
      TERM2=AZ*TERM2
      T1=TERM1+TERM2
      T1Y1=T1/Y1
      RETURN
      END
```

REGRESSION PROGRAMS

PUTT AND DODO3

Programs fit a data set to polynomials of the form

$$y = P' + Q'x + R'x^2 + S'x^3$$

by the method of least squares.

PROGRAM PUTT

This program fits a data set to first, second or a third order polynomial - a polynomial per data set.

Coefficient P' is evaluated by the program.

INPUT

Card 1

FORMAT 1 - The order of the polynomial, J, and the number of data points, NO.

Cards 2 → NO + 1

FORMAT 2 - A value of x and y per card.

Card NO + 2

Next system or blank card before EOF.

OUTPUT

The coefficients of the polynomial, their standard errors, the deviation between input and calculated y for each data point and the standard error of the fit of the data to the polynomial.

SUBROUTINES - INVERSE and TERR.

PROGRAM DODO3

This program fits a data set to second, third and fourth order polynomials - a nominated order per data set.

Coefficient P' is fixed.

INPUT

Card 1

FORMAT 1 - The order of the polynomial, J, the number of data points, N, and the coefficient P', INTERC.

Cards 2 → N + 1

FORMAT 2 - As PUTT.

Card N + 2

Next system or blank card before EOF.

OUTPUT

As PROGRAM PUTT.

SUBROUTINES - INVERSE and YERR.

```
      PROGRAMPUTT(INPUT,OUTPUT)
      DIMENSION X(50),Y(50),A(10,10),B(10),C(10,10),CO(10),YY(50),Z(50)
C     J IS THE ORDER OF POLYNOMIAL
C     NO IS THE NUMBER OF VALUES OF X AND Y
   20 READ1,J,NO
    1 FORMAT(I1,I2)
      IF(NO.EQ.0) GO TO 90
      READ2,(X(I),Y(I),I=1,NO)
    2 FORMAT(2F10.0)
      PRINT100
  100 FORMAT(1H1,*PRINT OUT DATA BEFORE PROCESSING BEGINS*)
      PRINT101
  101 FORMAT(1H0,3X,*X(I)*,7X,*Y(I)*)
      PRINT102,(X(I),Y(I),I=1,NO)
  102 FORMAT(1X,2E14.7)
      PRINT103,J,NO
  103 FORMAT(1H0,*ORDER OF POLYNOMIAL = *,I1,4X,*NO. OF VALUES OF X AND
     *Y = *,I2)
C     CLEAR ARRAYS A AND B
      DO4L=1,10
      DO4K=1,10
      C(L,K)=0.0
    4 A(L,K)=0.0
      DO5NIX=1,10
      CO(NIX)=0.0
    5 B(NIX)=0.0
C     FILL LOCATION B(1)
      DO6I=1,NO
    6 B(1)=B(1)+Y(I)
C     FILL REMAINDER OF ARRAY B
      JK=J
      DO7M=1,JK
```

```
      DO7I=1,NO
    7 B(M+1)=B(M+1)+(X(I)**M)*Y(I)
      JS=J+1
C.... FILL ARRAY A BY ROWS
C.... FILL ROW    A(1,K)
   11 A(1,1)=NO
      JL=J
      DO12JO=1,JL
      DO12I=1,NO
   12 A(1,JO+1)=A(1,JO+1)+(X(I)**JO)
C.... FILL ROW    A (2,K)
      JK=J+1
      DO13JO=1,JK
      DO13I=1,NO
   13 A(2,JO)=A(2,JO)+(X(I)**JO)
      IF(J.EQ.1) GO TO 200
C.... FILL ROW    A(3,K)
      JK=J+2
      DO50JO=2,JK
      DO50I=1,NO
   50 A(3,JO-1)=A(3,JO-1)+(X(I)**JO)
      IF(J.EQ.2) GO TO 200
C.... FILL ROW    A(4,K)
      JK=J+3
      DO60JO=3,JK
      DO60I=1,NO
   60 A(4,JO-2)=A(4,JO-2)+(X(I)**JO)
  200 CALL INVERSE(A,B,C,CO,JS)
      CALLTERR(X,Y,CO,C,NO,J,JS,YY,S)
      GO TO 20
   90 STOP
      END
```

```
      PROGRAM DODO3(INPUT,OUTPUT)
      DIMENSION X(50),Y(50),A(10,10),B(10),C(10,10),CO(10),S(10),YI(50)
      REAL INTERC
   10 PRINT100
  100 FORMAT(1H1,*       INPUT  DATA  *)
      READ102
      PRINT102
  102 FORMAT(78H
     2                       )
      READ1,J,N,INTERC
    1 FORMAT(I1,I2,F10.0)
      IF(N.EQ.0) GO TO 11
      JS=J
      READ2,(X(I),YI(I),I=1,N)
    2 FORMAT(2F10.0)
      PRINT101
  101 FORMAT(1H0,*VALUES OF X $ Y RESP.*)
      PRINT103,(X(I),YI(I),I=1,N)
  103 FORMAT(2X,E14.7,2X,E14.7)
      DO3L=1,10
      DO3K=1,10
      C(L,K)=0.0
    3 A(L,K)=0.0
      DO4K=1,10
      CO(K)=0.0
      S(K)=0.0
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM DODO 3 CONTINUED   $$$$$$$$$$$$$$$$

    4 B(K)=0.0
      DO5I=1,N
    5 Y(I)=YI(I)-INTERC
      K=2*J
      DO6L=2,K
      DO6I=1.N
    6 S(L)=S(L)+(X(I)**L)
      LL=J
      DO7K=1,LL
      DO7I=1,N
    7 B(K)=B(K)+(X(I)**K)*Y(I)
      A(1,1)=S(2)
      A(1.2)=A(2,1)=S(3)
      A(2,2)=S(4)
      IF(J.EQ.2) GO TO 50
      A(3,1)=A(1.3)=S(4)
      A(3,2)=A(2.3)=S(5)
      A(3,3)=S(6)
      IF(J.EQ.3) GO TO 50
      A(4.1)=A(1,4)=S(5)
      A(4.2)=A(2,4)=S(6)
      A(4,3)=A(3.4)=S(7)
      A(4,4)=S(8)
   50 CALL INVERSE(A.B,C,CO,JS)
      CALLYERR(X.YI.CO,C,N,J,JS,INTERC)
      GO TO 10
   11 STOP
      END
```

```
      SUBROUTINE INVERSE(A,H,C,B,N)
      DIMENSION A(10,10),H(10),C(10,10),B(10)
C..... MATRIX ALGEBRA SUBROUTINES GENERAL INFORMATION MANUAL
C..... CONTROL DATA 6000 SERIES COMPUTER SYSTEMS
C..... CONTROL DATA CORPORATION,PALO ALTO ,CALIFORNIA ,U.S.A.
C..... PUBLICATION NO. 60154800.DECEMBER,1965
      CALLMATRIX(1,N,N,0,A,10,C,10)$CALLMATRIX(1,N,1,0,H,10,C(1,N+1),10)
      CALLMATRIX(10,N,N+1,2,C,10,Z)$CALLMATRIX(1,N,1,0,C(1,N+1),10,B,10)
      RETURN$END
```

```
      SUBROUTINETERR(X,Y,CO,C,N,J,JS,YY,STER)
      DIMENSION X(50),Y(50),CO(10),C(10,10),FRED(50),ERR(50),VARC(10),ST
     *ERCO(10),YY(50),SOB(10)
C.... ESTIMATE THE RESIDUALS ... ERR(I).
      IF(J-2)8,9,10
    8 DO4I=1,N
    4 YY(I)=CO(1)+CO(2)*X(I)
      GO TO 11
    9 DO5I=1,N
    5 YY(I)=CO(1)+CO(2)*X(I)+CO(3)*(X(I)**2)
      GO TO 11
   10 DO6I=1,N
    6 YY(I)=CO(1)+CO(2)*X(I)+CO(3)*(X(I)**2)+CO(4)*(X(I)**3)
   11 PRINT113
  113 FORMAT(1H0,4X,*x(I)*,14X,*Y(I)*,14X,*YY(I)*,14X,*ERR(I)*)
      DO21I=1,N
      ERR(I)=YY(I)-Y(I)
   21 PRINT114,X(I),Y(I),YY(I),ERR(I)
  114 FORMAT(1X,4(E14.7,5X))
      SR=0.0
      DO22I=1,N
      FRED(I)=ABS(ERR(I))**2.
   22 SR=SR+FRED(I)
      R=N-JS
C.... CALCULATE THE VARIANCE .. VIA ESTIMATED RESIDUALS .. ERR(I) .
```

```
$$$$$$$$$$$$$$$$$$$$$$$   SUBROUTINE TERR CONTINUED   $$$$$$$$$$$$$$$$$$
      VAR=SR/R
      PRINT115,VAR
  115 FORMAT(1H0,*ESTIMATED VARIANCE VIA RESIDUALS = *,E14.7)
      STER=(VAR)**0.5
      PRINT116,STER
  116 FORMAT(1H0,*STANDARD ERROR OF FIT ..(EST. RESIDUALS)= *,E14.7)
C.... CALCULATE THE STANDARD ERRORS OF COEFFICIENTS
      PRINT501,R
  501 FORMAT(1H0,*NUMBER OF DEGREES OF FREEDOM  FOR T TEST = *,F3.0)
      PRINT118
  118 FORMAT(1H0,5X,*COEFFICIENT*,7X,*ST. ERR. OF COEFF.*,7X,*T TEST*)
      DO23L=1,JS
      VARC(L)=VAR*C(L,L)
      STERCO(L)=(VARC(L))**0.5
      SOB(L)=CO(L)/STERCO(L)
   23 PRINT117,L,CO(L),STERCO(L),SOB(L)
  117 FORMAT(1H0,3X,I1,2X,E14.7,4X,E14.7,7X,E14.7)
      RETURN$END
```

```
      SUBROUTINEYERR(X,Y,CO,C,N,J,JS,TER)
C.....  SUBROUTINE ERR FOR FIXED INTERCEPT LEAST SQUARES
      DIMENSION X(50),Y(50),CO(10),C(10,10),FRED(50),ERR(50),VARC(10),ST
     *ERCO(10),YY(50),SOB(10)
C.... ESTIMATE THE RESIDUALS ... ERR(I).
      IF(J-3)8,9,10
    8 DO4I=1,N
    4 YY(I)=TER+CO(1)*X(I)+CO(2)*(X(I)**2)
      GO TO 11
    9 DO5I=1,N
    5 YY(I)=TER+CO(1)*X(I)+CO(2)*(X(I)**2)+CO(3)*(X(I)**3)
      GO TO 11
   10 DO6I=1,N
    6 YY(I)=TER+CO(1)*X(I)+CO(2)*(X(I)**2)+CO(3)*(X(I)**3)+CO(4)*(X(I)**
     *4)
   11 PRINT113
  113 FORMAT(1H0,4X,*X(I)*,14X,*Y(I)*,14X,*YY(I)*,14X,*ERR(I)*)
      DO21I=1,N
      ERR(I)=YY(I)-Y(I)
   21 PRINT114,X(I),Y(I),YY(I),ERR(I)
  114 FORMAT(1X,4(E14.7,5X))
      SR=0.0
      DO22I=1,N
      FRED(I)=ABS(ERR(I))**2
   22 SR=SR+FRED(I)
```

```
$$$$$$$$$$$$$$$$$$$$$$$   SUBROUTINE YERR CONTINUED   $$$$$$$$$$$$$$$$$$
      JR=JS
      R=N-JR
C.... CALCULATE THE VARIANCE .. VIA ESTIMATED RESIDUALS .. ERR(I) .
      VAR=SR/R
      PRINT115,VAR
  115 FORMAT(1H0,*ESTIMATED VARIANCE VIA RESIDUALS = *,E14.7)
      STER=SQRT(VAR)
      PRINT116,STER
  116 FORMAT(1H0.*STANDARD ERROR OF FIT ..(EST. RESIDUALS)= *,E14.7)
      PRINT500,TER
  500 FORMAT(1H0,* INTERCEPT = *,F10.6)
C.... CALCULATE THE STANDARD ERRORS OF COEFFICIENTS
      PRINT501.R
  501 FORMAT(1H0.*NUMBER OF DEGREES OF FREEDOM  FOR T TEST = *,F3.0)
      PRINT118
  118 FORMAT(1H0,5X,*COEFFICIENT*,7X.*ST. ERR. OF COEFF.*,7X,*T TEST*)
      DO23L=1,JS
      VARC(L)=VAR*C(L,L)
      STERCO(L)=SQRT(VARC(L))
      SOB(L)=CO(L)/STERCO(L)
   23 PRINT117.L,CO(L),STERCO(L),SOB(L)
  117 FORMAT(1H0.3X.I1,2X,E14.7,4X,E14.7,7X,E14.7)
      RETURN$END
0000000000000000000000   END OF RECORD
```

PROGRAM ROOTEQ

This program, written by D.E. Mulcahy*, fits a set of density-concentration data to the Root equation** by the method of least squares.

INPUT DATA

Card 1

FORMAT 20

N = Number of data points.

M = An option parameter which is equated to zero or unity.

If M = 1 in conjunction with the upper and lower limits together with the increment defined on card N + 3, then values of d are computed at nominated values of C with the evaluated coefficients of the Root equation.

A = The density of the solvent.

Card 2

FORMAT 102 - System identification.

Cards 3 → N + 2

U = Concentration.

Y = The density of the solution.

Card N + 3

If M = O, the next system or a blank card before EOF.

If M = 1

FORMAT 23

HI = Initial value of the concentration range in which computed density-concentration data are desired.

ST = Increment between points in this range.

HA = The upper limit of the range.

Card N + 4

As N + 3 with M = O.

OUTPUT

The coefficients of the Root equation, their standard errors,

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* Reference (47) Chapter 5; ** Equation 5.2 of Chapter 5.

the standard error of the fit of the density-concentration data to the Root equation and the deviation between experimental and computed values of the density for each data point. If the option M = 1 is exercised, then the computed value of the density at each nominated value of concentration is also printed out.

```
      PROGRAM ROOTEQ(INPUT,OUTPUT)
C.... PROGRAM FITS DENSITY $ CONCENTRATION DATA TO EQUN. OF W.C.ROOT
C.... REF. HARNED$OWEN P CHEM OF ELECTROLYTE SOLNS. 3RD. EDN. PAGE 358
C.... N=NO. DATA POINTS,M OPTION PARAMETER M=1 FOR ROUNDED VALUES OF
C.... CONCENTRATION AND DENSITY,A=DENSITY OF SOLVENT
      DIMENSION U(30),Y(30),X(30),YC(30),DEL(30),Z(30)
   10 READ 20,N,M,A
   20 FORMAT(2I2,F10.0)
      IF(N)11,11,12
   12 PRINT 21
   21 FORMAT(1H1)
      READ102
  102 FORMAT (78H
     1                                              )
      PRINT102
      PRINT100,A
  100 FORMAT(1H0,*SOLVENT DENSITY = *,F8.6)
      E=F=G=S=T=V=0
   24 READ 22,(U(I),Y(I),I=1,N)
   22 FORMAT(2F10.0)
      DO4I=1,N
      X(I)=SQRT(U(I))
      Z(I)=Y(I)-A
      E=E+X(I)**4
      F=F+X(I)**5
```

```
$$$$$$$$$$$$$$$$$$$$$$$$$$   PROGRAM ROOTEQ CONTINUED   $$$$$$$$$$$$$$$$
      G=G+X(I)**6
      S=S+Z(I)*X(I)**2
      T=T+Z(I)*X(I)**3
      V=V+Z(I)**2
    4 CONTINUE
      D=(S*F-T*E)/(F**2-E*G)
      B=(S-D*F)/E
      XXN=N
      SD=(V-B*S-D*T)*E/((XXN-2.)*(E*G-F**2))
      SED=SQRT(SD)
      SB=(V-B*S-D*T)*G/((XXN-2.)*(E*G-F**2))
      SEB=SQRT(SB)
      PRINT 13
   13 FORMAT(30H           C01           C02        )
      PRINT 1,B,D
    1 FORMAT(2E15.6)
      PRINT 18
   18 FORMAT(//30H           SE1           SE2        )
      PRINT 17,SEB,SED
   17 FORMAT(2E15.4)
      PRINT 15
   15 FORMAT(//54H          C          RC          DCAL          DEXP          DIFF
     1)
      SDEL=0.0
      N=XXN
```

$$$$$$$$$$$$$$$$$$$$$$$$$$ PROGRAM ROOTEQ CONTINUED $$$$$$$$$$$$$$$$

```
      DO5I=1,N
      YC(I)=A+B*U(I)+D*(X(I)**3)
      DEL(I)=YC(I)-Y(I)
      PRINT 3,U(I),X(I),YC(I),Y(I),DEL(I)
    3 FORMAT(2F11.7,2F10.6,E10.1)
      SDEL=SDEL+DEL(I)*DEL(I)
    5 CONTINUE
      SDEV=SQRT(SDEL/(XXN-3.))
      PRINT103,SDEV
  103 FORMAT(1H0,*STANDART DEV OF DATE = *, F10.7)
      IF(M)10,10,6
    6 READ 23,HI,ST,HA
   23 FORMAT(F9.7,F10.7,F10.7)
      PRINT 16
   16 FORMAT(//40H        C       RC       DCAL           )
    8 HO=SQRT(HI)
      YO=A+B*HO**2+D*HO**3
      PRINT 7,HI,HO,YO
    7 FORMAT(2F11.7,F10.6)
      HI=HI+ST
      IF(HA-HI)9,8,8
    9 GOTO10
   11 CONTINUE
      END
```