ELECTROCHEMICAL STUDIES OF SOME
UNSYMMETRICAL ELECTROLYTES IN
NONAQUEOUS SOLVENT

A Thesis
submitted to the University of Surrey
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in the Faculty of Chemical and Biological Sciences

By

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TO MY PARENTS
Summary

The work reported in this thesis has been concerned with the study of the electrochemical behaviour of unsymmetrical electrolytes in propylene carbonate.

Zinc halides were found to be soluble in this solvent, while zinc oxide, sulphate and carbonate and potassium carbonate were sparingly soluble.

The electrical conductances of zinc halides, zinc perchlorate and ferric chloride in PC have been measured at 25°C.

The results indicate that all of these solutes behave as "weak" electrolytes. Zinc perchlorate was found to be anomalous in showing unusually high molar conductance in this solvent, and in exhibiting a pronounced maximum conductance at low concentration.

The Murphy-Cohen equation was modified to allow for "weak" electrolytes and for different modes of ionisation of unsymmetrical electrolytes. The conductance data were analysed by a minimisation technique using the modified Murphy-Cohen equation and the limiting law. It was found that for zinc salts in propylene carbonate solution at 25°C, the mode of ionisation is specific.
for the anion involved.

The effect of the variation of the distance parameter $a$ on the values of $\Lambda_0$ and $K_A$ was fully investigated.

Single ion conductances, calculated from conductance and transport number data, suggested that the mobilities of the cations decreases along the series: $\text{ZnI}^+ > \text{ZnBr}^+ > \text{Zn}^{2+}$.

Electrodeposition of zinc from a solution of zinc chloride in propylene carbonate proceeded with very high efficiency.

Polarographic reduction of cations was possible, with a range of half wave potentials similar to those for aqueous solutions.
Acknowledgements

The work described in this thesis was carried out under the supervision of Dr. W.H. Lee, Reader in Physical Chemistry, University of Surrey. I wish to express my deepest gratitude to Dr. W.H. Lee for his advice, guidance, and encouragement throughout the work.

I would like to thank Mrs. P. Lowe for her much appreciated work on the typewriter and to Pat and Mary for their help.

Finally, the leave of absence from University of Ain Shams, Egypt, is greatly appreciated.
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CHAPTER I
PROPYLENE CARBONATE AS ELECTROCHEMICAL SOLVENT
Although the solvent powers of nonaqueous solvents have been recognized for centuries, investigations of electrochemical properties of nonaqueous solutions were begun only in the latter part of the nineteenth century. Nonaqueous electrolyte solutions, particularly in organic solvents, have received more attention in recent years. Studies have been made on conductances, transference numbers, diffusion coefficients, electrode potentials and on the nature of the ionic species present in nonaqueous solutions. Less quantitative investigations have been made on the electrodeposition of certain metals not now obtainable by electrolysis of aqueous solutions.

The purpose of this research was to investigate the behaviour of some unsymmetrical electrolytes in a particular nonaqueous solvent.

4-Methyl-1,3-dioxolan-2-one [108-32-7] or 1,2 propanediol carbonate, a cyclic ester (which will be referred to by its common name, propylene carbonate, abbreviated to PC), was chosen because it possesses many of the properties desirable in an ionizing medium used to conduct electrochemical reactions. It is an odourless, colourless, mobile liquid, not readily hydrolysable nor corrosive. It is characterized by a high dielectric constant, medium donor properties, low vapour pressure, high chemical stability, relatively
low toxicity, and nonreactivity with anodically liberated halogens\(^{(10)}\).

Some physical properties of the pure material are summarized in Table 1.

The following is a brief account of previous studies which have been carried out in this solvent.

The dielectric constant is high, not very different from that of water. The solution chemistry of PC, however, differs considerably from that of water; in particular, the viscosity is significantly higher, and some, although not all, of the differences in behaviour can be explained by this property. Because it is a racemic mixture\(^{(18)}\) of forms I and II, the liquidus range is broad (-49\(^{\circ}\) to 241\(^{\circ}\)C) compared with that of ethylene carbonate\(^{(12)}\) (III) (36\(^{\circ}\) to 238\(^{\circ}\)C).

\[
\begin{align*}
\text{I} & \quad \text{II} & \quad \text{III} \\
\begin{array}{c}
\text{CH}_3 \\
\text{H}
\end{array} & \begin{array}{c}
\text{H} \\
\text{CH}_3
\end{array} & \begin{array}{c}
\text{H}
\end{array}
\end{align*}
\]
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>102.9</td>
<td></td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>-49.2</td>
<td>(11)</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>241.7</td>
<td>(11)</td>
</tr>
<tr>
<td>Density, gm·ml⁻¹</td>
<td>1.198</td>
<td>(10)</td>
</tr>
<tr>
<td>Refractive index (nD)</td>
<td>1.4193</td>
<td>(13)</td>
</tr>
<tr>
<td>Dielectric constant (D)</td>
<td>64.4b</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td>65.1c</td>
<td>(14)</td>
</tr>
<tr>
<td></td>
<td>64.92d</td>
<td>(15)</td>
</tr>
<tr>
<td>Dipole moment (μ), debye</td>
<td>4.94e</td>
<td>(12)</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>(9)</td>
</tr>
<tr>
<td>Donor number DN₅SbCl₅</td>
<td>15.1</td>
<td>(9)</td>
</tr>
<tr>
<td>Viscosity (η), poise</td>
<td>0.0253</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td>0.0248</td>
<td>(16/17)</td>
</tr>
<tr>
<td>Kirkwood correlation factor (g)</td>
<td>1.18</td>
<td>(13)</td>
</tr>
<tr>
<td></td>
<td>1.04</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td>1.01</td>
<td>(15)</td>
</tr>
<tr>
<td>Trouton constant, Cal. mole⁻¹ deg⁻¹</td>
<td>23.19</td>
<td>(9)</td>
</tr>
<tr>
<td>Specific conductivity (S), ohm⁻¹ cm⁻¹</td>
<td>1•2x10⁻⁸</td>
<td>(17)</td>
</tr>
<tr>
<td></td>
<td>2x10⁻⁷</td>
<td>(10)</td>
</tr>
</tbody>
</table>

(a) at 25°C  (b) at 100KHz  (c) at 200KHz  (d) at 1MHz  
(e) extrapolation of data in benzene solution, by the method of reference (24).
The solvent can be supercooled by about 25°C resulting in a glassy phase; solutes such as lithium aluminium chloride depress the freezing point to -80°C. Although the pure solvent boils at 241°C, thermal decomposition can occur at 150°C. Acid-base hydrolysis is the principal chemical decomposition reaction. The solvent can be electrochemically decomposed on the graphite cathode to propylene gas and carbonate ion, with almost 100% coulombic efficiency.

While the acetonitrile molecule is small and rod-like in shape, the PC molecule is large and bulky; this may account for a number of differences observed between these two solvents of similar donor number.

PC is readily available commercially in reasonable purity. General methods for the preparation of cyclic carbonates were reviewed by Idris Jones. The synthesis of PC from propylene oxide and carbon dioxide, with an alkali metal or tetraalkylammonium halide, together with an oxide or carbonate of a group II or III metal as catalyst, has been reported in the open and patent literature.

PC is principally used in applied electrochemistry as the primary electrolyte solvent for ambient temperature batteries employing an alkali metal or an alkaline earth metal as the negative electrode. It has, so far, been
of major interest as a solvent for high capacity nonaqueous primary\(^{(27)}\) and secondary\(^{(28)}\) batteries, capable of meeting the needs of today's military, aerospace, and commercial enterprises.\(^{(29)}\)

Previous to these studies, nonaqueous primary batteries could deliver about 100 watt-hour/pound during discharge, which is only about 50.\% of the energy theoretically available from the system SiO/Ag in PC, involving the Ag (II) state. Moreover, the theoretical energy of the Li/CuF\(_2\) couple is 746 w-hr/lb., and of Li/CoF\(_3\) 970 w-hr/lb.; this would triple the useful flight time of a space vehicle using a primary battery power system, or allow an equivalent increase in weight of the instrument load.\(^{(30)}\)

PC has also found some application as a dielectric for capacitors.\(^{(31)}\)

Chend et al.\(^{(32)}\) suggest the use of this solvent to acquire specificity for the electrochemical sensing of nitrogen in the presence of sulphur dioxide.

Applications as a chemical solvent and a reaction medium have been described.\(^{(11)}\) It has been used in separating hydrocarbons according to their degree of aromaticity, and commercially as a solvent for nylon and polyacrylonitrile, and as a plasticizer. It may also
be of value as an intermediate in the preparation of agricultural chemicals, resins, fungicides, and pharmaceuticals. It has been recommended as a good solvent for EPR studies, especially suitable for "in situ" generation of organic radicals,\(^{(33)}\) as well as in the study of quaternisation kinetics.\(^{(34)}\)

Harris\(^{(10)}\) was one of the pioneer workers on the electrochemistry of PC and other cyclic esters. He measured several properties of the pure liquid and of different ionic solutions. A number of common inorganic salts were found to be readily soluble, and some of the highly electropositive metals could be electrodeposited from solutions of their salts. This work was quickly followed by a series of exploratory projects on the development of lithium batteries with PC as solvent.\(^{(35)}\) This interest has caused an increase in the number of investigations of electrochemical phenomena in PC solutions. However, before PC can be used as a solvent, it must be as pure as possible, so that the observed properties will not be traced to the effects of impurities.

**Purification of PC**

Considerable attention has been given to the purification of PC and a large number of publications report the precise conditions for collecting the purified material, and for its analysis.\(^{(10, 20b, 33 & 36)}\)
Galvanostatic and potential sweep experiments were performed with PC solutions, to investigate the role of water in PC. The presence of small traces of water, in the range of PPM, has a remarkable effect on the performance of this solvent. For example, 1PPM of water in 1ml of an otherwise pure solvent, would produce an oxide film 1000 Å thick on 1 cm² of smooth, clean lithium surface; this could change substantially the electrochemical properties of the surface. Similarly, measurements of the solubility of CuF₂ showed that the solubility was dependent on the concentration of water in the solvent, even at a concentration below 100 PPM. The presence of other "natural" impurities in PC, e.g. propylene oxide, propylene glycol and propionaldehyde, has been reported to increase the solubility of CuCl₂. On the other hand, the effect of water, as an impurity, on the solubility of halide salts of copper, silver, mercury and lead has been analysed. The results indicate that an increase in water content of the solvent increases the solubility of salts that are soluble in water; traces of water have no effect on the solubility of salts that are inherently sparingly soluble in aqueous media.

Trace amounts of water in PC have been determined by differential infrared spectrophotometry, employing the 1.9μ near-infrared absorption band. This
method appears to give reasonable results above 20 PPM; between 10 and 20 PPM the results are to be considered as semiquantitative only. Alternative methods for measuring traces of water in this solvent are: gas-liquid chromatography (36a) Karl-Fischer titration, and nuclear magnetic resonance. (42) The electrochemical behaviour of the intensively dried solvent has been investigated. (43) The elimination of the last traces of water, using sodium-potassium alloys, yields a solvent free from active hydrogen but contaminated with traces of alkali metal glycolate, potassium carbonate and an unidentified coloured product of PC decomposition. (36b) Fluoride-containing solutions in PC cannot be dried by storing over zeolites; NMR-19F measurements demonstrated that zeolites in this solvent are attacked by fluoride ions, removing about 1% of the fluoride in 1.8 hours. (44)

**Electrochemical Properties**

Kempa and Lee (12) have made extensive dielectric measurements on various cyclic carbonates among them PC. They determined the dipole moment and suggested the possibility of intermolecular association in the pure compound, and more particularly in ethylene carbonate. Simeral and Amey (13) measured the equilibrium dielectric permittivity, density and refractive index over a wide range of temperature. The Kirkwood correlation factor is essentially unity over this temperature range, suggesting that PC behaves as a normal polar liquid with strong dipole-dipole interactions, but with little or
no specific association present. Their infrared and NMR measurements provide further evidence which is consistent with the dielectric results. Payne and Theodorou\textsuperscript{(15)} studied the dielectric properties of PC by a pulse reflection technique and concluded that the equilibrium dielectric constants for the pure PC and for mixtures with other liquid dielectrics are consistent with the absence of specific intermolecular forces. Temperature coefficients of density, viscosity and dielectric constant have been determined.\textsuperscript{(45)} Choi and Joncich\textsuperscript{(46)} measured the vapour pressure of PC at several temperatures and obtained the molar enthalpy of vaporization. While Vasilev and Korkhov\textsuperscript{(47)} calculated the free energy parameters, $\Delta G$, $\Delta H$, $\Delta S$, over the temperature range $50^\circ\text{C}-310^\circ\text{K}$.

The NMR analysis of PC has shown that its molecular skeleton is planar in the liquid state.\textsuperscript{(48)} A semiempirical molecular orbital calculation was performed,\textsuperscript{(49)} to obtain the electron density distribution of the PC molecule. This calculation employs the CNDO/2 method\textsuperscript{(50)} and assumes that the ring system is planar, with the double bond in the plane. The results show a considerable electron density on all PC oxygen atoms and a diffuse positive end of the molecular dipole, Figure 1.
Electron density distribution of the PC molecule.

In a recent infrared and Raman spectroscopic study,\textsuperscript{(51)} the authors conclude that the cyclic carbonates possess slightly distorted planar, reasonably rigid, ring structures. The mass spectrum of PC has been given\textsuperscript{(52)} and the principal fragmentation pathway described.

**Solvent Properties**

There have been few previous quantitative solubility studies of electrolytes in PC.

Harris\textsuperscript{(10)} found that the relatively low-melting covalent compounds are quite soluble. The solubility increased, for a series K < Na < Li with a common anion, due to the relative gain in solvation energy compared with lattice energy as the cation size decreases, and
the same is true of Ba < Ca. For a given alkali metal cation, solubility increased in the order Cl < Br < I, except that lithium bromide is more soluble than lithium iodide. He concluded, from solubility studies, that PC will solvate cations to a much larger degree than anions, and that simple multivalent ions do not seem to exist in PC solutions, with the possible exception of calcium ion from Ca(BF$_4$)$_2$. However, as the present study has shown, not all of his solubility data are reliable, probably because of traces of water in the solvent or solutes used.

The tetraalkylammonium chlorides are soluble in PC, except for tetramethylammonium chloride.\(^{(53)}\)

The equilibria of silver chloride in PC solutions, and in the presence of excess chloride ions, have been studied potentiometrically.\(^{(54)}\) The equilibrium constants were fitted by a nonlinear least-squares pit-mapping technique.\(^{(55)}\) Only mononuclear complexes, AgCl$_n$, were found. The main complex present, in silver halide solutions, is AgX$_2^-$, where X is chloride or bromide.\(^{(56)}\) While in the case of iodide the stable I$_3^-$ complexes were observed.\(^{(57)}\)

The coordination of transition metal ions in PC is discussed in Gutmann's monograph\(^{(9a)}\). It appears that hexacoordinated species are formed, with competitive anion inclusion in the coordination sphere; anion coordination is four-fold for cobalt (II), nickel (II),
manganese (II) and vanadium (II) with halide, cyanide and thiocyanate anions, with the exception of manganese (II) chloride; and six-fold for titanium (III), vanadium (III), chromium (III) and iron (III).

The solubilities of the thallium (I) halides in PC were measured by potentiometric titration, and their solubility products were calculated. Single-ion medium effects were calculated from the solubility and EMF data, with reference to water.\(^{(58)}\)

Lee\(^{(59)}\) measured the surface tension of PC and found that this solvent obeyed the Hildebrand-Scott equation\(^{(60)}\) for the relation between the solubility parameters and surface tensions of liquids, in the case of nonelectrolyte solutions.

The heats of solution of the alkali metal trifluoroacetates, tetraphenylborates, iodides, and perchlorates,\(^{(45)}\) and of the tetraalkylammonium halides,\(^{(61)}\) in PC have been measured. The standard heats of transfer from water to PC and heats of transfer of ions relative to that of sodium have been determined. Krishnan and Friedman\(^{(62)}\) have made an extensive study of enthalpies of solution and transfer of non-electrolytes (normal alcohols and hydrocarbons) and of tetraalkylammonium ions to PC from water and from dimethylsulphoxide. These studies have led to a simple picture of additive contribution from the CH\(_2\) groups to the free energy of solvation of
the hydrocarbon chains in PC.

Salomon\(^{(63)}\) studied the thermodynamic properties of lithium halides and of sodium and potassium iodides in PC by EMF measurements. He calculated the free energies and enthalpies of solvation for these alkali halides, and concluded that ion pairing effects were negligible in the solutions. The solvation of anions increased from chloride to iodide.

**Viscosity and Conductance Studies**

Viscosities of various electrolyte solutions in PC have been given in the literature in connection with attempts to produce high-energy nonaqueous batteries.\(^{(64)}\)

The maximum conductances of a variety of salts in PC have been reviewed by Jasinski\(^{(19)}\) but the data is generally fragmentary. Almost all solute-PC combinations have maximum specific conductances below \(10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}\).

The specific conductance, at higher concentrations, does not increase uniformly with increasing concentration; ion association becomes important and ion pairs as well as larger charged ion multiplets are formed. In effect, the solvent becomes unable to shield satisfactorily one ion from another and as a result the specific conductance - concentration plots pass through a maximum, and the specific conductance then decreases with increasing salt concentration until saturation is reached,
Figure 2. This effect cannot be explained entirely in terms of increasing viscosity of the solutions.

An extensive study has been made of viscosities and conductances for moderately concentrated solutions, 0.05 to 0.41 molal, of tetraalkylammonium bromide and iodide in PC over a wide range of temperature, (65) -50°C to 125°C. Molar conductances, viscosities and densities were well described by empirical polynomials. The log \( A \) vs. \( m^2 \) plot is linear over this concentration range, except at the temperatures \( \leq 0°C \). The Walden products \( (A_0\eta) \) decrease 10-15% with increasing temperature over the 175°C range and at any temperature, \( (A\eta) \) decreases 20-25% with increasing concentration over the 0.36 range. It is concluded that there is no significant ion-solvent interaction in these systems.

Reports on conductances of electrolytes at low concentrations, in PC, however, are few and indicate lack of correlation in some instances. Fuoss et al. (66) studied the conductance of tetra-butylammonium tetraphenylboride in PC and concluded that ion association was negligible in this case. Wu and Friedman (45) in their preliminary studies indicated that the perchlorates in general were strong electrolytes, whereas the corresponding trifluoroacetates gave evidence of considerable ion association. They
FIGURE 2

Specific conductances in PC at 25°C

- △ KCNS
- ○ LiClO₄
- □ NH₄CNS
- × LiBr

$S$ Specific conductance ohm$^{-1}$ cm$^{-1}$

C molar concentration
suggested that the predominant associated form of lithium trifluoroacetate was an ion pair dimer, \( \text{Li}_2(\text{CF}_3\text{CO}_2)_2 \). In the case of lithium perchlorate solutions, the conductance data indicated negligible ion association, whereas heats of solution showed a strong concentration dependence, indicating the existence of large ionic interactions.

Mukherjee et al.\(^{(17 \& 67)}\) have made precise viscosity and conductance measurements on solutions of certain lithium, potassium and tetraalkylammonium halides and perchlorates in PC. They have discussed the significance of the viscosity coefficient in interpreting their conductance data. Lithium chloride and bromide were found to be pairwise associated, having association constants of 557 and 19, respectively, whereas no association could be detected in the other systems. Comparison of the limiting conductances of the perchlorates, suggests that the mobility of Li\(^+\) is lower than that of n-Bu\(_4^+\)N\(^+\) and Et\(_4^+\)N\(^+\); indicating that the lithium ions in PC are substantially solvated, as in water. It is of further interest to note that, in the case of the lithium salts, unlike the tetraalkylammonium salts, the agreement between the sum of the crystallographic radii and the a-parameters (distances of closest approach of ions, \( p63 \)) is generally good. So that in the event of ion-ion contacts, the bare ions rather than their solvated co-spheres are presumably involved. Courtot-Coupez and L'Her\(^{(68)}\) measured the conductances of alkali metal perchlorates in PC. Their results are
in general consistent with those of Mukherjee et al.

High precision viscosity and conductance measurements for several additional alkali metal and tetraalkylammonium halides, perchlorates, trifluoroacetates and nitrates in PC have been made by Jansen and Yeager. Lithium trifluoroacetate was confirmed to be extensively associated, with the formation of a variety of ion aggregate species. Although it was not possible to evaluate all equilibrium constants for these processes, the value of 1900 for the ion pair formation constant was estimated, with uncertainty of about 30%. The other alkali metal trifluoroacetates also showed a significant degree of ion pairing in contrast to the corresponding perchlorates, which were found to be unassociated. The degree of association for the trifluoroacetates decreases with increasing size of the alkali metal ion. Their results thus confirm the previous conclusions of Wu and Friedman.

Further evidence for the existence of ion pairs in these systems was provided by studies of $^{23}\text{Na}$ chemical shifts in PC. These shifts were essentially independent of salt concentration for sodium perchlorate and tetraphenylborate, but were strongly concentration dependent for sodium iodide and thiocyanate. An approximate value of 36.6 ± 10.6 M$^{-1}$
was computed for the ion pair formation constant of sodium thiocyanate.

Table 2 gives some conductance parameters for the electrolytes reported in PC.

Moreover, single ion conductances, $\lambda^0$, were derived, using the reference electrolyte tetraisoamylammonium tetraisoamylboride for which it is assumed that the cation and the anion have equal mobilities, i.e. $\lambda^0+ = \lambda^0-$. Large cations show a normal size-mobility dependence, but alkali metal ions produce a reverse trend, in terms of bare-ion radii. Anions have much higher mobilities than cations, relative to their crystallographic size, indicating relatively poor solvation of anions by PC.

Table 3 gives limiting conductances for single ions in PC collected from various sources. Agreement is not very good in some instances.

Very little work has been done on the solubilities and conductances of electrolytes other than uni-univalent in PC; indeed, this is true of organic solvents in general. The only unsymmetrical electrolyte which has been studied in PC is aluminium chloride; this is perhaps unfortunate in view of the known reactivity of this substance with organic compounds.\(^{25}\) Keller et al.\(^ {42}\) measured the specific conductances
TABLE 2

Conductance Parameters For Some 1-1 Electrolytes in PC at 25°C

<table>
<thead>
<tr>
<th>SALT</th>
<th>$\Lambda^0$ ohm$^{-1}$ cm$^2$ mole$^{-1}$</th>
<th>$K_A$ mole$^{-1}$</th>
<th>$a$, Å</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>27.50</td>
<td>557</td>
<td>2.52</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td></td>
<td></td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>26.1</td>
<td>437</td>
<td></td>
<td>71</td>
</tr>
<tr>
<td>LiBr</td>
<td>26.2</td>
<td></td>
<td></td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>27.35</td>
<td>19</td>
<td>2.66</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>25.3</td>
<td>5.6</td>
<td></td>
<td>71</td>
</tr>
<tr>
<td>LiClO$_4$</td>
<td>25.6</td>
<td></td>
<td></td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>26.08</td>
<td>2.75</td>
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<td>17</td>
</tr>
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<td></td>
<td>26.1</td>
<td></td>
<td></td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>27.33</td>
<td></td>
<td></td>
<td>69a</td>
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<tr>
<td>LiAsF$_6$</td>
<td>22.2</td>
<td>84.7</td>
<td></td>
<td>72</td>
</tr>
<tr>
<td>Na I</td>
<td>28.0</td>
<td></td>
<td></td>
<td>10</td>
</tr>
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<td></td>
<td>27.81</td>
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<td></td>
<td>27.89</td>
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<td>NaCF$_3$CO$_2$</td>
<td>27.2</td>
<td>189±54</td>
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<tr>
<td>KI</td>
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<td></td>
<td>30.75</td>
<td>3.70</td>
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<td>69a</td>
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### TABLE 3

**Single-Ion Conductances**

in PC at 25°C

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<tr>
<th>Ion</th>
<th>Ohm cm⁻¹ mol⁻¹</th>
<th>Ref</th>
<th>Ion</th>
<th>Ohm cm⁻¹ mol⁻¹</th>
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<td>Na⁺</td>
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<td>Br⁻</td>
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<td>I⁻</td>
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of dilute solutions of aluminium chloride in PC. The equivalent conductance plotted versus the square root of the concentration, showed both a maximum and a minimum with decreasing solute concentration, unlike the phoreogram\(^{(74)}\) for aluminium chloride in the presence of lithium chloride, Figure 3. The occurrence of this minimum for aluminium chloride at fairly low concentration was attributed to the water content of the solvent. However, an alternative interpretation of the data has been suggested.\(^{(75)}\) It is assumed that the effect is not due to imperfect drying of the solvent, since the anomalous behaviour occurs with a water concentration less than 20 PPM. Furthermore, the phoreogram of lithium tetrachloroaluminate, LiAlCl\(_4\), does not show this behaviour in the same solvent. The rapid increase in the equivalent conductance with increasing concentration is then explained by equilibria in which the number of ions per mole of solute increases with increasing concentration. The following equilibria fulfill this requirement:

\[
\begin{align*}
3 \text{AlCl}_3 & \rightleftharpoons \text{AlCl}_2^+ + \text{Al}_2\text{Cl}_7^- \\
4 \text{AlCl}_3 & \rightleftharpoons \text{AlCl}_4^- + \text{Al}_3\text{Cl}_8^+
\end{align*}
\]

However, there is always the possibility of chemical interaction of aluminium chloride with PC; the reaction with ethylene carbonate (III) to form ethylene oxide, is rapid.\(^{(25)}\) For this reason we have not included aluminium chloride in our present study.
FIGURE 3

Equivalent conductances in PC at 25°C
Densities and specific conductances of solutions of alkali metal chlorides in a molal solution of aluminium chloride in PC have been measured.\(^{(76a)}\) The results are interpreted in terms of ion solvation and formation of the complex ion \(\text{AlCl}_4^-\), together with structural changes of the solvent. Assuming the solvation:\(^{(42)}\)

\[
\text{AlCl}_3 + 6/4 \text{PC} + 1/4 \text{Al[PC]}_{6}^{3+} 3/4 \text{AlCl}_4^- \\
\text{the alkali metal ions react:}
\]

\[
x \text{MCl} + 1/4 \text{Al[PC]}_{6}^{3+} + 3/4 \text{AlCl}_4^- + \\
x \text{M}^+ + (1-x)/4 \text{Al[PC]}_{6}^{3+} + (3+x)/4 \text{AlCl}_4^- + 3x/2 \text{PC}
\]

Electrode kinetics in these systems have been studied using micropolarization measurements and the kinetic parameters of the deposition - dissolution process of the complex ions were evaluated.\(^{(76b)}\)

Relating the conductance data to ionic conductances and to the modes of ionisation of electrolytes, requires a knowledge of transference numbers \(t^+\) and \(t^-\). Very few of these are available for nonaqueous electrolytes in general and for PC in particular. Some of the available data were obtained by the Hittorf method. Keller et al.\(^{(42)}\) determined the transference number for lithium ion in a molar solution of lithium chloride in PC and found \(t^+ = 0.19 \pm 0.08\), while Dey and Rao\(^{(77)}\) reported a value of
t^+ = 0.2. Lyall et al.\(^{(73)}\) reported a value of 0.11 for the transference number of potassium ion in 0.45 mole l\(^{-1}\) KPF\(_6\)/PC. The use of concentration EMF cells has also been used to measure transference numbers in PC. The transference number of the perchlorate ion has been determined in a concentration cell using Li-amalgam electrodes. The results, extrapolated to zero concentration, gave t^- = 0.72 and t^+ = 0.28 for ClO\(_4^-\) and Li^+ respectively\(^{(67)}\). These values are in poor agreement with those reported by Hoare and Wiese\(^{(78)}\) t^- = 0.68 and t^+ = 0.32 for ClO\(_4^-\) and Li^+ respectively, using the same method but with lithium electrodes. On the other hand, a very different value of t^+ = 0.39 for the lithium ion has been calculated from chronopotentiometric data.\(^{(79)}\) Thus transference number data in the solvent is not very precise.

**Electrolysis of Solutions in PC**

The deposition of metals from solutions of their salts in PC has been investigated.\(^{(10)}\) Lithium, sodium and potassium were readily deposited from their halides; no deposition of magnesium, calcium, aluminium, titanium, niobium and uranium was obtained. Zinc, cadmium, iron, manganese, cobalt, bismuth and lead were only obtained from PC solutions at certain current densities. Doussek et al.\(^{(36c)}\) obtained 100\% faradaic efficiency in the deposition of potassium from KPF\(_6\) in intensively dried PC. However, the efficiency for redissolution was 25-30\% only.
Electromotive Force Studies

Butler\(^{(80)}\) discussed the setting up of reference electrodes in aprotic organic solvents, including PC. Earlier work with glass electrodes in this solvent showed the EMF to be linear with respect to \(\log (\text{metal concentration, } M^+)\), between \(10^{-2}\) and \(10^{-5}\) molar.\(^{(54 \text{ & 81)}}\) Slopes of the EMF vs. \(\log [M^+]\) plots are less than the Nernstian value. Calomel and Zn\(^{2+}/\text{Zn}\) electrodes are said to be unsatisfactory in PC (see, however, reference \(86\), where the Calomel electrode was used as reference electrode); Tl(I), Pb and Cd are possible halide-ion reversible electrodes.\(^{(53 \text{ & 82)}}\)

The Nernstian behaviour of the Li\(^{+}/\text{Li}\) couple in PC has been established,\(^{(83)}\) and a lithium ribbon electrode in a molar solution of lithium perchlorate proved satisfactory as a reference system for general electrochemical applications.\(^{(84)}\) The I\(_3^-/\text{I}^-\) reference electrode has been investigated in PC solution.\(^{(85)}\) Two separate equilibria exist; whenever \(\text{I}^-\) is present in excess of \(\text{I}_2\), the \(\text{I}_3^-/\text{I}^-\) couple is formed, and whenever the concentration of \(\text{I}_2\) exceeds that of \(\text{I}^-\), only the \(\text{I}_2/\text{I}_3^-\) couple exists. Matsuura et al.\(^{(86a)}\) have measured the standard electrode potentials of metal/ion couples in PC, dimethylformamide and dimethylsulfoxide, relative to the aqueous saturated Calomel electrode SCE. The thallium (I)-perchlorate ion electrode was found to be stable enough to be used as a reference electrode. The Debye-Hückel equation,
for estimating the activity coefficient, equation (3:5) was said to be applicable in these solvents; provided the proper value was chosen for the ionic radius parameter \( a \). This parameter was estimated to be zero in PC.

Electrochemical charge and discharge characteristics at copper electrodes in molar lithium tetrachloroaluminate solution in PC, show that oxidation produces sparingly soluble cuprous chloride, and reduction of this product gives soluble chlorocuprate complexes.

Anodic stripping of lithium deposited on magnesium from lithium perchlorate solution, shows both elementary and alloyed lithium to be present.

**Polarography in PC**

Diffusion coefficients have been measured in PC solution, from the change in weight of a porous disc, filled with the solution and suspended in the pure solvent. These coefficients are required in relating the polarographic current to the concentration of the ion being reduced, by the Ilkovic equation. McComsey and Spritzer have published a preliminary report on polarography in PC. The choice of salt bridge, reference electrode and supporting electrolyte are discussed, as well as, the polarographic behaviour of acids and molecular oxygen in PC. A platinum mesh reference electrode
was used in the polarographic investigation of poly-
methine dyes in PC.\(^{(91)}\)

The oxidation of halide ions in PC at a rotating
platinum anode has been investigated.\(^{(92)}\) Oxidation of
chloride ion is a single stage process, whereas bromide
and iodide are oxidised in two-stage processes:

\[
\begin{align*}
2 \text{Cl}^- &\rightarrow \text{Cl}_2 \\
3 \text{X}^- &\rightarrow \text{X}_3^- \\
2 \text{X}_3^- &\rightarrow 3 \text{X}_2
\end{align*}
\]

where \(\text{X}\) is \(\text{I}^-\) or \(\text{Br}^-\).

Half wave d.c., \(E_{1/2}\), and peak a.c., \(E_p\), potentials
have been measured against aqueous SCE, for alkali
metal ions in PC.\(^{(86b)}\) Table 4 gives the values of
\(E_{1/2}\) and \(E_p\), where \(I_d\) is the diffusion current constant;
\(i_d/cm^{2/3} t^{1/6}\). \(\delta E_p/2\) is the half width of the a.c.
current peak. \(i_p/i_d \tau^{1/2}\) is the reversibility factor,
with drop time at a.c. peak equal to \(\tau\) second.

The PC-Water System

Water and PC are not miscible in all proportions;
separation of phases occurs between 0.036 and 0.700 mole
fraction of water.\(^{(93a)}\) The complete liquid-liquid
phase diagram at atmospheric pressure is reproduced by
permission of the authors\(^{(94)}\), Figure 4. In the
TABLE 4

Polarographic Potentials of Alkali Metal Cations in PC at 25°C

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<th>ac polarography</th>
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<tr>
<td>Cs$^+$</td>
<td>1.982</td>
<td>1.25</td>
<td>43</td>
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</tbody>
</table>

(a) Values obtained from maximum current polarogram.
(b) Values obtained from mean current polarogram.

Reduction of water in PC at a platinum disc electrode, with tetraethylammonium perchlorate, as supporting electrolyte, hydroxyl ion is formed, which then reacts with the solvent to form $\text{HCO}_3^-$ and propanediol. (95a) At lower vapour pressures of water, propylene is evolved. (95b) If ions are present, they are usually solvated preferentially by the water, which is not then decomposed until present in excess above the solvation requirements. (37) The relative solvation of ions by the two constituents is considered by L'Her et al. (93a) and the physical properties of water-PC solutions were recorded, (93b) as well as the activity coefficients of transfer for a number.
FIGURE 4

Phase diagram for PC - water system at 1 - atm pressure

1 liquid

2 liquids

ice + liquid

propylene carbonate/wt fraction

temp °C
of cations, and their polarographic half-wave potentials. (93c)

To conclude this literature survey, previous studies of PC electrolyte solutions, utilizing a variety of techniques, generally have indicated strong cation solvation, weak anion solvation and reasonable degrees of dissociation for electrolytes. However, the tendency for ion pair and higher complex formation is greater than in aqueous solutions and we would expect this process to be enhanced with increasing charge on the cation. Few reliable transport data are available and there is some uncertainty regarding reference electrode potentials in this solvent.

As most of the previous work had dealt with symmetrical electrolytes, the present investigation was orientated towards the behaviour of the as yet unexplored field of unsymmetrical electrolytes in PC, such as the 1:2 electrolyte potassium carbonate, 2:1 electrolytes zinc halides and perchlorates and the 3:1 electrolyte ferric chloride.
CHAPTER II

SOLUBILITIES OF ELECTROLYTES IN PC
The solubility of an electrolyte in PC is important in determining the various techniques available to study the electrochemical behaviour of this electrolyte. Although conductances can be measured in extremely dilute solution, the results are usually only precise above about $5 \times 10^{-5}$ molar concentration, because of the relatively large solvent correction, and the possibility of adsorption of a significant number of ions on the electrodes or the conductivity cell wall, at lower concentrations.

For transference number studies, on the other hand, much more concentrated solutions $> 0.1$ molar are required, if the voltage across the transport cell is to remain reasonably small and, in the case of the Hittorf method, if the concentration changes are to be appreciable.

In addition to more traditional techniques, spectroscopic studies also must be carried out at concentrations very much greater than those which are suitable for conductance studies.

Thus, it was decided to investigate the solubilities of zinc and potassium carbonates, zinc oxide, sulphate, bromide and iodide, which had not previously been measured, as well as to make a precise measurement of the solubility of zinc chloride.
Experimental

Saturated solutions of various anhydrous inorganic electrolytes in PC were prepared by allowing the system PC-excess solute to equilibrate under a dry nitrogen atmosphere in a long-necked glass flask submerged in a thermostat at 25°C. In order to obtain true solubilities, the saturated solutions were prepared by allowing a supersaturated solution obtained with occasional shaking at a higher temperature, 35°C to cool down to the temperature of the thermostat and to equilibrate. The excess solid was then separated from the saturated solution by filtration in a dry nitrogen atmosphere, inside a glove box. A weighed amount of the liquid phase was then analysed by recommended analytical procedures. No investigation of the composition of the solid phase was carried out.

Materials

The solvent, PC and most of the solutes selected for these studies, were highly hygroscopic in character. It was, therefore, necessary that these chemicals should be stored and handled exclusively in a glove box, Gallenkamp type MA-950, containing an inert atmosphere. Dry and prepurified nitrogen was used as the inert gas. Trace oxygen was removed from the nitrogen by BASF catalyst type R 3-11, which consists of about 30% copper in highly dispersed form stabilized on a Carrier,
and activated by various additional compounds. Water vapour was removed by passing the gas over anhydrous magnesium perchlorate, and the humidity was checked by a hair hygrometer, Griffin type HV - 450. The glassware used in this work was treated according to the following procedure: After cleaning in hot nitric acid-water 1:1, the glassware was rinsed thoroughly with conductivity water, dried in a regulated oven and finally heated to 250°C in a special oven for several hours under a current of dry nitrogen. After the glassware was dried in such a manner, it was immediately transferred to the inert atmosphere box.

(i) Solvent

During the first period of this work a sample of PC, supplied by Chemische Werke Hüls, Germany (C.W.H), was used. This material contained up to 10% impurities, which were identified as mainly water, propylene glycol and propylene oxide. During the later part of the work described in this thesis, the PC used was supplied by British Drug Houses, England (B.D.H.). The quality of this material was found to be superior to that of C.W.H.

Purification of PC

The methods described for purifying PC were extensively investigated. The best results were achieved by stirring the solvent over molecular sieves,
type 4A, for 48 hours, followed by fractional
distillation twice under reduced pressure in a dry
nitrogen atmosphere. A distillation column 70 cm.
long and 1.2 cm in diameter was packed with glass
helices. The outside of this column was electrically
heated to a temperature below the working temperature.
The kettle temperature was maintained at 110°-111°C;
the column head temperature levelled off between 72°
and 75°C. In practice, a vacuum of 0.5 torr was
achieved at the distillation kettle to avoid decomp­
osition. The first 30% of distillate was discarded,
and the useful fraction collected was the middle 60%.
The remaining 10% was undistilled. The solvent
was immediately transferred to the dry atmosphere
in the glove box, and used within two weeks.

Tests of Purity (a) Chromatography

The purified PC was analysed by gas chromatography
to identify the impurities that remained after the
distillation. The apparatus used for the determination
of water was the Pye 104 series gas chromatograph
model 34, equipped with thermal conductivity cells.
The experiments were performed with a column con­
taining Porapak Q; (ethylvinylbenzene-divinylbenzene
polymer) 2 feet in length. Helium was used as the
carrier gas to minimise tailing of the water peak.
The basic analytical conditions are summarised as
follows:
In order to detect the organic impurities a flame ionisation detector was used, with Perkin-Elmer gas chromatograph model F 11 A. The analytical conditions are shown below:

- **Column packing**: Porapak Q
- **Carrier gases**
  - Nitrogen: 35 cm³ min⁻¹
  - Air: 300 cm³ min⁻¹
  - Hydrogen: 30 cm³ min⁻¹
- **Detector temperature**: 165°C
- **Injector temperature**: 110°C
- **Sample size**: 0.1 μl

A composite chromatogram of PC as received from B.D.H. is shown in Figure 5. The components were identified by matching the retention times of pure material injected at concentrations of the same order as those present in the solvent. The areas under the chromatographic peaks were measured by the Disc Chart-Integrator unit model 252-A. By measuring the area under the PC peak and assuming this value corresponded to 100%,
FIGURE 5

Composite chromatogram of impurities in PC as-received (B.D.H.)

(A) Carbon dioxide and
(B) Water (Using thermal conductivity detector)
(1) Propylene oxide,
(2) Allyl alcohol,
(3) 1, 2-Propylene glycol, and
(4) 1, 3-Propylene glycol (Using flame ionization detector)
an approximate value for the concentrations of the impurities could be obtained.

Figure 6 shows the chromatograms of the purified PC used in this work; curve A is for the flame ionization detector, and curve B for the thermal conductivity detector.

The water content of the purified product was 10 PPM; other detectable impurities were propylene oxide <1PPM, 1,2 propylene glycol 10 PPM and allyl alcohol < 2 PPM. The purified product had a specific conductance of $4 \sim 8 \times 10^{-8} \text{ohm}^{-1} \text{cm}^{-1}$. The resultant specific conductance of PC was considered a good criterion of its purity.

(b) **Density**

The density of PC was measured by a new device, the Precision Density Meter DMA 02C. The instrument depends upon the variation of the natural frequency of a hollow oscillator when filled with different liquids or gases. The mass, and thus the density, of the liquid or gas changes this natural frequency because of the gross mass change of the oscillator.

To illustrate the calculation, we may consider an equivalent system represented by a hollow body
FIGURE 6

Chromatograms of purified PC used in these studies

Curve A, flame ionization detector
Curve B, thermal conductivity detector
of mass $M$ and volume $v$ which is suspended by a spring of force-constant $s$. This volume shall be filled with a sample of density $d$.

The natural frequency of this system will be

$$f = \frac{1}{2} \pi \left( \frac{s}{(dv+M)} \right)^{\frac{1}{2}} \tag{1:1}$$

therefore the period $\tau$

$$\tau = 2 \pi \left( \frac{(dv+M)}{s} \right)^{\frac{1}{2}} \tag{1:2}$$

taking the square of this expression and inserting

$$A = (4\pi^2v)s; \quad B = (4\pi^2M)/s$$

we obtain

$$\tau^2 = A \ d + B \tag{1:3}$$

for the difference of the densities of two samples.

$$d_1 - d_2 = \frac{1}{A} \left( \tau_1^2 - \tau_2^2 \right) \tag{1:4}$$

The constant $A$ could be obtained from two calibration measurements on samples of known density e.g. water and air.

$\tau$ is obtained by automatic recording of the number of oscillations in a selected period of time, fixed by the instrument.

The density measurements were performed at $25^\circ\text{C} \pm 0.01$, giving a density of $1.1993 \text{ g cm}^{-3} \pm 0.0001$ for the purified PC; corresponded to $79045 \pm 1$ oscillations.
(ii) Solutes

Zinc Chloride

Anhydrous zinc chloride was prepared by the method described by Christov et al. (97), which involved the distillation of Analar zinc metal in powder form with an excess amount of absolute ethanol. Analar acetyl chloride was added dropwise for 15-30 minutes before the distillation and platinum foil was used as a catalyst. The unreacted metal was filtered off and the filtrate, containing zinc chloride, distilled in vacuum until crystallisation started. The solute was recrystallised from a nonpolar solvent, benzene, under a dry nitrogen atmosphere.

\[
\begin{align*}
2 \text{CH}_3\text{COCl} + 2 \text{C}_2\text{H}_5\text{OH} + \text{Zn} & \rightarrow 2 \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{ZnCl}_2 + \text{H}_2 \\
2 \text{CH}_3\text{COCl} + 2 \text{H}_2\text{O} + \text{Zn} & \rightarrow 2 \text{CH}_3\text{CO}_2\text{H} + \text{ZnCl}_2 + \text{H}_2 \\
2 \text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} + \text{Zn} & \rightarrow \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{CH}_3\text{CO}_2\text{H} + \text{ZnCl}_2 + \text{H}_2
\end{align*}
\]

The product dissolved readily in water, alcohol and ether to give perfectly clear solutions, free from oxychloride.

The recrystallised solute was stored over phosphorus pentoxide for several days in the dry box before use.

Analysis for zinc content by titration with the disodium salt of EDTA, using eriochrome black
T as indicator, and for chloride by the Volhard method, showed excellent agreement with the theoretical composition:

- **Found by EDTA titration:** 47.90% Zn and
- **by Volhard method:** 52.00% Cl
- **Theory for ZnCl₂:** 47.97% Zn and 52.03% Cl

A second source of this anhydrous solute was the Alfa product, USA, Ultrapure zinc chloride which has been used as received.

**Zinc Bromide**

The Fisher Certified Reagent Grade salt was dried by heating at 300°C under reduced pressure; 0.02 mmHg, for one hour, followed by sublimation. (98)

**Zinc Iodide**

The Merck Reagent Grade product was treated as for zinc bromide.

All the zinc halides were stored over phosphorus pentoxide in the dry box.

**Zinc Oxide**

The Ultrapure, Alfa product, USA, was used without further purification.
**Zinc Sulphate**

The Analar BDH hydrated salt was recrystallised from ethanol and dried at $300^\circ C$ for three hours.

**Zinc Carbonate**

The Fisher Certified Reagent Grade was dried by heating at $100^\circ C$ under reduced pressure for one hour.

**Potassium Carbonate**

The Analar BDH salt was treated as for zinc carbonate.
(2) Solubility Results

The results of the solubility determinations are given in Table 5. Each value is the mean of three independent determinations. The equilibration time in each case was about 100 hours at 25°C ± 0.01.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solubility molal</th>
<th>Method of Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Chloride</td>
<td>0.1184*</td>
<td>EDTA &amp; Flame photometric</td>
</tr>
<tr>
<td>Zinc Bromide</td>
<td>0.325</td>
<td>EDTA</td>
</tr>
<tr>
<td>Zinc Iodide</td>
<td>0.402</td>
<td>EDTA</td>
</tr>
<tr>
<td>Zinc Sulphate</td>
<td>0.0465</td>
<td>Flame photometric</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>0.0285</td>
<td>Flame photometric</td>
</tr>
<tr>
<td>Zinc Carbonate</td>
<td>1.46 x 10^{-6}</td>
<td>Flame photometric</td>
</tr>
<tr>
<td>Potassium Carbonate</td>
<td>9.05 x 10^{-6}</td>
<td>Flame photometric</td>
</tr>
</tbody>
</table>

* The value quoted is much lower than that of reference (10) and refers to the vigorously dried PC as described before.
(3) **Discussion**

The above results show that for zinc halides, the solubility increases along the series $\text{Cl}^- < \text{Br}^- < \text{I}^-$; this may be due to the decrease in the lattice energy as the anion size increases with little change in the free energy of solvation of the anion. The same is true of cadmium halides, calcium chloride, calcium bromide, manganese (II) chloride and manganese(II) bromide, in this solvent; see Table 6. Also the solubility is greater for zinc halides than for the corresponding cadmium salts, and is greater for calcium bromide than for barium bromide; see Tables 5 and 6. This is probably due to the relative gain in solvation energy compared with the lattice energy as the cation size decreases.

**TABLE 6**

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solubility molal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium Chloride</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Cadmium Bromide</td>
<td>0.0450</td>
</tr>
<tr>
<td>Cadmium Iodide</td>
<td>0.0454</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>$5 \times 10^{-3}$</td>
</tr>
<tr>
<td>Calcium Bromide</td>
<td>0.745</td>
</tr>
<tr>
<td>Manganese Chloride</td>
<td>$2 \times 10^{-3}$</td>
</tr>
<tr>
<td>Manganese Bromide</td>
<td>1.50</td>
</tr>
<tr>
<td>Barium Bromide</td>
<td>$7.8 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

* Data from reference (10)
Further consideration of the data shows that the solubilities of zinc sulphate and zinc oxide are less than those of the halides, as could be expected, due to their high lattice energies, 739 and 985 K. cals. mole\(^{-1}\) respectively\(^{(99)}\), and to the poor solvation of the anion in PC.\(^{(49)}\) The carbonyl oxygen of PC with its relatively high negative charge and exposed position will readily solvate cations. The positive end of the PC dipole will, however, be spread over a number of atoms and will be much less accessible than in the case of water, which because of the exposed charge distribution, solvates both anions and cations to a comparable degree. Moreover, in water potassium carbonate is very soluble and zinc carbonate is sparingly soluble but in PC this is not the case. This is because the increase in the lattice energy, as the charge of the cation increases, is not compensated by a corresponding gain in the solvent-anion interaction.

We may divide the free energy of solvation of gaseous ions into two parts; the first is an electrostatic term due to the separation of ions in a dielectric medium; the second is due to specific chemical interaction between the ions and the polar-solvent molecules. The electrostatic part of the free energy can be approximated by the Born equation:\(^{(100)}\)

\[
\Delta G = - \frac{Nz^2e^2}{8\pi\varepsilon_0r} \left(1 - \frac{1}{\varepsilon_r}\right)
\]  

(1 : 5)
where $Z$ is the numerical value of the charge on the ion, of radius $r$, $\varepsilon_o$ is the permittivity of a vacuum, and $\varepsilon_r = \varepsilon/\varepsilon_o$ is the relative permittivity or dielectric constant, where $\varepsilon$ is the permittivity of the solvent.

The energy of interaction of the ion with its first solvation shell is based on the interaction between solvent dipoles and the ion. This interaction will be enhanced by solvents having larger dipole moments, by ions of higher charge density and by a more exposed charge distribution in the solvent molecule. Moreover a small solvent molecule will promote a greater amount of coordination and a greater ion dipole interaction, because of the greater number of molecules that may surround a given ion in solution. Usually the greater (more positive) the difference between the lattice energy and the enthalpy of solvation of a solute, the greater the solubility will be. In general, a high solvation energy for an electrolyte will be favoured by ions of high charge density in a medium of high dielectric constant; by greater separation of charge (i.e. larger dipole moment) in the solvent molecule; and by specific chemical interaction between the ions and the solvent. Thus, these factors lead to high solubility; however, the high ionic charge density will also give rise to a large lattice energy.
In conclusion, zinc halides are sufficiently soluble in PC to allow for conductance and transference number measurements.
CHAPTER III

CONDUCTANCE OF ELECTROLYTES IN PC
The different theories of conductance of electrolytes have been fully reviewed by Al-Najar\(^{101}\) so only a brief account will be given here. The modern theory of electrolyte conductance was founded by Debye and Hückel.\(^{102}\) Their theory ascribed the variation of equivalent conductance \(\Lambda\) with the molar concentration \(C\) to the effect of interionic forces and led to the explanation of the empirical limiting law of Kohlrausch:

\[
\Lambda = \Lambda_0 - S C^{1/2}
\]  

(2:1)

where \(\Lambda_0\) is the equivalent conductance at infinite dilution.

Soon after the Debye-Hückel result, Onsager\(^{103}\) gave an improved derivation of the coefficient \(S\).

In an electrolyte solution, the ionic distribution is not random and this results from the competition between Coulombic electrical forces and the thermal motions of the ions. Each ion in solution at equilibrium is at the centre of an associated, spherically symmetric region of opposite charge, known as the "ion atmosphere". When an external electric field is applied, at any finite concentration, the ion atmosphere loses its symmetry and the mobility of the ion decreases from its value at zero concentration, this effect being known as the "asymmetry" or "relaxation" effect. The
other influence on the mobility of an ion is known as the "electrophoretic" effect; this arises from counter-
motion of the solvent bound to the ions in its
atmosphere so that the motion of the ion is apposed
by a "frictional" resistance described by Stokes's
law. The ions are here represented as point charges.
The above reasoning led to the Debye Hückel-Onsager
limiting equation for symmetrical electrolytes.

\[ \Lambda = \Lambda_0 - (S_1 \Lambda_0 + S_2) C^{\frac{1}{2}} \]  \hspace{1cm} (2:2)

where \(S_1 \Lambda_0\) is the relaxation term and \(S_2\) is the elec-
trophoretic term. \(S_1\) and \(S_2\) are function of temperature
T, the valence type of the electrolyte \(Z_i\) and \(Z_j\) and the
dielectric constant of the solvent \(D\); \(S_2\) also depends
upon the viscosity of the solvent \(\eta\).

For unsymmetrical electrolytes equation (2:2)
takes the form:

\[ \Lambda = \Lambda_0 - \left[ 2.80 \times 10^6 \frac{q |z_i| z_j}{\Lambda_0 (D T)^{3/2}} \left( 1 + q^{\frac{1}{2}} \right) + 41.25 \left( \frac{|z_i| + |z_j|}{\eta (D T)^{1/2}} \right) R^{\frac{1}{2}} \right] \]  \hspace{1cm} (2:3)

where \(q = (e_i w_i - e_j w_j) / (e_i - e_j) (w_i - w_j)\)  \hspace{1cm} (2:4)

\(e_i\) and \(e_j\) are the charges on the ions and \(w_i\) and \(w_j\)
are the mobilities of the ions of species \(i\) and \(j\)
respectively.
I is the ionic strength of a solution containing n ionic species of charge \( Z_i \) and molarity \( C_i \) defined by:

\[
I = \frac{1}{2} \sum_{i=1}^{n} C_i Z_i^2
\]  

(2.5)

Equation (2.2) may be regarded as a first approximation to a description of a plot of \( \Lambda \) against \( C^{\frac{1}{2}} \). In fact it represents the tangent to the phoreogram\(^{(74)}\) at concentration zero.

Other workers have attempted to extend and improve the theory, in order to produce conductance equations that represent, more closely, the phoreograms of different electrolytes. One of the first attempts to improve the limiting law was made by Falkenhagen, Leist and Kelbg\(^{(104)}\) who considered the ions to possess finite size. Their conductance equation, based on a distribution function\(^{(105)}\) which allowed that not more than one ion could occupy the same site, contrary to the Boltzmann distribution function used in the limiting law. Moreover, they introduced the distance of closest approach between the ions; the \( a \) parameter, in the boundary conditions. The equation was formulated as:

\[
\Lambda_c = \Lambda_o - \Lambda_{cI} - \Lambda_{cII}
\]  

(2.6)

Where \( \Lambda_{cI} \) and \( \Lambda_{cII} \) are the relaxation and electrophoretic terms respectively in the molar conductance \( \Lambda_c \).

\[
\Lambda_{cI}(D,T,\vec{E},\Lambda_o) \quad \Lambda_{cII}(D,T,n,\vec{E}_o)
\]
It is interesting to note that the Falkenhagen school alone has not limited its considerations to very low-frequency 'applied fields. $\Lambda_{C1}$ and $\Lambda_{CII}$ in (2:6) are functions of frequency, and the stationary field is considered as a special case.

A series of conductance equations has been developed by Fuoss and others\(^{(106)}\), based on a model in which the ions were represented by charged spheres. The Fuoss-Onsager equation\(^{(107)}\) was in the form of a series in $C$ to the first order:

$$\Lambda = \Lambda_o - SC^{\frac{1}{2}} + EC\ln C + JC$$  \(2:7\)

where $S$ is the Onsager coefficient of the limiting law (2:1), $E$ a constant defined by the same variables as $S$. $J$ is a function of ion size.

Later, they\(^{(108)}\) evaluated partially the coefficient of $C^{3/2}$ term to give an equation of the form:

$$\Lambda = \Lambda_o - SC^{\frac{1}{2}} + Ec \ln C + J_1C - J_2C^{3/2}$$  \(2:8\)

Falkenhagen and Kremp\(^{(109)}\) gave a new conductance equation of the form (2:7). The coefficients of this equation together with those of Fuoss-Onsager and of the Onsager limiting law are shown in Table 7.
\[ b = \left( \frac{Z + Z^- |e^2|}{c a DkT} \right) \]

<table>
<thead>
<tr>
<th></th>
<th>Onsager</th>
<th>Fuoss-Onsager</th>
<th>Falkenhagen-Kremp</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S</strong></td>
<td>( S = S_1 \Lambda_0 + S_2 ); ( S_1 = \frac{e^2 K c^{-\frac{1}{4}}}{3DkT(2+\sqrt{2})} ); ( S_2 = \frac{F e K 10^{-11}}{3 \pi n c^2} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>E</strong></td>
<td>0</td>
<td>( E = E_1 \Lambda_0 - E_2' ); ( E_1' = \frac{(Kab)^2}{24c} ); ( E_2' = \frac{S_2 K_{ab}}{16c^2} )</td>
<td>( E = E_1 \Lambda_0 )</td>
</tr>
</tbody>
</table>
| **J_1** | 0            | \( J_1 = \sigma \Lambda_0 + \sigma_2 \) | \( \sigma_1 = \frac{(Kab)^2}{12c} \left[ -1/b^3 + 2/b^2 + 2/b + \ln \frac{K_{ab}}{c^2} \right] \)
|       |               | \( \sigma_2 = S_2 \left[ S_1 + 11K_{ab}/12c^2 - K_{ab}/8c^2 \left( 1.0170 + \ln a/c^2 \right) \right] \) | \( \sigma_1 = \frac{(Kab)^2}{12c} \left[ -1/b^3 + 1/b^2 + 9/4b + 0.96 + \ln K_{ab}/c^2 \right] \)
|       |               |                                           | \( \sigma_2 = S_2 . K_{ab}/c^2 \) |
| **J_2** | 0            | \( J_2 = \sigma_3 \Lambda_0 + \sigma_4 \) | \( \sigma_3 = \sqrt{2} \frac{(Kab)^3}{24c^{3/2}} \left[ 1/b^3 + 2/b^2 - 1.0776/b \right] \)
|       |               | \( \sigma_4 = S_2 \frac{(K_{ab})^2}{c} \) | \( \sigma_3 = 0 \)
Fuoss and Hsia\textsuperscript{(110)} completed the $C^{3/2}$ terms to yield an equation of the form:

$$A = (\Lambda_0 - \Delta \Lambda)(1 + \Delta X/X)/(1 + 3 \phi/2) \quad (2:9)$$

where $\Delta \Lambda$ is the electrophoretic term, $\Delta X/X$ is the relaxation term and $\phi$ is the volume fraction of one species of ions. A revised version of this equation has been given by D'Aprano\textsuperscript{(111)}, omitting the volume term to give:

$$A = \Lambda_0 (1 + \Delta X/X) - \Delta \Lambda \quad (2:10)$$

The Fuoss-Hsia equation (2:9) has been put into the series form (2:8) by Fernandez-Prini and Prue\textsuperscript{(112)}, who expanded the equation in powers of $C$ and neglected terms above $C^{3/2}$. We refer to this expanded equation as the "modified" form. The expressions for the $S$, $E$, $J_1$ and $J_2$ coefficients for the modified Fuoss-Hsia equation are shown in Table 8.

Murphy and Cohen\textsuperscript{(113)} improved the Fuoss-Onsager equation (2:8) by using a different method to solve the differential equation, and in doing so they obtained a corrected value for $J$ (or $\Lambda_2$) equation (2:11). However, Chen\textsuperscript{(114)} has pointed out that they, as well as Fuoss and Onsager, have neglected a contribution to the conductivity that effects the value of both $E$ (or $\Lambda_2$) and $J$ (or $\Lambda_2$).
<table>
<thead>
<tr>
<th>S</th>
<th>$S = \lambda_0 S_1 + S_2$; $S_1 = \frac{e^2 K c^{-\frac{1}{2}}}{3DKT(2+\frac{1}{2})}$; $S_2 = \frac{Fe K 10^8 c^{-\frac{1}{2}}}{3\pi \gamma C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>$E = E_1 \lambda_0 - E_2$; $E_1' = \frac{(K a b)^2}{24c}$; $E_2' = \frac{S_2 K a b}{16c^2}$; $0.4343E_1 = E_1'$; $0.4343E_2 = E_2'$</td>
</tr>
<tr>
<td>$J_1$</td>
<td>$J_1 = \sigma_1 \lambda_0 + \sigma_2$; $\sigma_1 = f_1(b)$; $\sigma_2 = f_2(b)$</td>
</tr>
<tr>
<td>$J_2$</td>
<td>$J_2 = \sigma_3 \lambda_0 + \sigma_4$; $\sigma_3 = f_3(b)$; $\sigma_4 = f_4(b)$</td>
</tr>
</tbody>
</table>

**Table 8**

Modified Fuoss-Hsia

<table>
<thead>
<tr>
<th>$\sigma_1$</th>
<th>$[\frac{(K a b)^2}{24c}] [1.8147 + 2\ln(K a/c^2) + (2/b^3)(2b^2 + 2b - 1)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_2'$</td>
<td>$S_1 S_2 + S_1 (K a/c^2) - S_2 (K a/b) / 16c^2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\sigma_3'$</th>
<th>$[b^2(K a)^3 / 24c^5 / 2] [0.6094 + (4.4748/b) + (3.8284/b^2)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_4'$</td>
<td>$[S_2 (K a b)^2/24c] [1.9384] + S_1 S_2 (K a/c^2) + S_2 [K a] / b$</td>
</tr>
<tr>
<td></td>
<td>$- [S_2 b (K a)^2 / 16c] [1.5405 + (2.2761/b)]$</td>
</tr>
<tr>
<td></td>
<td>$- (S_2^2 K a b / 16 \lambda_0 c^2) [(4/3b) - 2.2194]$</td>
</tr>
</tbody>
</table>
In 1970, Murphy and Cohen (115) produced a corrected equation in which they used a higher-order expression for the equilibrium pair distribution function to extend the applicability of the theory to asymmetric electrolytes, whereas all the extensions to (2:2) previously described were restricted to symmetric electrolytes. This form of the Murphy-Cohen equation is formulated as a series in BK:

\[ \Lambda = \Lambda_0 + BK \Lambda_1 + (BK)^2 \ln(BK) \Lambda_2 + \ldots \] \hspace{1cm} (2:11)

where \( B = -e_1 e_2 / DkT \)

and \( K \) is the reciprocal of "Debye length" i.e.

\[ 1/K = (4\pi \sum n_i e_i^2 / DkT)^{-1/2} \]

\( \Lambda_1, \Lambda_2 \) and \( \Lambda_2 \) are the relaxation, electrophoretic and osmotic terms, which are defined in the original paper. (115)

At present, the equation (2:11) is formulated to the first order in concentration i.e. to order \( (BK)^2 \). The conductance expression depends on the experimentally measurable quantities \( \Lambda_0, w_1 \) the mobility of an ion of species \( i \), viscosity \( \eta \) of the medium, \( D \) dielectric constant and \( T \) absolute temperature, as well as the single arbitrary parameter \( a \).
The Murphy-Cohen conductance equation was used, with some modification, in this work for the interpretation of experimental data, since this is the only available extended equation capable of analysing the conductance data for unsymmetrical electrolytes. (equation 2:3 is of course the limiting law).

The equations described above are taken to be valid up to concentrations corresponding to $K_a = 0.2$, which corresponds to the limiting concentrations in Table 9, assuming complete dissociation in aqueous solution at 25°C:

<table>
<thead>
<tr>
<th>$\frac{a}{\Delta}$</th>
<th>$K$</th>
<th>Concentration mole $1^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Solute type</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1 : 1$</td>
</tr>
<tr>
<td>3</td>
<td>0.067</td>
<td>0.04433</td>
</tr>
<tr>
<td>10</td>
<td>0.020</td>
<td>0.00399</td>
</tr>
<tr>
<td>14</td>
<td>0.014</td>
<td>0.00204</td>
</tr>
</tbody>
</table>

TABLE 9
While in the case of the Murphy-Cohen equation (2:11) the limit is $BK = 0.2$ which corresponds to the following concentrations, Table 10.

**TABLE 10**

<table>
<thead>
<tr>
<th>Solute type</th>
<th>Concentration mole $\text{l}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 1</td>
<td>0.00796</td>
</tr>
<tr>
<td>1 : 2</td>
<td>0.00066</td>
</tr>
<tr>
<td>2 : 2</td>
<td>0.00012</td>
</tr>
</tbody>
</table>
The equations that have been considered so far have been concerned mainly with the theoretical prediction of the conductance behaviour of strong electrolytes; with the exception of the Murphy-Cohen equation they are restricted to symmetrical species. The phoreograms of some electrolytes in different solvents show large negative deviations from the limiting law. This may be explained by postulating the existence of ion association to form non-conducting species in solution, either molecules or ion aggregates. However, with unsymmetrical electrolytes the position is more complicated since the ion pair is now a new charged entity contributing to the measured conductance. There will be an equilibrium between free ions and ion pairs:

\[
\begin{align*}
M^{z_1^+} + A^{z_j^-} & \rightleftharpoons [MA]^{(z_i^-z_j^+)} \\
\text{(3:1)}
\end{align*}
\]

which can be described by the equilibrium constant for ion pair formation:

\[
K_A = \frac{(1 - \alpha) f}{C} \alpha^2 f_\pm \alpha^2 \\
\text{(3:2)}
\]

where \(K_A\) is the association constant, \((1 - \alpha)\) is the fraction of solute associated to pairs, \(f_\pm\) is the mean ion activity coefficient of the free ions at molarity \(\alpha C\) and \(f\) is the activity coefficient of the ion pair at molarity \(C(1 - \alpha)\), which can be taken to be unity for low concentrations of chargeless pairs.
In general, the deviation may be explained by postulating the existence of a new species, the ion pair or complex of mononuclear (116) and polynuclear (117) species in the solution. If only mononuclear species are formed, the ion association can be regarded as a stepwise process involving the equilibria:

\[
\begin{align*}
M^{z_i+} + A^{z_j-} & \rightleftharpoons MA (z_i - z_j) + \\
MA (z_i - z_j) + + A^{z_j-} & \rightleftharpoons MA_2 (z_i - 2z_j) + \\
& \vdots \\
MA_p [z_j - (p-1)z_j] + + A^{z_j-} & \rightleftharpoons MA_p [z_j - (p-1)z_j] + A^{z_j-}
\end{align*}
\]

(3:3)

where \( p \) is the maximum coordination number of the metal ion \( M^{z_i+} \), hence:

\[
K_A = \frac{[MA_p] (z_i - p z_j) +}{[MA]_p [z_i - (p-1)z_j] + A_j z_j} \times
\]

\[
f_{MA_p} (z_i - p z_j) + \quad f_{MA_p} [z_i - (p-1)z_j] + f_A z_j
\]

(3:4)

If the Debye-Hückel law is applicable, the mean ion activity coefficient will be:

\[
\log f_+ = -A \left| z_i z_j \right| I^{1/2}/(1 + B \cdot I^{1/2})
\]

(3:5)

where \( A = 1.8246 \times 10^6 / DT^{3/2} \) and \( B = 50.29 \times 10^8 / DT^{1/2} \)

Murphy and Cohen (115) derived another expression for the mean activity coefficient to order of \((BK)^2\)
based on the same "primitive" model as their conductance formula, assuming rigid charged spheres in a continuum, and depending on the minimum centre to centre distance between ions. The extent to which the centre to centre distance thus obtained for the nonequilibrium case agrees with that obtained for the equilibrium case, will give an indication of the degree of validity of Fuoss-Onsager theory, as well as, of the degree of applicability of the primitive model to actual ionic solutions.

The mean activity coefficient expression can be derived from the pair distribution function, as well as from Mayer's statistical expression\(^{(118)}\) to give the following equation:

\[
\ln f_+ = f_1(BK) + f_2(BK)^2 \ln (BK) + f_2(BK)^2 + \ldots \quad (3:6)
\]

where \(f_1 = -\frac{1}{2}, \ f_2 = (e_1 + e_2)^2 / 6e_1 e_2\) and the function \(f_2\) is defined in the original paper.\(^{(115)}\)

When ion association is included in the treatment of conductances, the electrolyte concentration is modified from stoichiometric \(C\) to ionic \(\alpha C\) and the theoretical conductance function will be changed from

\[
\Lambda = f(C; \Lambda_0, a, z)
\]

\[
\Lambda = \alpha f(\alpha C; \Lambda_0, a, z)
\]
Fuoss, Onsager and Skinner\(^{(119)}\) published an equation in which the Boltzmann distribution function was used and ion association term \(K_A aC f^2_\pm A\) was built in:

\[
\Lambda = \Lambda_0 - S\left(\alpha C\right) + E\alpha C \ln(\alpha C) + J\alpha C - K_A \alpha C f^2_\pm A \quad (3:7)
\]

Nevertheless, this equation, like the other Fuoss-Onsager equations, contains series-expanded Boltzmann function, truncated at terms linear in the electrolyte concentration, to agree with the superposition theorem.\(^{(120)}\)
(3) The Distance Parameter, 间隙.

The question arises as to how close the ions have to be before they can be considered to have lost their independent mobility. This problem was tackled by Bjerrum who, from purely electrostatic considerations, defined a distance between oppositely charged ions within which they are to be considered as being associated into ion pairs. The ionic separation \( q \), where the mutual potential energy is equal to twice the thermal energy, represents the position of minimum probability of finding an ion of opposite charge anywhere on a spherical shell of radius \( q \) surrounding the central ion, where:

\[
q = \sqrt[\text{e}^{2}/2D\cdot\text{KT}}
\]

For aqueous solutions at 25°C, \( q = 3.57 \text{ Å} \) for 1:1 electrolytes, and increases rapidly as the product of \( Z_iZ_j \) is raised to give 7.14 Å for 1:2 electrolytes, 14.32 for 2:2 electrolytes and 33.1 Å for 3:3 valent types. In PC \( q \) for 1:1 electrolytes is 4.34 Å and 8.69, 17.38 and 39.11 for 1:2, 2:2 and 3:3 valent types respectively. Distances above about 10 Å are too large to be meaningful.

An alternative approach due to Denison and Ramsay (121a) and Fuoss (121b) suggested that two ions should constitute an ion pair only when they were in contact, with no intervening molecules between them. Hence, the
distance of closest approach was the contact distance \( a \) and could be set equal to the sum of the crystallographic radii of the ions in question.

A more refined picture has been proposed by Eigen\(^{(122)}\). Associated ions could have one or two interposing solvent molecules between the ions, "outer sphere ion pairs", or they could exist with the ions in contact, "inner sphere or contact ion pairs". The upper limit, \( a \) in this case, is given by the sum of the ionic radii plus the diameters of one or two solvent molecules.

Each of the three models described above implies a different value for \( a \). Generally, for electrolytes whose ionic volumes are large compared to the volume of the solvent molecules e.g. tetrabutylammonium tetraphenylboride in acetonitrile, good correlation is found between the three distance parameters. But in cases where ionic and solvent volumes are comparable, usually all three vary in a seemingly erratic way for a given electrolyte in different solvents, or with composition, for solutions in mixed solvents.\(^{(123)}\)

Moreover, for 2:2 electrolytes in aqueous solutions at 25°C the disagreement is large; the Bjerrum distance is 14.32 Å, the Eigen value is about 10 Å and the centre to centre distance is of the order of 4 Å. However, for 2:1 electrolytes in PC at 25°C, \( q = 8.69 \) Å,
the Eigen value is about 12 Å and the centre to centre distance is about 3 Å.
(4) **Experimental**

The conductance measurements in the present work were made using two types of conductance bridge: a modified Wheatstone bridge and the Wayne-Kerr Autobalance Universal Bridge, type B642.

(4-1) **Apparatus**

(i) **Modified Wheatstone Bridge**

Conductance measurements were made at 1kHz i.e. at audio-frequency. A conventional Wheatstone bridge was used, having a slide wire modified for increased precision of balance. This circuit is essentially the one proposed by Davies\(^{124}\) for conductance work; the circuit details are shown in Figure 7. The slide wire xy of low temperature coefficient of resistance, was stretched over a metre rule. This arrangement together with the sliding contact s was obtained as a slide wire detector unit from Messrs. Griffin and George. Non-reactive 100 ohm resistors \(r_1\) and \(r_2\) were connected to each end of the wire. The wire had a resistance of 2 ohms so that the whole arrangement was equivalent to a 101 meter wire, and each mm of the wire had 1/101,000 of the resistance of the whole. The position of the balance point was read to 0.5 mm.

The non-reactive resistance \(R\) was a five-decade Sullivan box type A.C.1013 of total resistance 11,111 ohms. The capacitance of the cell was balanced out with a General Radio decade
FIGURE 7

DIAGRAM OF WHEATSTONE BRIDGE CIRCUIT

[Diagram of Wheatstone Bridge Circuit]
capacitor C having a capacitance range of 1µF to 50pF. Components R and C were standardised by the National Physical Laboratory (NPL). The conductance cell was connected in the remaining arm of the bridge. The cell and R could be interchanged with respect to the bridge wire to give two positions of balance. These two positions were not equivalent since the values of \(r_1\) and \(r_2\) were not identical and so the true balance position was determined from the mean of two or more measurements.

The bridge source was a Farnell Instruments oscillator type LFM2. The oscillator had a frequency range of 1 to \(10^6\) Hz but the normal frequency of operation was 1KHz. The source was connected to the bridge with screened cables and was situated as far as possible from the bridge, to reduce pick-up of stray signals by the bridge network. The symmetry of the bridge with respect to earth was checked by reversing the oscillator leads; no change in resistance measurement was detected.

The detector D was a General Radio tuned amplifier and null detector type 1232-A connected to the bridge with screened cables. This detector was tuned to the output frequency of the oscillator and the gain on the detector was increased as the balance point was approached. The other bridge connections were made of thick copper wire and their resistance was determined by filling the cell with mercury. (The Wheatstone bridge as described had an accuracy of about 0.03%).
For the measurement of a very high resistance, one of the 100 ohm resistors could be short-circuited. The centre point of the bridge wire then corresponded to a ratio of 1 : 101 for resistance \( R \) to that of the unknown. With this arrangement, an accuracy of about 0.2% could be attained.

**Calibration of the bridge**

The Wheatstone bridge was calibrated by the method of Davies.\(^{(124)}\)

A N.P.L. calibrated resistance box was substituted for the cell in the circuit. Setting this resistance at 1000 ohms, various balance positions of \( s \) were obtained for different resistances \( R \) corresponding to the ratio of \( R : 1000 \). A plot of \( R/1000 \) vs. the bridge reading thus enabled the ratio corresponding to any bridge reading to be interpolated.

The bridge was also calibrated for very high resistances by shorting out \( r_1 \) and obtaining a graph of balance positions vs. \( R/(\text{Resistance of standard}) \).

Recalibration of the bridge was carried out several times during the course of this work and coincident straight line graphs were always obtained.

(ii) **Autobalance Universal Bridge**

During the later part of the work described in this thesis
the Autobalance Universal bridge type B642 for measuring conductances was used. The B642 shown in Figure 8 is an autobalance transformer ratio arm bridge for the measurement of admittance or impedance at audio frequencies. Capacitance and conductance readings are displayed simultaneously on two meters as soon as the test component is connected. Eight decades, four for capacitance and four for conductance, are operated in succession, each decade being provided with a numbered readout. The three left-hand controls in each group are twelve position switches, the right-hand control being a potentiometer. Decimal points are indicated by small signal lamps mounted between the decade control knobs, the correct lamp being selected automatically by operation of the range switch.

The sensitivity of the instrument can be adjusted manually by setting the meter sensitivity switch to one of the three manual positions. Alternatively, by setting the meter sensitivity switch to "Auto", the meter sensitivity will change automatically as the first two decade controls are set. Bridge accuracy using the internal source is 0.1% provided all decades are in use. An external standard can be connected to the bridge to replace the internal bridge standards.

Calibration of the bridge

The bridge was calibrated by recording the bridge reading
FIGURE 8

Wayne-Kerr Autobalance Universal Bridge Type B 642
at balance positions for different standard resistances R.

A N.P.L. calibrated resistance box was connected to the unknown sockets E and I of the bridge by the instrument measurement cables. The legend E signifies the source side of the instrument, whilst I signifies the detector side. In each case the side arm of the cable is the neutral connection. The exposed metal sleeve between the two moulded sections is also connected to neutral, Figure 9.

A graph of standardised resistance R vs. the bridge reading was obtained. This was repeated from time to time during the work; coincident line plots were always obtained.

(iii) The Conductance Cell

The cell, Figure 10, consisted of a cylindrical vessel, of about 250 ml capacity, with an S-shaped capillary side tube; the latter enabled dry nitrogen to be passed into the cell through the electrolyte.

The cell was fitted with a ground glass cone (B20) neck. The B20 cap fitting on the neck contained two mercury tubes for connection to the platinum electrodes. A third tube in this cap allowed for successive addition of the stock solution, and served as a gas outlet. The electrodes were two parallel platinum sheets of 2 x 1 cm., spaced 1.5 cm. apart, and were
FIGURE 9
Measurement Connections to B 642 Bridge
FIGURE 10

THE CONDUCTANCE CELL
lightly coated with platinum-black in order to reduce any polarisation effects. Detailed accounts of the platinisation of electrodes have been made by Jones and Bollinger\(^{(126a)}\), and by Feltham and Spiro\(^{(126b)}\), and this procedure was followed.

The cap and the cell body carried location marks, to enable the positioning of the cap on the body, and the level of the solvent in the cell, to be reproduced in each experiment.

(iv) **Temperature Control**

The conductance cell and its contents were maintained at 25.00 ± 0.01 °C by means of a constant temperature cabinet. The cabinet was made from aluminium, and efficiently insulated by one inch thick polystyrene sheet lagging. The lower half of the cabinet contained a glass tank (30 litres) filled with light transformer oil.\(^{(127)}\) The bath was set to 25.00°C with a standard calibrated thermometer graduated in 0.01°C divisions. No temperature difference between the various parts of the bath could be detected with this thermometer. The air temperature of the upper half of the cabinet was maintained at 25.0 ± 0.1 °C by means of a heater connected to an air bellows, microswitch and fan.

The conductance cell was placed in the oil bath through two double-thickness perspex doors in the upper half of the cabinet. The measuring leads from the bridge were dipped into two small tubes of mercury in the oil bath. Two further leads
from these tubes were dipped in the mercury in the cell
electrode tubes.\textsuperscript{(120 & 124)}

(4-2) Materials

(i) Solvents

Conductivity Water

The conductivity water used for the determination of
cell constants was prepared by the method described by Al-Najar\textsuperscript{(101)}
It had a specific conductance in the range $0.2 - 0.4 \times 10^{-6}$ ohm\textsuperscript{-1} cm\textsuperscript{-1} at 25°C.

Propylene Carbonate was purified in the manner previously
described.

(ii) Solutes

Potassium chloride: "Analar" grade potassium chloride,
B.D.H., was recrystallised three times from conductivity water,
dried at 110°C, and then heated to dull red heat in a platinum
 crucible. The purified salt was allowed to cool in a desiccator,
where it was stored, over phosphorus pentoxide.

Zinc halides: were purified and handled as described
previously.

Lithium chloride: The Fisher Certified Reagent grade salt
was dried for 5 hours at 130°C.

Zinc perchlorate: was prepared by dissolving Analar zinc
oxide in redistilled (about 72%) perchloric acid and concentrating
the solution on a water-bath to effect crystallisation. The solution was cooled to give fine crystals, which were washed with a small quantity of distilled water containing ice, and then recrystallised from distilled water to give well-formed crystals of zinc perchlorate hexahydrate. This is stable in air, and could be kept indefinitely in a desiccator over potassium hydroxide. Analysis for zinc content by E.D.T.A. titration, and for water content by thermogravimetric analysis, T.G.A., indicated that the material was 99.73% $\text{Zn(ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. The T.G.A. analysis also showed that heating zinc perchlorate hexahydrate leads to a gradual dehydration with the loss of hygroscopic water, the conversion of the hexahydrate into the dihydrate, and finally decomposition of the dihydrate. Thus the water of crystallisation is not removed completely before decomposition, and it is impossible to obtain anhydrous zinc perchlorate by heating the hexahydrate.

The compound of zinc perchlorate with dioxane was then prepared by gradually dissolving zinc perchlorate-hexahydrate in an excess of carefully purified dioxane, with stirring and gentle heating on the water-bath. On cooling the above solution, a fine white crystalline precipitate readily formed; this material was recrystallised thrice from purified dioxane. Analysis for zinc content by E.D.T.A. titration and for dioxane by T.G.A. showed that the crystals were zinc perchlorate-6-dioxane, with up to 20-25 wt% of absorbed dioxane. The latter volatilises readily in a desiccator over calcium chloride. Attempts to prepare anhydrous zinc perchlorate from
this compound following the method described by Chudinovskii\textsuperscript{129} were unsuccessful. Heating Zn(ClO$_4$)$_2$ \times C$_4$H$_8$O$_2$ leads to loss of both absorbed and combined dioxane and the formation of Zn(ClO$_4$)$_2$.C$_4$H$_8$O$_2$. At atmospheric pressure this compound is stable up to 100°C; above this temperature, part is converted into Zn(ClO$_4$)$_2$, but with appreciable decomposition to zinc oxide and chloride.

Ferric chloride: 'Analar' ferric chloride hexahydrate (B.D.H) was purified by the method described by Cocking\textsuperscript{130} with some modification. A long glass tube with three compartments separated by narrow constrictions was employed. The hydrated ferric chloride was placed in the first compartment and the tube was connected to a vacuum pump via a series of traps. The salt was sublimed under vacuum into the second compartment by heating with an electric tape wrapped round the compartment. The procedure was repeated to sublime this ferric chloride from the second to the third compartment; this was fitted with a break seal, so that a vacuum ampoule was obtained.
(5) **Experimental Techniques**

(5-1) **Preparation of Stock Solutions**

The stock solutions were prepared in the dry box, by weighing approximately the required amount of the purified salt under examination in a small stoppered glass tube. This was removed from the dry box, weighed accurately on an analytical balance, and then returned to the dry box, where it was introduced into a stoppered flask containing a known weight of purified solvent. Weighings were made to ± 0.0001 g., and buoyancy corrections were applied throughout. A fresh stock solution was made up for each experimental run.

(5-2) **Measurement of Conductance**

Before starting an experimental run the conductance cell was first cleaned, dried, and weighed accurately. Dry nitrogen was passed into the cell, which was then filled with the solvent up to the location mark, in the dry box. The cell and contents were re-weighed; a buoyancy correction was applied to the weight of solvent. The cell was then removed from the dry box, firmly clamped in the thermostat, and left to reach thermal equilibrium whilst a slow stream of dry nitrogen was passed through the cell.
The purpose of the dry nitrogen was threefold: to prevent contamination of the solvent and solutions by moisture from the atmosphere, to facilitate mixing of the solutions, and to inhibit electrolyte adsorption on the electrodes. To minimise the shaking effect\(^{(131)}\), and to obtain consistent resistance readings, the bridge was balanced immediately after the nitrogen flow had been shut off. When no readings were being taken, the solution was always kept agitated by a slow stream of dry nitrogen.

The solvent usually attained thermal equilibrium after one hour in the thermostat. Beyond this period, resistance readings were constant for up to ten hours, therefore it was assumed that the resistance of the solvent would remain constant for the duration of a run. Solutions of the electrolytes being studied were made up in the cell by the addition of small quantities of stock solution from a syringe, which was weighed before and after the addition. This addition was repeated at intervals of fifteen minutes, when once again thermal equilibrium had been reached, and the resistance became constant.

The following procedure was adopted for the measurement of the resistance of a solution, using the modified Wheatstone bridge. The resistance of the cell was first determined approximately by adjusting the resistance and capacitance boxes.
The gain of the detector was then increased and two null positions on the slide wire were found corresponding respectively to the usual circuit of the bridge, and that with the leads to the ratio arm reversed. These balance points were then redetermined accurately. The mean of the resistances measured was then taken to be the resistance of the solution. The frequency of measurement was 1 KHz; the waveform of the oscillator was checked periodically, and was found to be accurately sinusoidal. Possible errors due to polarisation were checked by taking series of readings at 1 KHz and 3 KHz. The maximum difference was 0.02%, so it was assumed that, for the electrolytes and concentrations studied, polarisation effects could be neglected.

The following procedure was adopted for the measurement of the conductance of a solution, using the autobalance universal bridge B642. The most suitable range was selected and all the decade controls set to zero positions. With the meter sensitivity switch at the most sensitive position, and the leads open-circuited both the trim controls were adjusted for zero reading of the capacitance and conductance meters; then with the meter sensitivity switch at the "calibrate" position, the capacitance meter was adjusted to +10 by means of the 'F.S.D.' control, while the conductance meter was set to zero by the 'Zero' control. As there is slight interaction between these controls, the adjustments were repeated till constant readings were obtained.
Finally, with the meter sensitivity switch at the 'Auto' position, the conductance of the cell was immediately displayed by the conductance meter.

The concentration of the solution was calculated from the known weights of stock solution and solvent used. The concentration was converted to volume concentration using the density of the solvent. The effect of the very small amount of the solute on the density of the solution was neglected. The specific conductance of the electrolyte $S$ was then determined by the equation:

$$ S = \left( \frac{1}{R} - \frac{1}{R_s} \right) \times \text{cell constant} \quad (4:1) $$

where $R$ is the resistance of the cell + solution;

$R_s$ is the resistance of the cell + solvent.

The cell constant was determined as described below.

The molar conductance of the electrolyte $\Lambda_{\text{exp}}$ could be obtained from the equation:

$$ \Lambda_{\text{exp}} = S \times 10^3 / \text{molar concentration} \quad (4:2) $$

(5-3) Determination of the Cell Constant

The cell constant was accurately determined by measurement of the conductances of a series of potassium chloride solutions of known concentration, whose resistances fell in the required range. The equivalent conductances were calculated from the semi-
empirical equation of Lind, Zwolenik and Fuoss\textsuperscript{(132)}:

\[ A = 149.93 - 94.65 C^{\frac{1}{2}} + 58.74 C \log C + 198.4 C \] (4:3)

This equation represents the equivalent conductances of potassium chloride solutions in water, at 25°C, and at any concentration \( C \) up to about 0.012 mole l\(^{-1}\), with an accuracy of about 0.013%.

A cell constant was obtained for each concentration by comparison of the observed conductance with the calculated specific conductance. From a series of measurements of the cell constant a mean value of 0.21385 ± .00004 cm\(^{-1}\) was obtained at 25°C. The individual values are shown below:

<table>
<thead>
<tr>
<th>( 10^4 C ) mole l(^{-1} )</th>
<th>Cell Constant cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.22951</td>
<td>0.21390</td>
</tr>
<tr>
<td>2.72408</td>
<td>0.21381</td>
</tr>
<tr>
<td>5.27293</td>
<td>0.21389</td>
</tr>
<tr>
<td>7.84071</td>
<td>0.21387</td>
</tr>
<tr>
<td>10.31588</td>
<td>0.21379</td>
</tr>
<tr>
<td>13.96394</td>
<td>0.21382</td>
</tr>
<tr>
<td>18.04376</td>
<td>0.21387</td>
</tr>
</tbody>
</table>

The cell constant was re-checked several times during the course of this work.
(6) Conductance Results

The experimental molar conductances $\Lambda_{\text{exp}}$ of zinc perchlorate, chloride, bromide, and iodide and of ferric chloride were measured in this work at different molar concentrations $C$; the results are given in Tables 12 to 16 respectively. Figures 11 and 12 show $\Lambda_{\text{exp}}$ vs. $C$ for zinc perchlorate and bromide, while Figure 13 shows these plots for zinc chloride and iodide.

The conductances of mixtures of lithium chloride and zinc chloride, each of 0.01 molar in PC, are given in Tables 17 to 19 and shown graphically in Figure 14.
<table>
<thead>
<tr>
<th>Soln.</th>
<th>$10^4 C$</th>
<th>$\Lambda_{\text{exp}}$</th>
<th>Soln.</th>
<th>$10^4 C$</th>
<th>$\Lambda_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mole $1^{-1}$</td>
<td>ohm$^{-1}$ cm$^{2}$ mole$^{-1}$</td>
<td></td>
<td>mole $1^{-1}$</td>
<td>ohm$^{-1}$ cm$^{2}$ mole$^{-1}$</td>
</tr>
<tr>
<td>1</td>
<td>0.3310</td>
<td>84.943</td>
<td>11</td>
<td>6.9822</td>
<td>92.595</td>
</tr>
<tr>
<td>2</td>
<td>0.6303</td>
<td>86.687</td>
<td>12</td>
<td>8.0820</td>
<td>92.021</td>
</tr>
<tr>
<td>3</td>
<td>0.9714</td>
<td>89.840</td>
<td>13</td>
<td>9.2685</td>
<td>91.465</td>
</tr>
<tr>
<td>4</td>
<td>1.4950</td>
<td>92.644</td>
<td>14</td>
<td>10.5360</td>
<td>90.803</td>
</tr>
<tr>
<td>5</td>
<td>1.9009</td>
<td>93.573</td>
<td>15</td>
<td>11.8897</td>
<td>90.097</td>
</tr>
<tr>
<td>6</td>
<td>2.5774</td>
<td>93.774</td>
<td>16</td>
<td>13.2856</td>
<td>89.371</td>
</tr>
<tr>
<td>7</td>
<td>3.2491</td>
<td>93.903</td>
<td>17</td>
<td>14.7811</td>
<td>88.611</td>
</tr>
<tr>
<td>8</td>
<td>4.2049</td>
<td>93.841</td>
<td>18</td>
<td>16.2667</td>
<td>87.841</td>
</tr>
<tr>
<td>9</td>
<td>5.0613</td>
<td>93.449</td>
<td>19</td>
<td>17.8080</td>
<td>87.084</td>
</tr>
<tr>
<td>10</td>
<td>5.9570</td>
<td>93.130</td>
<td>20</td>
<td>19.2859</td>
<td>86.426</td>
</tr>
</tbody>
</table>
### TABLE 13

Experimental Conductance Data of Zinc chloride in PC at 25°C

<table>
<thead>
<tr>
<th>Soln.</th>
<th>$10^4 C$ mole $^{-1}$</th>
<th>$\Lambda_{exp}$ ohm$^{-1}$cm$^2$mole$^{-1}$</th>
<th>Soln.</th>
<th>$10^4 C$ mole $^{-1}$</th>
<th>$\Lambda_{exp}$ ohm$^{-1}$cm$^2$mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3258</td>
<td>21.309</td>
<td>13</td>
<td>6.2779</td>
<td>6.157</td>
</tr>
<tr>
<td>2</td>
<td>0.4155</td>
<td>21.082</td>
<td>14</td>
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TABLE 14

Experimental Conductance Data of Zinc Bromide in PC at 25°C

<table>
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<tr>
<th>Soln.</th>
<th>$10^4 C$ mole $^{-1}$</th>
<th>$\Lambda_{\text{exp}}$ ohm$^{-1}$cm$^2$ mole$^{-1}$</th>
<th>Soln.</th>
<th>$10^4 C$ mole $^{-1}$</th>
<th>$\Lambda_{\text{exp}}$ ohm$^{-1}$cm$^2$ mole$^{-1}$</th>
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### TABLE 15

Experimental Conductance Data of Zinc Iodide in PC at 25°C

<table>
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<th>Soln.</th>
<th>$10^4 C$ mole $^{-1}$</th>
<th>$\Lambda_{\text{exp}}$ ohm$^{-1}$ cm$^2$ mole$^{-1}$</th>
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</thead>
<tbody>
<tr>
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</tr>
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</table>


TABLE 16

Experimental Conductance Data of Ferric Chloride in PC at 25°C

<table>
<thead>
<tr>
<th>Soln.</th>
<th>$10^4 C$ mole $^{-1}$</th>
<th>$\Lambda_{\text{exp}}$ ohm$^{-1}$cm$^{2}$mole$^{-1}$</th>
<th>Soln.</th>
<th>$10^4 C$ mole $^{-1}$</th>
<th>$\Lambda_{\text{exp}}$ ohm$^{-1}$cm$^{2}$mole$^{-1}$</th>
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</table>
FIGURE 11

Molar conductance in PC at 25°C

\[ \text{Zn} \left( \text{ClO}_4 \right)_2 \]
FIGURE 12

Molar conductance in PC at 25°C

ZnBr₂
FIGURE 13

Molar conductances in PC at 25°C

+ ZnCl\textsubscript{2}

○ ZnI\textsubscript{2}
### TABLE 17

**Experimental Conductance of mixed Electrolyte**

LiCl - ZnCl$_2$ in PC at 25°C

<table>
<thead>
<tr>
<th>Soln.</th>
<th>$10^4 C$ mole $^{-1}$</th>
<th>$\Lambda_{exp}$ ohm$^{-1}$cm$^2$mole$^{-1}$</th>
<th>Soln.</th>
<th>$10^4 C$ mole $^{-1}$</th>
<th>$\Lambda_{exp}$ ohm$^{-1}$cm$^2$mole$^{-1}$</th>
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### TABLE 18

Experimental Conductance of mixed Electrolyte

LiCl - ZnCl$_2$ in PC at 25°C

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<th>$\Lambda_{exp}$ ohm$^{-1}$cm$^2$mole$^{-1}$</th>
<th>Soln.</th>
<th>$10^4$C mole $^{-1}$</th>
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TABLE 19

Experimental Conductance of mixed Electrolyte
LiCl - ZnCl₂ in PC at 25°C.

<table>
<thead>
<tr>
<th>Soln.</th>
<th>10⁴C mole⁻¹</th>
<th>( \Lambda_{\text{exp}} ) ohm⁻¹cm²mole⁻¹</th>
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<tr>
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</table>
FIGURE 14

Molar conductances of LiCl-ZnCl₂ mixtures in PC at 25°C

- 100% LiCl
- 80% LiCl + 20% ZnCl₂
- 60% LiCl + 40% ZnCl₂
- 40% LiCl + 60% ZnCl₂
- 20% LiCl + 80% ZnCl₂
(7) Treatment of Results

In the present work, the Murphy–Cohen conductance equation (2 : 11) was modified to allow for various forms of ion association which produce a pair of ions:

\[ A = \alpha \left[ A_0 + B K^* A_1 + (B K^*)^2 \ln (B K^*) A_2 + (B K^*)^2 A_2 \right] \quad (5 : 1) \]

where \( \alpha \) is the fraction of the electrolyte present as free ions i.e. the degree of dissociation. \( K^* \) is here a function of the ionic concentration \( \alpha C \).

The activity coefficients were calculated by means of the extended form of the Debye-Hückel equation (3 : 5) and compared to those of the Murphy–Cohen equation (3 : 6).

The effect of the choice of the \( \alpha \) parameter upon the interpretation of the conductance data has been fully investigated; see the discussion on page 116.

Extrapolation methods (133) provide a useful means of evaluation of \( K_A \) and \( A_0 \) using a preselected range of \( \alpha \) values. However, in order to obtain an independent set of these three parameters, it is necessary to treat the conductance data by one of the minimisation methods (134).

Several computer programs have been developed to compute the three parameters \( A_0 \), \( \alpha \) and \( K_A \) or \( \alpha \), based on
the following minimisation technique. An example of their structures is given in the Appendix. The program calls for the following sequence of operations:

Given a set of conductance data \( C_n \), \( n = 1 \ldots N \), and solvent properties \( D \) and \( \eta \) and temperature \( T \), the three parameters are obtained by successive approximations. For a selected value of \( K_A \), \( \alpha \) is calculated at each concentration by the preselected expression for \( K_A \). The extended forms of the Debye-Hückel (3:5) and Murphy-Cohen (3:6) equations are used to calculate the activity coefficients. Since \( f_+ \) in turn depends on \( \alpha \) through \( I \), the solution must be obtained by successive approximations. The cycle is repeated until two successive values of \( \alpha \) differ by less than \( \alpha \times 10^{-6} \). Estimated initial values of \( \Lambda_0 \) and \( \alpha \) are used to start the cycle of approximations. The difference \( (\Lambda_{\text{calc}} - \Lambda_{\text{exp}}) \) is computed for each experimental point and the parameters \( S^2 \) and \( \delta \) are calculated for the given \( K_A \), \( \Lambda_0 \) and \( \alpha \) where

\[
S^2 = \sum_1^N (\Lambda_{\text{calc}} - \Lambda_{\text{exp}})^2; \quad \delta = (S^2/N)^{\frac{1}{2}} \quad (5:2)
\]

The three parameters are then changed by predetermined incremental amounts to give new values of \( S^2 \) and \( \delta \). The final values of the three parameters that minimise \( S^2 \) are then found by visual inspection. This technique not only gives the best fit of the experimental results by a set of
parameters but also examines the latitude available in varying the parameters while obtaining an acceptable fit to the data, and enables one to investigate separate concentration ranges of the data, in which different equilibria may obtain.

(7-1) Tests of the Murphy-Cohen Equation

The Murphy-Cohen equation (2 : 11) is applicable to both symmetrical and unsymmetrical electrolytes. The modified form, equation(5 : 1), has been tested with "strong" electrolytes such as potassium chloride and calcium chloride in water, as well as "weak" or ion paired electrolytes such as magnesium sulphate and acetic acid in water. A satisfactory fit was obtained in all cases. A selection of these results is shown in Tables 20 to 23.

However, the equation is not able, by the present treatment, to yield a satisfactory interpretation of the conductance data in low dielectric media. The critical value of dielectric constant below which the method fails is D=20, as can be seen from Table 24.
**Potassium Chloride** (135)

**Test of Equation (5:1)**

<table>
<thead>
<tr>
<th>$10^4 C$ mole $^{-1}$</th>
<th>$\Lambda_{exp}$ ohm$^{-1}$cm$^2$ mole$^{-1}$</th>
<th>$\Delta \Lambda = \Lambda_{calc} - \Lambda_{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9825</td>
<td>148.61</td>
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</tr>
<tr>
<td>3.0907</td>
<td>148.29</td>
<td>0.005</td>
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<tr>
<td>4.1381</td>
<td>148.10</td>
<td>0.073</td>
</tr>
<tr>
<td>5.2151</td>
<td>147.81</td>
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<td>8.1535</td>
<td>147.30</td>
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</tr>
<tr>
<td>9.8869</td>
<td>147.09</td>
<td>0.090</td>
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</tbody>
</table>

**Best fit values:**

- $\Lambda_0 = 149.95 \pm 0.01$
- $a = 3.2 \pm 0.1 \text{Å}$
- $s^2 = 0.015$
- $\delta = 0.050$
TABLE 21

Calcium Chloride

Test of Equation (5:1)

<table>
<thead>
<tr>
<th>$10^4 C$ mole $^{-1}$</th>
<th>$\Lambda_{\text{exp}}$ ohm$^{-1}$cm$^2$equiv.$^{-1}$</th>
<th>$\Delta \Lambda = \Lambda_{\text{calc}} - \Lambda_{\text{exp}}$</th>
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<tr>
<td>0.7805</td>
<td>133.657</td>
<td>0.038</td>
</tr>
<tr>
<td>1.7618</td>
<td>132.594</td>
<td>0.069</td>
</tr>
<tr>
<td>4.0585</td>
<td>130.926</td>
<td>0.055</td>
</tr>
<tr>
<td>8.2218</td>
<td>128.909</td>
<td>0.021</td>
</tr>
<tr>
<td>12.7435</td>
<td>127.317</td>
<td>0.003</td>
</tr>
<tr>
<td>18.1780</td>
<td>125.812</td>
<td>-0.002</td>
</tr>
<tr>
<td>21.8466</td>
<td>124.948</td>
<td>-0.004</td>
</tr>
</tbody>
</table>

Best fit values:

\[ \Lambda_0 = 135.85 \pm 0.01 \]
\[ a = 6.05 \pm 0.01 \text{ Å} \]
\[ S^2 = 0.0096 \]
\[ \delta = 0.0371 \]
## TABLE 22

**Magnesium Sulphate**

(137)

**Test of equation (5:1)**

<table>
<thead>
<tr>
<th>$10^4$C mole $^{-1}$</th>
<th>$\Lambda_{exp}$ ohm$^{-1}$cm$^2$equiv.$^{-1}$</th>
<th>$\Lambda_{calc} - \Lambda_{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8511</td>
<td>127.11</td>
<td>0.017</td>
</tr>
<tr>
<td>1.9936</td>
<td>123.13</td>
<td>0.023</td>
</tr>
<tr>
<td>3.0899</td>
<td>120.33</td>
<td>0.037</td>
</tr>
<tr>
<td>4.2701</td>
<td>117.89</td>
<td>0.032</td>
</tr>
<tr>
<td>5.5970</td>
<td>115.50</td>
<td>-0.098</td>
</tr>
<tr>
<td>7.1965</td>
<td>113.14</td>
<td>-0.062</td>
</tr>
</tbody>
</table>

Best fit values:

- $K_A = 198 \pm 1$
- $\Lambda_0 = 133.38 \pm 0.01$
- $\bar{\sigma} = 7.7 \pm 0.1 \AA$
- $s^2 = 0.017$
- $\delta = 0.053$
**TABLE 23**

(101)

**Acetic Acid**

Test of Equation (5:1)

<table>
<thead>
<tr>
<th>$10^4 C_\text{mole}^{-1}$</th>
<th>$\Lambda_{\text{exp}} \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$</th>
<th>$\Delta \Lambda = \Lambda_{\text{calc}} - \Lambda_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.9636</td>
<td>74.25</td>
<td>-0.002</td>
</tr>
<tr>
<td>5.9636</td>
<td>61.84</td>
<td>-0.001</td>
</tr>
<tr>
<td>10.1661</td>
<td>48.33</td>
<td>0.004</td>
</tr>
<tr>
<td>12.4782</td>
<td>43.92</td>
<td>-0.002</td>
</tr>
<tr>
<td>14.4782</td>
<td>40.62</td>
<td>0.007</td>
</tr>
<tr>
<td>17.3467</td>
<td>37.62</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Best fit values:

- $K_A = 57260 \pm 10$
- $\Lambda_o = 390.51 \pm 0.01$
- $a = 5.7 \pm 0.1\AA$
- $s^2 = 0.001$
- $\delta = 0.0036$
TABLE 24
Tetrabutylammonium Bromide in Methanol-Carbon Tetrachloride Mixtures (138)

<table>
<thead>
<tr>
<th>D</th>
<th>$K_A$</th>
<th>$\Lambda_o$</th>
<th>$a$</th>
<th>$s^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.63</td>
<td>11.7</td>
<td>96.2</td>
<td>5.8</td>
<td>0.003</td>
</tr>
<tr>
<td>29.74</td>
<td>16.0</td>
<td>88.3</td>
<td>6.4</td>
<td>0.008</td>
</tr>
<tr>
<td>26.72</td>
<td>36.0</td>
<td>81.7</td>
<td>5.0</td>
<td>0.007</td>
</tr>
<tr>
<td>23.80</td>
<td>72.0</td>
<td>75.1</td>
<td>4.8</td>
<td>0.015</td>
</tr>
<tr>
<td>22.23</td>
<td>111</td>
<td>72.7</td>
<td>4.8</td>
<td>0.008</td>
</tr>
<tr>
<td>20.13</td>
<td>193</td>
<td>68.5</td>
<td>5.35</td>
<td>0.099</td>
</tr>
<tr>
<td>15.31</td>
<td>2920</td>
<td>57.6</td>
<td>5.25</td>
<td>56.63</td>
</tr>
<tr>
<td>12.02</td>
<td>1900</td>
<td>36.2</td>
<td>5.7</td>
<td>22514</td>
</tr>
</tbody>
</table>

Nevertheless, the treatment is applicable to the experimental results of this work, since PC has a dielectric constant of 64.4.
Possible Modes of Ionisation of 2:1 Electrolytes

We have tested four possible single modes of ionisation of 2:1 electrolytes:

\[ \text{MA}_2 \rightleftharpoons \text{MA}^+ + \text{A}^- \quad (6:1) \]
\[ \text{MA}_2 \rightleftharpoons \text{M}^{2+} + 2\text{A}^- \quad (6:2) \]
\[ 2 \text{MA}_2 \rightleftharpoons \text{MA}^+ + \text{MA}_3^- \quad (6:3) \]
\[ 2 \text{MA}_2 \rightleftharpoons \text{M}^{2+} + \text{MA}_4^{2-} \quad (6:4) \]

The association constant describing reaction (6:1) will be

\[ K_A = \frac{(1 - \alpha)}{C_\alpha^2 f_{1.1}^2} \quad (6:5) \]

hence

\[ \alpha = \frac{-1 + (1 + 4C f_{1.1}^2 K_A)^{1/2}}{2C f_{1.1}^{3/2} K_A} \quad (6:6) \]

where \( f_{1.1} \) is the activity coefficient calculated from equation (3:5) or (3:6). The ionic strength of this solution is

\[ I = C_\alpha \text{ mole l}^{-1}, \text{ equation (2:5).} \]

The association constant for reaction (6:2) is

\[ K_A = \frac{(1 - \alpha)}{4C_\alpha^2 \alpha^3 f_{1.2}^3} \quad (6:7) \]

hence

\[ 4K_A C_\alpha^2 f_{1.2}^3 \alpha^3 + \alpha - 1 = 0 \quad (6:8) \]

To solve the above cubic equation in \( \alpha \) the method of Grant and Hitchins\(^{(139)}\) was used, employing the CO2ACA NAG
library program. This routine finds all the roots of a polynomial with real coefficients. The ionic strength in this case is

\[ I = 3C \, \alpha \, \text{mole} \, l^{-1} \]

For the third mode of ionisation, equation (6.3), the association constant is given by

\[ K_A = \frac{4(1-\alpha)^2}{\alpha^2 f^2_{1,1}} \]  

(6.9)

hence

\[ \alpha = \frac{-4+2(K_A f^2_{1,1})^{1/2}/(K_A f^2_{1,1} - 4)}{2} \]  

(6.10)

and

\[ I = C \, \alpha/2 \, \text{mole} \, l^{-1} \]

Finally, for reaction (6.4)

\[ K_A = \frac{4(1-\alpha)^2}{\alpha^2 f^2_{2,2}} \]  

\[ I = 2C \, \alpha \, \text{mole} \, l^{-1} \]  

(6.11)

On the other hand, if there are two stages of ionisation

\[
\begin{align*}
\text{MA}_2 & \rightleftharpoons \text{K}_1 \to \text{MA}^+ + \text{A}^- \\
C(1-\alpha_1) \quad & \begin{array}{c} \downarrow \text{K}_2 \\ \text{M}^{2+} + \text{A}^- \end{array} \\
C\alpha_1(1-\alpha_2) \quad & \begin{array}{c} \downarrow \text{K}_2 \\ \text{C} \alpha_1 \alpha_2 \end{array} \\
C\alpha_1(1-\alpha_2) \quad & \begin{array}{c} \downarrow \text{K}_2 \\ \text{C} \alpha_1 \alpha_2 \end{array}
\end{align*}
\]  

(6.12)
we will have a mixed electrolyte solution.

There are at present no satisfactory equations for this situation. If we assume additivity of ion conductances, we can derive the equation:

$$1000 S_{\text{soln}} = \sum_i C_i \lambda_i$$  \hspace{1cm} (6:13)

Summation is over all ionic species present;

$C_i$ and $\lambda_i$ must be in compatible units: equivalent $1^{-1}$ and ohm $^{-1}$ cm$^2$ equivalent $^{-1}$, or moles $l^{-1}$ and ohm $^{-1}$ cm$^2$ mole$^{-1}$.

We have taken the limiting Debye-Hückel - Onsager equation for a single ionic species $\lambda_i$ where

$$\lambda_i = \lambda_i^0 \left[ 2.801 \times 10^6 q_i z_i^z_i |\lambda_i^0/(DT) |^{3/2} (1+q_i) + 41.25 |z_i|/\mu(DT)^{1/2} \right] I_i^{1/2}$$  \hspace{1cm} (6:14)

and $[I_i] = \frac{1}{2} \left[ 4[M^2+]+[MA^+]\right]+[A^-] \hspace{1cm} (6:15)$

Onsager and Kim$^{(140)}$ introduced a modification for the effect of mixed ions upon the relaxation term. We find little improvement over equation (6:14) when tested by the conductance data for oxalic acid$^{(141a)}$, for which equation (6:13) takes the form:

$$1000 S_{\text{soln}} = C_{H^+} + \lambda_{H^+} + C_{HOX^-} \lambda_{HOX^-} + C_{OX^2-} \lambda_{OX^2-}$$  \hspace{1cm} (6:16)
In (6:16), the ion concentrations are known from the well-defined values of $K_1$ and $K_2$.

In Table 25, the experimental data for Oxalic acid in aqueous solution at 25°C is tested by equation (6:14).

**TABLE 25**

**Oxalic Acid**

$$K_1 = 16.95 \quad K_2 = 15.625 \times 10^2$$

$$\lambda_{H^+} = 349.8 \quad \lambda_{HOX^-} = 40.20 \quad \lambda_{OX^{2-}} = 74.15$$

<table>
<thead>
<tr>
<th>$10^4 C$ equiv l$^{-1}$</th>
<th>$\lambda_{exp \ ohm^{-1} cm^2 equiv^{-1}}$</th>
<th>$\lambda_{calc \ ohm^{-1} cm^2 equiv^{-1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6224</td>
<td>289.807</td>
<td>289.753</td>
</tr>
<tr>
<td>0.7023</td>
<td>284.039</td>
<td>283.980</td>
</tr>
<tr>
<td>0.7863</td>
<td>278.749</td>
<td>278.685</td>
</tr>
<tr>
<td>1.1830</td>
<td>260.694</td>
<td>260.608</td>
</tr>
<tr>
<td>2.1110</td>
<td>238.739</td>
<td>238.606</td>
</tr>
<tr>
<td>7.6480</td>
<td>206.333</td>
<td>205.963</td>
</tr>
<tr>
<td>11.50</td>
<td>199.594</td>
<td>199.068</td>
</tr>
<tr>
<td>13.55</td>
<td>197.139</td>
<td>196.532</td>
</tr>
<tr>
<td>17.74</td>
<td>193.311</td>
<td>192.539</td>
</tr>
<tr>
<td>19.68</td>
<td>191.865</td>
<td>191.018</td>
</tr>
</tbody>
</table>
Within the concentration range $0.6 - 20 \times 10^{-4}$ equiv. $l^{-1}$,
$A_{\text{calc}}$ from equation (6:14) and $A_{\text{exp}}$ agree within 0.8%. We are therefore justified in using this equation to interpret the conductance data, where applicable.
In the present work, conductances were measured over the concentration range $0.20$ to $20.00 \times 10^{-4}$ molar. The results for zinc perchlorate are shown in Table 12 and Figure 11. It is interesting to note that a maximum $\Lambda$ is observed at a concentration about $3 \times 10^{-4}$ molar. This phenomenon has been observed in other solvents of high dielectric constant. Dawson et al.\textsuperscript{(142)} found maxima for cerium perchlorate and several other salts in N-methylacetamide ($D = 165.5$ at $40^\circ$C) at $C < 3 \times 10^{-4}$ molar. Jones et al.\textsuperscript{(143)} reported similar maxima for some transition metal salts in formamide ($D = 111.5$ at $20^\circ$C) at $C$ about $1.5 \times 10^{-3}$ molar.

In order to explain the rapid increase in $\Lambda$ as the concentration is increased, a reaction is required in which the number of ions per mole of solute increases with increasing concentration, such as:

\begin{align*}
3 MA_2 & \rightleftharpoons MA^+ + M_2A_5^- & \quad (7:1) \\
4 MA_2 & \rightleftharpoons MA^+ + M_3A_7^- & \quad (7:2)
\end{align*}

Let $K_{A_1}$ and $K_{A_2}$ be the association constants for $(7:1)$ and $(7:2)$ respectively, then
Therefore, (7:3) or (7:4) predicts that the number of ions per mole of solute will increase with increasing concentration. Consequently, the conductance calculated as: \( \Lambda = 1000 \text{ S/C} \) will also increase.

Alternatively, if the ionisation takes place in the two stages

\[
3 \text{M}^{2+} + 6\text{A}^- \xrightleftharpoons[K_1]{K_2} 3 \text{M} \text{A}_2 \xrightleftharpoons[]{} \text{M}^+ + \text{M}_2\text{A}_5^- \quad (7:5)
\]

as the stoichiometric concentration \( C \) increases, the total ionic concentration increases, at first more slowly than \( C \) and then more rapidly; thus, if we assume that, at these concentrations, the specific conductance \( S \) is proportional to \( C \) (i.e. the ionic velocities are constant), then \( \Lambda \) (proportional to \( S/C \)) passes through a maximum, see Table 26 and Figure 15. \( I' \) (which is not the usual ionic strength \( I \)) gives the total ionic concentration in equiv.\( l^{-1} \).

Thus, the shape of this curve and the maximum \( \Lambda \) observed, could be attributed to the fact that different ionic species predominate in different concentration regions. However, it is difficult to suggest what the complex ions might be, in the present case; the species \( \text{Zn}_2(\text{ClO}_4)_5^- \) does not seem
\[ K_1 = 10^{24} \text{ mole}^{-6} \quad K_2 = 10^3 \text{ mole} \quad \alpha = 0.9831 \]

\[ \Sigma I' = 2[M^{2+} 2A^{-}] + [MA^+ M_2A_5^-] \]

<table>
<thead>
<tr>
<th>( C ) mole ( l^{-1} )</th>
<th>( \Delta C )</th>
<th>( \Delta I' )</th>
<th>( \Delta I'^{'} )</th>
<th>( \frac{I'^{'}}{C \alpha A} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-6} )</td>
<td>1.99( \times 10^{-6} )</td>
<td>1.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 3 \times 10^{-6} )</td>
<td>6.00( \times 10^{-6} )</td>
<td>2.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.33</td>
<td>2.28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 7 \times 10^{-6} )</td>
<td>1.37( \times 10^{-5} )</td>
<td>1.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.42</td>
<td>1.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 10^{-5} )</td>
<td>1.92( \times 10^{-5} )</td>
<td>1.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 3 \times 10^{-5} )</td>
<td>4.75( \times 10^{-5} )</td>
<td>1.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.33</td>
<td>1.67</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 7 \times 10^{-5} )</td>
<td>7.95( \times 10^{-5} )</td>
<td>1.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.42</td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 10^{-4} )</td>
<td>9.57( \times 10^{-5} )</td>
<td>0.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 3 \times 10^{-4} )</td>
<td>1.71( \times 10^{-4} )</td>
<td>0.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.33</td>
<td>1.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 7 \times 10^{-4} )</td>
<td>1.82( \times 10^{-4} )</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.42</td>
<td>2.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 10^{-3} )</td>
<td>3.80( \times 10^{-4} )</td>
<td>\textbf{0.38}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 5 \times 10^{-3} )</td>
<td>1.52( \times 10^{-3} )</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 10^{-2} )</td>
<td>2.97( \times 10^{-3} )</td>
<td>0.297</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 15

Theoretical variation of $S$ and $\Lambda$ with concentration, calculated from equation (7:5).
very likely. Alternatively, the effect of changes in the nature of the solvent environment with concentration of the multivalent cation might provide an explanation. In a solvent like PC, which is known to solvate the cations intensively, such an influence cannot be neglected completely. Measurements did not reveal any marked change in the macroscopic viscosity of the solution, within the concentration range of the conductance maxima. However, diffusion studies could provide evidence of solute - solvent interaction and indicate if the variation between the macroscopic viscosity of the solution, and the microscopic viscosity in the immediate vicinity of the ionic species, is operative. It is known that the dielectric constant, in the immediate vicinity of an ion, is very much lower than in the bulk of the solution; and both effects (of changes in viscosity and in dielectric constant) may become important in very dilute solution.

Considering the zinc perchlorate conductance data at a concentration higher than $3 \times 10^{-4}$ molar, we may analyse the data by the Murphy-Cohen equation (5:1) with the various modes of ionisation considered above. The experimental results are best fitted by the equilibrium (6:2) as shown in Table 27, where $C$ is the molar concentration and $\Lambda_{\text{exp}}^\gamma$ is the experimental equivalent conductance on this basis. The best fit values of the three parameters $K_A$, $\Lambda_0$, and $\bar{g}$ are listed
### TABLE 27

\[ \text{Zn}(\text{ClO}_4)_2 \rightleftharpoons \text{Zn}^{2+} + 2\text{ClO}_4^- \]

\[ t = 25^\circ \text{C} \]

<table>
<thead>
<tr>
<th>Soln.</th>
<th>(10^4 \text{ C mole}^{-1})</th>
<th>(\Lambda_{\text{exp}} \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1})</th>
<th>(\Delta \Lambda = \Lambda_{\text{calc}} - \Lambda_{\text{exp}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.2049</td>
<td>46.92_1</td>
<td>-0.03_8</td>
</tr>
<tr>
<td>2</td>
<td>5.0613</td>
<td>46.72_5</td>
<td>-0.02_1</td>
</tr>
<tr>
<td>3</td>
<td>5.9570</td>
<td>46.56_5</td>
<td>0.03_8</td>
</tr>
<tr>
<td>4</td>
<td>6.9822</td>
<td>46.29_8</td>
<td>0.02_0</td>
</tr>
<tr>
<td>5</td>
<td>8.0820</td>
<td>46.01_1</td>
<td>0.00_8</td>
</tr>
<tr>
<td>6</td>
<td>9.2685</td>
<td>45.73_3</td>
<td>0.02_4</td>
</tr>
<tr>
<td>7</td>
<td>10.5360</td>
<td>45.40_2</td>
<td>0.01_1</td>
</tr>
<tr>
<td>8</td>
<td>11.8897</td>
<td>45.04_9</td>
<td>-0.00_1</td>
</tr>
<tr>
<td>9</td>
<td>13.2856</td>
<td>44.68_6</td>
<td>-0.01_0</td>
</tr>
<tr>
<td>10</td>
<td>14.7811</td>
<td>44.30_6</td>
<td>-0.01_2</td>
</tr>
<tr>
<td>11</td>
<td>16.2667</td>
<td>43.92_1</td>
<td>-0.02_2</td>
</tr>
<tr>
<td>12</td>
<td>17.8080</td>
<td>43.54_2</td>
<td>-0.01_5</td>
</tr>
<tr>
<td>13</td>
<td>19.2859</td>
<td>43.21_3</td>
<td>0.02_2</td>
</tr>
</tbody>
</table>

**Best fit Values:**

\[ K_A = 14910 \pm 10 \]

\[ \Lambda_0 = 48.89 \pm 0.01 \]

\[ a = 2.4 \text{ Å} \]

\[ \delta = 0.0214 \]

\[ s^2 = 0.0059 \]
together with the corresponding values of $S^2$ and $\delta$
eq(5:2). Tables 28 gives the values of $a$
eq(6:8) at each concentration, together with $f_{\pm DH}$ and $f_{\pm MC}$ calculated from equations (3:5) and (3:6) respectively. As can be seen, $f_{\pm MC}$ is slightly higher than $f_{\pm DH}$; this could be attributed to the additional term $f_2(BK)^2$ in the Murphy-Cohen expression.

The value of the $a$ parameter affects $\Lambda_0$ and $K_A$ as shown in Table 29 and Figure 16; $a$ values from 2.1 to 9 yield entirely acceptable agreement as shown by $S^2$ and $\delta$. The minimum in $S^2$ obtained at 2.4 $\AA$ could be reproduced, but at a much higher value of $a$. The very large variation of $K_A$, over the range of $a$ values studied, adds weight to the argument of Prue et al [134b] that an association constant cited without specifying the other parameters involved, in particular $a$, is meaningless. The indeterminacy of $K_A$, when $a$ is not specified, has also been noted by Guggenheim [145].

It is interesting to note that the final values of $\Lambda_0$ will also depend on $a$. Although the variation is only about 1%, there is no reason for the mobilities of ions at infinite dilution to depend on the location of the boundary between free and associated ions, but possibly this variation results from treating $\Lambda_0$ as a variable parameter to fit the data.
TABLE 28

$$\text{Zn(Clo}_4\text{)}_2 \rightleftharpoons \text{Zn}^{2+} + 2\text{ClO}_4^-$$

$t = 25^\circ C$

<table>
<thead>
<tr>
<th>Soln.</th>
<th>$\alpha$</th>
<th>$f_{\pm\text{Dh}}$</th>
<th>$f_{\pm\text{MC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9926</td>
<td>0.8942</td>
<td>0.9032</td>
</tr>
<tr>
<td>2</td>
<td>0.9898</td>
<td>0.8847</td>
<td>0.8950</td>
</tr>
<tr>
<td>3</td>
<td>0.9864</td>
<td>0.8758</td>
<td>0.8872</td>
</tr>
<tr>
<td>4</td>
<td>0.9821</td>
<td>0.8665</td>
<td>0.8793</td>
</tr>
<tr>
<td>5</td>
<td>0.9771</td>
<td>0.8575</td>
<td>0.8716</td>
</tr>
<tr>
<td>6</td>
<td>0.9713</td>
<td>0.8486</td>
<td>0.8640</td>
</tr>
<tr>
<td>7</td>
<td>0.9648</td>
<td>0.8399</td>
<td>0.8566</td>
</tr>
<tr>
<td>8</td>
<td>0.9575</td>
<td>0.8314</td>
<td>0.8494</td>
</tr>
<tr>
<td>9</td>
<td>0.9497</td>
<td>0.8234</td>
<td>0.8426</td>
</tr>
<tr>
<td>10</td>
<td>0.9411</td>
<td>0.8154</td>
<td>0.8359</td>
</tr>
<tr>
<td>11</td>
<td>0.9325</td>
<td>0.8081</td>
<td>0.8297</td>
</tr>
<tr>
<td>12</td>
<td>0.9235</td>
<td>0.8010</td>
<td>0.8237</td>
</tr>
<tr>
<td>13</td>
<td>0.9148</td>
<td>0.7947</td>
<td>0.8183</td>
</tr>
</tbody>
</table>
TABLE 29

\[ \text{Zn(ClO}_4\text{)}_2 \rightleftharpoons \text{Zn}^{2+} + 2\text{ClO}_4^- \]

\[ t = 25^\circ C \]

<table>
<thead>
<tr>
<th>( a ) (°)</th>
<th>( A )</th>
<th>( \Lambda_0 )</th>
<th>( 10^3 K_A )</th>
<th>( S^2 )</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>49.40</td>
<td>6.400</td>
<td>0.0453</td>
<td>0.0590</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>49.07</td>
<td>12.360–12.380</td>
<td>0.0132</td>
<td>0.0319</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>48.93</td>
<td>14.650–14.660</td>
<td>0.0072</td>
<td>0.0235</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>48.89</td>
<td>14.910–14.920</td>
<td>0.0059</td>
<td>0.0214</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>48.92</td>
<td>14.350–14.360</td>
<td>0.0087</td>
<td>0.0228</td>
<td></td>
</tr>
<tr>
<td>2.6</td>
<td>48.97</td>
<td>13.330–13.340</td>
<td>0.0088</td>
<td>0.0260</td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>49.04</td>
<td>12.300</td>
<td>0.0114</td>
<td>0.0297</td>
<td></td>
</tr>
<tr>
<td>2.8</td>
<td>49.11</td>
<td>11.250</td>
<td>0.0152</td>
<td>0.0341</td>
<td></td>
</tr>
<tr>
<td>2.9</td>
<td>49.16</td>
<td>10.200</td>
<td>0.0191</td>
<td>0.0384</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>49.22</td>
<td>9.400</td>
<td>0.0237</td>
<td>0.0427</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>49.45</td>
<td>5.550</td>
<td>0.0530</td>
<td>0.0639</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>49.47</td>
<td>5.350</td>
<td>0.0555</td>
<td>0.0654</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>49.43</td>
<td>5.850</td>
<td>0.0497</td>
<td>0.0618</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>49.39</td>
<td>6.650</td>
<td>0.0432</td>
<td>0.0574</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>49.37</td>
<td>7.450</td>
<td>0.0365</td>
<td>0.0530</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>49.29</td>
<td>8.250</td>
<td>0.0309</td>
<td>0.0488</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 16

Plots of the "best fit" values of $K_A$ (△), $\Lambda_0$ (○), and $\delta$ (×) calculated from the experimental data of zinc perchlorate in PC against the value of $a$ chosen.
Increasing the value of \( a \) would necessitate increasing that of \( K_A \). This could be predicted in a qualitative sense as follows: If \( a \) is changed from \( a_1 \) to \( a_2 \) \((a_2 > a_1)\), then an ion in the spherical shell \( \frac{4}{3\pi} (a_2^3 - a_1^3) \), opposite in sign to a reference ion, was formerly regarded as being free and will now be classed as associated. Therefore the numerical value of \( K_A \) should increase.

It seems that the general pattern of the variation of the three parameters \( K_A \), \( \Lambda_0 \) and \( a \) in both aqueous and non-aqueous solution falls into two categories. In the first, there is a range of values of \( a \) over which the goodness of the "best fit" attainable changes but the values of \( K_A \) and \( \Lambda_0 \) required to obtain that fit remain unaltered. This is well illustrated by Meites\(^{(146a)}\) using the conductance data of Shedlovsky\(^{(146b)}\) for aqueous solutions of acetic acid, Figure 17. This behavior would not be predicted on algebraic grounds, and is certainly not universal. The conditions under which it will arise are as yet not clear.

In the second category, varying the value of \( a \) will give a sharp minimum for certain \( K_A \) and \( \Lambda_0 \) values. Probably this is the more common situation\(^{(101)}\).

In conclusion, the most satisfactory means of expressing the characteristic parameters of an
Plots of the "best fit" values of $K_A$ (▲), $\Lambda_0$ (●), and $\delta$ (×) calculated from the experimental data for Acetic Acid solutions in water reference (146b) against the value of $a$ chosen.
electrolyte solution is always to quote $K_A$, $\Lambda_0$ and $\alpha$ since all are doubtless inter-related.

(8-2) **Zinc Chloride**

The results of the present work on zinc chloride are given in Table 13 and Figure 13. The analysis of these data are given in Table 30. The best fit values of the three parameters $K_A$, $\Lambda_0$ and $\alpha$ are listed together with the corresponding values of $S^2$ and $\delta$. This analysis assumes the following mode of ionization:

$$\text{ZnCl}_2 \rightleftharpoons \text{Zn}^{2+} + 2\text{Cl}^-$$

Table 31 gives the values of $\alpha$, $f_{DH}$, ml $f_{MC}$ at each concentration. It is interesting to note that $\alpha$ is very small even at these concentrations, due to the very large value of $K_A$ obtained.

The effect of $\alpha$ on $K_A$ and $\Lambda_0$ in this case falls into the first category in which there is a range of $\alpha$ values which change very slightly the best attainable fit, but do not alter the values of $K_A$ and $\Lambda_0$ required to obtain that fit, as can be seen from Table 32.

The method of continuous variations$^{(147)}$ was employed in this work to investigate the system lithium chloride-zinc chloride in PC. A typical set of data is shown in Figure 14, in which plots of $\Lambda_{exp}$
TABLE 30

\[
\text{ZnCl}_2 \xrightarrow{\text{t = 25°C}} \text{Zn}^{2+} + 2\text{Cl}^- \\
\]

<table>
<thead>
<tr>
<th>Soln.</th>
<th>(10^4 \text{ C}) mole (^{-1})</th>
<th>(\Lambda_{\text{exp}}^{-}) ohm(^{-1}) cm(^2) equiv(^{-1})</th>
<th>(\Delta\Lambda = \Lambda_{\text{calc}} - \Lambda_{\text{exp}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.2449</td>
<td>3.458</td>
<td>-0.036</td>
</tr>
<tr>
<td>2</td>
<td>6.2779</td>
<td>3.079</td>
<td>-0.080</td>
</tr>
<tr>
<td>3</td>
<td>7.3387</td>
<td>2.804</td>
<td>0.002</td>
</tr>
<tr>
<td>4</td>
<td>8.2538</td>
<td>2.631</td>
<td>-0.133</td>
</tr>
<tr>
<td>5</td>
<td>9.4308</td>
<td>2.457</td>
<td>-0.082</td>
</tr>
<tr>
<td>6</td>
<td>10.6897</td>
<td>2.316</td>
<td>-0.027</td>
</tr>
<tr>
<td>7</td>
<td>11.9427</td>
<td>2.209</td>
<td>0.027</td>
</tr>
<tr>
<td>8</td>
<td>13.2102</td>
<td>2.122</td>
<td>0.077</td>
</tr>
<tr>
<td>9</td>
<td>14.4637</td>
<td>2.053</td>
<td>0.124</td>
</tr>
<tr>
<td>10</td>
<td>15.6951</td>
<td>1.998</td>
<td>0.168</td>
</tr>
<tr>
<td>11</td>
<td>17.0699</td>
<td>1.945</td>
<td>0.061</td>
</tr>
<tr>
<td>12</td>
<td>18.4395</td>
<td>1.908</td>
<td>0.042</td>
</tr>
<tr>
<td>13</td>
<td>19.7029</td>
<td>1.871</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Best fit Values:

\[
K = 3.005 \times 10^8 \\
\Lambda_0 = 26.29 \pm 0.01 \\
a = 8 \text{ Å} \\
S^2 = 0.0888 \\
\delta = 0.0827
\]
### TABLE 31

\[ \text{ZnCl}_2 \rightleftharpoons \text{Zn}^{2+} + 2\text{Cl}^- \]

\( t = 25^\circ\text{C} \)

<table>
<thead>
<tr>
<th>Soln.</th>
<th>( \alpha )</th>
<th>( f_{\pm\text{DH}} )</th>
<th>( f_{\pm\text{MC}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1440</td>
<td>0.9536</td>
<td>0.9567</td>
</tr>
<tr>
<td>2</td>
<td>0.1287</td>
<td>0.9520</td>
<td>0.9553</td>
</tr>
<tr>
<td>3</td>
<td>0.1167</td>
<td>0.9506</td>
<td>0.9542</td>
</tr>
<tr>
<td>4</td>
<td>0.1083</td>
<td>0.9496</td>
<td>0.9532</td>
</tr>
<tr>
<td>5</td>
<td>0.0996</td>
<td>0.9484</td>
<td>0.9521</td>
</tr>
<tr>
<td>6</td>
<td>0.0920</td>
<td>0.9472</td>
<td>0.9511</td>
</tr>
<tr>
<td>7</td>
<td>0.0857</td>
<td>0.9461</td>
<td>0.9502</td>
</tr>
<tr>
<td>8</td>
<td>0.0804</td>
<td>0.9452</td>
<td>0.9494</td>
</tr>
<tr>
<td>9</td>
<td>0.0759</td>
<td>0.9443</td>
<td>0.9486</td>
</tr>
<tr>
<td>10</td>
<td>0.0720</td>
<td>0.9435</td>
<td>0.9479</td>
</tr>
<tr>
<td>11</td>
<td>0.0682</td>
<td>0.9427</td>
<td>0.9472</td>
</tr>
<tr>
<td>12</td>
<td>0.0649</td>
<td>0.9419</td>
<td>0.9465</td>
</tr>
<tr>
<td>13</td>
<td>0.0622</td>
<td>0.9412</td>
<td>0.9460</td>
</tr>
</tbody>
</table>
TABLE 32

\[
\text{ZnCl}_2 \rightleftharpoons \text{Zn}^{2+} + 2\text{Cl}^-
\]

\[t = 25^\circ\text{C}\]

<table>
<thead>
<tr>
<th>(a) Å</th>
<th>(s^2)</th>
<th>(a) Å</th>
<th>(s^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.5861</td>
<td>8</td>
<td>0.0888</td>
</tr>
<tr>
<td>3</td>
<td>0.0956</td>
<td>9</td>
<td>0.0887</td>
</tr>
<tr>
<td>4</td>
<td>0.0899</td>
<td>10</td>
<td>0.0886</td>
</tr>
<tr>
<td>5</td>
<td>0.0894</td>
<td>11</td>
<td>0.0886</td>
</tr>
<tr>
<td>6</td>
<td>0.0891</td>
<td>12</td>
<td>0.0885</td>
</tr>
<tr>
<td>7</td>
<td>0.0889</td>
<td>13</td>
<td>0.8885</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14</td>
<td>0.0884</td>
</tr>
</tbody>
</table>
against C for a series of mixtures of 0.01 molar lithium chloride and 0.01 molar zinc chloride are shown. Curves of y, the composition of these mixtures, against ΔS, the difference between the experimental value of the specific conductance and the value calculated assuming no interaction, are shown in Figure 18. It can be seen from these curves at different concentrations, $1.5 \times 10^{-3}$ to $2.0 \times 10^{-3}$ molar that only a single compound is formed. At concentrations $> 1.5 \times 10^{-3}$ molar ΔS shows a maximum at 66 mole % of LiCl, indicating the formation of a 2:1 complex. The stability of this complex increased as the concentration increased. At a concentration below $1.5 \times 10^{-3}$ molar the maximum is ill defined, indicating that this compound may not be formed at low concentration. This result suggests the formation of the species $\text{ZnCl}_4^{2-}$ at a concentration above $1.5 \times 10^{-3}$ molar in the presence of excess chloride in zinc chloride PC solutions.

Our results, table 30 do not show evidence for this anion.

(8-3) Zinc Bromide

Analysis of the experimental conductance data, Table 14, of this salt by the Murphy-Cohen equation (5:1), using all four modes of ionisation, equations (6:1) to (6:4), did not give a satisfactory fit. Another approach
FIGURE 18

$\Delta S$ for the specific conductances of mixtures of 0.01 M LiCl with 0.01 ZnCl$_2$ at 25°C

1 at $2.0 \times 10^{-3}$ molar
2 at $1.9 \times 10^{-3}$ molar
3 at $1.75 \times 10^{-3}$ molar
4 at $1.60 \times 10^{-3}$ molar
5 at $1.50 \times 10^{-3}$ molar
is to consider different ranges of concentration separately. At low concentration $3.5 \times 10^{-5}$ to $9.5 \times 10^{-5}$, a fit was obtained assuming the following ionisation:

$$\text{ZnBr}_2 \rightleftharpoons \text{Zn}^{2+} + 2 \text{Br}^-$$

At higher concentration $> 2 \times 10^{-4}$ molar, a fit was obtained with:

$$2 \text{ZnBr}_2 \rightleftharpoons \text{Zn}^{2+} + \text{ZnBr}_4^{2-}$$

Neither of these was satisfactory, as can be seen from Tables 33 and 34.

Alternatively this behaviour could be attributed to successive modes of association, equation (6:12). Analysis of the data according to this assumption employing equation (6:14) gave a better fit, Table 35.
TABLE 33

\[ \text{ZnBr}_2 \rightleftharpoons \text{Zn}^{2+} + 2\text{Br}^- \]
\( t = 25^\circ\text{C} \)

<table>
<thead>
<tr>
<th>Soln.</th>
<th>(10^4\text{C}) mole (^{-1})</th>
<th>(\Lambda_{\text{exp}}) ohm(^{-1})cm(^2)equiv(^{-1})</th>
<th>(\Delta\Lambda = \Lambda_{\text{calc}} - \Lambda_{\text{exp}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3515</td>
<td>18.051</td>
<td>1.058</td>
</tr>
<tr>
<td>2</td>
<td>0.4577</td>
<td>15.770</td>
<td>0.644</td>
</tr>
<tr>
<td>3</td>
<td>0.5490</td>
<td>14.300</td>
<td>0.255</td>
</tr>
<tr>
<td>4</td>
<td>0.6482</td>
<td>12.574</td>
<td>-0.199</td>
</tr>
<tr>
<td>5</td>
<td>0.7862</td>
<td>10.772</td>
<td>-0.785</td>
</tr>
<tr>
<td>6</td>
<td>0.9497</td>
<td>9.113</td>
<td>-1.329</td>
</tr>
</tbody>
</table>

Fit values:

\[ K_A = 3.02 \times 10^8 \]
\[ \Lambda_0 = 26.99 \pm 0.01 \]
\[ a = 6 \ \text{\AA} \]
\[ S^2 = 4.0210 \]
\[ \delta = 0.8186 \]
TABLE 34

\[ 2 \text{ZnBr}_2 \rightleftharpoons \text{Zn}^{2+} + \text{ZnBr}_4^{2-} \]

\[ t = 25^\circ\text{C} \]

<table>
<thead>
<tr>
<th>Soln.</th>
<th>(10^4 C)</th>
<th>(\Lambda_{\text{exp}})</th>
<th>(\Lambda_{\text{calc}} - \Lambda_{\text{exp}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.3987</td>
<td>7.668</td>
<td>1.194</td>
</tr>
<tr>
<td>2</td>
<td>2.7484</td>
<td>7.256</td>
<td>0.826</td>
</tr>
<tr>
<td>3</td>
<td>3.1674</td>
<td>6.881</td>
<td>0.504</td>
</tr>
<tr>
<td>4</td>
<td>3.5721</td>
<td>6.612</td>
<td>0.280</td>
</tr>
<tr>
<td>5</td>
<td>4.2380</td>
<td>6.323</td>
<td>0.062</td>
</tr>
<tr>
<td>6</td>
<td>4.8530</td>
<td>6.114</td>
<td>-0.087</td>
</tr>
<tr>
<td>7</td>
<td>5.6458</td>
<td>5.922</td>
<td>-0.207</td>
</tr>
<tr>
<td>8</td>
<td>6.2008</td>
<td>5.802</td>
<td>-0.280</td>
</tr>
<tr>
<td>9</td>
<td>6.5632</td>
<td>5.732</td>
<td>-0.321</td>
</tr>
<tr>
<td>10</td>
<td>7.0251</td>
<td>5.667</td>
<td>-0.350</td>
</tr>
<tr>
<td>11</td>
<td>7.7229</td>
<td>5.576</td>
<td>-0.389</td>
</tr>
<tr>
<td>12</td>
<td>8.6114</td>
<td>5.481</td>
<td>-0.421</td>
</tr>
<tr>
<td>13</td>
<td>9.5172</td>
<td>5.360</td>
<td>-0.481</td>
</tr>
<tr>
<td>14</td>
<td>10.6094</td>
<td>5.264</td>
<td>-0.503</td>
</tr>
</tbody>
</table>

Fit values:

\[ K_A = 28.71 \pm 1 \quad \Lambda_0 = 64.97 \pm 0.01 \]

\[ a = 6 \text{ Å} \]

\[ s^2 = 3.6109 \quad \delta = 0.5079 \]
TABLE 35

\[
\begin{aligned}
\text{ZnBr}_2 & \xrightleftharpoons{K_1} \text{ZnBr}^+ + \text{Br}^- \\
\text{ZnBr}^+ & \xrightleftharpoons{K_2} \text{Zn}^{2+} + \text{Br}^-
\end{aligned}
\]

\( t = 25^\circ C \)

<table>
<thead>
<tr>
<th>Soln.</th>
<th>(10^4) C</th>
<th>(\Lambda_{\text{exp}})</th>
<th>(\Delta\Lambda = C_{\text{calc}} - C_{\text{exp}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mole (^{-1})</td>
<td>ohm (^{-1}) cm(^2) mole (^{-1})</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.3987</td>
<td>7.668</td>
<td>0.424</td>
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<tr>
<td>2</td>
<td>2.7484</td>
<td>7.256</td>
<td>0.481</td>
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<td>3.1674</td>
<td>6.881</td>
<td>0.492</td>
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<td>4</td>
<td>3.5721</td>
<td>6.612</td>
<td>0.458</td>
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<td>5</td>
<td>4.2380</td>
<td>6.323</td>
<td>0.325</td>
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<td>4.8530</td>
<td>6.114</td>
<td>0.209</td>
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<td>7</td>
<td>5.6458</td>
<td>5.922</td>
<td>0.049</td>
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<tr>
<td>8</td>
<td>6.2008</td>
<td>5.802</td>
<td>-0.042</td>
</tr>
<tr>
<td>9</td>
<td>6.5632</td>
<td>5.732</td>
<td>-0.098</td>
</tr>
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<td>10</td>
<td>7.0251</td>
<td>5.667</td>
<td>-0.182</td>
</tr>
<tr>
<td>11</td>
<td>7.7229</td>
<td>5.576</td>
<td>-0.294</td>
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<td>12</td>
<td>8.6114</td>
<td>5.481</td>
<td>-0.425</td>
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<tr>
<td>13</td>
<td>9.5172</td>
<td>5.360</td>
<td>-0.506</td>
</tr>
<tr>
<td>14</td>
<td>10.6094</td>
<td>5.264</td>
<td>-0.623</td>
</tr>
</tbody>
</table>
### TABLE 35 Cont'd/...

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$7.5 \times 10^3$</td>
<td>mole$^{-1}$</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$4.1 \times 10^8$</td>
<td>mole$^{-1}$</td>
</tr>
<tr>
<td>$\lambda_{Zn}^{o}$</td>
<td>8.00</td>
<td>ohm$^{-1}$ cm$^2$ equiv$^{-1}$</td>
</tr>
<tr>
<td>$\lambda_{ZnBr}^{o}$</td>
<td>12.80</td>
<td>ohm$^{-1}$ cm$^2$ equiv$^{-1}$</td>
</tr>
<tr>
<td>$\lambda_{Br}^{-}$</td>
<td>18.94</td>
<td>ohm$^{-1}$ cm$^2$ equiv$^{-1}$</td>
</tr>
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<td>$A_0$</td>
<td>26.94</td>
<td>ohm$^{-1}$ cm$^2$ equiv$^{-1}$</td>
</tr>
<tr>
<td>$s^2$</td>
<td>1.9726</td>
<td>$\delta = 0.3754$</td>
</tr>
</tbody>
</table>

The single ion conductances quoted above were also obtained by the minimisation method.
Zinc Iodide

The results for zinc iodide are given in Table 15 and shown graphically in Figure 13. Table 36 gives the results of analysis of this data together with the best fit values obtained, assuming the following mode of ionisation:

\[
\text{ZnI}_2 \rightleftharpoons \text{ZnI}^+ + \text{I}^- \quad (7:1)
\]

This assumption is in agreement with the conclusion of Bonner et al.\cite{148} from their conductance measurements of zinc iodide in ethylene carbonate(III) at 40°C.

Table 37 gives the values of \(\alpha, f_{\text{iDH}}\) and \(f_{\text{iMC}}\) at each concentration. It can be seen that \(\alpha\) is very small at these concentrations.

The effect of the \(\alpha\) value on \(K_A\) and \(\Lambda_0\) is shown in Figure 19. It is interesting to note that this behaviour falls into the second category in which there is a minimum for certain \(K_A\) and \(\Lambda_0\) values. The minimum occurs at \(\alpha = 9\) to \(10\) \(\Lambda\), as can be seen.

Analysis of the data at very low concentration \(< 3.5 \times 10^{-4}\) molar gives rather a poor fit for all of the modes of ionisation considered in this work, equations (6:1) to (6:4). A fit was obtained assuming the mode:

\[
\text{ZnI}_2 \rightleftharpoons \text{Zn}^{2+} + 2\text{I}^- \quad (7:2)
\]
TABLE 36

\[ \text{ZnI}_2 \xleftrightarrow{t = 25^\circ C} \text{ZnI}^+ + \text{I}^- \]

<table>
<thead>
<tr>
<th>Soln.</th>
<th>$10^4 C$ mole$^{-1}$</th>
<th>$\Lambda_{\text{exp}}$ ohm$^{-1}$cm$^2$mole$^{-1}$</th>
<th>$\Delta \Lambda = \Lambda_{\text{calc}} - \Lambda_{\text{exp}}$</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>4.0532</td>
<td>9.674</td>
<td>0.151</td>
</tr>
<tr>
<td>2</td>
<td>4.6266</td>
<td>9.078</td>
<td>0.069</td>
</tr>
<tr>
<td>3</td>
<td>5.2309</td>
<td>8.370</td>
<td>-0.182</td>
</tr>
<tr>
<td>4</td>
<td>5.8444</td>
<td>7.982</td>
<td>-0.173</td>
</tr>
<tr>
<td>5</td>
<td>6.8418</td>
<td>7.522</td>
<td>-0.096</td>
</tr>
<tr>
<td>6</td>
<td>8.2350</td>
<td>6.968</td>
<td>-0.057</td>
</tr>
<tr>
<td>7</td>
<td>9.6320</td>
<td>6.531</td>
<td>-0.024</td>
</tr>
<tr>
<td>8</td>
<td>11.0936</td>
<td>6.073</td>
<td>-0.082</td>
</tr>
<tr>
<td>9</td>
<td>12.4542</td>
<td>5.908</td>
<td>0.065</td>
</tr>
<tr>
<td>10</td>
<td>13.9650</td>
<td>5.674</td>
<td>0.126</td>
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<td>11</td>
<td>15.5537</td>
<td>5.363</td>
<td>0.079</td>
</tr>
<tr>
<td>12</td>
<td>17.0227</td>
<td>5.153</td>
<td>0.082</td>
</tr>
<tr>
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<td>18.6497</td>
<td>4.942</td>
<td>0.079</td>
</tr>
<tr>
<td>14</td>
<td>20.4052</td>
<td>4.736</td>
<td>0.070</td>
</tr>
</tbody>
</table>

Best fit values:

\[ K_A = 23000 \pm 100 \quad \Lambda_0 = 34.10 \pm 0.01 \]
\[ a = 9 \text{ Å} \]
\[ S^2 = 0.1546 \quad \delta = 0.1051 \]
TABLE 37

\[ \text{ZnI}_2 \rightleftharpoons \text{ZnI}^+ + \text{I}^- \]

\[ t = 25^\circ C \]

<table>
<thead>
<tr>
<th>Soln.</th>
<th>( \alpha )</th>
<th>( f_{+DH} )</th>
<th>( f_{+MC} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2822</td>
<td>0.9833</td>
<td>0.9842</td>
</tr>
<tr>
<td>2</td>
<td>0.2671</td>
<td>0.9826</td>
<td>0.9837</td>
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<tr>
<td>3</td>
<td>0.2536</td>
<td>0.9820</td>
<td>0.9831</td>
</tr>
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<td>4</td>
<td>0.2420</td>
<td>0.9814</td>
<td>0.9826</td>
</tr>
<tr>
<td>5</td>
<td>0.2262</td>
<td>0.9805</td>
<td>0.9819</td>
</tr>
<tr>
<td>6</td>
<td>0.2087</td>
<td>0.9795</td>
<td>0.9810</td>
</tr>
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<td>7</td>
<td>0.1948</td>
<td>0.9786</td>
<td>0.9802</td>
</tr>
<tr>
<td>8</td>
<td>0.1830</td>
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<td>0.9795</td>
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<td>9</td>
<td>0.1738</td>
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<td>0.9789</td>
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<td>0.1651</td>
<td>0.9763</td>
<td>0.9783</td>
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<td>0.1573</td>
<td>0.9756</td>
<td>0.9777</td>
</tr>
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<td>0.1510</td>
<td>0.9750</td>
<td>0.9772</td>
</tr>
<tr>
<td>13</td>
<td>0.1449</td>
<td>0.9744</td>
<td>0.9767</td>
</tr>
<tr>
<td>14</td>
<td>0.1391</td>
<td>0.9737</td>
<td>0.9762</td>
</tr>
</tbody>
</table>
FIGURE 19

Effect of \( a \) values upon \( \sum_{1}^{N} (\Lambda_{\text{calc}} - \Lambda_{\text{exp}})^2 \) for ZnI\(_2\) in PC at 25°C.

Note: \( N = \Delta S^2 \), equation (5:2)
as can be seen in Table 38. The agreement is not very satisfactory. Thus, again two stages of ionisation may be present, equation(6:12). Between $1.89 \times 10^{-4}$ and $3.5 \times 10^{-4}$ molar both modes(7:1)and(7:2)may be operative, and only at very low concentrations is (7:2) complete.

In the course of this investigation, attempts were made to identify the species present in this system by Raman spectrum. Evidence has been found for the ZnI$^+$ species, in 0.1 molar solution.

(8-5) **Ferric Chloride**

The experimental conductance data of this salt are given in Table 16. The graph of Figure 20 shows that these solutions are quite highly conducting at very low concentrations, but A falls off very rapidly with increasing concentration. This indicates the following possibilities: some of the molecules are not fully ionised, polyhalide ions are being formed, ion pair formation is extensive, or a combination of these factors. Because of this complexity we have not analysed the data further at present.
TABLE 38

\[ \text{ZnI}_2 \rightleftharpoons \text{Zn}^{2+} + 2 \text{I}^- \]

\[ t = 25^\circ \text{C} \]

<table>
<thead>
<tr>
<th>Soln.</th>
<th>(10^4 \text{ C/mole} )</th>
<th>( \Lambda_{\text{exp}}^{-} \text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1} )</th>
<th>( \Delta \Lambda = \Lambda_{\text{calc}} - \Lambda_{\text{exp}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.8893</td>
<td>11.73</td>
<td>0.169</td>
</tr>
<tr>
<td>2</td>
<td>2.2064</td>
<td>9.76</td>
<td>0.547</td>
</tr>
<tr>
<td>3</td>
<td>2.6697</td>
<td>7.77</td>
<td>-0.501</td>
</tr>
<tr>
<td>4</td>
<td>3.0658</td>
<td>6.68</td>
<td>-0.956</td>
</tr>
<tr>
<td>5</td>
<td>3.5148</td>
<td>5.73</td>
<td>-1.311</td>
</tr>
</tbody>
</table>

fit Values

\[ K_A = 8.24 \times 10^7 \]

\[ \Lambda_o = 26.42 \pm 0.01 \]

\[ a = 6 \text{ \AA} \]

\[ \delta = 1.1002 \]

\[ S^2 = 6.0519 \]
FIGURE 20

Molar conductance in PC at 25°C

FeCl₃
CHAPTER IV
ANCILLARY EXPERIMENTS
(1) Electrodeposition of Zinc

The electro-reduction experiments were undertaken as they were believed to be one of the simplest kinds of reactions that could be advantageously employed in characterising a new system. Although quite qualitative in nature, they provide information concerning the species present, and indicate the condition under which metals may be electrodeposited.

In order to investigate the system zinc chloride-PC an attempt was made to electrodeposit zinc from this system.

The experiments were performed in an H-shaped stoppered cell. Provision was made for magnetic stirring of cathode and anode compartments. The cell, as normally used, contained a total batch of 100 ml of solution. Prepurified and dried nitrogen gas was bubbled through the solution by means of gas diffuser tubes in each compartment. Smooth platinum electrodes, 0.4 mm thick each of 5 cm$^2$ area per face, were employed. This means that the current measurement can be changed to current density measurement by division by 10 cm$^2$. It is assumed that both faces of the electrode participate in the electro-chemical reaction. In some experiments a silver electrode with the same surface area was used as anode. The electrodes were parallel and 15 cm apart.
The solution was made up by weight, adopting the dry box technique, as described before.

The quantity of electricity passed was measured by a copper coulometer\(^{(149)}\) in series with the cell. To maintain cell currents of 25 and 50 mA, cell voltages of 14 V and 25.5 V were required, respectively.

A typical procedure was as follows: the platinum electrodes were cleaned with concentrated nitric acid, distilled water, and acetone, then dried in a desiccator, and finally weighed accurately. The electrolytic solution was added to the cell in the dry box, and the cell stoppered by the electrode assembly. Dry nitrogen was then passed through the cell and the solution for one hour, whilst the cell attained thermal equilibrium in the thermostat. A continuous stream of dry nitrogen was passed above the solution during the performance of the experiment. At the end of the run, the electrodes were removed immediately from the solution, rinsed with distilled water and then acetone, dried in a desiccator, and weighed accurately. From a "saturated" solution of zinc chloride in PC, a grey crystalline adherent deposit of zinc was obtained over a range of 5 - 10 mA/cm\(^2\) with 100% efficiency. For example in one of the experimental runs the quantity of electricity passed = 22.5 Coulomb

wt. of Pt cathode before the experiment = 4.45840 g

wt. of Pt cathode after the experiment = 4.46600 g
wt. of zinc deposited = 0.00760 g

If 1 coulomb deposits 0.000338 g of zinc

The theoretical amount of zinc metal expected = 0.00762 g

Cathodic current efficiency = 99.69%

This high efficiency indicates that the cathodic reaction is of the form \((\text{ZnX})^{2+} + 2e^- \rightarrow \text{Zn} + X\)

eg.

\[\text{Zn}^{2+} \text{(solvated)} + 2e^- \rightarrow \text{Zn} + \text{Solvent}.\]

(2) Polarographic Studies

(2-1) Materials

Zinc chloride: was used as previously described.

Potassium nitrate: The Analar BDH salt was dried for 12 hours under vacuum at 70°C.

Tetraethylammonium chloride: TEAC Eastman Organic white label grade was used without further treatment.

Mercury: The Alfa pure mercury\(^{(150)}\) was used.

The typical impurity levels in ppm are:

Ag, 2 Cu, 1 and other impurities < 1 ppm.

(2-2) Apparatus

Polarograms were obtained with a Polariter type PO4g recording polarograph. The polarographic cell employed is essentially that described by Kalousek\(^{(151)}\) with some modification. It consists of two compartments separated by a tap. The left-hand compartment contains the electrolyte to be analysed, the dropping capillary and a tube to pass dry nitrogen through the electrolyte; a small hole serves as the gas outlet. The mercury pool forms the depolarised electrode; the used mercury is
collected in the lower end of the compartment and could be drawn off by the bottom tap when necessary. The right-hand compartment serves as the reference electrode, of the mercury-saturated calomel-tetraethylammonium chloride type, SCTE.\(^{(53)}\)

The potential between this electrode and an aqueous saturated calomel electrode, SCE, was measured following the recommendations of Tsuji and Elving\(^{(152)}\) and it was found to be 47 ± 10 mV.

(2.3) Procedures

A typical polarogram was obtained as follows.

The electrolyte solution was prepared as previously described, adopting the dry box technique. The exact amount of the electrolyte under test and 25 cc. of the supporting electrolyte solution were poured into the cell. Dry nitrogen was bubbled through the electrolyte for 30 minutes, as the cell attained thermal equilibrium in the thermostat. Whilst the polarogram was being recorded, the dry nitrogen inlet was raised so that the gas flowed over the surface of the electrolyte. The centre tap connecting the electrolyte compartment to the reference electrode was opened only during the actual measurements, to prevent undesirable mixing of the solutions.
Results and Discussion

All potential values are given against the SCTE electrode in PC.

The solvent gave a nearly linear background, Figure 21 curve (A), between -0.28 and -1.8 V. This curve could be reproduced up to 3 h. under the above experimental condition. Hence, it could be used as a test for the stability of the solvent and as a purity check.

Figure 21 curve (B) shows a polarogram of the cathodic wave of a cation having a half wave potential of -1.48 V. An increase of ten fold in zinc chloride concentration did not change this potential, nor did a new wave appear, Figure 22. It is probable that the same positively charged species, \( \text{Zn}^{2+} \), exists over the whole concentration range (0.6 to 19.0 x \( 10^{-3} \) molar).

In addition to the cathodic wave, an attempt was made to obtain the anodic waves in zinc chloride solutions. The supporting electrolyte used in this case was 1 molar potassium nitrate solution. Again there was only one anodic wave, that of single anion having a half-wave potential of 0.02 V, Figure 23. The cathodic half-wave potential in this supporting electrolyte was -1.20 V, Figure 24. It is difficult to compare our results with those of Matsuura et al. (86), since different reference electrodes were used.
FIGURE 21

Polarograms of (A) Purified PC and (B) Solution of Zinc Chloride in PC with 1 mole $1^{-1}$ TEAC.
Polarograms of Zinc Chloride solutions in PC (A) 0.0006 M, (B) 0.0019 M, (C) 0.019 M with 1 mole l⁻¹ TEAC.
FIGURE 23

Polarogram of Zinc Chloride in PC (Anodic wave) with 1 mole \(1^\text{st} \) Potassium Nitrate.
FIGURE 24

Polarogram of Zinc Chloride in PC with 1 mole l\(^{-1}\) Potassium Nitrate.
The inference is that zinc chloride solutions in PC contain a single reducible cation and a single oxidizable anion, in agreement with the mode of ionisation (6:2) suggested by the conductance study of this solute.

(3) Determinations of Transport-Numbers in PC Solutions

Transport-number measurements were made on solutions of zinc chloride and zinc perchlorate in PC. The cell employed for these experiments was the Hittorf type cell; the three compartments were separated by taps sealed with the electrolyte in the cell. The cell was usually filled with a total of 50 ml of the electrolyte solution. The solutions were made up by weight, adopting the dry box technique as described before. Platinum wires were used in the first experiments for both electrodes. However, in the case of zinc chloride if chlorine is evolved at the anode it may react with the solvent, so that a silver wire was substituted as the anode. The experiments were performed in the thermostat at 25°C. A constant current was maintained, typically about 0.45-0.50 milliamperes (limited by the conductance of the solution) for a period of 5 hours, corresponding to $8.39 \times 10^{-5}$ to $9.32 \times 10^{-5}$ Faraday. The exact quantity of electricity passed was measured by a copper coulometer in series with the Hittorf cell. The copper sulphate solution used was of the composition specified by Findlay (149). At the end of the electrolysis, the taps were closed and the compartments siphoned into weighed stoppered bottles and mixed well. The weight
of each compartment was found, then weighed samples were withdrawn and analysed for both anion and cation. Under these experimental conditions, the centre compartment should undergo no change. This is necessary in order to consider the interpretation of concentration changes in terms of the proposed ionisation of the solute and of the possible electrode reaction, as follows:

1. If the species present in zinc chloride solution are Zn$^{2+}$ and Cl$^{-}$ and if the electrode reactions are:

$$\text{Zn}^{2+} + 2\bar{e} \rightarrow \text{Zn} \quad \text{at the cathode,}$$

$$\text{Cl}^{-} \rightarrow \frac{1}{2} \text{Cl}_2 + \bar{e} \quad \text{at the anode}$$

then, for each Faraday passed through the cell the following changes occur:

**Cathode:**
- $t^-$ equivalents of Cl$^{-}$ leave,
- $t^+$ equivalents of Zn$^{2+}$ enter and
- one equivalent of Zn$^{2+}$ is discharged

**Overall change** = loss of $t^-$ equivalent of ZnCl$_2$/F.

**Anode:**
- $t^+$ equivalents of Zn$^{2+}$ leave,
- $t^-$ equivalents of Cl$^{-}$ enter and
- one equivalent of Cl$^{-}$ is discharged

**Overall change** = loss of $t^+$ equivalent of ZnCl$_2$/F

2. Now suppose the species present in the solution are Zn$^{2+}$ and ZnCl$_4^{2-}$ and that the reaction at the anode may be represented:

$$\frac{1}{2} \text{ZnCl}_4^{2-} \rightarrow \frac{1}{2} \text{Zn}^{2+} + 2\bar{e} + \text{Cl}_2$$
then, the following changes should result from the passage of one Faraday through the solution:

Cathode:  $t^-$ equivalents of $\text{ZnCl}_4^{2-}$ leave,  
$\text{t}^+$ equivalents of $\text{Zn}^{2+}$ enter and  
one equivalent of $\text{Zn}^{2+}$ is discharged  
Overall Change = loss of $t^-$ equivalent of Zn.$\text{ZnCl}_4/F$  
= $t^-$ mole of $\text{ZnCl}_2/F$

Anode: $t^+$ equivalents of $\text{Zn}^{2+}$ leave,  
$t^-$ equivalents of $\text{ZnCl}_4^{2-}$ enter,  
$\frac{1}{2}$ equivalents of $\text{ZnCl}_4^{2-}$ discharged and  
$\frac{1}{2}$ equivalents of $\text{Zn}^{2+}$ formed.  
Overall Change = gain of $(\frac{1}{2}-t^+)$ equivalent of Zn.$\text{ZnCl}_4$  
= $(\frac{1}{2}-t^+)$ mole of $\text{ZnCl}_2/F$

3. Finally, if the species present in the solution are $\text{ZnCl}^+$ and $\text{ZnCl}_3^-$ and the electrode reactions are:

$\text{ZnCl}^+ + e \rightarrow \text{ZnCl}$  
$\text{ZnCl} \rightarrow \frac{1}{2} \text{Zn} + \frac{1}{2} \text{ZnCl}_2$  
$\frac{1}{2} \text{ZnCl}_2 \rightarrow \frac{1}{4} \text{Zn} \text{Cl}^+ + \frac{1}{4} \text{ZnCl}_3^-$  

$\frac{3}{4} \text{ZnCl}^+ + e \rightarrow \frac{1}{2} \text{Zn} + \frac{1}{4} \text{ZnCl}_3^-$ at the cathode and  
$\text{ZnCl}_3^- \rightarrow \text{ZnCl}_3 + e$  
$\text{ZnCl}_3 \rightarrow \text{ZnCl}_2 + \frac{1}{2} \text{Cl}_2$  
$\text{ZnCl}_2 \rightarrow \frac{1}{2} \text{ZnCl}^+ + \frac{1}{2} \text{ZnCl}_3^-$  

$\frac{1}{2} \text{ZnCl}_3^- \rightarrow \frac{1}{2} \text{ZnCl}^+ + \frac{1}{2} \text{Cl}_2 + e$ at the anode.
then, for each Faraday passed the following changes occur: Cathode:

- A loss of \((t^- - \frac{1}{4})\) \(\text{ZnCl}^-\) and
- A loss of \((\frac{3}{4} - t^+)\) \(\text{ZnCl}^+\)

Overall changes = loss of \((\frac{3}{4} - t^+)\) equivalent of \(\text{ZnCl}.\text{ZnCl}_3/F\)

\[= (\frac{3}{4} - t^+) \text{ moles of ZnCl}_2/F\]

Anode:

- A loss of \((t^+ - \frac{1}{2})\) \(\text{ZnCl}\) and
- A loss of \((\frac{1}{2} - t^-)\) \(\text{ZnCl}_3\)

Overall change = loss of \((\frac{1}{2} - t^-)\) equivalent of \(\text{ZnCl}.\text{ZnCl}_3/F\)

\[= (\frac{1}{2} - t^-) \text{ moles of ZnCl}_2/F\]

In the case of zinc chloride in PC, zinc deposited at the cathode only, with high efficiency; no deposit was observed at the anode. Moreover, chlorine gas was evolved at the platinum anode, while no gas evolved at the cathode. This could be in support of the first assumption.

Example of calculation:

- Wt. of Cu deposited = \(2.668 \times 10^{-3}\) g
- No. of Faradays passed = \(8.398 \times 10^{-5}\)
- Wt. of ZnCl\(_2\) lost from anode compartment = \(1.723 \times 10^{-3}\) g
- Wt. of ZnCl\(_2\) lost from cathode compartment = \(3.553 \times 10^{-3}\) g
- Change in wt. of ZnCl\(_2\) present in the centre compartment = \(0.10 \times 10^{-3}\) g

From the anode change,

\[t^+ = 1.723 \times 10^{-3} / 68.138 \times 8.39 \times 10^{-5}\]

\[= 0.301\]
From the cathode change, \( t^- = 3.553 \times 10^{-3}/68.138 \times 8.398 \times 10^{-5} \)
\[ = 0.621 \]

The agreement between the anode and cathode values of \( t^+ \) is thus within about 10% and the centre compartment change is about 4% of that in the other compartments. This low standard of accuracy may be due to the difficulty of the analysis; with such small changes of concentration, the transport-numbers are very dependent upon the results of the analyses.

In the experiments involving zinc perchlorate, the cathode process will be the same as for zinc chloride. But there is uncertainty as to the reaction at the anode; silver perchlorate unlike silver chloride is quite soluble in PC. We have therefore used only the loss per Faraday from the cathode compartment \( t^- \), to calculate the transport number.

The results are summarised in Table 39, over the concentration range 7.166 to 9.92 \( \times 10^{-3} \) molar.

No conclusive results could be obtained over a range of concentration due to the low solubility of the solute in PC and the high resistance of these electrolyte solutions. The interpretation and reliability of these results is uncertain, because these systems are not sufficiently well defined as yet.
TABLE 39

<table>
<thead>
<tr>
<th>Solute</th>
<th>Zn Cl₂</th>
<th></th>
<th>Zn (ClO₄)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t⁺</td>
<td>t⁻</td>
<td>t⁺</td>
</tr>
<tr>
<td>Soln.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.308</td>
<td>0.690</td>
<td>0.419</td>
</tr>
<tr>
<td>2</td>
<td>0.312</td>
<td>0.687</td>
<td>0.427</td>
</tr>
<tr>
<td>3</td>
<td>0.300</td>
<td>0.695</td>
<td>0.430</td>
</tr>
<tr>
<td>4</td>
<td>0.306</td>
<td>0.708</td>
<td>0.404</td>
</tr>
<tr>
<td>Average</td>
<td>0.307</td>
<td>0.695</td>
<td>0.420</td>
</tr>
</tbody>
</table>
CHAPTER V
CONCLUSIONS
The work described in this thesis has mainly been concerned with the study of the electrochemical behaviour of unsymmetrical electrolytes in propylene carbonate.

Zinc halides were found to be sufficiently soluble in this solvent to allow for electrochemical studies, while zinc oxide, sulphate and carbonate and potassium carbonate were not.

The conductances of zinc halides, zinc perchlorate and ferric chloride as well as mixtures of lithium chloride and zinc chloride solutions, have been measured at 25°C. The results indicate that all these solutes behave as "weak" electrolytes.

Zinc perchlorate is anomalous in showing unusually high molar conductances, and a pronounced maximum in conductance, at low concentration. The presence of this maximum may be explained in terms of a change of the physico-chemical properties of the solvent in the immediate vicinity of the ions, as compared with the "bulk" values.

The Murphy-Cohen equation (5:1) and the Debye-Hückel Onsager limiting law for unsymmetrical electrolytes equation (2:3) were used for the evaluation of the conductance data. The Murphy-Cohen equation has been modified to allow for various possible modes of ionisation of 2:1 electrolytes. The
equation has been treated, by a minimisation technique, as a three-parameter equation in terms of the association constant $K_A$, the distance of closest approach of free ions $a$ and the conductance at infinite dilution $\Lambda_0$.

The effect of variation of the value of the $a$ parameter on the values of $\Lambda_0$ and $K_A$ was investigated. The general pattern of these variations in both aqueous and nonaqueous solutions of symmetric and unsymmetrical electrolytes falls into two categories. Either there is a range of values of $a$ over which the values of $K_A$ and $\Lambda_0$ remain unaltered, or the variation of $a$ alters the values of $K_A$ and $\Lambda_0$ sharply.

Analysis of the experimental conductance data suggests that, for the zinc salts, the mode of ionisation is specific for the type of anion involved. The most likely modes of ionisation of the electrolytes over the range of concentrations considered appear to be:

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$a = K_A$</th>
<th>$\Lambda_0$</th>
<th>$aA$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Zn(ClO}_4\text{)}_2$</td>
<td>$\rightleftharpoons$</td>
<td>$\text{Zn}^{2+} + 2\text{ClO}_4^-$</td>
<td>48.89</td>
</tr>
<tr>
<td>$\text{ZnCl}_2$</td>
<td>$\rightleftharpoons$</td>
<td>$\text{Zn}^{2+} + 2\text{Cl}^-$</td>
<td>26.29</td>
</tr>
<tr>
<td>$\text{ZnBr}_2$</td>
<td>$\rightleftharpoons$</td>
<td>$\text{ZnBr}^+ + \text{Br}^-$</td>
<td>26.94</td>
</tr>
<tr>
<td>$\text{ZnBr}^+$</td>
<td>$\rightleftharpoons$</td>
<td>$\text{Zn}^{2+} + \text{Br}^-$</td>
<td>4.10$\times10^8$</td>
</tr>
<tr>
<td>$\text{ZnI}_2$</td>
<td>$\rightleftharpoons$</td>
<td>$\text{ZnI}^+ + \text{I}^-$</td>
<td>34.10</td>
</tr>
<tr>
<td>$\text{ZnI}^+$</td>
<td>$\rightleftharpoons$</td>
<td>$\text{Zn}^{2+} + 2\text{I}^-$</td>
<td>not observed</td>
</tr>
</tbody>
</table>
From the trend of $\Lambda$ at low concentration, we consider that these salts are fully ionised at extreme dilution.

Electrodeposition, polarography and transport-number measurements of zinc chloride are in good agreement with the above analysis.

In Table 40, the values of $\Lambda_0$ and of single ion conductances at infinite dilutions $\lambda_+^0$ and $\lambda_-^0$ obtained in this work are summarised; the last column shows the literature values for $\lambda_-^0$.

<table>
<thead>
<tr>
<th>Solute</th>
<th>$\Lambda_0$</th>
<th>$\lambda_+^0$</th>
<th>$\lambda_-^0$</th>
<th>Previous work(^{(a)}) $\lambda_-^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$^{2+}$ 2Cl$^-$</td>
<td>26.29</td>
<td>8.07</td>
<td>18.22</td>
<td>18.26 - 20.20</td>
</tr>
<tr>
<td>Zn$^{2+}$ 2Br$^-$</td>
<td>26.94</td>
<td>8.00</td>
<td>18.94</td>
<td>18.91 - 20.00</td>
</tr>
<tr>
<td>ZnBr$^+$ Br$^-$</td>
<td></td>
<td>12.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnI$^+$ I$^-$</td>
<td>34.10</td>
<td>15.53</td>
<td>18.57(^{(b)})</td>
<td>18.35 - 18.78</td>
</tr>
<tr>
<td>Zn$^{2+}$ 2ClO$_4^-$</td>
<td>48.89</td>
<td>20.53</td>
<td>28.36</td>
<td>18.44 - 19.60</td>
</tr>
</tbody>
</table>

\(^{(a)}\) see Table 3
\(^{(b)}\) estimated value

Utilizing the conductance data obtained, the following series of decreasing cation conductances in PC may be established:
ZnI$^+$ > ZnBr$^+$ > Zn$^{2+}$

The low $\lambda^0_+$ of the zinc ion can be accounted for by assuming substantial coordination of this ion in PC. The values of $\lambda^0_-$ obtained from the conductance and transport number data are in good agreement with the literature values, with the exception of the values of $\lambda^0_+$ and $\lambda^0_-$ of zinc perchlorate. These could be attributed to the fact that the solute used was Zn(ClO$_4$)$_{2}$.C$_4$H$_8$O$_2$. If the zinc ion retains its partial solvation shell of dioxane, and is prevented from coordinating with the solvent, its mobility may be increased considerably; however, it is unlikely that the presence of the dioxane at these very low concentrations will have such a marked effect. We consider that these $\lambda^0_\pm$ values are approximate only, and further study is required of these unsymmetrical electrolytes in nonaqueous solvents in general.
APPENDIX
The following is an example of the minimisation programs used in this work. The program was written in Algol for an ICL 1905F computer, and minimises the differences between the experimental conductance data and those calculated by the modified Murphy-Cohen equation \((5:1)\) at the appropriate concentrations. The data is fed in as \(N\) pairs of \(C_n A_n\) values, and the three parameters \(K_A, A_0,\) and \(a\) are varied over preselected ranges; \(K_A\) runs from value \(KA\) to \(KAMAX\) in steps of \(DKA, A_0\) runs from \(LO\) to \(LOMAX\) in steps of \(DLO\) and \(a\) runs from \(A\) in steps of \(DA\) to \(AMAX\). The mode of ionisation selected by a switch in the program \(SW\). The input is required in the following order:

- \(D\), dielectric constant of the solvent
- \(T\), absolute temperature
- \(ETA\), viscosity of the solvent
- \(N\), number of \(C_n A_n\) pairs
- \(SW\), mode of ionisation required
- \(Z_C\), valency of cation
- \(Z_A\), valency of anion
- \(N_C\), number of cation
- \(KA, DLO, DKA, LOMAX, KAMAX, A, DA,\) and \(AMAX\)
- \(T_C\), transport-number of cation (unsymmetrical electrolytes only)
- \(T_A\), transport-number of anion (unsymmetrical electrolytes only)
- \(CM[x, y]\), \(N\) pairs of \(C_n A_n\) values (molar scale)

The output consists of \(S^2\) and \(\delta\) equation \((5:2)\) and the corresponding values of \(K_A, A_0,\) and \(a\).
'LIBRARY' (ED, SUBGROUP NAGA)

'PROGRAM' (CM1L)

'TRACE' 2

'BEGIN' REAL D, T, ETA, PEB, BK, L1, L2, L21, L, Z, LO, B, BETA,
FN, FN1, E3, E4, K, S1,
DA, AMAX, AZ, AF, AG, PQ, E1, E2,
LA, LC, G, I, ACT, TA, TC, NA, SS, KK, DK, D1,
SWSET, AM1, CK, ZL,
KA, DKA, DL0, LOMAX, KAMAX, KAMIN,
AL, T, ACTDH, ACTMC, ACTIV, QQ, EIB,
A, F, E, X, Y, J, S, L3, AA, BB, KB;

'INTEGER' N, M, PNC, N2, N3, ZC, ZA, SW, U1, U, OUTPUT,
I, N1;

'PROCEDURE' C02ACA(A1, N1, REZ, IMZ, D1);

'VALUE'A1, N1;

'INTEGER' N1;

'ARRAY'A1, REZ, IMZ, D1; 'EXTERNAL';

'REAL' 'ARRAY'A1[0:3], REZ, IMZ, D1[1:3];

N1:=3;

'NEW SOLVENT': D:=READ;

'IF' D=0 'THEN' 'GOTO' 'EXIT';

T:=READ; ETA:=READ;

WRITETEXT ("'CORRECTED'MURPHY-COHEN'EQUATION'');

'NEW SALT': NEWLINE(1);

COPYTEXT (<*)>;

OUTPUT:=READ; U1:=READ;

'CALC': N:=READ;

'IF' N=0 'THEN' 'GOTO' 'NEW SALT';

'IF' 'ACTIV=A' THEN 'GOTO' 'DEHU';

WRITETEXT ("'MURPHY-COHEN % ACTIVITIES'"');

'GOTO' 'MCG';

DEHU:

WRITETEXT ("'DEBYE-HUCKEL % ACTIVITIES'"');

'MCG': M:=0;

'BEGIN' 'ARRAY' CL[1:N, 1:2], CM[1:N, 1:2];

'NEW SALT':

'SW': :=READ;

'IF' 'SW=0' 'THEN' 'GOTO' 'NEW SALT';

'IF' 'SW=99' 'THEN' 'GOTO' 'EXIT';

'NEW LINE'(1);

WRITETEXT ("'MCGDE%'OF%'IONISATION%'SW=%'"');

PRINT('SW, 1, 3); 'NEW LINE'(1);

'NEW L0': L0:=READ;

'IF' 'L0=0' 'THEN' 'GOTO' 'NEW SALT';

'IF' 'L0=2' 'THEN' 'GOTO' 'CHECK';

'IF' 'L0=3' 'THEN' 'GOTO' 'NEW SALT';

'IF' 'L0=99' 'THEN' 'GOTO' 'EXIT';

ZC:=READ; ZA:=READ;

'IF' 'ZC=-ZA' 'THEN' 'BEGIN'

Q:=SQRT(.5);

'END';

CHECK:

NC:=READ;
P := 0;
KA := READ; KMIN := KA;
IF KA = 0 THEN GOTO STRONG;
DL0 := READ; DKA := READ;
LOMAX := READ; KAMAX := READ;
STRONG:
A := READ; DA := READ; AMAX := READ;
AMIN := A;
NA := -NC*ZC/ZA;
N2 := 0;
BB := L0;
AZ := 0;
REPEAT: IF A = 0 THEN GOTO NEWLO;
IF A = 44 THEN GOTO EXIT;
IF KA = 0 THEN BEGIN
WRITETEXT (' ( % STRONG % ELECTROLYTE % ) ' ); NEWLINE (1);
END;
WRITETEXT (' ( % A = % ) '); PRINT (A, 3, 3);
AA := A*1.68;
PEB := 18.84954*ETA*1.6705*3/(D*T);
PEB := PEB*ABS(ZC*ZA);
E1 := 4.803*10*ZC;
E2 := 4.803*10*ZA;
E := (E1 + E2)*2/(2*E1*E2);
DKT := D*T*1.38054*1.6;
B := -E1*E2/(DKT*AA);
NEWB:
Z := 1; BETA := 0;
FOR U := 1 STEP 1 UNTIL 40 DO
BEGIN
Z := Z*(U);
BETA := BETA + B*(U/Z);  
END;
EIB := 0.5772+LN(B)+BETA;
J := EIB;
WRITETEXT (' ( L0 = ) '); PRINT (L0, 3, 2);
WRITETEXT (' ( % KA = % ) '); PRINT (KA, 9, 9);
NEWQ:
IF ZC = -ZA THEN GOTO Q2;
IF AZ # 0 THEN GOTO Q2;
TC := READ; TA := READ;
IF TC = 0 THEN GOTO PRINTLL;
LC := L0*TC; LA := TA*L0;
PRINTLL:
Q := (L0/((ZA-ZC)*(LC/ZC-LA/ZA)));
Q0 := ABS(Q); Q := SQRT(QQ);
Q2 := NEWLINE (1);
FF := F := 96487*(ABS(E1)+ABS(E2))/(PEB*299.97);
IF ZC = -ZA THEN GOTO PQ;
PQ:
L1 := -(Q + 2*L0/ (3*(1+Q)))/F;
L21 := Q + 2*L0/6 - F*(Q + 2/2 - E);
L2 := \(-1.15442 + (6Q + 15Q^2 + 21Q^3 - 13Q^4 - 35Q^5 + 6Q^6) / (12Q^2 + 1Q)\)
L3 := \((2Q + 2Q^2 + 2Q^3 - 13Q^4 + 2Q^5 + 3Q^6) / (2(1 - Q^2))\)
L2 := L2 - L3;
L3 := \((1 - 2Q + 2) / \ln(1 + 2Q) / (1 - Q^2)\);
L2 := L2 - \((1 - Q + 2) / \ln(1 + Q) / (2 - Q^2)\);
L2 := L2 - L3;
L2 := L2 + J \cdot (\exp(B) \cdot (2B + 2Q + 1B + 1) - 6B^3 - 9B^2 - 9B - 12) / (18B + 3);  
L3 := E \cdot (1 + 3 - 2Q + 2\ln(3/(2Q))) / (1 - Q^2);
L2 := L2 - L3;
L2 := L2 + J \cdot (\exp(B) \cdot (23B^2 + 9B^3 + 12) - 6B^3 - 8B^2 - 9B - 12) / (18B + 3);
L3 := E \cdot (1 + 3 - 2Q + 2\ln(3/(2Q))) / (1 - Q^2);
L2 := L2 - L3;
L2 := L2 + J \cdot (\exp(B) \cdot (-5B^2 - 36B^3 + 30B^4 + 30B^3 + 30B^2 + 2B - 36) / (108B^5)) - 6B^4 - 45B^3 - 6B^2 - 54B + 36) / (8Q^3);
E3 := E1 \cdot &10;  
E4 := E2 \cdot &10;
BETA := 0;
FN := 2;
H := B / (E3 \cdot E4);
'FOR' U := 3 \cdot 'STEP' 1 \ 'UNTIL' 40 \ 'DO';
'BEGIN' FN := FN \cdot U;
BETA := BETA + H \cdot (U - 2) / ((E3 \cdot U - E4 \cdot U) / (E3 - E4)) \cdot U;
'END';
L3 := L3 - BETA / (Q^2 \cdot E3 \cdot E4)  
- F \cdot (\exp(B) \cdot (B^4 + 5B^3 + 3B^2 - 12B + 6) - 9B^4) / 2  
- 3B^3 + 6B^2 + 6B - 6) / (12L0B^4);
L3 := L3 + E \cdot (57721 + \ln(3) - \ln(B) + 1/6) / (Q^2);
L3 := L3 + F \cdot Q^2;
L2 := L2 - L3;
'IF' 'OUTPUT' = 0 'THEN' 'GOTO' 'NEWONE';
WRITETEXT('"B% = %")'; PRINT(B, 3, 3);
WRITETEXT('"EIB% = %")'; PRINT(E1B, 3, 3);
'IF' 'ZC' = 'ZA' 'THEN' 'GOTO' 'HI';
WRITETEXT('"L+ = %")'; PRINT(LC, 3, 2);
WRITETEXT('"L- = %")'; PRINT(LA, 3, 2);
HI:
WRITETEXT('"C% = %")'; PRINT(Q, 1, 3); NEWLINE(1);
WRITETEXT('"L1% = %")'; PRINT(L1, 3, 3);
WRITETEXT('"L21% = %")'; PRINT(L21, 3, 3);
WRITETEXT('"BETA"'); PRINT(BETA, 2, 3);
WRITETEXT('"L2% = %")'; PRINT(L2, 3, 3);
NEWLINE(1);
NEWONE:
'IF' 'M' = 2 'THEN' 'GOTO' 'COMPUTE';
'FOR' X := 1 'STEP' 1 'UNTIL' N 'DO';
'FOR' Y := 1 'STEP' 1 'UNTIL' 2 'DO';
CM[X, Y] := READ;
COMPUTE;
SS := 0;
'FOR' X := 1 'STEP' 1 'UNTIL' N 'DO';
'BEGIN'
NEWG:
G := 1;
NEW I := CM[X, 1] * G;
'IF' I < 0 THEN 'BEGIN' WRITETEXT ('"I NEGATIVE\"") ;
NEWLINE(1);
M := 2; 'GOTO' ZAZ; 'END';
'IF' SV = 111 THEN 'BEGIN' CL[X, 2] := CM[X, 2];
'GOTO' EKB; 'END';
'IF' SV = 112 THEN 'BEGIN' CL[X, 2] := CM[X, 2]/2;
I := 3*I; 'GOTO' EKB; 'END';
'IF' SV = 211 THEN 'BEGIN' CL[X, 2] := CM[X, 2]*2;
I := I/2; 'GOTO' EKB; 'END';
'IF' SV = 222 THEN 'BEGIN'
I := 2*I; CL[X, 2] := CM[X, 2]; 'GOTO' EKB; 'END';
BKB:
CL[X, 11] := CM[X, 11];
EKB := (3.556*9*SQRT(G*CL[X, 11])*SQRT(NA*ZA + NC*ZC + 2)) / (SQRT(D*T));
EKB := BK*(-E1*E2/DKT);
L := L0 + G*BN + L1*G + BK + 2*KL + BK + L2*G;
L3 := CL[X, 2] - L;
ACT := 2.303*ABS(ZC*ZA)*SQRT(I*(1.8247*6/(D*T) + 1.5)/(1 + (50.29*AA*SQRT(D*T)) - 5));
ACT := EXP(-ACT);
ACTDH := ACT;
FN1 := 6; BETA := 0;
'FOR' U := 3 'STEP' 1 'UNTIL' 50 'DO'
'BEGIN'
FN1 := FN1 * (U + 1);
BETA := BETA + H(U-2)/(FN1*(U-2))*(E3tU-E4tU)/(E3-E4) + 2);
'END';
MCAS:
I := (E3+E4)*2*(5.772 - LN(B/3) + .25)/6 + E3+E4*(1/(3+B/3) + 1/(2*B));
I := (I - BETA) / (E3+E4);
ACT := EXP(-BK/2 + E*LX*BN*BK + BK + 2/3 + BK + 2); 1+
ACTMC := ACT;
'IF' 'ACTIV = 4 THEN 'BEGIN'
ACT := ACTDH;
'END'; 'GOTO' mode;
ACT := ACTMC;
MODE:
'IF' 'KA = 0 THEN 'GOTO' PRINTOUT;
'IF' 'SV = 112 THEN 'BEGIN'
CFK := 4*CL[X, 1] + 2*ACT + 3*KA;
A[0] := CFK;
A[1] := 0;
C02ACA(A1, N1, REZ, IMZ, D1);
'IF' 'UI = 0 THEN 'GOTO' KS;
WRITETEXT ('"%%%ZERO%OBTAINED\"');
NEWLINE(1);
WRITETEXT ('"REAL%PART%%%IMAGINARY%PART%%%MOD(F1(Z))\"');
NEWLINE(1);
'FOR' U1 := 1 'STEP' 1 'UNTIL' N1 'DO'

PRINT(REZ[II], 0.9);
PRINT(IM[II], 0.9);
PRINT(D[II], 0.9); NEWLINE(1);
'IF' IMZ[II] = '0' 'AND' REZ[II] 'LE' '1' 'THEN' AL:=REZ[II];
'END';
KS: 'IF' U1=0 'THEN' 'BEGIN'
FOR 'II:=1' STEP '1' UNTIL 'N1' 'DO' 'BEGIN' 'IF' IMZ[II] = '0' 'AND'
REZ[II] 'LE' '1' 'THEN' AL:=REZ[II]; 'END'; 'END';
ZL:=CFK*AL+3+AL-1;
'GOTO' MODAL;
'END';
'IF' SW=222 'THEN' 'GOTO' AL112;
'IF' SW=211 'THEN' 'GOTO' AL112;
'GOTO' AL111;
AL112:
AL:=2*(SQRT(KA*ACT+2)-4)/(KA*ACT+2-4);
'GOTO' MODAL;
AL111:
AL:=(SQRT(1+4*ACT+2*KA*CLX, 1)-1)/(2*ACT+2*KA*CLX, 1);
MODAL:
'IF' ABS(G-AL)>AL/10000 'THEN' 'BEGIN'
G:=AL; 'GOTO' NEW1; 'END';
PRINTOUT:
'IF' OUTPUT=0 'THEN' 'GOTO' NEWDATA;
'IF' KA=0 'THEN' 'GOTO' STRONG1;
NEWLINE(1);
WRITETEXT('('AL%=')'); PRINT(AL, 0.9);
'IF' SW=112 'THEN' 'BEGIN'
WRITETEXT('('CFK%=')'); PRINT(CFK, 0.9);
WRITETEXT('('TEST%=')'); PRINT(ZL, 0.9); 'END';
NEWLINE(1);
STRONG1:
WRITETEXT('('BK%=')');
PRINT(BK, 3.4);
PRINT(CLX, 1, 1, 6);
WRITETEXT('('L*EXPT.=')');
PRINT(CLX, 21, 3, 2);
WRITETEXT('('L*CALC.=')');
PRINT(L, 3, 3);
NEWLINE(1);
'IF' KA=0 'THEN' 'GOTO' PL3;
WRITETEXT('('G%=')');
PRINT(G, 0.9);
PL3:
WRITETEXT('('L3=')');
PRINT(L3, 2, 3);
NEWLINE(1);
WRITETEXT('('F+-, D/H=')');
PRINT(ACTDH, 0.9);
WRITETEXT('('F+-, M/C=')');
PRINT(ACTMC, 0.9);
NEWLINE(1);  
NEWDATA:  
SS:=SS+L3t2;  
'END';  
WRITETEXT('('SS=%')');PRINT(SS,3,4);  
K:=SQRT(SS/N);  
WRITETEXT('('SIGMA%=%)');PRINT(K,2,4);  
NEWLINE(1);  
NEWLINE(1);  
SS:=0;  
'IF'KA=0'THEN'GOTOCMIT;  
L0:=L0+DL0;  
P:=2;  
M:=2;  
AZ:=AZ+1;  
'IF'L0<LOMAX'THEN'GOTO'REPEAT;  
L0:=BB;  
KA:=KA+DKA;  
'IF'KA<KMAX'THEN'GOTO'REPEAT;  
KA:=KMIN;  
'GOTO'NEXTA;  
CMIT:M:=2;  
N2:=0;  
P:=2;  
NEWLINE(1);  
NEWLINE(1);  
NEXTA:A:=A+DA;  
AZ:=AZ+1;  
'IF'A<AMAX'THEN'GOTO'REPEAT;  
ZAZ:  
AZ:=0;  
A:=AMIN;  
'GOTO'NEWSW;  
'END';  
EXIT:'END';  
'END';
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