

A CONDUCTIMETRIC STUDY OF SOME ELECTROLYTES IN  
ETHYLENE CARBONATE-WATER MIXTURES AT 25 AND 40 °C

By

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## DEDICATION

This dissertation is dedicated to my wife, Gaylia, and my son, Benjamin, for their support, encouragement, and patience.

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There has been much interest recently in the study of the solvent properties of n-methylacetamide and n-methylpropionamide and related compounds. Probably the major reason for this interest is because of their high dielectric constants. However, these amide derivatives all form hydrogen-bonded chains, and it would be interesting to study a system of high dielectric constant incapable of forming hydrogen bonds. Ethylene carbonate, with a dielectric constant of 90.36 at 40 °C, is aprotic and was chosen for such a study. Ethylene carbonate is a solid at room temperature, melting at 36.4 °C, and a mixed solvent system of ethylene carbonate-water was used to avoid this difficulty. This also allowed the study of intermediate compositions.

The electrolytes studied in this solvent system were NaCl, NaAc, HCl, and HAc. Kraus cells were used, in conjunction with a bridge based on the design of Janz and McIntyre, to determine equivalent conductances. Analysis of the results was accomplished by the use of Pitt's conductance equation or log-log plots.

The study showed decreasing limiting equivalent conductances and increasing ion association with increasing concentrations of ethylene

carbonate (and hence increasing dielectric constant). There was also evidence for dimer and trimer formation for the two acids, as well as complex association species. Trends of association constants were, in general, opposite to that expected from Bjerrum's simple electrostatic model.

Ethylene carbonate is a dipolar aprotic solvent of high dielectric constant with minimal self-association. Water structure is broken down by addition of the ethylene carbonate, resulting in reduced solvating power for the mixed solvent. This poor solvating power is probably due primarily to poor anion solvation. Nevertheless, the solvent mixture is well suited for both practical and theoretical studies.

CHAPTER I  
INTRODUCTION

Ethylene carbonate, with a dielectric constant of 90.36 at 40 °C,<sup>1</sup> is one of the few solvents possessing a dielectric constant greater than water which is not an amide derivative or extremely exotic, as, for example, hydrogen cyanide. Ethylene carbonate is aprotic and hence incapable of forming hydrogen bonds with itself. However, the presence of the carbonyl oxygen permits hydrogen bonding if appropriate hydrogens are available. There has been much interest in using both ethylene carbonate<sup>2,3</sup> and propylene carbonate<sup>4</sup> as nonaqueous battery solvents. Pistoia<sup>2</sup> et al. suggest that ethylene carbonate is superior to propylene carbonate with respect to viscosity and specific conductance.

Despite theoretical and applied interest in ethylene carbonate as an electrolytic solvent, very little research has been published to date. This is probably because of the high melting point (36.6 °C) and the poor solubility of many common salts (the alkali metal halides, for example<sup>5</sup>) in ethylene carbonate. The use of an ethylene carbonate-water mixed solvent system removes both of these difficulties, and as an added bonus allows studies to be done in mixtures approaching isodielectric properties. Because of its high dielectric constant and dipole moment, the solvating power of ethylene carbonate is expected to be high. This is based on two properties of solutions. First, the electrostatic forces of attraction between oppositely charged ions are inversely proportional to the dielectric constant. This would imply less ion interaction in

solvents of higher dielectric constant. Second, higher dipole moments would imply stronger ion-dipole interaction between the solvent and the solute. Hence, ion-ion interactions are expected to be small and ion-solvent interactions are expected to be large, resulting in negligible ion association. The use of ethylene carbonate-water mixtures provides an excellent opportunity to test theoretical relations between ion association and dielectric constant.

Conductivity is a useful technique for the study of electrolytes in solvent systems because of its high accuracy<sup>6,7</sup> and general value in assessing ionic solution properties.<sup>7</sup> It was the major tool used in this work.

## CHAPTER II

### THEORETICAL BACKGROUND AND DEVELOPMENT

#### General Theory

The modes of conduction of electricity can be divided into two main types: that characteristic of metals, involving the transfer of electrons; and the conduction of electrolyte solutions. In the latter, the transfer is of free ions. While both modes of conduction are basically similar in that charge transfer is involved in each, there are significant differences in their modes of transfer. This is evidenced, for example, by changes in conduction with temperature. Metallic conduction is inversely proportional to temperature, while solution conduction is directly proportional. Although this work was concerned for the most part with electrical conduction in solutions and its implications to solution theory, metallic conduction played a major role in the collection of the data on solution conductance.

At this point, it may be helpful to discuss some basic concepts concerning the forces between charges and relate them to aspects of solution behavior.\*

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\*For a more detailed description, see, for example, G. Körtum, Treatise on Electrochemistry, second edition, Elsevier Publishing Co., Amsterdam, 1965.

Coulomb's law states that the force,  $F$ , acting on two point ions of charges  $z_1e$  and  $z_2e$  separated by a distance  $r$  in a vacuum is proportional to:

$$F \propto \frac{z_1 z_2 e^2}{r^2} \quad (1)$$

Here  $e$  is the unit of elementary charge of the proton.

However, solution studies are not done in a vacuum. The parameter which allows the determination of the change in field strength resulting when the vacuum is replaced by a fluid is called the dielectric constant. The dielectric constant, generally symbolized by  $\epsilon$ , is a measurable property of the fluid and enters the expression of Coulomb's law in the denominator:

$$F \propto \frac{z_1 z_2 e^2}{\epsilon r^2} \quad (2)$$

If an electric field of strength  $E$  is applied to an electrolyte solution, each ion present will experience a force proportional to its charge  $z_i$  and to the applied field:

$$F = z_i e E \quad (3)$$

The ions will move under the influence of this force and attain a velocity  $v_i$  proportional to the field and inversely related to the ion size,  $r_i$ , and the viscosity of the solvent,  $\eta$ :

$$v_i = \frac{F}{6\pi\eta r_i} \quad (4)$$

In the special case of unity field strength, the final velocity, called the absolute mobility of that ion, is symbolized by  $u_i$ . Combining equations (3) and (4) gives:

$$u_i = \frac{|z_i| e}{6\pi\eta r_i} \quad (5)$$

The mobility is characteristic of the ion and also depends on external conditions such as concentration, solvent properties, and the temperature.

A cubic centimeter of an electrolyte solution contains  $N_+$  cations and  $N_-$  anions of  $z_+$  and  $z_-$  charges respectively. The net number of unit charges crossing a unit plane ( $\text{cm}^2$ ) per second is the current, symbolized by  $I$ , and is given by:

$$I = eE(N_+z_+u_+ + N_-z_-u_-) \quad (6)$$

Combining this relationship with Ohm's law allows the calculation of the resistance of a unit cube of solution. This parameter is symbolized by  $\rho$ , and called the specific resistance. The inclusion of the distance between electrodes,  $l$ , and their area,  $A$ , allows the determination of the resistance of the volume of solution between any pair of electrodes,

$R_m$ .

$$R_m = \frac{l}{e(N_+z_+u_+ + N_-z_-u_-) A} = \rho \frac{l}{A} \quad (7)$$

The inverse of  $\rho$  is  $\kappa$ , the specific conductance. The specific conductance is dependent on concentration, and it is advantageous to remove this dependence by dividing  $\kappa$  by the concentration  $c$ . A factor of 1000 is introduced because the initial unit size was one cubic centimeter, and concentration is based on the liter (1000cc). Hence  $\Lambda$ , the equivalent conductance, is given by:

$$\Lambda = \frac{\kappa 1000}{c} \quad (8)$$

Now the equivalent conductance can be related to a measurable resistance and concentration by:

$$\Lambda = \frac{l 1000}{A R_m c} \quad (9)$$

By definition, an electrolyte placed in a solvent forms a conducting medium. For conduction to occur, the presence of charged, mobile

particles, called ions, is necessary. In general, there are two basic types of electrolytes. In one type, the ions are present before the addition of solvent, as, for example, inorganic salts. The other type forms ions by interaction with the solvent, as do the organic acids. However, both types are solvated by various interactions, as described below.

The most straightforward force possible between a molecule and an ion is simply due to the electrostatic forces that exist between charges. The charge associated with a neutral solvent molecule is the result of its dipole moment. These electrostatic ion-molecule interactions are particularly important in the solvation of ions. Of course, interactions involving dipolar and quadrupolar geometries are more complex than the case of simple point charges.

In the absence of a permanent dipole moment, the field of the ion can induce a dipole in the solvent molecule. The forces thus generated are called induction forces and are independent of temperature. Induction forces are strongly dependent on the polarizability of the neutral molecule.

Dispersion forces are the most general in nature and are responsible for the cohesion of molecules without charge or permanent dipole moments. Dispersion forces are the result of instantaneous dipole formations caused by random fluctuations in the electron cloud distribution of the molecules. These forces are additive for the interaction of several molecules and can result in a significant attractive force.

In addition to these non-specific coulombic forces, which generally result in non-stoichiometric associations, different types of specific interactions are also possible. These specific interactions lead to definite compositions.

A good example of a specific interaction is hydrogen bonding. Generally associated with the presence of hydrogen bonding are several unique properties, including a high boiling point, low intermolecular separations, and unusual solvent structure. There is some evidence that the hydrogen bond is somewhat electrostatic in nature, since stronger bonds are only formed in conjunction with the highly electronegative atoms fluorine, chlorine, oxygen, and nitrogen. A complete explanation of all the properties of hydrogen bonds has not yet been formulated.

Another specific force results from charge transfer processes between neutral molecules. Here an electron is transferred from one molecule to another. Some degree of electron sharing is evident, indicating a similarity to chemical bonding. The resulting species generally possesses a high dipole moment. A good example of such a species is  $\text{BF}_3 \cdot \text{O}(\text{CH}_3)_2$ . The  $\text{BF}_3$  contains an incomplete external electron shell, while the ether  $\text{O}(\text{CH}_3)_2$  has free pairs of electrons, which serve to complete the shell in boron trifluoride.

From the above discussion it is evident that there are many possible interactions between molecules and ions. The relative strengths of these various interactions are responsible for the differences between solvents with respect to their ion-solvent interactions. Specific interactions are strong enough in some instances to overcome the more general associations. For example, the fact that electrostatic forces of attraction are inversely proportional to the dielectric constant implies that ionization should be more probable with increasing dielectric constant. This conclusion, generally referred to as the Nernst -- Thomson<sup>8</sup> rule, has been disproved repeatedly, and is

inadequate to handle the complex interplay of interactions recognized in modern solution chemistry. This study has attempted to shed light on the solvent properties of a specific solvent system, ethylene carbonate-water.

### Basic Measurement Techniques

The measurement of the electrical conductance of solutions is a very sensitive technique, requiring strict attention to details in order to obtain precise results. For example, the temperature coefficient of the conductance of many aqueous solutions is approximately 2 percent per °C. Thus temperature control good to  $\pm 0.005$  °C is required to obtain data with a precision of  $\pm 0.01$  percent. Other conditions of measurement are equally important and are discussed below.

The measurement of solution conductance is a precise resistance determination, and this is most conveniently done using a Wheatstone bridge, diagrammed schematically in Figure 1.

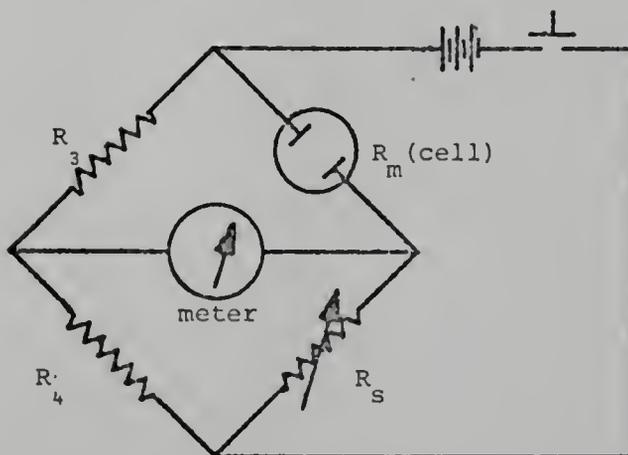


Figure 1. Circuit diagram of a Wheatstone bridge.

Basically, the standard resistance,  $R_s$ , is adjusted until the meter indicates a null (that is, no flow of current). At the null, the potential across the meter is equal to zero, and the relationship between the resistive components of the bridge circuit is:

$$\frac{R_m}{R_3} = \frac{R_s}{R_4} \quad (10)$$

However, under direct current conditions, the ions migrate to the electrodes in response to the applied field. The effects of electrolysis would obviously change the bulk concentration and consequently the resistance. Kohlrausch<sup>9</sup> eliminated the problem of direct current polarization by the use of alternating current where no net flow of ions takes place. However, the use of alternating current in conjunction with the standard cell configuration of parallel plates requires the capacitances of the circuit to be balanced as well. The major change that the use of alternating current introduces is the balancing of impedance rather than resistances.

Early work by Grinnell Jones et al.<sup>10-17</sup> and Shedlovsky<sup>18</sup> forms the basis for most aspects of precision bridges today. More recent work by Feates, Ives, and Pryor<sup>19</sup> demonstrates the usefulness of the transformer bridges found in many commercial impedance comparators for conductance measurements. The instrument used in this study is based on a design of Janz and McIntyre<sup>20</sup> and is discussed in more detail in the experimental section.

A frequency dependence of the measured resistance remains with even the most refined bridges of today. Hence, a reliable method of removing this frequency dependence is required to obtain accurate and precise conductance data. Fortunately, a large fraction of these

frequency variations have been removed by cell design and the use of mineral oil of low dielectric constant<sup>10</sup> as the thermostated bath fluid. There remain additional effects due to complex electrode processes which require careful study. Platinizing, or coating the electrodes with platinum black, reduces these effects.<sup>16</sup> However, platinization produces a coating of high surface area and high catalytic activity. Problems of adsorption and reaction associated with the platinum black coating have resulted in the choice of shiny platinum for the electrodes.

The generally accepted equivalent circuit of a conductance cell is that given by Ives,<sup>19</sup> with the addition of the so-called Warburg impedance<sup>21</sup> (symbolized by  $\text{W}$ ). A schematic of the components of this model is shown in Figure 2.

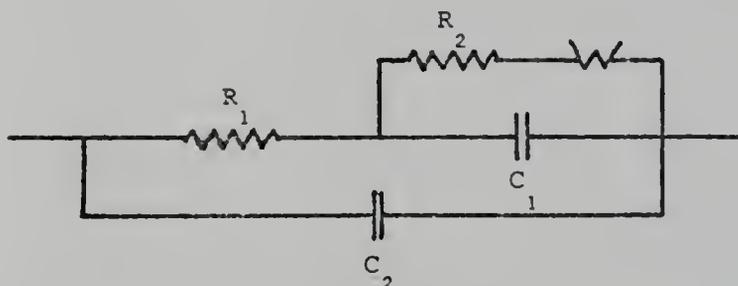


Figure 2. Schematic diagram of Ives model of a conductance cell.

$R_1$  is the true ohmic resistance of the cell, the quantity to be determined. It is independent of frequency in the range over which the measurements are made (generally between 1 and 20 kHz). Electronic relaxation times do not become an important factor until radio frequencies are reached. In series with the ohmic resistance of the solution is the double layer capacitance,  $C_1$ , which is also independent of frequency in the frequency range of the measurements. The capacitance  $C_2$  is the external capacitance of the leads, and generally is negligible in well designed cells immersed in oil baths.

While no actual discharge or ion formation occurs at the electrodes at the potentials used in this study (0.3 volt), some spontaneous electrolysis does occur. This electrolysis is due to the depolarizing action of dissolved oxygen or possibly ion discharge, and represents a Faradaic leakage in parallel with the double layer capacitance. This leakage generally can be represented by a pure resistance  $R_2$  and a Warburg impedance in series. The Warburg impedance can be considered to be equivalent to a resistance and capacitance in series with equal impedances at any one frequency. Both impedances vary inversely with  $\omega^{1/2}$ .

Feates, Ives, and Pryor<sup>19</sup> have solved the bridge balance conditions for their model (assuming a negligible Warburg impedance). These conditions revealed the frequency dependence of  $R_m$ , the measured resistance, to be of the form:

$$R_m = R_1 + \frac{R_2}{1 + a\omega^2} \quad (11)$$

where:

$$a = \frac{R_1 R_2^2 C_1^2}{R_1 + R_2}$$

and:

$$\omega = 2\pi\nu, \nu \text{ being the frequency.}$$

Hoover<sup>22</sup> has compared this model and other theoretical bridge balance conditions and concluded that equation (11) is sufficiently accurate for extrapolation to infinite frequency. A more detailed description of the extrapolation calculations is given in the experimental section of this work.

### Conductivity Concepts

Svante Arrhenius<sup>23</sup> was the first to suggest the existence of unbound ions in electrolyte solutions. These unbound ions are free to move under the influence of external forces. The concept of ions remains today as the basis for understanding electrolyte solution theory. However, it has undergone considerable refinement since its introduction, and today we have a much clearer understanding of ionic solution processes. Nevertheless, the picture is still far from complete, and the present work is an attempt to further the understanding of solution processes and interactions of a specific solvent system.

Kohlrausch<sup>24</sup> studied the behavior of the equivalent conductance at low solute concentrations and observed a linear dependence on the square root of the concentration,  $c$ . Thus the behavior of the equivalent conductance can be expressed as an equation of a straight line, as shown in equation (12):

$$\Lambda = \Lambda^{\infty} + A\sqrt{c} \quad (12)$$

$\Lambda^{\infty}$  is the limiting equivalent conductance at zero concentration.

Kohlrausch also advanced the concept of independent migration of ions, which assumes that ions in their movements do not interact with each other. This is only true at infinite dilution, and in this limit the individual contributions of each ion to the total conductance can be separated, as shown in equation (13):

$$\Lambda^{\infty} = \lambda_{+}^{\infty} + \lambda_{-}^{\infty} \quad (13)$$

Now a term to express the fraction of the total conductance associated with a single ion can be introduced. This term is called the transference number, symbolized by  $t_i^{\infty}$ , and is related to conductance by:

$$\lambda_i^{\infty} = t_i^{\infty} \Lambda^{\infty} \quad (13a)$$

In tables of single ion conductances, anomalously high values are noticed for hydrogen and hydroxide ions. The reason for these high conductances is due to the fact that these ions are fragments of the solvent, water. Actual physical transport of these ions in water is not necessary due to the existence of a proton jump mechanism. The proton is transferred from an  $\text{H}_3\text{O}^+$  group to a neighboring water molecule. No major movement of ions results, but the charge moves rapidly along a chain of water molecules. Figure 3 shows this schematically.



Figure 3. Schematic of the proton jump mechanism.

A similar process occurs with the hydroxide ion, except that the negative ion acts as a proton acceptor rather than a proton donor.

An increase in temperature reduces the anomaly between the conductance of hydrogen and that of more "normal" ions. This suggests a reduced probability of proton jumping due to the disruption of the water structure at high temperatures. A disruption in the structure of water by means other than thermal forces would be expected to result in a decrease of the proton jump effect as well.

#### Variation of Conductance with Concentration

Under the conditions of infinite dilution, ions are considered to be far enough apart for their interactions to be negligible. For non-zero concentrations, ions do influence one another, and the simple infinite dilution approximations are no longer appropriate to handle these complex interactions. Ionic interaction theory has made a good start in quantitatively explaining how conductance varies with concentrations, but over only a limited concentration range, up to perhaps 0.1M for 1:1

electrolytes in aqueous solutions. There are two major effects of ion interactions: the electrophoretic effect and the relaxation effect.

The electrophoretic effect is the result of solvent flow due to ion migration. An ion moving in a viscous medium drags along nearby solvent. The solvent can be directly associated with the ion (that is, the ion is solvated). Also, nearby solvent is pulled along to some extent by frictional forces. Hence, neighboring ions experience a net solvent flow rather than static conditions. This flow of solvent is either with or against the movement of this neighboring ion, depending on its charge. This effect vanishes at infinite dilution.

Since distances between ions are involved, Boltzmann distribution functions can be used to express these effects.\* If a single electrolyte is used, all velocities of ions of the same charge will be equal, and the Boltzmann symmetry is preserved. It can be shown that the electrophoretic increment to the velocity of the ion is:

$$\Delta v_+ = \sum_{n=1}^{\infty} A_n \frac{z_+^n (z_+^{n-1} k_+ - z_-^{n-1} k_-)}{a^n (z_+ - z_-)} \quad (14)$$

where:

$$A_n = \frac{(-1)^n}{n! 6\pi\eta} \left( \frac{e^2}{\epsilon kT} \right)^{n-1} \phi_n(ka)$$

In these relations,  $k_+$  and  $k_-$  are the forces acting on the ions;  $a$  is the distance of closest approach of the ions.  $\phi_n$  is a function of  $ka$  only and defined by:

$$\phi_n(ka) = (ka)^2 \left( \frac{e^{ka}}{(1+ka)} \right)^2 S_n(ka)$$

\*A detailed description of ionic distribution functions can be found in Chapter 4 of Electrolyte Solutions, R.A. Robinson and R.H. Stokes, second edition, 1970 revision, Butterworths, London.

$\kappa a$  is a convenient collection of frequently appearing natural constants:

$$\kappa a = \left( \frac{8\pi N e^2 I}{1000 \epsilon k T} \right)^{1/2} a$$

$S_n(\kappa a)$  is also a function of  $\kappa a$  only, and is given by:

$$S_n(\kappa a) = a^{n-2} \int_a^\infty \frac{e^{-nkr}}{r^{n-r}} dr$$

which is in the form of an exponential integral.  $T$  is the absolute temperature and  $N$  is the Avogadro number. Other terms have been defined previously, and the summation over  $n$  (all ionic species appears from the Boltzmann distribution, as does the Boltzmann constant,  $k$ ).

In an equilibrium situation, the average distribution of ions is spherically symmetric, and there is no net force acting on the central ion. In the presence of an electric field, the central ion will be moved off-center from the spherically symmetric distribution. As a result of this movement, the ion experiences a small restoring force before thermal fluctuations return the original spherical symmetry. This return to spherical symmetry is termed the relaxation of the ionic atmosphere and the average restoring force experienced by the central ion is called the relaxation effect.

Initial work on the problem of the relaxation effect was done by Debye and Hückel,<sup>25</sup> but a somewhat more successful treatment is given by Onsager.<sup>26</sup> Onsager's expression for the velocity of an ion, as modified by the relaxation effect, is given by:

$$v_j = v_j^\infty \left( 1 + \frac{z_1 z_2 e^2}{3 \epsilon k T} \cdot \frac{q \kappa}{1+q} \right) \quad (15)$$

where  $q$  is given by:

$$q = \frac{|z_1 z_2|}{|z_1| + |z_2|} \cdot \frac{\lambda_1^\infty \lambda_2^\infty}{|z_2| \lambda_1^\infty + |z_1| \lambda_2^\infty}$$

For symmetrical electrolytes, where  $z_1 = z_2$ ,  $q = 1/2$ .

However, this expression is valid only when  $\kappa a$  is small compared to unity, which generally occurs only in dilute solutions. Additional approximations also limit its usefulness to dilute solutions ( $<0.001$  M) where the relaxation effect is small. Combining this relation (15) for the relaxation effect with the electrophoretic effect (14) gives an expression for the variation of the equivalent conductance with concentration known as Onsager's limiting law:

$$\Lambda = \Lambda^\infty - \frac{|z_1 z_2| e^2 \Lambda^\infty q \kappa}{3 \epsilon k T (1 + \sqrt{q})} - \frac{F^2}{6 \pi \eta N} (|z_1| + |z_2|) \kappa \quad (16)$$

Here  $\kappa$  is of the form:

$$\kappa = \left( \frac{8 \pi N e^2 I}{1000 \epsilon k T} \right)^{1/2}$$

where  $I$ , the ionic strength, is:

$$I = \frac{c}{2} (v_1 z_1^2 + v_2 z_2^2)$$

and  $v$  represents the number of moles of ions formed from a mole of electrolyte.

If symbols are replaced by values of the corresponding physical constants, and a 1:1 electrolyte is assumed, equation (16) can be written as:

$$\Lambda = \Lambda^\infty - \left[ \frac{8.204 \times 10^5 \Lambda^\infty}{(\epsilon T)^{3/2}} + \frac{82.50}{\eta (\epsilon T)^{1/2}} \right] \sqrt{c} \quad (17)$$

Equation (17) has the linear dependence on  $\sqrt{c}$  that Kohlrausch first observed. However, there is now a theoretical basis for this behavior and a means of calculating the empirical constant  $A$ .

Shedlovsky<sup>27</sup> has proposed an expression suitable for extrapolation purposes based on this limiting expression. Putting (17) into a more symbolic form gives:

$$\Lambda = \Lambda^{\infty} - B_1 \Lambda^{\infty} \sqrt{c} - B_2 \sqrt{c} \quad (18)$$

and then rearranging (18) yields:

$$\Lambda^{\infty} = \frac{\Lambda + B_2 \sqrt{c}}{1 - B_1 \sqrt{c}} \quad (19)$$

For strong aqueous 1:1 electrolytes, this calculated value of  $\Lambda^{\infty}$  varies almost linearly with concentration up to ~0.1M. One can thus plot this varying  $\Lambda^{\infty}$  against  $c$ , whereupon extrapolation to zero concentration gives a better estimate of the true limiting conductance  $\Lambda^{\infty}$ .

Robinson and Stokes<sup>28</sup> have included the finite ion size in a similar expression:

$$\Lambda = \Lambda^{\infty} - \left( \frac{B_1 \Lambda^{\infty} + B_2}{1 + \kappa a} \right) \sqrt{c} \quad (20)$$

which can be similarly rearranged to give:

$$\Lambda^{\infty} = \Lambda + \frac{B_1 \Lambda^{\infty} + B_2}{1 + (B_1 a - B_2) \sqrt{c}} \sqrt{c} \quad (21)$$

Where  $B = \kappa/\sqrt{c}$ . Equation (21) is useful for  $\Lambda^{\infty}$  determinations by extrapolation using Shedlovsky's method.

#### Pitts' Equation

It is clear from the behavior of the  $\Lambda^{\infty}$  of equation (19) that data up to ~0.1M can be represented by:

$$\Lambda = \Lambda^{\infty} - (B_1 \Lambda^{\infty} + B_2) \sqrt{c} + bc(1 + B_1 \sqrt{c}) \quad (22)$$

if  $b$  is chosen to fit the data. This empirical relation has been shown

to be a fortuitous result of derived numerical values of more complete theoretical descriptions.<sup>29</sup>

There are two major theoretical equations relating electrolytic conductance to concentration and other physical quantities: that of Fuoss,<sup>29, 30</sup> and numerous modifications of his basic equation,<sup>31-33</sup> and the relation derived by Pitts<sup>34</sup> in the early 1950's. Both theories are based on the model of a charged sphere in a continuum and they have been put in the same form with only differences in coefficients.<sup>35</sup> The form is:

$$\Lambda = \Lambda^{\infty} - S\sqrt{c} + Ec \log c + J_1 c - J_2 c^{3/2} \quad (23)$$

The S term (Onsager's limiting law slope) and the E term are identical in the two treatments, but the ion size terms,  $J_1$   $J_2$ , are different. The differences arise from the different approaches used by Fuoss and Pitts and reflect differences in boundary conditions and details in the application of the model. There has been much discussion recently as to which treatment is better.<sup>35-40</sup> The most frequently cited difference has been a smaller value for  $a$ , the ion size parameter, resulting from the Pitts' treatment. However, large variations in  $a$  from different sets of data for even so well studied a salt as KCl<sup>40</sup> indicate a strong dependence on the precision of the data. Present techniques give the quantity  $a$  some of the characteristics of a variable modified to allow a better fit of the data. This of course limits its theoretical meaning. It is not yet possible to decide which treatment is superior. The KEQIVES program<sup>41</sup> which utilizes the Pitts' treatment was available and was used for the final analysis of the data.

The form of the Pitts' equation used in the KEQIVES program (written in Fortran IV and described more fully in the experimental section) was:

$$\Lambda^\infty - \Lambda = \Lambda^\infty \left( \frac{A\sqrt{c}}{(1+y)(\sqrt{2+y})} + BcS_1 \right) + G\sqrt{c} \left( \frac{1}{(1+y)} - \frac{A\sqrt{c}}{(1+y)^2(\sqrt{2+y})} - \frac{H\sqrt{c}}{1+y} T_1 \right) \quad (24)$$

where:

$$A = H(\sqrt{2} - 1)$$

$$B = 3H^2$$

$$G = \frac{\epsilon k T H N_1 10^3}{\pi \eta c^2}$$

$$H = \frac{z^2 e^2 \kappa}{3 \epsilon k T \sqrt{c}}$$

$$S_1 = \frac{9\sqrt{2} - 10 + y(3\sqrt{2} + 1) + 2y^2}{8(1+y)^2(\sqrt{2+y})^2} - \frac{e^y}{4(1+y)} E_i(y) + \frac{7\sqrt{2}}{16} \frac{e^{(2+\beta)y}}{(1+y)^2(\sqrt{2+y})} E_i((\beta+2)y) + \frac{\sqrt{2}}{16} \frac{e^{(1+\beta)y}}{(1+y)(\sqrt{2+y})} E_i((\beta+1)y)$$

$$T_1 = \frac{3}{4(\sqrt{2+y})} + \frac{3}{8} \left[ \frac{3\sqrt{2}e^{(\beta+1)y}}{\sqrt{2+y}} E_i((\beta+1)y) - 2e^y E_i(y) \right]$$

$$E_i(t) = \int_t^\infty \frac{e^{-u}}{u} du$$

$$y = \kappa a, \text{ where } \kappa = \left( \frac{8\pi N z^2 e^2 c}{1000 \epsilon k T} \right)^{1/2}$$

$$\beta = \frac{1}{\sqrt{2}}$$

C = speed of light

All other symbols have their previous meaning.

To make the program more general, concentrations were replaced by  $\alpha c$ , where  $\alpha$  is the degree of dissociation. Correspondingly, equivalent conductances calculated by the KEQIVES program were multiplied by  $\alpha$  to convert  $\Lambda_i$ , the value actually calculated ( $\Lambda_i$  is the conductance if the electrolyte were completely dissociated into ions of  $\alpha c$  concentration), to the equivalent conductance,  $\Lambda$  (that is,  $\Lambda/\Lambda_i = \alpha$ ).

A value for the association constant  $K_a$  can be derived from the mass balance equation by the use of  $\alpha$ :

$$K_a = \frac{1 - \alpha}{\alpha^2 c y_{\pm}^2} \quad (25)$$

In this expression,  $y_{\pm}^2$  is the mean activity coefficient (molar scale) of the electrolyte. Activity coefficients at very low ionic strengths can be derived by the Debye-Hückel expression:

$$f_{\pm}^2 = 10^{-\frac{2A|z_1 z_2| \sqrt{I}}{1 + Ba\sqrt{I}}}$$

Here A and B, the usual Debye-Hückel parameters, are given by:

$$A = \frac{1.8246 \times 10^6}{(\epsilon T)^{3/2}}$$

$$B = \frac{50.29 \times 10^8}{(\epsilon T)^{1/2}}$$

Equation (26) gives the activity coefficient,  $f_{\pm}$ , on the mole fraction scale; it is converted to the molar scale by the expression:

$$y_{\pm}^2 \approx \left( \frac{\rho}{\rho + 10^{-3} c (2M_{\text{solvent}} - M_{\text{solute}})} \right)^2 f_{\pm}^2 \quad (27)$$

where  $m$  = moles solute per kg of solvent

$M$  = molecular weight

$\rho$  = density of the solvent

## CHAPTER III

### EXPERIMENTAL

#### Materials

The primary source of ethylene carbonate was Eastman, a division of Eastman Kodak Company. The ethylene carbonate was obtained in 3kg quantities; the product, of practical grade, came from two different lots. Some initial trial experiments were done with ethylene carbonate from Matheson, Coleman, and Bell (MCB).

The solvent was purified by slow freezing of the 3kg quantities. Freezing was chosen because of its simplicity. Furthermore, the closely related compound, propylene carbonate, has been reported to decompose at temperatures greater than 110 °C.<sup>4, 42</sup> The purification procedure involved melting of the ethylene carbonate, followed by filtering through a fine sintered glass filtering funnel to remove insoluble material. The ethylene carbonate was then allowed to freeze slowly overnight. The remaining liquid was removed the following day and the crystals were remelted and then allowed to refreeze. This procedure was repeated until the initial color (light yellow) was removed. Despite an initial difference in color intensity between lots, no significant difference was observed in the number of melting and freezing steps required for color removal. A similar color has been reported to appear in propylene carbonate containing traces of water after contact with a sodium-potassium alloy.<sup>43</sup> The development of color has been suggested

to be due to the presence of a polymeric form.<sup>44</sup> Typical yields were on the order of 60 to 80 percent.

Due to the nearness of the melting point of ethylene carbonate (36.4 °C) to room temperature, the process of slow refreezing approximated the conditions of zone refining. The concentration of the color into the liquid remaining was readily apparent. This was responsible for the success of this technique of purification. The specific conductance of ethylene carbonate purified in this manner was on the order of  $5-10 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$ , as low as, or lower than, values reported in the literature.<sup>2,5,45</sup> Purified ethylene carbonate showed little or no tendency to absorb moisture from the air, as reported by Bonner *et al.*<sup>46</sup> Its rate of hydrolysis is very slow;<sup>47</sup> indeed, it has been reported to be immeasurably slow.<sup>48</sup> Base-catalyzed hydrolysis is much more rapid<sup>47</sup> but still not unmanageable in the times and concentrations studied in this work. Acid-catalyzed hydrolysis is also a potential problem, but EMF measurements indicate little or no problem up to about 0.1 molar in acid at 20 mole percent ethylene carbonate.<sup>49</sup> However, at 40 °C and high mole fractions of ethylene carbonate (>60 mole percent), the acid-catalyzed hydrolysis rate has increased enough to become a source of error.

Conductivity water was prepared by a single distillation of water which was treated by reverse osmosis followed by deionization. A Corning AG-11b Pyrex still was used. Conductivity water thus prepared had a specific conductance between  $0.8 - 1.2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ . This was expected, since no protection from the  $\text{CO}_2$  present in the air was provided.

The salts used in this study were recrystallized twice from conductivity water using standard procedures. The sodium chloride was

Fisher Certified reagent grade material, while the anhydrous sodium acetate and potassium chloride (for cell constant determinations) were Mallinckrodt Analytical Reagent chemicals. After recrystallization, salts were dried in a vacuum oven (initially at 60 °C, to avoid hydrate melting, then at 150 °C) and stored in a desiccator over indicating Drierite until used.

The glacial acetic acid was also a Mallinckrodt Analytical Reagent. Purification of the acetic acid consisted of three fractional freezings. The final fraction was stored in a desiccator over indicating Drierite.

Hydrogen chloride solutions were prepared by double distillation of constant boiling hydrogen chloride-water azeotrope. The final concentration was established by the gravimetric determination of chloride using silver nitrate. This concentration was found to be 6.053 M.

#### Instrument Description

The conductance bridge was based on a design of Janz and McIntyre,<sup>20</sup> slightly modified by Hoover<sup>50,51</sup> to allow the use of available capacitors. A schematic diagram of the bridge is shown in Figure 4.

The major component of the bridge is a General Radio model 1654 impedance comparator, modified by the manufacturer to operate at 1.0, 2.5, 5.0, and 10kHz. The transformer bridge used in this commercial instrument is of a toroidal design with a center-tapped secondary winding. The halves of the center-tapped secondary act as inductively coupled ratio arms of the bridge circuit, and they are equal within one part in  $10^6$ . The precision of this measurement is thus limited by the precision of the standard resistance used as a comparison to the unknown resistance.

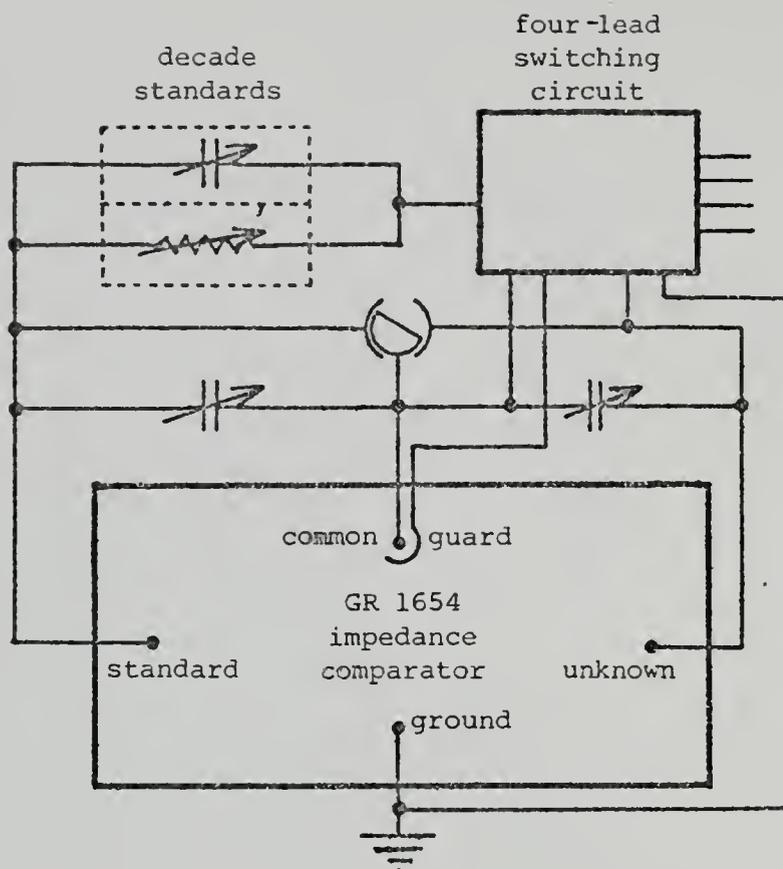


Figure 4. Block diagram of the conductance bridge.

The standard resistance used in conjunction with the comparator was a General Radio model 1433-F decade resistor. This model has seven decades of resistance ranging from  $10\text{k}\Omega$  steps down to  $0.01\Omega$  steps. For the resistances typically encountered during measurements ( $>100\Omega$ ), the precision of the resistance readings was 0.01 percent. A General Radio model 1412-BC decade capacitor was connected in parallel with the decade resistance to allow compensation for the cell capacitance. It is also possible to measure dielectric constants utilizing the measured capacitance of the cells.

To avoid problems associated with irreproducible contact resistances from the connections between the cells and the bridge circuitry, a four-lead measurement system was used. The four-lead system used is essentially the same as that employed with four-lead platinum resistance thermometers. Basically, a four-lead measurement requires two measurements with differing connections between bridge and unknown. The mean of the resulting two measurements contains no contribution from the inherent resistance of the leads. This system is shown schematically in Figure 5.

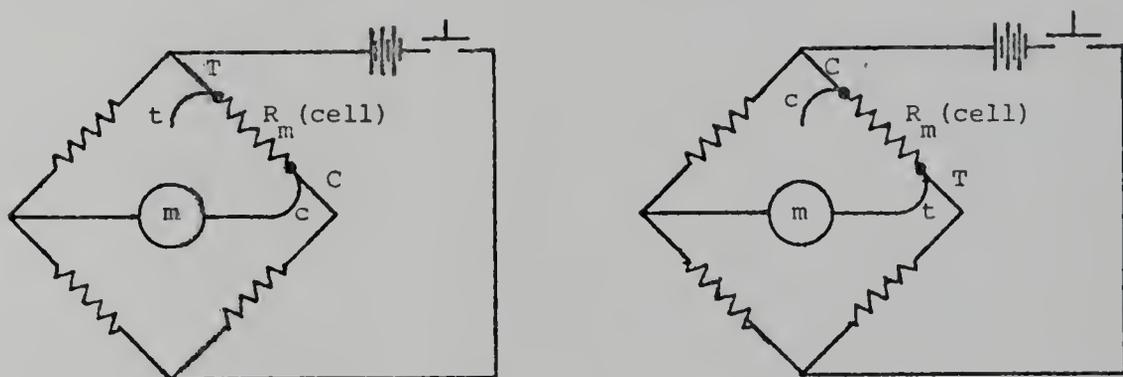


Figure 5. Circuit diagram of the two different connections in a four-lead measurement.

The connection between the conductance bridge and the cells consisted of printed circuit cards and edge connectors. Standard 15-contact hardware was used, which allowed three contact surfaces for each of the four leads. The contacts not used for connection purposes were utilized as spacers. The redundancy of contact for each lead insured positive contact and more reproducible connections. Figure 6 shows the physical arrangement of the system. As shown, this arrangement allows the measurement of two cells to be made simultaneously. One cell or the other may be balanced simply by inverting the circuit card connected to the bridge.

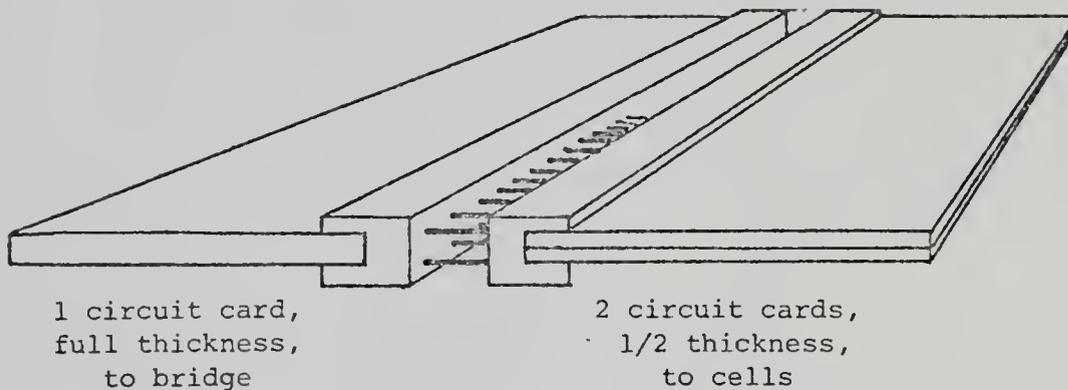


Figure 6. Drawing of the card connecting system.

The cells used were similar to the design suggested by Kraus et al.<sup>52</sup> Two were commercially manufactured by Beckman Instruments. The cell constants were 1.0534 and 0.12041  $\text{cm}^{-1}$ . A duplicate of the cell with the larger constant was made by the departmental glass shop. This cell had a cell constant of 0.93943  $\text{cm}^{-1}$ . All cell constants were determined at 25 °C. A drawing of the cell design is shown in Figure 7.

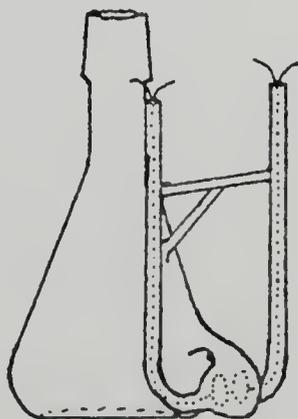


Figure 7. Drawing of a cell of the Kraus design.

The reason for the wide placement of the lead wires is to reduce the Parker effect.<sup>53</sup> This effect is the result of capacitance formed by the leads as they pass through the electrolyte solution. These capacitances produce a frequency dependence of the measured resistances. The electrodes are of shiny platinum, spot welded to platinum wire. The platinum wire is welded to tungsten for sealing purposes. Heavy gauge copper wire is brazed to the tungsten, and the copper is doubled at the top of the glass for four-lead measurements.

The constant temperature bath was constructed by the department machine shop. The bath itself is of stainless steel, with welded seams. The bath is insulated with Styrofoam, and supported by a phenolic board box frame. The box frame is secured in a welded angle iron cart. Circulation for temperature uniformity is provided by two 1.3-ampere American Instrument Company circulating pumps. The bath liquid was BP food grade white oil. This white oil, of low dielectric constant, was used to reduce further the lead capacitance effects<sup>10</sup> mentioned previously.

Temperature control to  $\pm 0.002$  °C was obtained by a Yellow Springs Instrument Company model 72 temperature controller. A 10-turn potentiometer was substituted for the standard three-quarters turn potentiometer to permit more precise control of the temperature setting. The temperature controller was used with a thermistor probe and two immersion heaters. One of the immersion heaters used was a standard 500 watt Vycor sheathed immersion heater. The other was constructed of Nichrome heating wire wrapped on a Plexiglas frame. This heater was placed to take advantage of the flow from the two circulation pumps. Cooling water was circulated through copper tubing immersed in the oil as an aid in temperature control. This water was cooled by a Blue M Constant Flow

cooling unit immersed in a auxiliary water bath. This cooling was in opposition to the immersion heaters used in conjunction with the temperature controller and allowed continuous control rather than cycling.

As a further aid in temperature control, and to keep dust and other debris out of the constant temperature bath, a Plexiglas cover, constructed by the departmental machine shop, was provided. A hinged box lid with an additional door was placed over the area where the cells were positioned. This simplified the addition of stock solution and manipulation of the cell assemblies.

Stirring for the cells was provided by a variable speed Poly Science Corporation model RZR-10 stirrer motor. This stirrer motor was connected to a Pic chain and sprocket mechanism by two Sears Craftsman right angle drives. The chain sprockets turned two large Teflon stirbars to provide stirring for two cells. Figure 8 shows a cross-sectional view of the constant temperature bath and the placement of the various components associated with it.

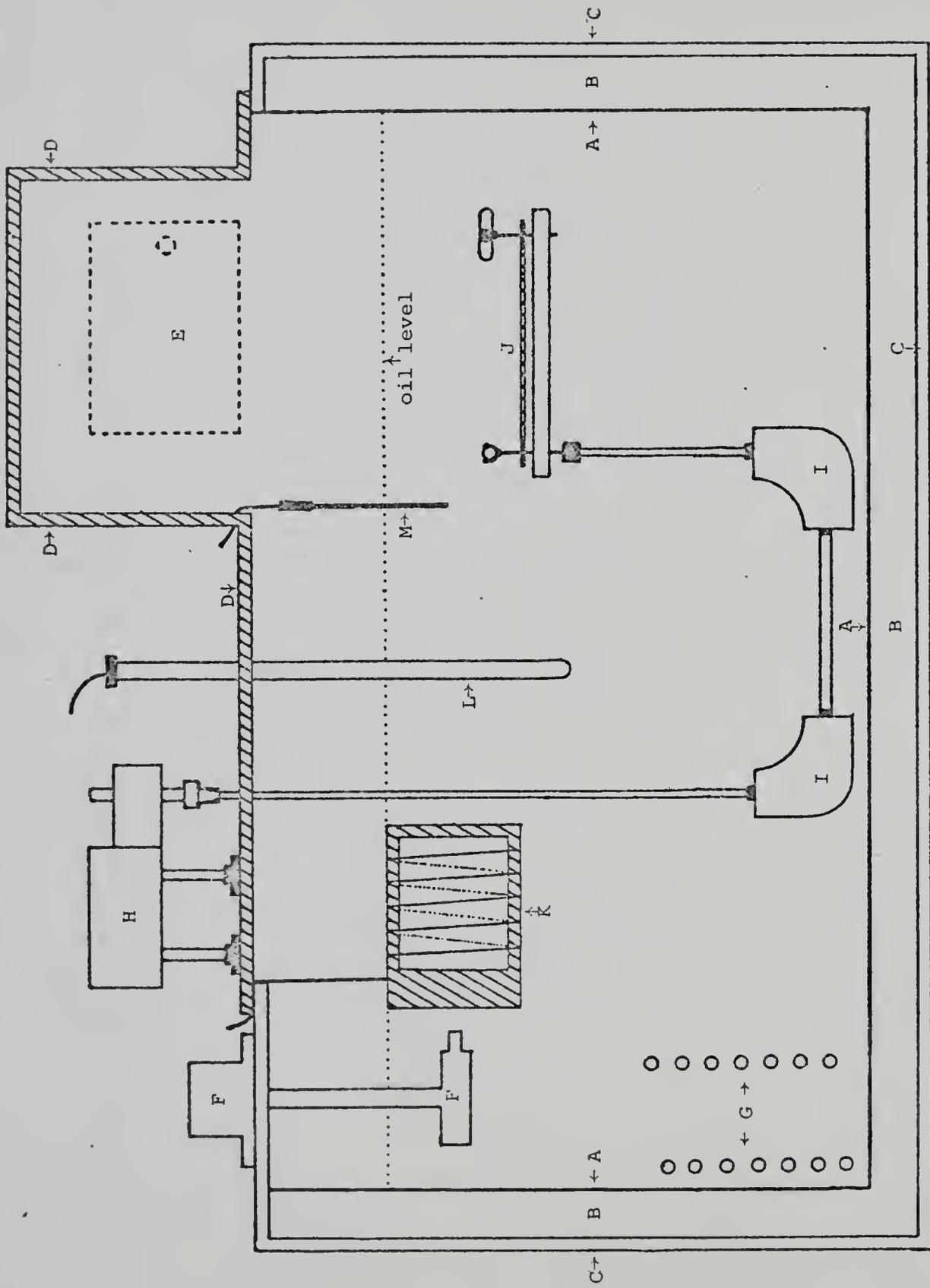
Densities were determined by three Fisher pycnometers with volumes of approximately 25 ml. Pycnometers were calibrated by multiple weighings of conductivity water. The values obtained from the three pycnometers were averaged together to get mean values for the densities.

Viscosities were determined with viscometers of the Cannon-Fenske design; they were also calibrated with conductivity water.

Figure 8. Drawing of a sectional view of the constant temperature bath and associated components.

KEY

- A Stainless steel inner wall.
- B Foam insulation.
- C Phenolic outer wall (for support).
- D Plexiglas cover, including access box lid.
- E Indicates position of door in access box lid.
- F Circulating pump.
- G Cooper coil for cold water circulation.
- H Poly Science variable speed stirrer moter.
- I Sears right angle drives.
- J Brass bearing support with Pic chain and sprockets, holding Teflon magnetic stirring bars.
- K Plexiglas frame wound with Nichrome wire for heating.
- L Standard Vycor immersion heater.
- M Probe used with temperature controller.



## CHAPTER IV

### METHODS

#### Method of Experiment

The properties of ethylene carbonate-water mixtures are such as to require pretreatment and conditioning to insure reproducible results. However, the experimental procedure followed was basically a stepwise addition method utilizing weights rather than volumes for higher accuracy. Thus, solute concentrations were initially low. Concentrations greater than that of the addition solution were produced by the addition of the electrolyte itself.

Ethylene carbonate has a tendency to leach ionizable impurities from glassware.<sup>4</sup> To reduce the magnitude of this problem, cells and other glassware in contact with ethylene carbonate during the experiments were filled with conductivity water when not in use. This was not sufficient, as a decrease in resistance with time was still observed when solvent was added. Thus, before starting a run, it was necessary to allow the cells to equilibrate overnight with solvent of the same composition as that used in the experiment. The cells were then rinsed and refilled with fresh solvent, and its specific conductance determined (for use in making solvent corrections).

The first addition of electrolyte after this pretreatment step exhibited behavior opposite to leaching. Drift of the measured resistance in this case was upward, implying a gradual loss of ions. The cell surfaces now had to come to equilibrium with the solute at its initial

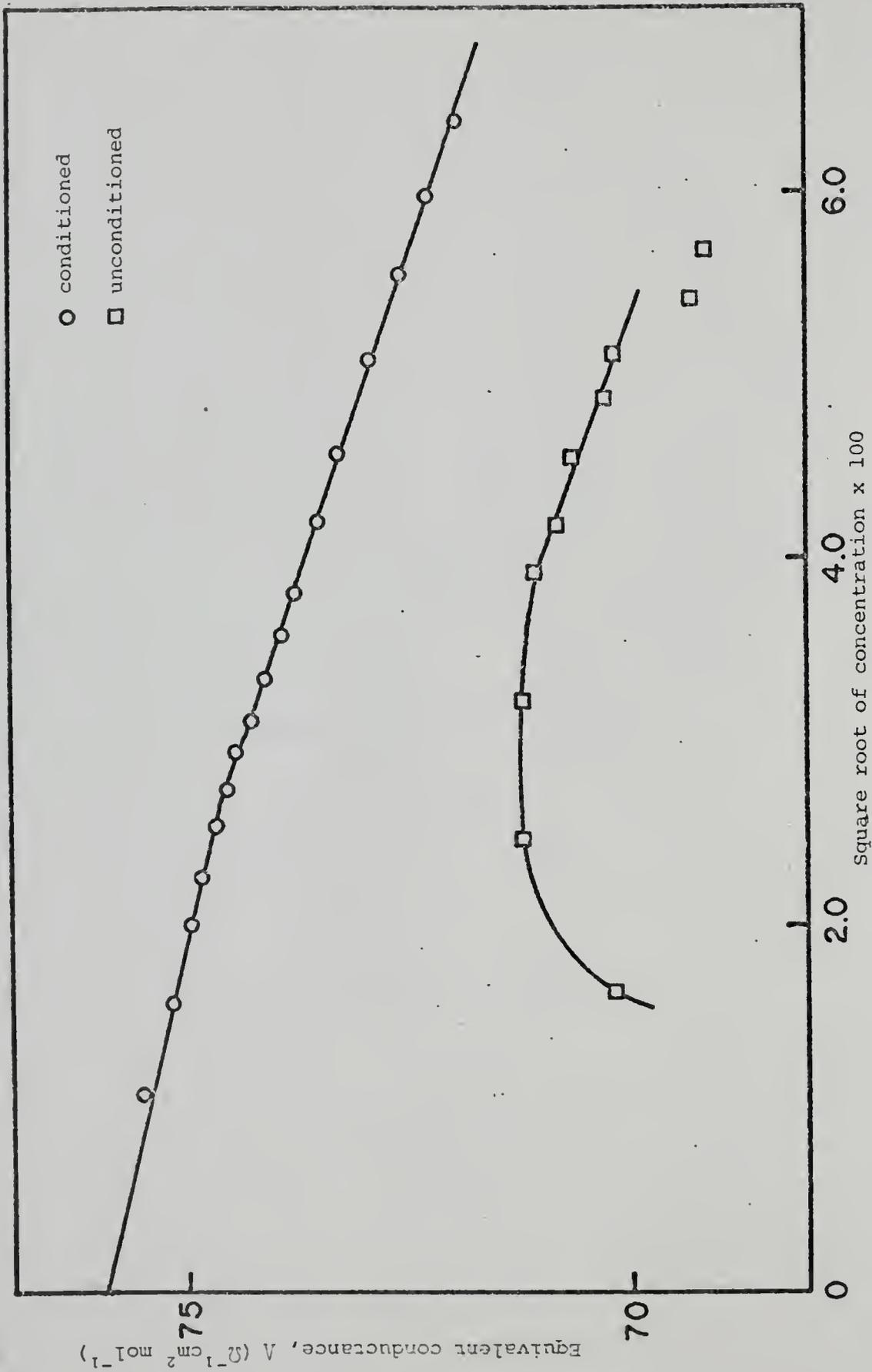


Figure 9. Comparison of a conditioned and an unconditioned run for HCl in 50 mole percent ethylene carbonate at 25 °C.

concentration. This problem was more pronounced for the acids than for the salts. Equilibrium was generally reached in 18 hours, as evidenced by a constant value of the measured resistance. The initial conditioning solution was then discarded; fresh solvent was added without rinsing and the weight of the cell and solvent determined. The first weighed increment of addition solution was added at this time. The cell was then placed in the constant temperature bath and allowed to reach thermal equilibrium. Figure 9 shows the difference between conditioned and unconditioned runs. The solution was indeed stable thereafter, as evidenced by relatively minor changes in measured resistance ( $<0.01\%$ ) which occurred overnight.

Addition of solutions directly into the cells resulted in splashing, and drops of more concentrated solution collected on the sides of the cells. The entire cell then had to be shaken to wash these drops into the bulk of the solution. When using two cells, however, the possibility of cell damage from shaking was significantly increased. To eliminate the necessity of shaking the cells, a special filling cap was designed, as shown in Figure 10.

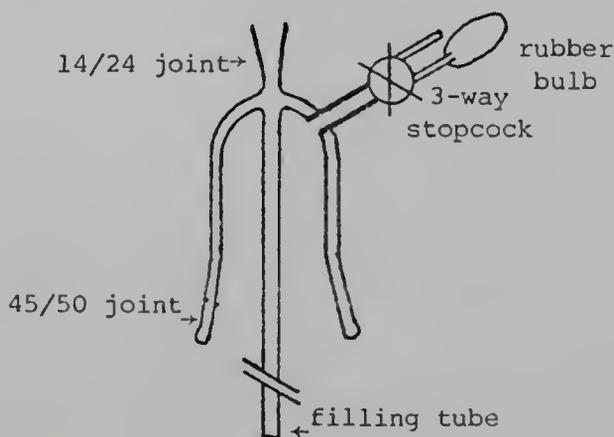


Figure 10. Drawing of a special filling cap.

The long fill tube extending to the solution level prevented splashing, and the bulb and three-way stopcock allowed solution to be pushed up into the fill tube to rinse it out. Both caps and stirbars were stored, as were the cells, in conductivity water. They were also subjected to the pretreatment and conditioning steps.

Addition solutions were kept in a weight buret or capped polyethylene wash bottle. In earlier experiments, the ground glass joints of the weight buret were frequently covered with crystals, causing potential weighing problems. This "creeping" was the result of evaporation of water from the solution. The crystals resulting from this evaporation formed capillaries which then drew more solution up, leading to further evaporation. Crystals would frequently cover the entire bottom of the buret. This experience made it necessary to find alternatives to the weight buret. The use of polyethylene wash bottles eliminated this problem and offered other advantages as well.

#### Preliminary Data Handling

As the conductance bridge was designed to use the four-lead technique, all resistance data are the means of the resulting two readings. Measurements were made with alternating current rather than direct current to eliminate composition changes resulting from electrolysis. Hence, provision had to be made for separating the ohmic resistance from capacitance effects and other frequency dependent terms. This is generally done by taking measurements at various frequencies and then extrapolating to infinite frequency. Many of the various methods of frequency extrapolation have been discussed by Hoover,<sup>22</sup> and his recommendations were followed. The technique used is also discussed by

Robinson and Stokes,<sup>54</sup> who consider it applicable to bright platinum electrodes in aqueous solutions. It is based on an equation of the form:

$$R_{\text{measured}} = R_{\text{ohmic}} + \frac{R}{1 + a\omega^2} \quad (28)$$

where:

$$a = \frac{F - 1}{\omega_3^2 - F\omega_2^2}$$

and:

$$F = \frac{\omega_1^2 - \omega_3^2}{\omega_1^2 - \omega_2^2} \cdot \frac{R_2 - R_1}{R_3 - R_1}$$

$\omega$  has the usual form of  $2\pi\nu$ . The measured resistance was plotted against  $(1 + a\omega^2)^{-1}$ , and the intercept at infinite frequency (where the second term on the right of equation (28) = 0) gave the value of the ohmic resistance.

Equation (28) was only useful over a limited resistance range, however. When the measured resistance is very high (as with pure solvent or very dilute solutions), resistance increased with frequency rather than decreased, which is considered normal.<sup>12,15</sup> Application of equation (28) to these anomalous frequency results caused a reversal of the  $\omega^2$  dependence. This reversal of the dependence resulted in an intercept of unknown meaning. The effect has been described by Mysels *et al.*,<sup>55</sup> and is attributed to leakage to ground along a resistance and capacitance in series. They conclude that extrapolation to zero frequency is the correct procedure for extracting the ohmic resistance of the cell. This was the procedure followed in this work.

To convert the value of the ohmic resistance to the specific conductance, a knowledge of the cell constant is required. The cell

constant was determined by measuring the resistance of a solution of known specific conductance. The accepted standards for cell constant determinations are aqueous solutions of potassium chloride as described by Jones and Bradshaw.<sup>14</sup> A more recent work by Fuoss et al.<sup>56</sup> gives an expression which allows the calculation of the equivalent conductance of aqueous potassium chloride at 25 °C at any concentration up to about 0.04 M. Their equation is:

$$\Lambda = 149.93 - 84.65\sqrt{c} + 58.74c\log c + 198.4c \quad (29)$$

where  $c$  is the concentration in moles per liter.

The experimental procedure of the usual runs was followed in its entirety. This produced a set of measured ohmic resistances and concentrations. From equation (7), we can write an expression relating the specific conductance  $\kappa$  to the cell constant  $\theta$  (equal to  $\frac{l}{A}$ ) and the solution resistance  $R_s$ :

$$\kappa = \frac{\theta}{R_s} \quad (30)$$

If the assumption is made that  $R_s = R_m$  (the measured resistance after frequency extrapolation), equation (30) can be rearranged to give:

$$R_m = \frac{\theta}{\kappa} \quad (31)$$

If the experimental  $R_m$  is plotted against  $\kappa^{-1}$  (which can be calculated using equation (29) and equation (8)), the slope of the line will be the cell constant. As many points will be used in the determination, a linear least squares fit can be used. An example of such a plot is given in Figure 11. This plot includes data from three separate runs and demonstrates the reproducibility of the technique.

No definitive standards for solution conductivity have been proposed for temperatures other than 0, 18, and 25 °C.<sup>14</sup> Thus, cell

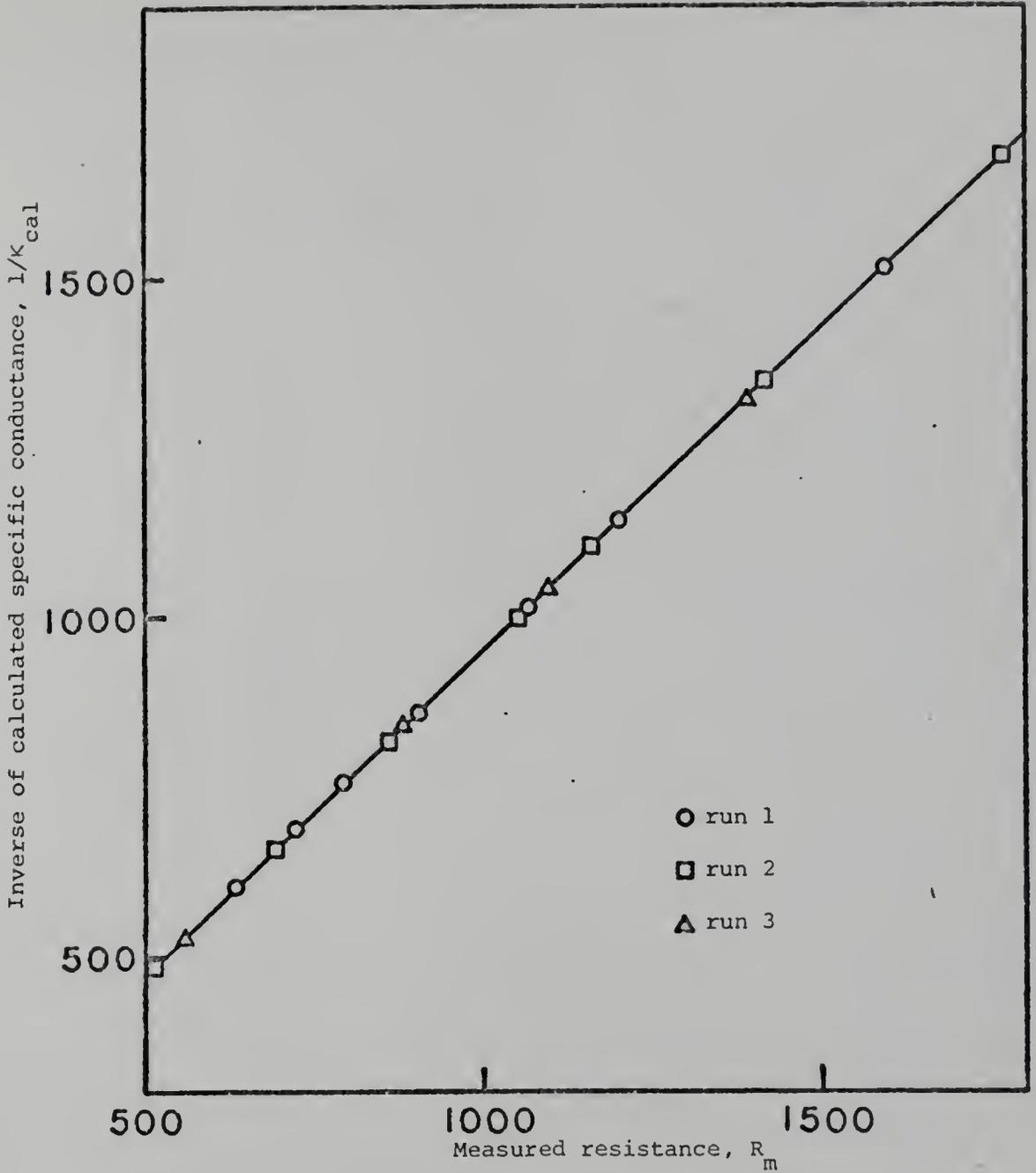


Figure 11. Plot of the inverse of the calculated specific conductance vs. the measured resistance.

constants at 40 °C were determined by calculations based on cell design and the coefficients of expansion of Pyrex glass and platinum. This calculation is described in detail by Robinson and Stokes.<sup>57</sup> The cell constants thus calculated were on the order of 0.02 percent less than the corresponding values at 25 °C.

The concentrations of the individual solutions were determined on the basis of the total amount of addition solution used and the initial weight of solvent present in the cell. Since all additions were in terms of weight, it was most convenient to use molality (moles per 1000 g of solvent) for these determinations. In calculating the equivalent conductance, however, the concentration is expressed in terms of moles per liter. A convenient relation between the molality,  $m$  and the molarity  $c$ , is given by:<sup>58</sup>

$$c = \frac{1000\rho m}{1000 + mM_{\text{solute}}} \quad (32)$$

To apply this equation one needs a knowledge of the solution density,  $\rho$ . Densities of the various solutions were determined at a single concentration. Densities at other concentrations were assumed to lie on the straight line defined by the measured solution density and the pure solvent value. Once the concentration was known, the equivalent conductance could be calculated using equation (8).

Calculations up to this point were all done on a Hewlett-Packard model 55 programable calculator. (Power series fits of mixed solvent parameters and the linear least squares fits of the potassium chloride cell constant determinations were done on a Wang 600 series programable calculator.) Several "programs" were written especially for the calculation of these results.

KEQIVES Program Description

The facilities of the Northeast Regional Data Center of the University of Florida were used for more complex calculations involving Pitts' relation (equation (24)). The Fortran IV program used for the final analysis of the equivalent conductance data was that of Duer, Robinson, and Bates.<sup>41</sup> Some modifications were added to increase program efficiency and alter the printout format.

The program utilized an iterative procedure of Ives,<sup>59,60</sup> which is based on an expression for the dissociation constant  $K_d$ :

$$K_d = \frac{c_i^2 y_{\pm}^2}{c_u} \quad (33)$$

Here the subscript  $i$  denotes quantities based on the ions present in the solution. The subscript  $u$  denotes undissociated molecules of electrolyte (the activity coefficient in this case is assumed to be equal to unity). The degree of dissociation can be expressed as:

$$\alpha = \frac{\Lambda}{\Lambda_i} \quad (34)$$

Hence, one can write:

$$c_i = \alpha c = \frac{\Lambda}{\Lambda_i} c \quad (35)$$

similarly, for  $c_u$ :

$$c_u = (1 - \alpha)c = \frac{c}{\Lambda_i} (\Lambda_i - \Lambda) \quad (36)$$

Combining equations (33), (34), and (36) yields:

$$K_d = \frac{\Lambda^2 c y_{\pm}^2}{\Lambda_i (\Lambda_i - \Lambda)} \quad (37)$$

In Ives' paper,<sup>59</sup> the theoretical basis for determining  $\Lambda_i$  was Onsager's limiting law, equation (16). In the present program, however, Pitts' equation is used. If  $\Lambda_r$  symbolizes Pitts' theoretical expression for determining  $\Lambda_i$  from  $\Lambda^\infty$ , equation (37) becomes:

$$K_d = \frac{\Lambda^2 c y_{\pm}^2}{\Lambda_i (\Lambda^\infty + \Lambda_r) - \Lambda} \quad (38)$$

This expression can be rewritten as:

$$\Lambda - \Lambda_r = \Lambda^\infty - \frac{\Lambda^2 c y_{\pm}^2}{\Lambda_i K_d} \quad (39)$$

which can be reduced to the form:

$$Y = \Lambda^\infty - X \frac{1}{K_d} \quad (40)$$

where:

$$Y = \Lambda - \Lambda_r$$

$$X = \frac{\Lambda^2 c y_{\pm}^2}{\Lambda_i}$$

Equation (40) is in the form of a straight line, and  $\Lambda^\infty$  and  $K_d$  (equal to  $\frac{1}{K_d}$ ) are intercept and slope, respectively. As  $\Lambda^\infty$  is used to calculate  $\Lambda_r$ , an initial estimate based on extrapolation of the  $\Lambda$  against  $\sqrt{c}$  was provided. After following the above procedure, least squares

analysis gives a new estimate of  $\Lambda^\infty$ . The procedure is repeated with this new  $\Lambda^\infty$ , generating another set of X and Y values and another  $\Lambda^\infty$  and  $K_a$ . Five of these interactions were more than sufficient to reach values of  $\Lambda^\infty$  and  $K_a$  which were constant.

In Ives' paper, the Debye-Hückel limiting law expression:

$$\log f_{\pm}^2 = -2A|z_1 z_2| \sqrt{I} \quad (41)$$

was used to determine the activity coefficients. However, the more complete expression (equation (26)) was used in the KEQIVES program.

As a check of the program the data of MacInnes and Shedlovsky<sup>61</sup> for acetic acid in water at 25 °C were analyzed. Table 1 compares the accepted values of  $\Lambda^\infty$  and  $K_a$  with those determined by the program (the ion size parameter in each case was 4 Å).

TABLE 1

Comparison of the accepted values of limiting equivalent conductance and association constant to the values determined by the KEQIVES program for acetic acid in water at 25 °C.

	$\Lambda^\infty$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	$K_a$ (liter $\text{mol}^{-1}$ ) $\times 10^5$
Accepted	390.71	1.753
KEQIVES	390.59	1.750

$a = 4.0\text{Å}$ , Accepted values from Robinson, R. A. and Stokes, R. H., Electrolyte Solutions, 2nd. ed., revised, Butterworths, London, 1970, pp 336, 339.

## CHAPTER V

### RESULTS AND DISCUSSION

#### Relevant Properties of Ethylene Carbonate

Ethylene carbonate is an interesting solvent with many unusual properties. It is generally considered to be a cyclic ester, and has been listed in Chemical Abstracts under the heading: Carbonic acid, cyclic ethylene ester. Since volume 76, it has been listed as 1, 3-dioxolan-2-one. The common name, ethylene carbonate, has been used throughout this study.

The structure of ethylene carbonate is that of a heterocyclic five-membered ring incorporating a carbonyl group. Bond lengths and angles have been reported by Brown<sup>62</sup> and are reproduced in Figure 12.

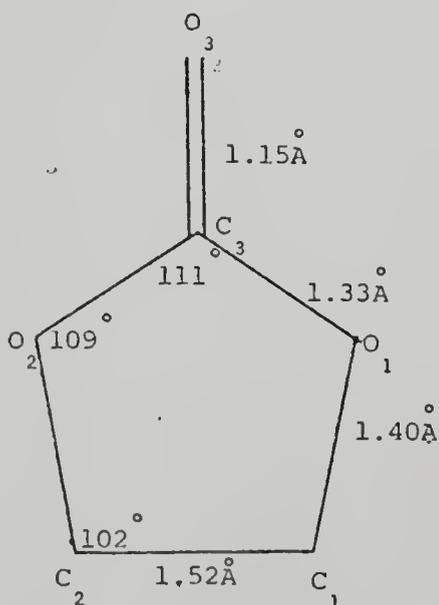


Figure 12. Ethylene carbonate molecule, showing bond angles and distances.

The large permanent dipole moment of 4.87 debyes<sup>63</sup> is responsible for its large dielectric constant (90.36 at 40 °C).

X-ray diffraction studies show that solid ethylene carbonate consists of layers.<sup>62</sup> The carbonyl groups are parallel in any given layer, but in alternate layers they are opposite in orientation. The unit cell of crystalline ethylene carbonate as determined by Brown<sup>62</sup> is shown in Figure 13.

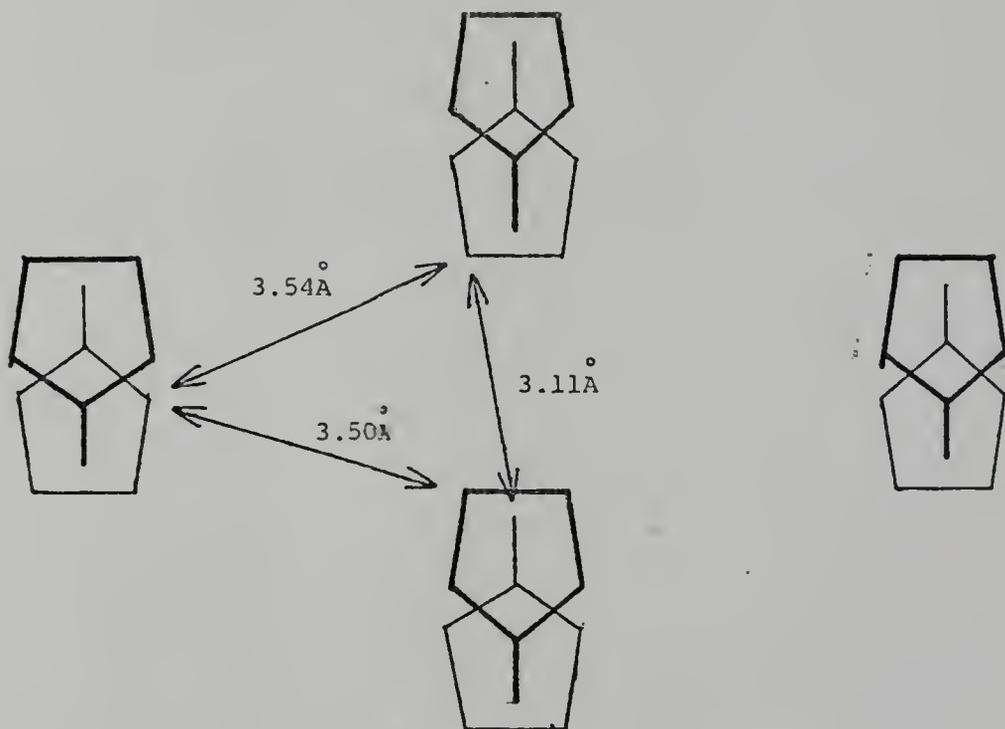


Figure 13. The unit cell of crystalline ethylene carbonate

The closest intermolecular distances between layers are associated with carbonyl oxygens and ethylene hydrogens. Various other C-H-O alignments occur as well, some of which are indicated in Figure 13. This close approach is an indication of strong dipole interactions, or possibly the presence of some hydrogen bond character.

In the solid state, the carbonate group is planar, with the  $C_1-C_2$  bond forming an angle of  $20^\circ$  to the carbonate plane. In the liquid state,

there is evidence that ethylene carbonate is planar except for the hydrogen atoms,<sup>64,65</sup> as postulated by Angell.<sup>66</sup> A more recent study concludes that the carbonate group remains planar, but there is a small nonplanar ring-puckering motion of the ethylene group.<sup>67</sup>

Ethylene carbonate is generally considered to be slightly associated. Values of the Harris-Alder correlation parameter<sup>68</sup> and the Kirkwood parameter<sup>69</sup> indicate slight association. Bonner and Kim<sup>70</sup> have studied osmotic coefficients of ethylene carbonate in benzene, and observed non-ideal behavior. They conclude that the primary reason for this non-ideality is association. They also report "clusters" in ethylene carbonate averaging 8.3 monomer units in size, and that the carbonyl group is involved in the association. However, the expected carbonyl association would result in a major cancellation of the dipole moments. The high dielectric constant is evidence against structures similar to those present in the solid state. An alternative possibility is the presence of hydrogen bonds, although this is also unlikely, as carbon is not considered electronegative enough for their formation. This would be an interesting area to investigate in future studies.

As an electrolytic solvent, ethylene carbonate is unusual. The alkali metal chlorides are almost insoluble, as mentioned previously. The chlorides of Hg(II), Fe(II), and other heavy metals are soluble,<sup>45</sup> as are alkali metal perchlorates and tetraalkylammonium halides.<sup>5</sup> This behavior is a result of poor anion solvation and the greater degree of solvation of the larger, more polarizable cations. Ethylene carbonate can be classified as a dipolar aprotic solvent using Kolthoff's<sup>71</sup> extension of Davis' classification scheme, and has moderate Lewis base properties.

Mixed Solvent Properties

Ethylene carbonate has a relatively high cryoscopic constant of 5.40 °C/mol.<sup>47</sup> Hence, mixtures with relatively small amounts of water should remain fluid at 25 °C. This behavior was observed, and compositions up to about 90 mole percent ethylene carbonate have been reported to exist as liquids at 25 °C.<sup>72</sup> The mixtures tend to supercool readily, as does ethylene carbonate itself.

Bonner and Kim<sup>70</sup> report self-association of ethylene carbonate in benzene but note that in solvents of high dielectric constant the association is much less. Hence, little self-association of ethylene carbonate in water mixtures is expected until the fraction of ethylene carbonate is quite high.

A plot of density vs. mole fraction is shown in Figure 14. The plot exhibits positive deviation from ideality, which usually indicates association between the two components. Geddes<sup>73</sup> has indicated that the composition at the maximum deviation from linearity is that of the associated species. As an aid in determining this point of maximum deviation of linearity, the excess density,  $\Delta d$ , is plotted with the density. The excess density was calculated from the expression:

$$\Delta d = d_m - (x_1 d_1 + x_2 d_2) \quad (42)$$

Here  $d_m$  is the experimentally determined density at a given mole fraction, while  $d_1$  and  $d_2$  are the densities of the two pure components of the mixed solvent system.  $x_1$  and  $x_2$  are the mole fractions of the two components. The excess density is plotted in the lower part of the figure using the same mole fraction axis as for the density. It displays a broad peak with a maximum at a mole percent of approximately 33 at both 25 and 40 °C. This corresponds to an association between one ethylene

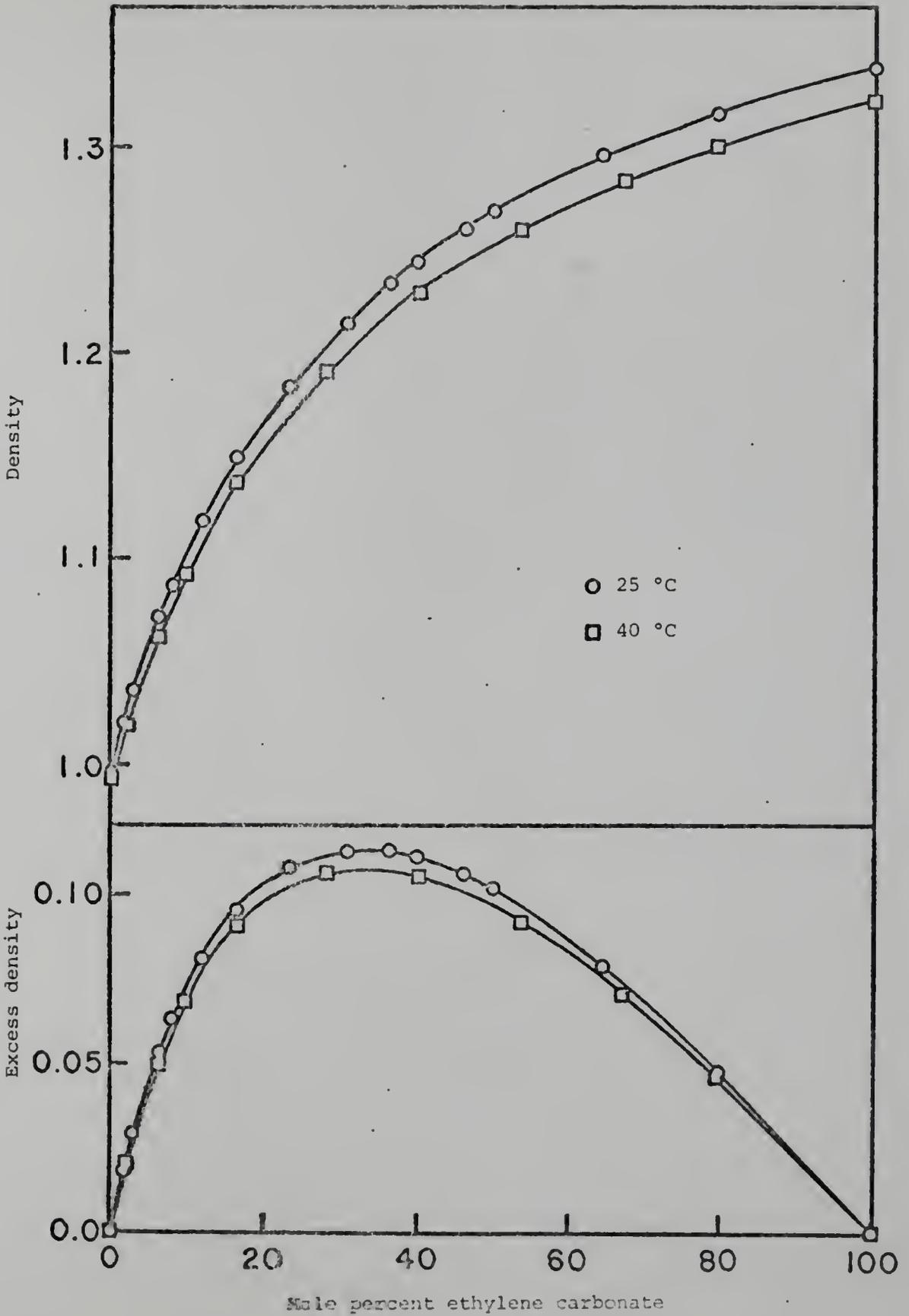
Figure 14. Plot of density and excess density vs. the mole percent ethylene carbonate.

Note: data for this plot were obtained from the following sources in addition to this work.

G. P. Cunningham, G. A. Vidulich, and R. L. Kay, *J. Chem. Eng. Data*, 12, 336 (1967).

A. D'Aprano, *Gazz. Chim. Ital.*, 104, 91 (1974).

R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed., revised, Butterworths, London, 1970.



carbonate molecule and two water molecules, most likely by hydrogen bonding involving the carbonyl oxygen. However, the peaks are broad and it is doubtful that any definite composition is present.

The change of the dielectric constant with composition also shows positive deviations. However, the corresponding excess values exhibit a shift with temperature, as shown in Figure 15. At 25 °C, the excess dielectric constant is a maximum at about 20 mole percent ethylene carbonate, while the maximum at 40 °C corresponds to 40 mole percent. The data for the dielectric constant appear less precise than those for the density. This fact must be taken into consideration when conclusions are drawn relating to the plot. Nevertheless, the possibility of some form of association with water exists. When the temperature is as high as 40 °C, the association is reduced through thermal agitation, and a composition closer to a 1:1 ratio may be favored.

As shown in Figure 16, the plot of viscosity vs. solvent composition also exhibits interesting behavior, again best illustrated by the excess quantity. While the viscosity does not go through a maximum as observed in the strongly associated dimethylsulfoxide (DMSO)-water system,<sup>74</sup> there is a point of inflection. In the region of low mole fractions, the plot behaves in the same manner as the previous two, a fairly rapid rise being followed by a slight leveling, which is earlier in this case. As the concentration of ethylene carbonate increases, a reduction in viscosity occurs possibly due to formation of the 1:1 species. This 1:1 species probably has less structure than either pure water or pure ethylene carbonate. However, the compositions with more water retain more of their structure than the compositions with higher ethylene carbonate concentrations. This is evidenced by the negative deviations of the

Figure 15. Plot of dielectric constant and excess dielectric constant vs. the mole percent ethylene carbonate.

Note: data for this plot were obtained from the following sources.

R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2nd ed., revised, Butterworths, London, 1970.

R. P. Seward and E. C. Vieira, *J. Phys. Chem.*, 62, 127 (1958).

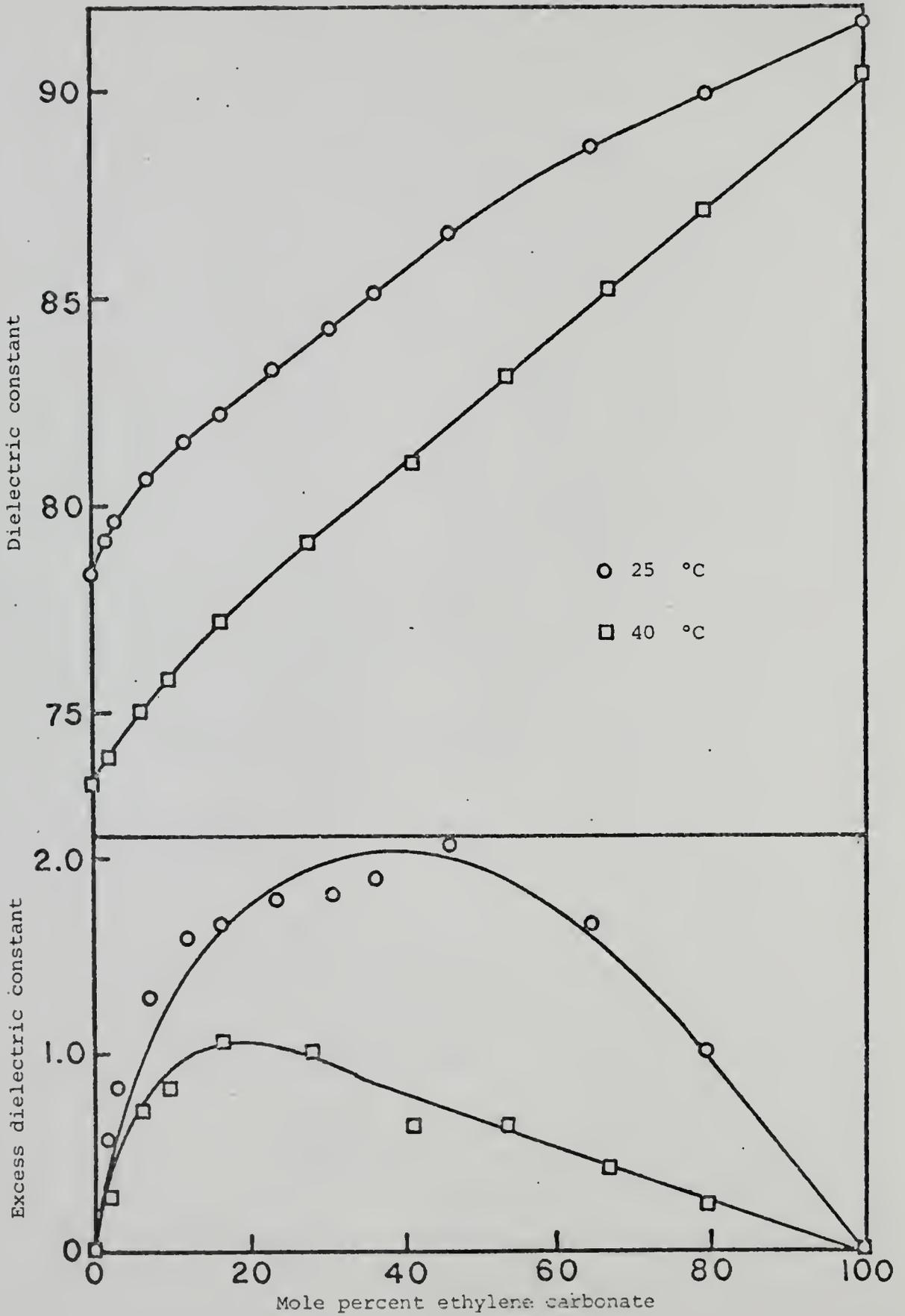
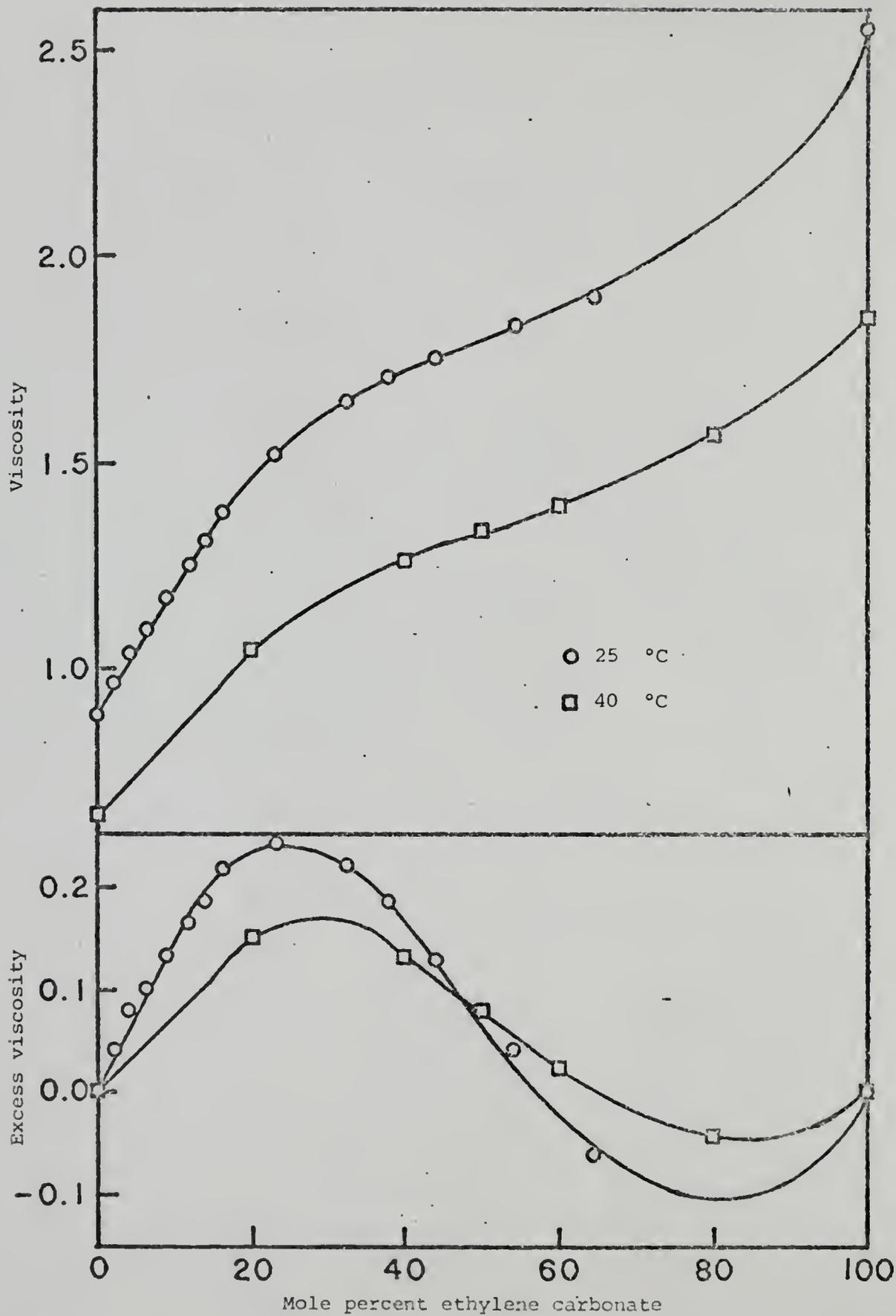


Figure 16. Plot of viscosity and excess viscosity vs. the mole percent ethylene carbonate.

Note: data for this plot were obtained from the following sources in addition to this work.

G. P. Cunningham, G. A. Vidulich, and R. L. Kay, *J. Chem. Eng. Data*, 12, 336 (1967).

R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2nd ed., revised, Butterworths, London, 1970.



excess function at the ethylene carbonate end of the plot. Apparently water is better at destroying the existing ethylene carbonate structure than ethylene carbonate is at breaking up the hydrogen bonded water structure.

Bonner and Choi<sup>75</sup> present evidence that propylene carbonate-water mixtures of low water concentrations (mole fraction less than 0.1) contain both a 1:1 species and a 1:2 species (one water molecule to two propylene carbonate molecules). This is perhaps the case with ethylene carbonate as well. The 1:2 species would be less likely to participate in further hydrogen bonding, and its formation is probably associated with the ethylene carbonate structure breakdown. As the concentration of water is increased, the 1:1 species would predominate, and the increased chance of hydrogen-bonded chains would be less disruptive to the water structure.

As compared to other mixed solvent systems containing ethylene carbonate, the relatively small positive deviations<sup>69</sup> from linearity are significant. One would expect that the addition of an organic species would disrupt the structure of the water. The lowering of temperature when the mixed solvent is prepared would be experimental evidence for such a breakdown of the water structure. Heat must be extracted from the solution to break the hydrogen bonds present in the water. Indeed, on mixing ethylene carbonate and water, the temperature was reduced sufficiently to cause the formation of crystals of ethylene carbonate. Considering this reduction in structure, large negative deviations from linearity would be expected, rather than the small positive deviations actually observed. Similar behavior has been observed in the DMSO-water system and attributed to a strong interaction between the two components.<sup>76</sup> Perhaps at lower mole fractions of ethylene carbonate,

the ethylene carbonate molecules can fit into the larger gaps of the diffuse quasi-lattice of water<sup>77</sup> with minimal disruption. However, as more ethylene carbonate molecules are added, smaller gaps must be used resulting in more structural breakdown and more association between the two species.

### Plots of $\Lambda$ vs. $\sqrt{c}$

The usual method of presenting conductance data is by plotting the equivalent conductance,  $\Lambda$ , vs. the square root of the molar concentration,  $c$ . Strong electrolytes with little or no association give linear plots, and extrapolation to the limiting equivalent conductance,  $\Lambda^\infty$ , at zero concentration is straightforward. Data for electrolytes with higher association constants exhibit curvature at the lower concentration regions when treated in this manner. In this case, extrapolation becomes more difficult without the aid of additional manipulations of the data.

Fuoss and Accascina<sup>78</sup> describe the changes in the conductance curves as the electrolyte is changed from one which is completely dissociated to one which is strongly associated. The curvatures described are arbitrarily divided into six types. As an aid to classification, the Onsager tangent is included with the conductance curve. The numerical value of the Onsager tangent has been given previously as the factor in brackets in equation (17):

$$\Lambda = \Lambda^\infty - \left[ \frac{8.204 \times 10^5}{(\epsilon T)^{3/2}} \Lambda^\infty + \frac{82.501}{\eta (\epsilon T)^{1/2}} \right] \sqrt{c} \quad (17)$$

The line showing the Onsager tangent in the following plots was generated by utilizing the experimental  $\Lambda^\infty$  and calculating the value of  $\Lambda$  at a concentration of 0.01 molar according to equation (17).

Figure 17 is an example of type I. This behavior is typical of the majority of 1:1 salts in water and other solvents of high dielectric constant. Type I plots exhibit increasing positive deviations from the Onsager tangent as the concentration is increased. The data of low concentration fall on the Onsager tangent.  $\Lambda^\infty$  is easily determined from this straight-line segment of the plot by simple extrapolation to zero concentration.

Behavior intermediate between Fuoss and Accascina's types I and II was exhibited by some of the data in 20 mole percent ethylene carbonate (see Figure 18). The experimental points fall on the Onsager tangent up to relatively high concentrations.  $\Lambda^\infty$  is again easily determined by extrapolation to zero concentration.

Type II is shown in Figure 19. It is characterized by a straight line with a slope somewhat less than the Onsager tangent.  $\Lambda^\infty$  can still be determined by extrapolation to zero concentration. Type II is generally characteristic of solvents with moderately low dielectric constants. Due to this decrease in dielectric constant, ion pairing is beginning to occur.

The majority of the data in this study exhibit type III behavior, as exemplified by Figure 20. The conductance curve is straight or concave to the Onsager tangent at relatively high concentrations, and approaches the tangent only at very low concentrations. A linear extrapolation to zero concentration will result in a value for  $\Lambda^\infty$  which is high. In this case, ion association has increased sufficiently to bring an inflection point with an associated linear behavior into the usual experimental region. With this behavior, it is suggested that the incorporation of  $\alpha$ , the degree of dissociation, into the theoretical

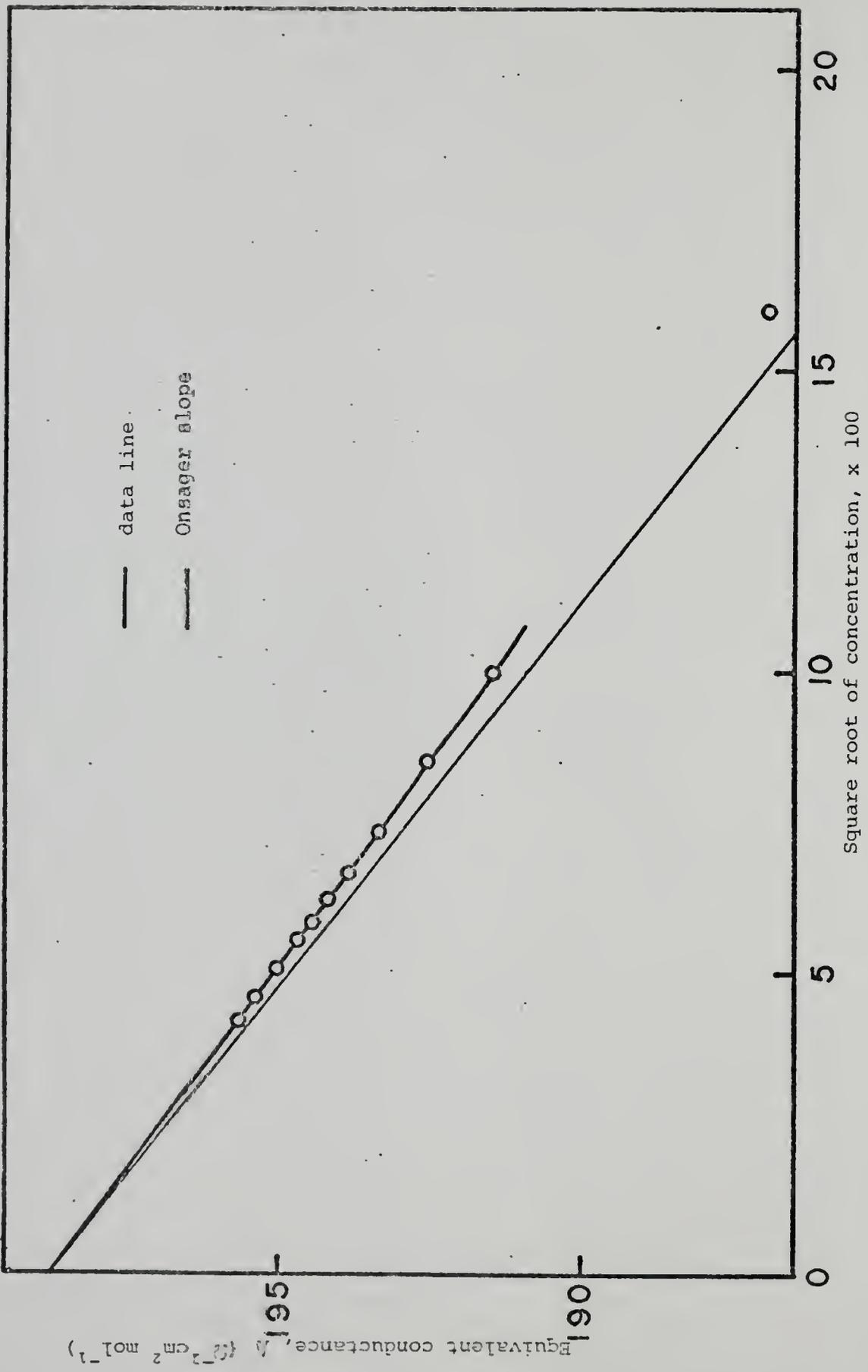


Figure 17. Example of type I behavior. Equivalent conductance vs. the square root of concentration for HCl in 20 mole percent ethylene carbonate at 25 °C.

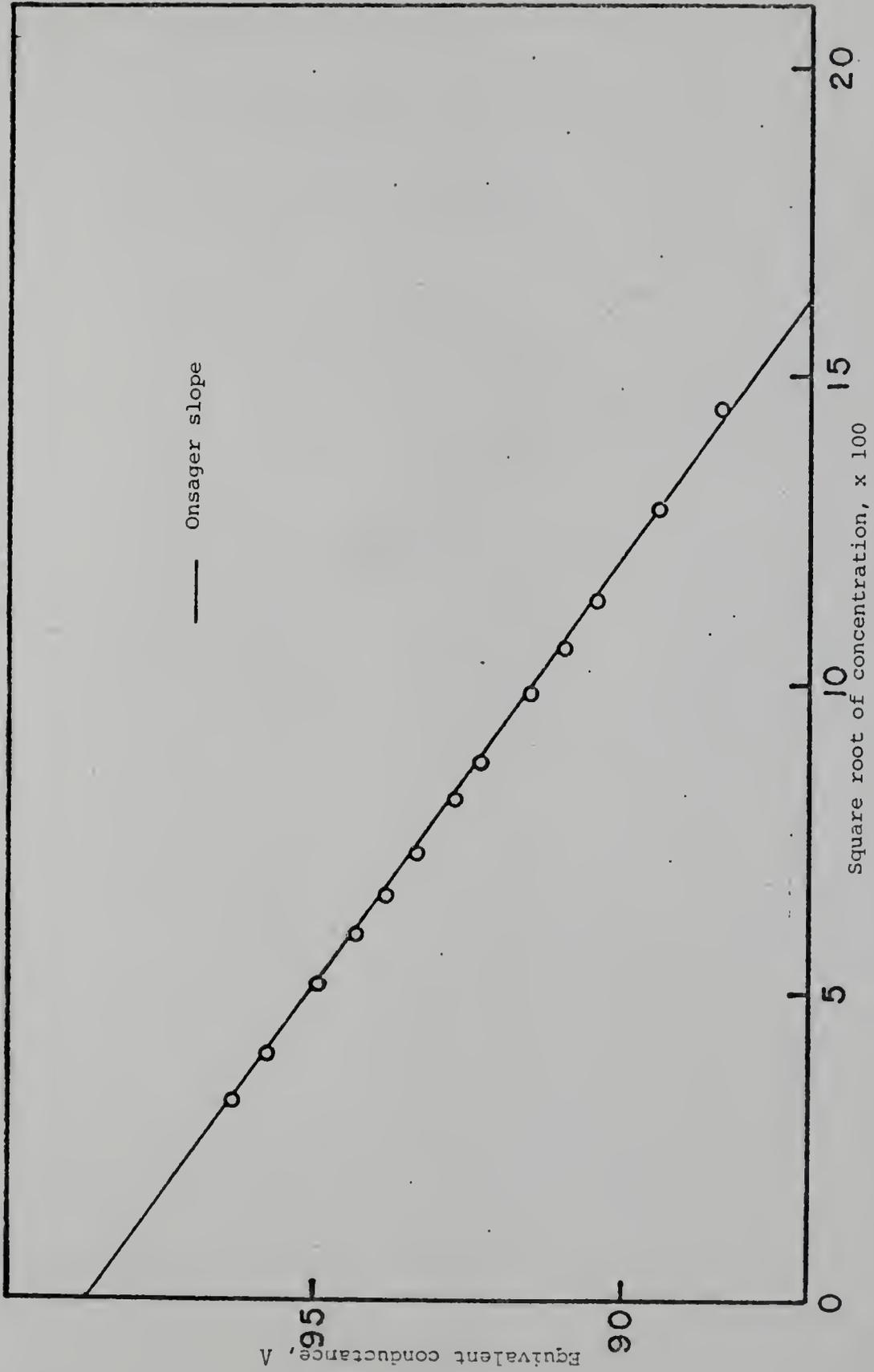


Figure 18. Example of behavior intermediate between type I and type II. Equivalent conductance vs. the square root of concentration for NaCl in 20 mole percent ethylene carbonate at 25 °C.

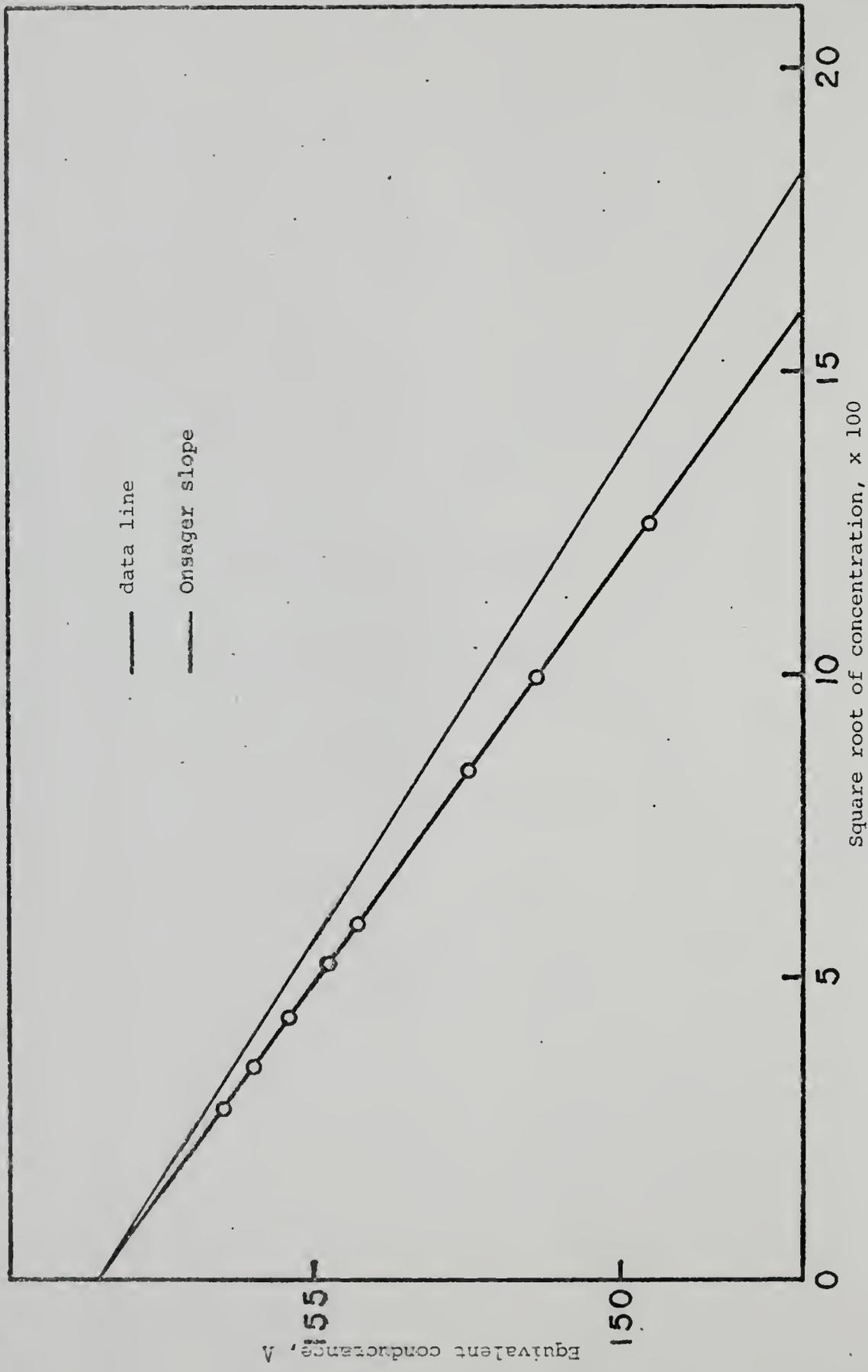


Figure 19. Example of type II behavior. Facsimile.

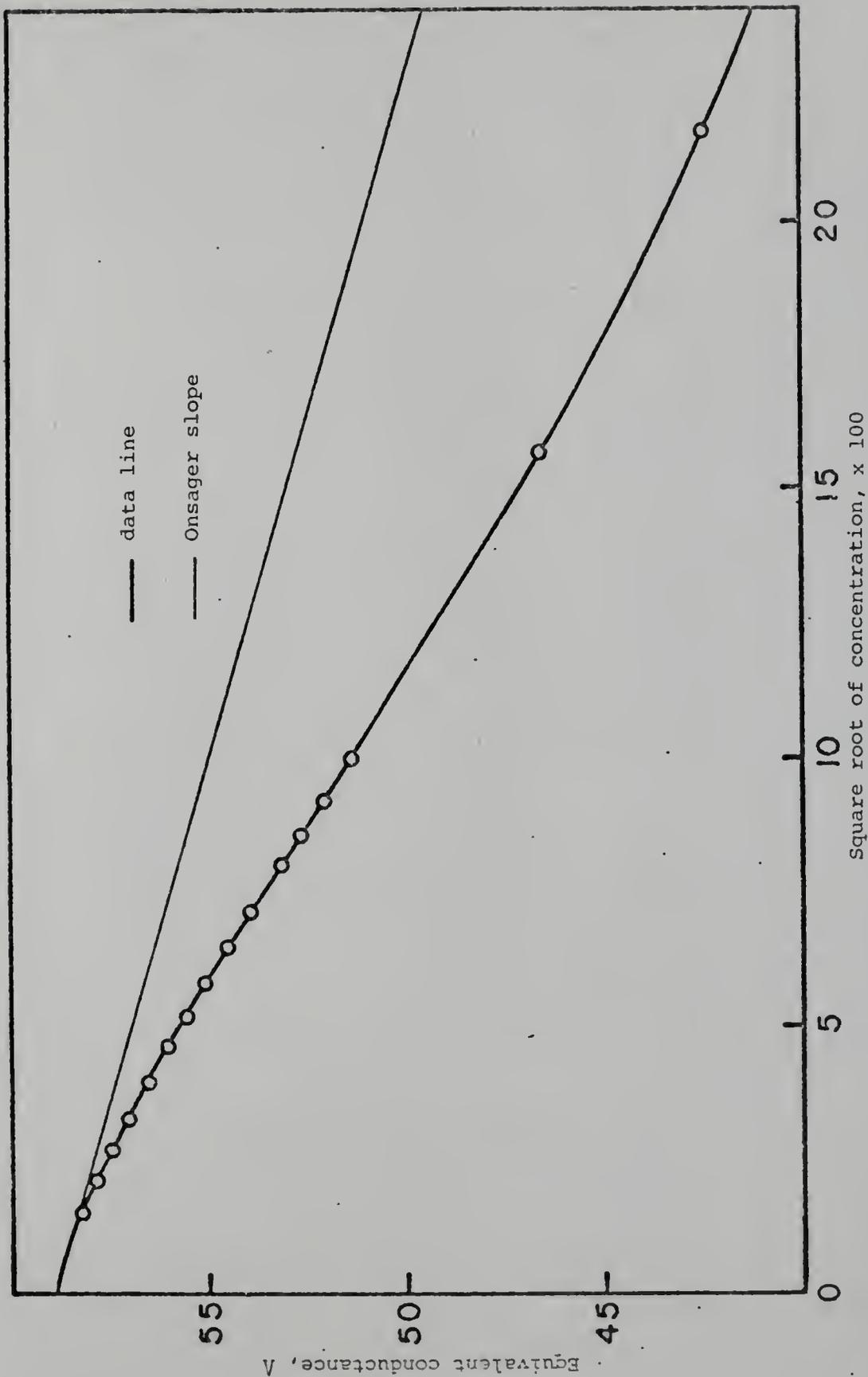


Figure 20. Example of type III behavior. Equivalent conductance vs. the square root of concentration for HCl in 60 mole percent ethylene carbonate at 25 °C.

expression is necessary to accurately describe the behavior of the curve. This is done simply by replacing the concentration  $c$  by  $\alpha c$ . One should recall, however, that this results in calculation of  $\Lambda_i$ . To generate a calculated  $\Lambda$ , it is necessary to multiply  $\Lambda_i$  by  $\alpha$ .

Type IV behavior occurs when ion association moves the inflection point to the low concentration region of the plot. An example is shown in Figure 21. Large errors in  $\Lambda^\infty$  result from linear extrapolation to zero concentration. Ion pairing is extensive, and the use of the mass action relation (equation (25)) is recommended.

All of the data for acetic acid exhibit type V behavior, as shown in Figure 22. As can be seen, type V typically exhibits extremely low values of the equivalent conductance and high curvature. However, type V usually goes through a minimum which is a result of triple ion formation. No such minimum was observed for either acetic acid data or hydrogen chloride data at any composition, including pure ethylene carbonate. Hence, it appears obvious that the solution properties of ethylene carbonate permit ion pairing to occur (producing the large  $K_a$  values). However, the high dielectric constant does not favor triple ion formation.

None of the data in this study are representative of type VI. This behavior is usually associated with the very low dielectric constants of hydrocarbon solvents and with complex structures due to multiple clustering.

It is interesting to note that this gradual progression from type I to type V (or VI) was attributed by Fuoss and Accascina<sup>78</sup> to decreasing dielectric constant. In the case of ethylene carbonate-water, the progression follows the increasing ethylene carbonate concentration, or

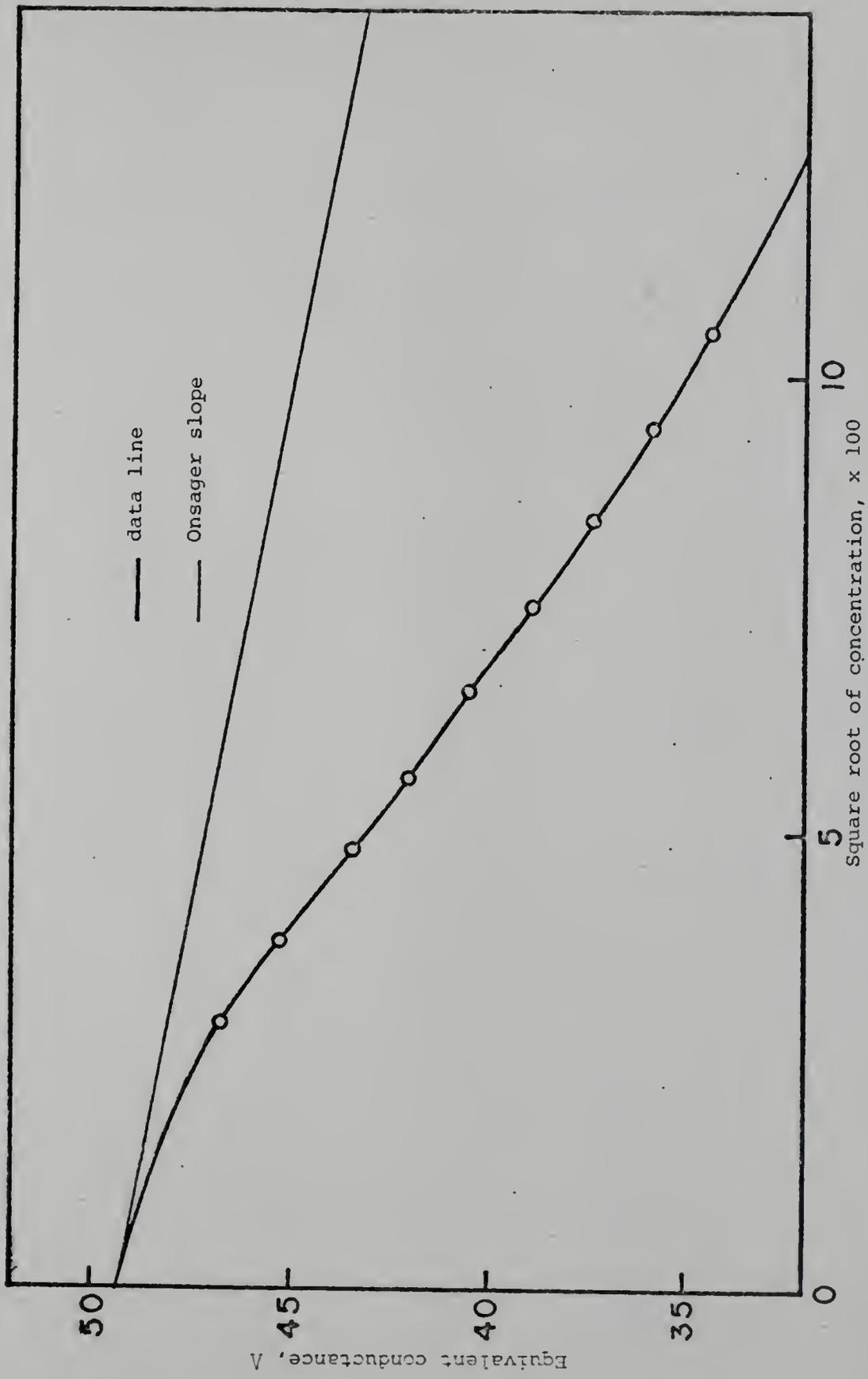


Figure 21. Example of type IV behavior. Equivalent conductance vs. the square root of concentration for HCl in 80 mole percent ethylene carbonate at 40 °C.

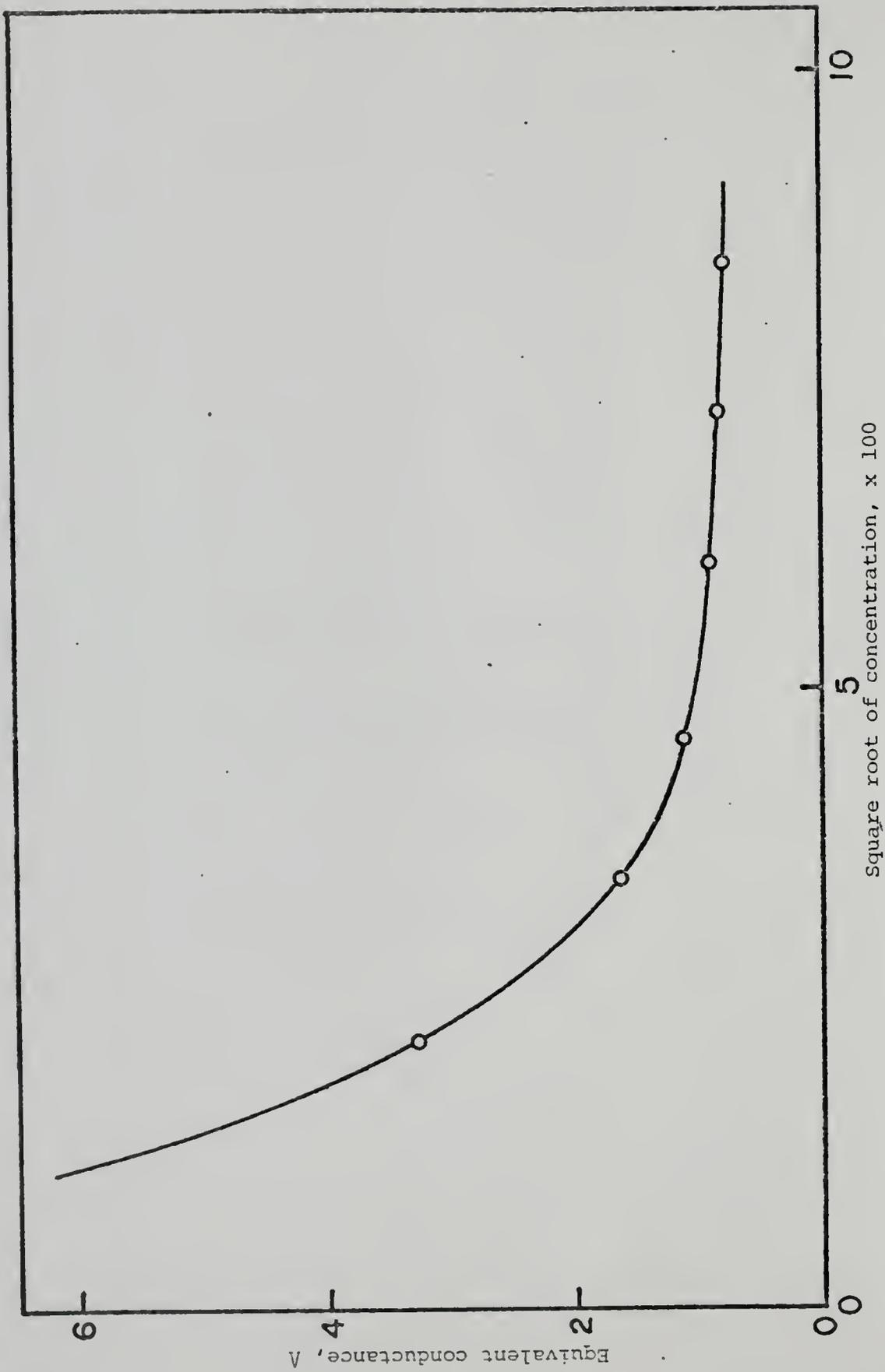


Figure 22. Example of type V behavior. Equivalent conductance vs. the square root of concentration for HCl in 100 mole percent ethylene carbonate at 40 °C.

increasing dielectric constant. The experimental data thus provide additional evidence that the patterns of ionic dissociation and association are as profoundly influenced by ion-solvent interactions as by changes in the electrostatic (Coulomb) forces between oppositely charged ionic species.

Fit to Pitts' Equation Assuming  $K_a = 0$

As evidenced by  $\Lambda$  vs.  $\sqrt{c}$  plots, the data at 20 mole percent ethylene carbonate suggest that little or no association is present for the salts or for hydrogen chloride. Accordingly, the program was modified to fit the  $\Lambda - c$  data assuming  $\alpha = 1.0$  and  $K_a = 0$ . However, no satisfactory fits were obtained using this procedure. The criterion usually used to determine the best fit (and consequently the best value of  $a$ , the ion size parameter) is the minimum value of the standard deviation between the experimental  $\Lambda$  values and calculated  $\Lambda$  values. The calculated  $\Lambda$  values are determined using the Pitts' equation and the  $\Lambda^\infty$  value determined by the coordinate transform line. The general trend of results using the modified program was increasingly poorer fits as  $a$  was increased, with no minimum observed (except perhaps, at unreasonably small values of  $a$ ). The results for  $a = 3.0\text{\AA}$ , a reasonable value based on Bjerrum's theory, are summarized in Table 2. Despite initially setting  $K_a = 0$ , the program still produced non-zero values for  $K_a$ .

As a check of the program, the data of Prue et al.<sup>79</sup> for lithium perchlorate in hexamethylphosphotriamide (HMPT) were treated by the program under the same conditions. In this case, the results were more reasonable. Values generated for  $K_a$  as the ion-size parameter was changed were negative at first. However, as  $a$  was increased,  $K_a$  became

positive, and was equal to zero when  $a$  was at the value reported by Prue et al. Hence, it appears that there is a nonzero value of  $K_a$  associated with the data for 20 mole percent ethylene carbonate.

TABLE 2

Summary of calculated conductance parameters for NaCl, NaAc, HCl in 20 mole percent ethylene carbonate at 25 and 40 °C assuming  $K_a = 0$ .

		$\Lambda^\infty$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	$K_a$ (liter $\text{mol}^{-1}$ )
25°	NaCl	73.26 ± 0.02	1.35 ± 0.06
	NaAc	55.99 ± 0.01	1.78 ± 0.07
	HCl	199.08 ± 0.03	0.346 ± 0.003
40°	NaCl	98.70 ± 0.01	1.08 ± 0.02
	NaAc	77.31 ± 0.04	2.11 ± 0.46
	HCl	248.26 ± 0.03	0.587 ± 0.007

$a = 3.0\overset{\circ}{\text{A}}$ , 95 percent confidence levels.

#### Fit to Pitts' Equation Assuming $K_a \neq 0$

Treatment of the data with the full, unmodified KEQIVES program (see appendix) gave satisfactory results for both salts and hydrogen chloride. Results of the data for acetic acid were unsatisfactory, with the only reasonable fits occurring at a composition of 20 mole percent ethylene carbonate. The analyses of the acetic acid data and the hydrogen chloride data in 80 mole percent ethylene carbonate and pure ethylene carbonate are discussed in a later section.

The results of the computer analysis for sodium chloride, sodium acetate, and hydrogen chloride are summarized in Table 3. The value of the ion size parameter  $a$  corresponding to the minimum in the standard deviation of the calculated and experimental equivalent conductances was taken to be the correct distance of closest approach. However, the fit is somewhat sensitive to experimental errors in the data. Of the calculated parameters, the value of  $\Lambda^\infty$  generally is changed the

TABLE 3

Summary of calculated conductance parameters for NaCl, NaAc, and HCl at 25 and 40 °C assuming  $K_a \neq 0$ .

	M	$\Lambda^\infty$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	$K_a$ (liter $\text{mol}^{-1}$ )	$a(\text{\AA})$	
25 °C	NaCl	20	73.15 ± 0.02	1.06 ± 0.03	2.85
		40	51.765 ± 0.004	3.30 ± 0.01	2.88
		50	46.477 ± 0.002	5.53 ± 0.01	5.55
		60	42.880 ± 0.005	7.93 ± 0.01	10.3
	NaAc	20	55.93 ± 0.01	4.38 ± 0.02	13.4
		40	41.413 ± 0.003	10.33 ± 0.01	17.0
		50	37.82 ± 0.01	14.2 ± 0.03	>24
		60	35.95 ± 0.01	19.7 ± 0.06	~24
	HCl	20	198.80 ± 0.01	1.35 ± 0.01	10.5
		40	102.06 ± 0.01	2.53 ± 0.02	2.40
		50	75.96 ± 0.01	5.67 ± 0.07	2.90
		60	58.75 ± 0.02	9.65 ± 0.07	2.70
40 °C	NaCl	20	98.69 ± 0.01	1.01 ± 0.02	2.80
		40	71.33 ± 0.01	3.53 ± 0.01	3.90
		50	63.20 ± 0.03	6.47 ± 0.03	13.5
		60	58.08 ± 0.01	8.31 ± 0.02	16.5
	NaAc	20	77.05 ± 0.01	6.15 ± 0.04	>24
		40	58.15 ± 0.01	9.98 ± 0.01	17.8
		50	52.81 ± 0.01	14.26 ± 0.01	>24
		60	49.21 ± 0.02	18.2 ± 0.1	>24
	HCl	20	248.26 ± 0.03	0.44 ± 0.02	2.50
		40	130.76 ± 0.06	2.09 ± 0.04	2.35
		50	97.28 ± 0.02	4.79 ± 0.03	2.40
		60	76.41 ± 0.04	8.21 ± 0.10	2.90
80		49.39 ± 0.08	49.1 ± 0.5	5.10	

95 percent confidence levels

M - mole percent ethylene carbonate

least by the inclusion of poor data, remaining essentially the same. The calculated values of  $K_a$  changed by a greater amount, but, in general, the standard deviations of  $K_a$  values were greater than those of  $\Lambda^\infty$ , and changes were less than the standard deviations. The value of  $a$ , the distance of closest approach, was much more significantly affected by the inclusion of poor data. The changes in  $\Lambda^\infty$  and  $K_a$  above reflect the change in the minimum point rather than the change in the data. For the same  $a$  value, for example, the  $\Lambda^\infty$  and  $K_a$  values for data sets with slightly different groupings of the total number of data points generally would be changed by an amount of the order of the standard deviation of the two parameters. At this point, then, it is possible that the variable parameter  $a$  has more of the character of an empirical fitting variable than that of a true physical parameter.

The sodium chloride data sets appear to be the best behaved. This is due to the fact that the solvent correction in the case of sodium chloride is unambiguous, and there is no possibility of reaction. The values of the parameter for sodium chloride are most likely to have a precise physical meaning, corresponding to the distance of closest approach of free ions.<sup>37</sup> Ions of opposite sign approaching closer than the association distance are assumed to be paired and do not contribute to the conductance. At this point, there is some ambiguity as to interpretation. Prue et al.<sup>37</sup> equate the  $a$  parameter generated by the Pitts expression (and other similar expressions) to a so-called "association distance"  $d$ . This is not the ion contact distance, which they symbolized by  $a$ . It is not clear if the association distance  $d$  is that of solvated ions in contact, or merely indicative of the fact that ion pairs can exist as stable entities while not in contact with each other. However, the

a parameter is generally taken as an ion size parameter.<sup>6</sup> From the data in Table III, we see that the size of the sodium chloride ions increases with increasing concentration of ethylene carbonate in the solvent mixture. This is expected, since solvation by the larger ethylene carbonate molecules would increase as the concentration of ethylene carbonate increases.

The data for hydrogen chloride are less consistent than those for sodium chloride. However, the trend is for  $\alpha$  to remain essentially constant throughout the entire composition range, rather than the increase observed with sodium chloride. This is due to the different natures of the hydrogen and sodium ions. The hydrogen ion is smaller than the sodium ion, and thus size would place steric limitations on solvation by large, bulky molecules. The larger sodium ion is more polarizable than the hydrogen ion, and the effects of size and polarization imply more solvation of the sodium ion. There is evidence that in the propylene carbonate-water system, water is strongly bound to the chloride ion.<sup>80</sup> One would expect similar behavior for ethylene carbonate, and the size of the solvated chloride ion is probably constant over the composition range of Table 3.

The poorest consistency is with the data for sodium acetate. This is possibly due to problems associated with solvent purity and the solvent correction. The purpose of the solvent correction is to eliminate the conductance of the solvent from the experimentally determined solution conductance. For sodium chloride, the normal solvent correction would simply involve the subtraction of the conductance of the solvent from the experimental conductance. For acids and bases, however, the application of the correction is not as straightforward. The major impurity

in the solvent mixture is the carbon dioxide present in the conductivity water. The recommended procedure for acid measurements in this case is to make no correction,<sup>81</sup> and this was followed for the measurements of hydrogen chloride. For salts of strong bases and weak acids (sodium acetate), a positive correction is recommended,<sup>81</sup> but its magnitude is not easily determined. However, the use of the normal correction appeared to be more satisfactory, and this procedure was followed. Possibly the data at low salt concentrations, where the solvent correction has its greatest effect, are responsible for the deviant  $\lambda$  values. However, the values are consistently high, and some form of solvation involving the carbonyl groups cannot be ruled out at the present time.

Figures 23, 24, and 25 show the behavior of the limiting equivalent conductance of hydrogen chloride, sodium chloride, and sodium acetate, respectively, as changes of solvent composition take place. The general trend of a rapid decrease as the concentration of ethylene carbonate increases is evident. The major portion of this decrease is probably a result of the reduction in ion mobilities due to the increase in viscosity of the solvent, as well as a reduction in the number of ions due to increasing association constants. The much larger drop-off observed for hydrogen chloride is the result of the high initial conductances in water, presumably due to the proton jump mechanism. The water structure favoring the jump mechanism is disrupted by the addition of the ethylene carbonate to the water. Hence, hydrogen ions behave more "normally" in solvents with large amounts of ethylene carbonate present.

A convenient parameter which allows one to remove the influence of the viscosity on the variations in ion conductance is the product

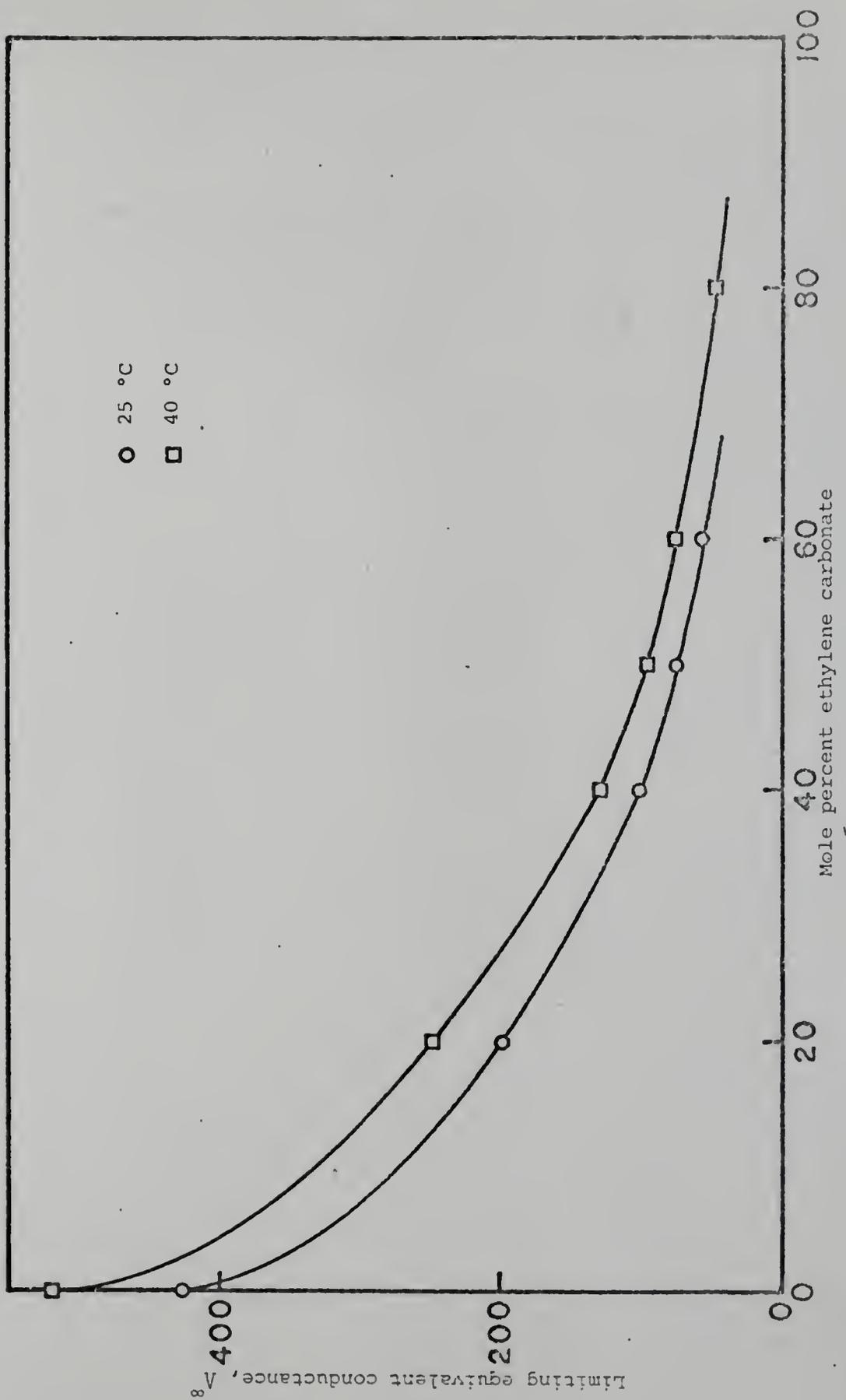


Figure 23. Plot of limiting equivalent conductance vs. mole percent ethylene carbonate for HCl at 25 and 40 °C.

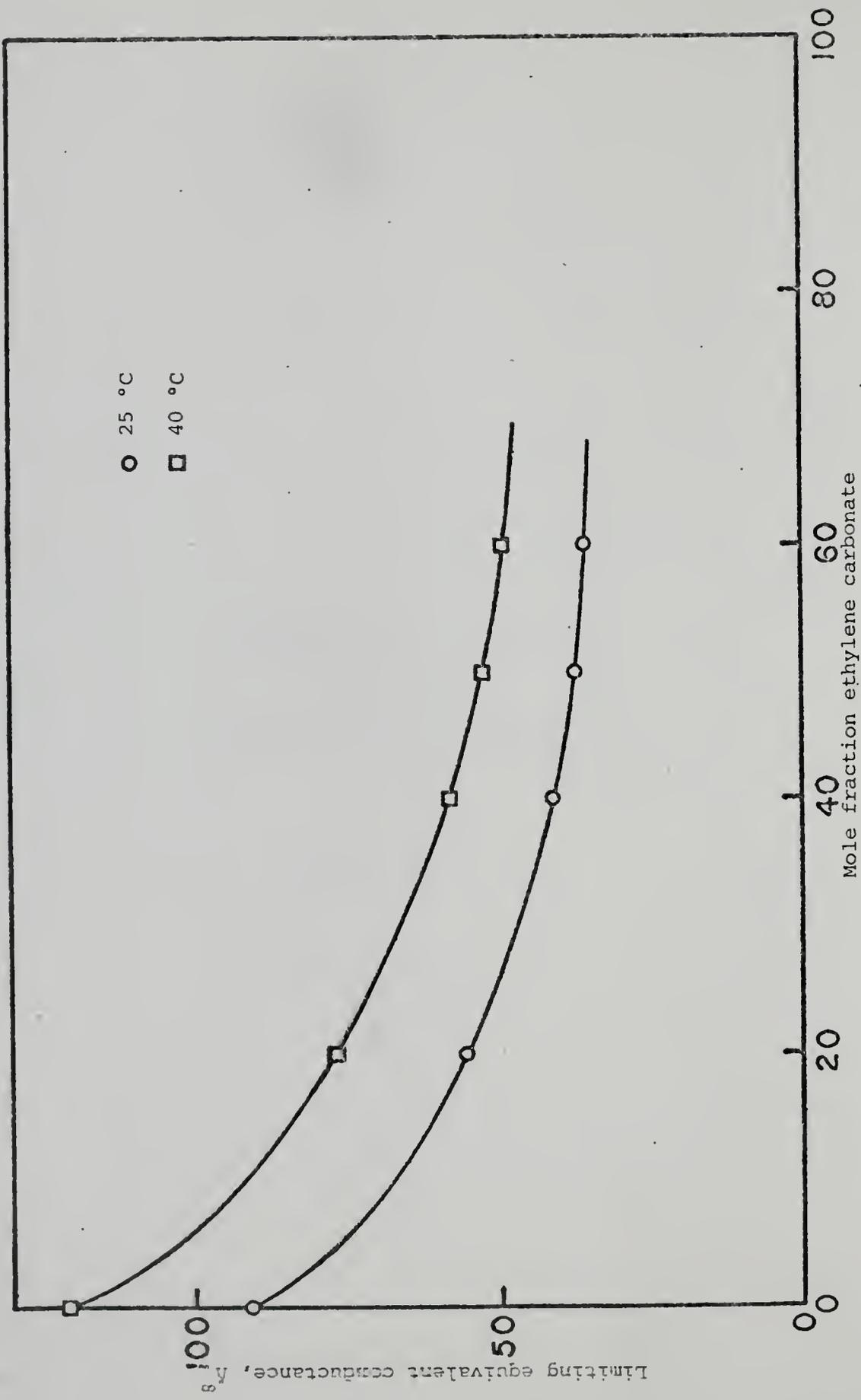


Figure 24. Plot of limiting equivalent conductance vs. mole percent ethylene carbonate for NaCl at 25 and 40 °C.

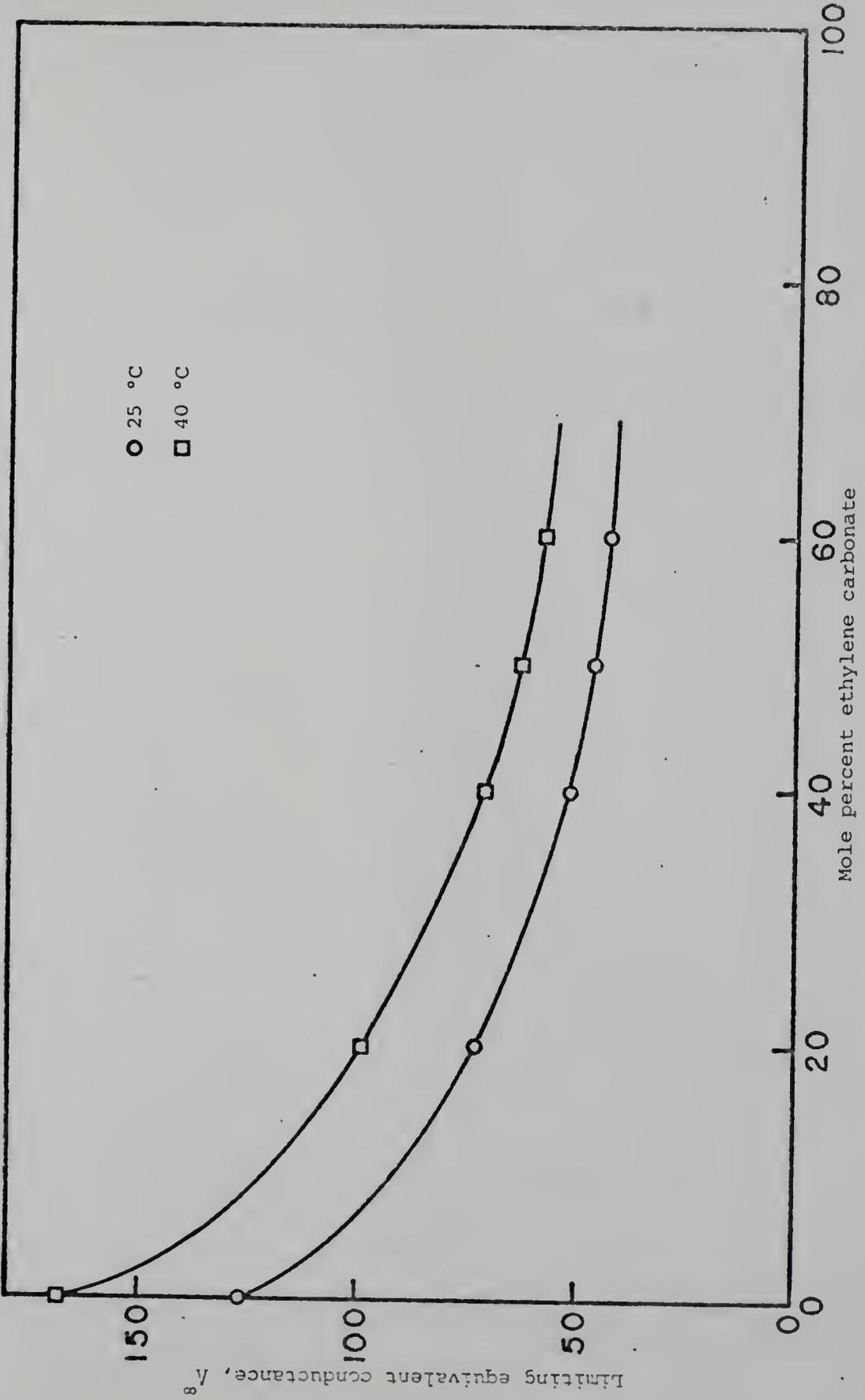


Figure 25. Plot of limiting equivalent conductance vs. mole percent ethylene carbonate for NaAc at 25 and 40°C.

of equivalent conductance and viscosity, called the Walden product, symbolized by  $\Lambda^\infty \eta$ . The Walden product was initially assumed to be constant<sup>82,83</sup> for different solvents, but later work revealed variations.<sup>84</sup> While today it is not considered quantitatively reliable, it is useful for limited comparison studies. As shown in Figure 26, a plot of the Walden product vs. solvent composition for the two salts does reveal approximate constancy. However, the Walden products for hydrogen chloride data show a decrease from an initial high value which is evidence for the disruption of the proton jump mechanism.

A somewhat clearer picture emerges if we plot the Walden product against the solvent parameter  $100/\epsilon$ , where  $\epsilon$  is the dielectric constant (see Figure 27). The conclusions reached above are still valid, but it is more apparent that the value of the Walden product for hydrogen chloride is approaching that for the salts as the fraction of ethylene carbonate increases. It also appears that each salt reaches a constant, though different, value of  $\Lambda^\infty \eta$ .

The association constant,  $K_a$ , behaves very much as expected as solvent composition is changed. As the mole fraction of ethylene carbonate is increased, the association constant increases, due to the decreased solvating power of the solvent system, as shown in Figure 28. Sodium acetate is apparently the most affected by the addition of ethylene carbonate, since its  $K_a$  increases more at lower concentrations than does that for the other electrolytes. This is due to the fact that the chloride ion is more easily solvated by water and perhaps also indicative of a specific interaction between ethylene carbonate and sodium acetate.

It is also interesting to compare the behavior of hydrogen chloride with the salts. At low concentrations of ethylene carbonate

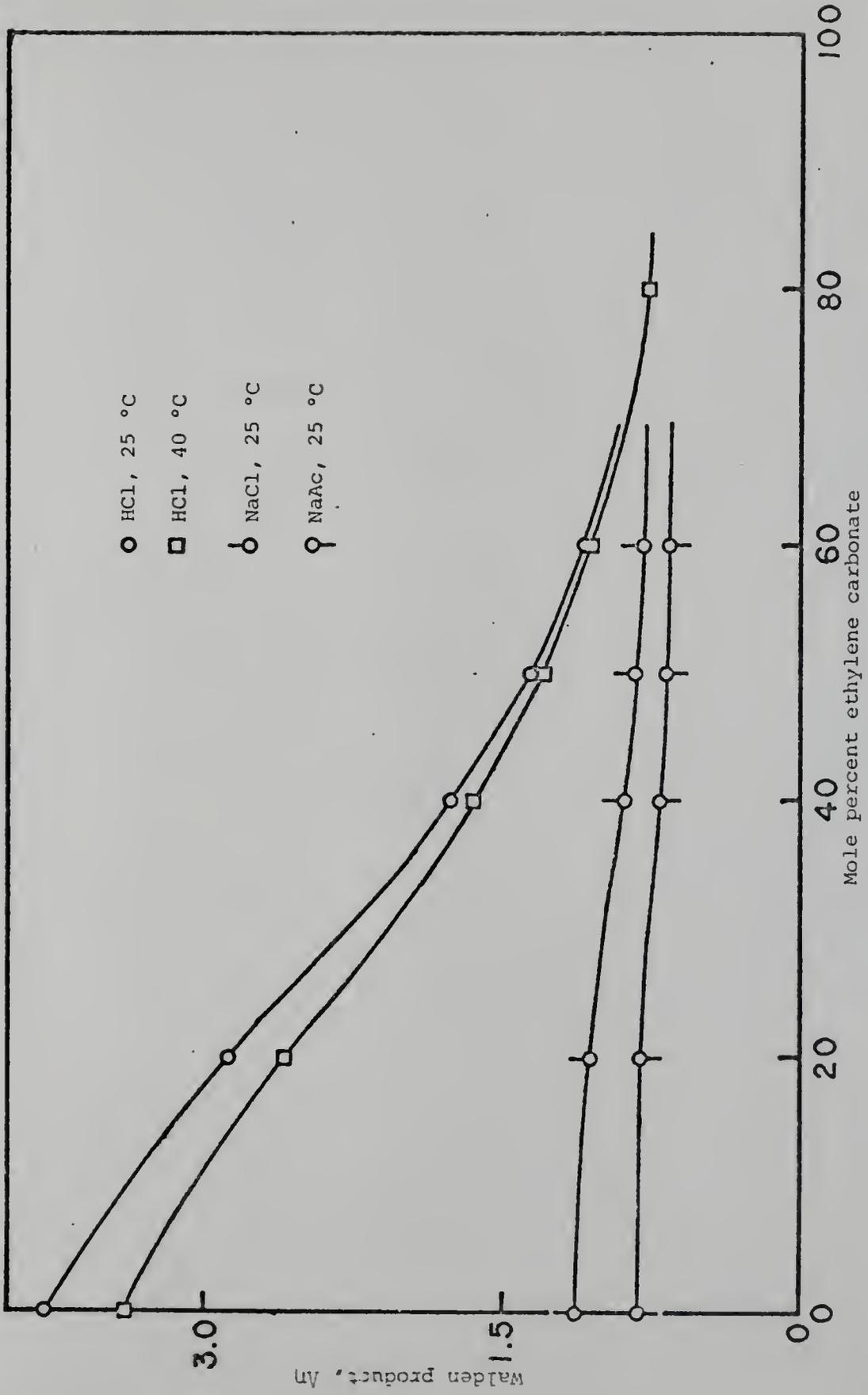


Figure 26. Plot of Walden product vs. mole percent ethylene carbonate for HCl, NaCl, and NaAc at 25 and 40 °C.

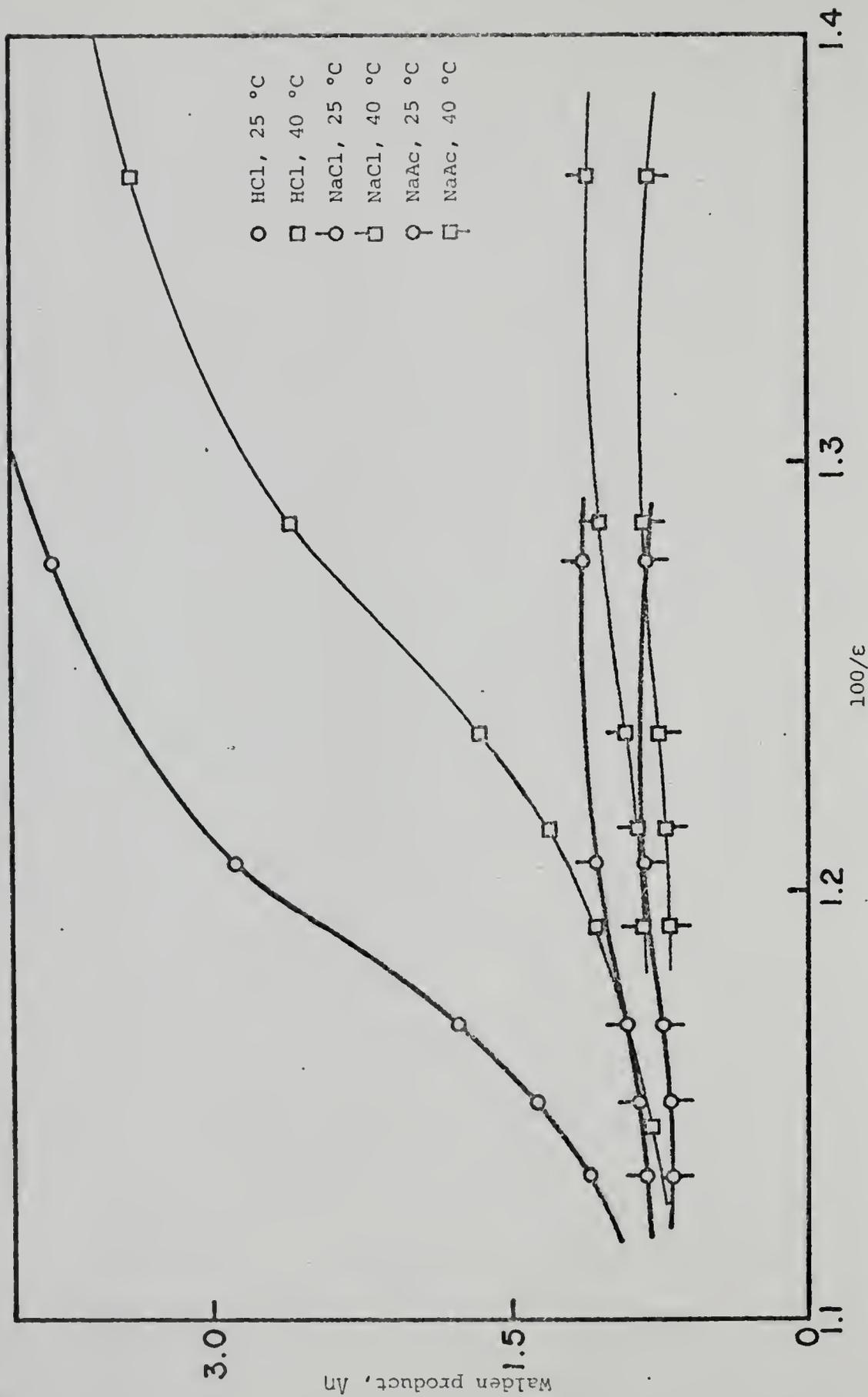


Figure 27. Plot of Walden product vs. the quantity  $100/\epsilon$  over the dielectric constant,  $100/\epsilon$  for HCl, NaCl, and NaAc at 25 and 40 °C.

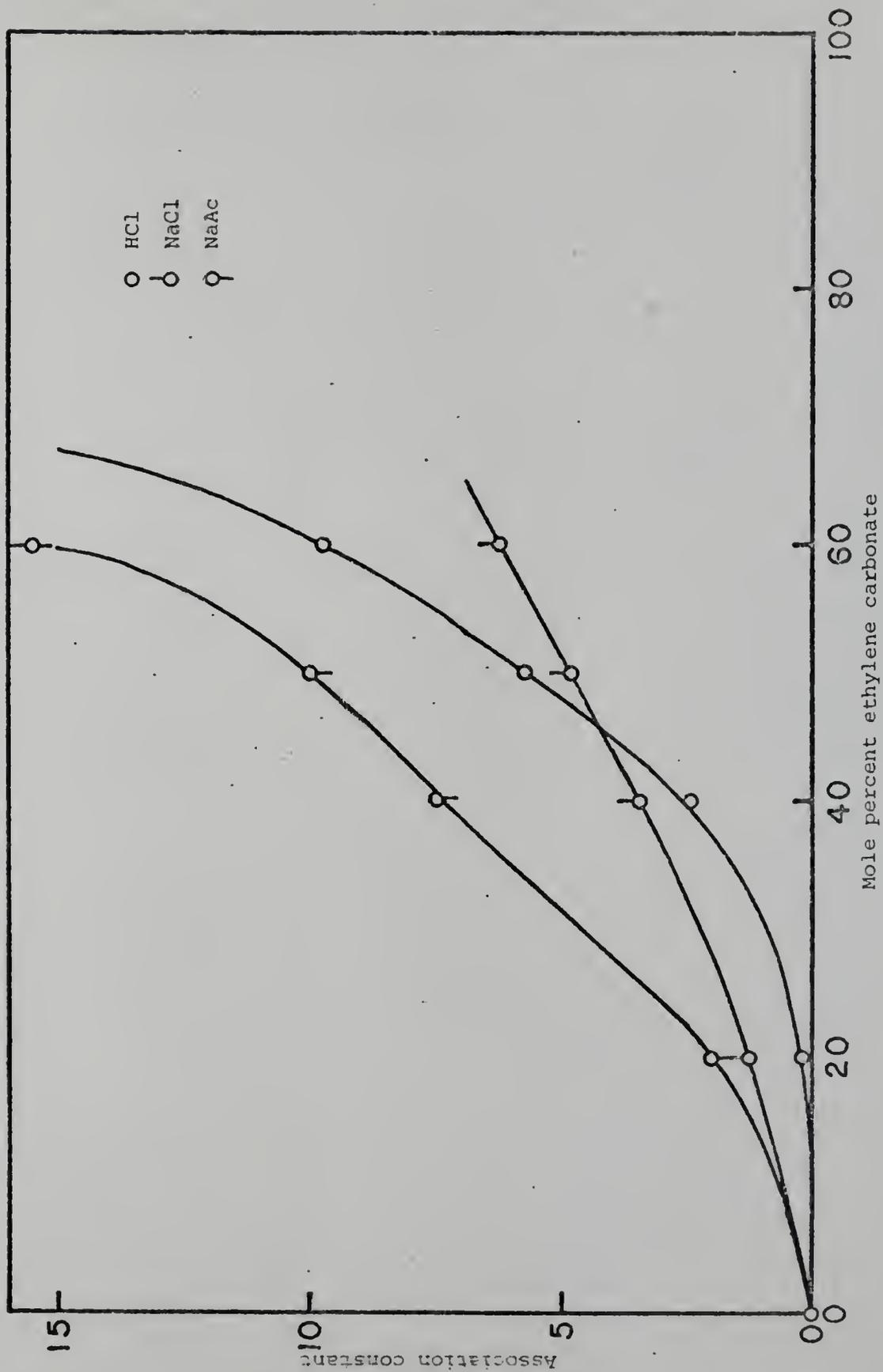


Figure 28. Plot of association constant vs. mole percent ethylene carbonate for HCl, NaCl, and NaAc at 25 °C.

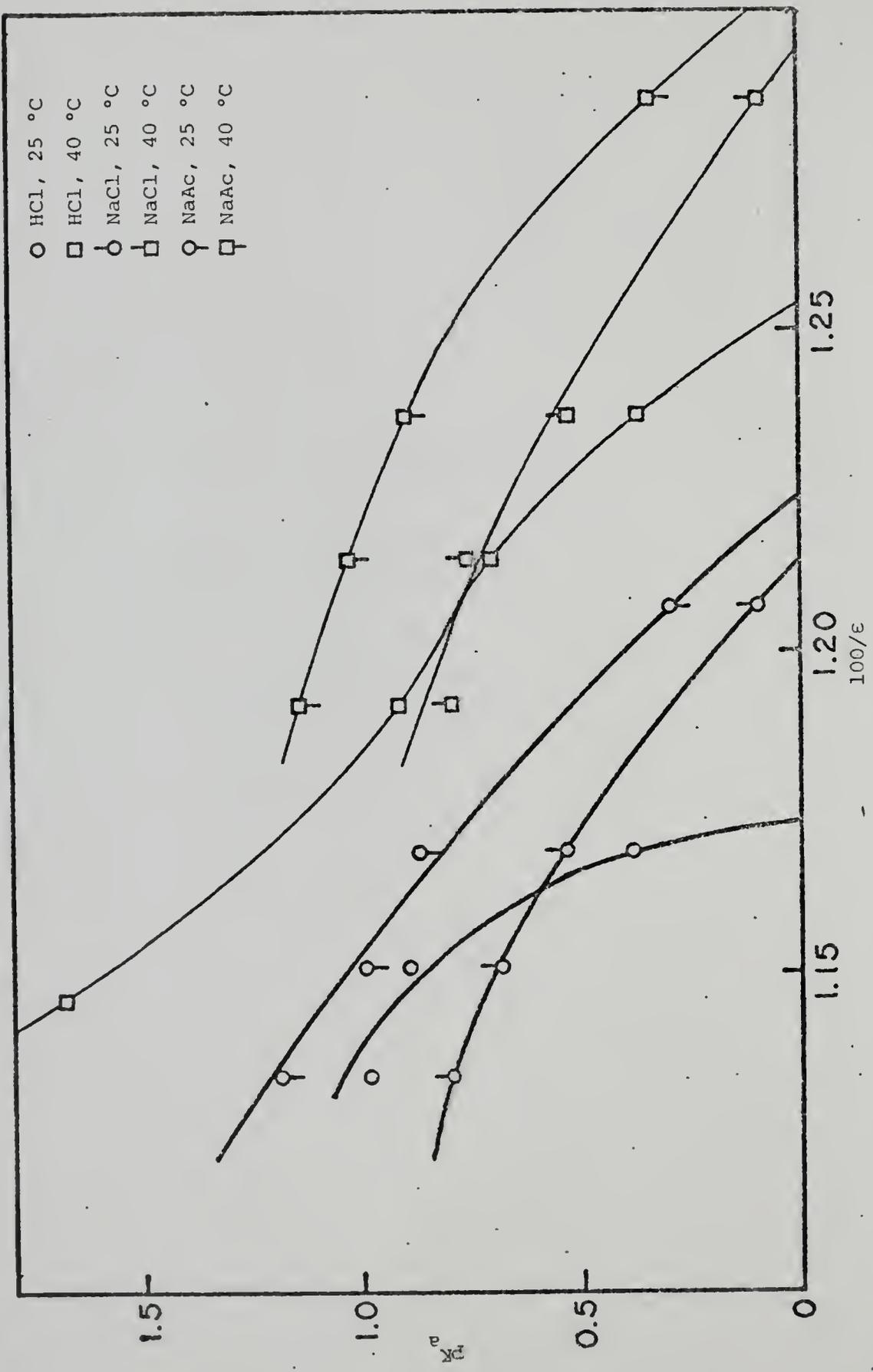


Figure 29. Plot of the log of the association constant,  $pK_a$ , vs. the quantity  $100/\epsilon$  over the dielectric constant  $100/\epsilon$ , for HCl, NaCl, and NaAc at 25 and 40 °C.

the  $K_a$ 's are lower for hydrogen chloride than for the salts. As the mole fraction of ethylene carbonate continues to increase, the hydrogen chloride curve crosses the sodium chloride curve and perhaps even the curve for sodium acetate. This is a further indication of the basic difference between the hydrogen ion and the sodium ion. It is the result of the greater ease of solvation of the sodium ion and the consequent increased probability that dissociation will occur.

Plotting the association constant vs. the parameter  $100/\epsilon$ , as before, reveals a clear distinction between the behavior at the two temperatures (see Figure 29). At each temperature, the sodium acetate curves are higher than the others, supporting the conclusions made earlier, although this method of presentation perhaps makes the distinctions clearer. However, in general the slopes are positive rather than negative. Thus, another example of a reversal of the usual dependence on dielectric constant is illustrated by these results.

#### Bjerrum Theory of Ion Association

One of the problems relating to ion association concerns the definition of an ion pair. The problem is basically whether or not actual physical contact between ions is necessary for association. The basis for most of the relationships concerning ion association is the work of Bjerrum.<sup>85</sup>

By definition, ion pairs must retain their identity for a long enough time for their existence to affect the surrounding solution. Bjerrum proposed that all oppositely charged ions within a certain critical distance be considered associated into ion pairs. Based on considerations of the Poisson-Boltzmann distribution of electrostatic forces, this critical distance,  $q$ , is found to be the distance where

the electrostatic potential energy of the two ions is  $2kT$ . Hence, the expression for  $q$  is:

$$q = \frac{|z_1 z_2| e^2}{2\epsilon kT} \quad (43)$$

Bjerrum, using standard procedures, formulated an expression for determining the number of ions  $N$  of opposite charge about a central ion in a shell of thickness  $dr$ , at a small distance,  $r$ , from the central ion:

$$N = 4 n_i \exp \left( - \frac{|z_1 z_2| e^2}{\epsilon kTr} \right) r^2 dr \quad (44)$$

where  $n_i$  is the number of ions per cc. The interplay between nearness to the central ion (where one would expect to find more ions due to attractive forces) and the increase in the shell volume as  $r$  is increased results in a minimum. The expression for  $q$ , the critical distance, can be derived from equation (44).

The degree of association,  $(1-\alpha)$ , can be determined by finding the number of ions in the shell starting at the distance of closest approach to the critical distance. This is a simple integration, as shown:

$$(1 - \alpha) = 4\pi n_i \int_a^q \exp \left( - \frac{|z_1 z_2| e^2}{\epsilon kTr} \right) r^2 dr \quad (45)$$

Using suitable transformations, equation (45) becomes:

$$(1 - \alpha) = \frac{4\pi Nc}{1000} \left( \frac{|z_1 z_2| e^2}{\epsilon kT} \right) Q(b) \quad (46)$$

where:

$$b = \frac{|z_1 z_2| e^2}{\epsilon k T a}$$

and:

$$Q(b) = \int_2^b x^{-4} e^{-x} dx$$

In this case:

$$2 = \frac{|z_1 z_2| e^2}{\epsilon k T q}$$

and:

$$x = - \frac{|z_1 z_2| e^2}{\epsilon k T r}$$

From the law of mass action, one can write:

$$K_d = \frac{\alpha^2 y_{\pm}^2 c}{1 - \alpha} \quad (47)$$

If the assumption is made that the solutions are very dilute,  $\alpha \approx 1$  and  $y_{\pm} \approx 1$ . Now, combining (47) and (46) results in:

$$\frac{1}{K_d} = K_a \approx \frac{1 - \alpha}{c} \approx \frac{4\pi N}{1000} \left( \frac{|z_1 z_2| e^2}{\epsilon k T} \right)^3 Q(b) \quad (48)$$

Values of the integral  $Q(b)$  have been tabulated,<sup>85,86</sup> and a more recent statistical treatment results in an asymptotic expansion of  $Q(b)$  giving:<sup>87</sup>

$$K_a = \frac{4\pi N a^3}{1000} \frac{e^b}{b} \quad (49)$$

Fuoss,<sup>88</sup> however, suggests that only ions in contact can correctly be considered associated. His analysis of the problem results in:

$$K_a = \frac{4\pi N a^3 e^b}{3000} \quad (50)$$

Experimentally determined  $K_a$  values for the electrolytes are compared with the calculated values in Table 4. Equation (49) is used rather than Bjerrum's original expression, as the high dielectric constant resulted in values of  $b$  less than 2, the lower limit of the tables.  $B_j$  is the value calculated using Bjerrum's expression, while  $F$  is the value resulting from Fuoss' expression, equation (50). The value of the ion size parameter  $a$  for HCl appeared to be constant, and hence  $a$  was arbitrary set equal to  $3.0\text{\AA}$ . Table 5 shows the results if the Bjerrum critical distance is used as the ion size parameter.

The ion size parameter is approximately constant for the HCl data in Table IV and for all electrolytes in Table 5. In this case, when the experimental values of  $K_a$  are increasing, the calculated values are decreasing. Indeed, only a change in the ion size parameter can counteract the increasing dielectric constant. The NaCl data are an example of the behavior as the ion size increases. However, even in this case, agreement is not good, with Bjerrum's expression greatly overcompensating at high values for  $a$ . The existence of the minimum in the sodium chloride data at  $25\text{ }^\circ\text{C}$  is also a result of a constant value for  $a$ . This reverse behavior has been reported previously.<sup>89</sup>

It is obvious from these calculations that a simple electrostatic model of ion association is totally inadequate to deal with the complex interplay of forces present in electrolyte solutions. Factors relating specifically to ion-solvent interactions must be considered. A solvation term has been proposed by Fuoss,<sup>88, 90</sup> based on the molar free energy of solvation,  $E_a$ . The derived relation by Gilkerson<sup>91</sup> is:

TABLE 4

Comparison of calculated and experimental  $K_a$  values.

	M	$a$ (Å)	$K_a$ (liter mol <sup>-1</sup> )	$B_j$	F	
25 °C	NaCl	20	2.85	1.06	0.79	0.63
		40	2.88	3.30	0.77	0.59
		50	5.55	5.53	3.56	1.38
		60	10.3	7.93	24.8	5.11
	HCl	20	10.5	1.35	25.9	5.56
		40	2.40	2.23	0.59	0.54
		50	2.90	5.67	0.77	0.57
	40 °C	NaCl	20	2.80	1.01	0.79
40			3.90	3.53	1.44	0.81
50			13.5	6.47	62.7	10.0
60			16.5	8.31	130.5	16.7
HCl		20	2.50	0.44	0.67	0.67
		40	2.35	2.09	0.58	0.54
		50	2.40	4.79	0.58	0.52
		60	2.90	8.21	0.75	0.55
		80	5.10	49.1	2.78	1.11

 $B_j$  - value of  $K_a$  calculated using Bjerrum equation (49).F - Value of  $K_a$  calculated using Fuoss' equation (50).

TABLE 5

Comparison of calculated and experimental  $K_a$  values using the Bjerrum distance as the ion size parameter.

	M	$a$ (Å)	NaCl	NaAc	HCl	$B_j$	F
25 °C	20	3.38	1.25	2.01	0.23	1.08	0.72
	40	3.28	3.45	7.53	2.43	0.99	0.66
	50	3.22	4.83	9.98	5.76	0.93	0.62
	60	3.18	6.27	15.5	9.80	0.90	0.60
40 °C	20	3.43	1.23	2.20	0.72	1.13	0.75
	40	3.30	3.37	7.98	2.36	1.00	0.67
	50	3.24	5.77	10.8	5.05	0.95	0.63
	60	3.18	6.27	13.9	8.30	0.90	0.60
	80	3.06	-	-	48.4	0.80	0.53

$$K_a = \frac{4\pi N a^3}{3000} e^b e^{E_s/RT} \quad (51)$$

This expression should take into account specific solvation in the association process. Unfortunately, almost no work has been done with ethylene carbonate-water mixtures, and values for the parameter  $E_s$  have not been found to date.

#### Treatment of the Acetic Acid Data

The KEQIVES program was unable to calculate convergent values for the various parameters for either the data for acetic acid at ethylene carbonate concentrations greater than 20 mole percent or for hydrogen chloride at 100 mole percent ethylene carbonate. The problem was associated with an iterative procedure that determined the value for  $\alpha$ , the degree of dissociation. An alternative method was therefore used for the analysis of these data. This method was based on a procedure of Sellers, Eller, and Caruso.<sup>92</sup> While the method is not original with them, they have provided a strong theoretical background for the original technique.

The procedure involves plotting  $\log \Lambda$  vs.  $-\log c$ . The resulting plot is generally a straight line whose slope gives information concerning the type of association present in the system. The intercept gives quantitative information about  $K_a$  and  $\Lambda^\infty$ .

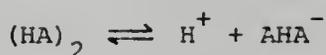
The data for solvents containing large amounts of water have slopes with a value of -0.5, with deviations from a straight line present only at low concentrations. This behavior is consistent with simple dissociation into ions,



which is the dissociation process in water. A plot exhibiting this behavior is shown in Figure 30. An increase in temperature results in a downward shift in the plot, with no change in the slope. This is a result of the changes in  $K_a$  due to thermal and kinetic processes.

As the concentration of ethylene carbonate increases, the slope increases to more negative values. At 60 mole percent ethylene carbonate at 25 °C, the slope is still -0.50. At 40 °C, however, the slope has increased to -0.75. This slope corresponds to the formation of acetic acid dimers. It thus appears that dimer formation is enhanced by an increase in temperature, an unusual occurrence.

However, there is some ambiguity in the interpretation of results using this method. A slope of -0.50 may also correspond to dimer formation coupled with triple ion formation, as shown below:



Since the slope increases slightly at lower concentrations as well, this would imply dimer formation rather than simple ionization. This is because increasing solute concentration would favor triple ion formation rather than simple ionization and result in the behavior observed.

However, there was no increase in  $\Lambda$  as solute concentration was increased, a characteristic of triple ion formation. Therefore, it may be that the small increase in slope at lower solute concentrations is a result of impurities and the fact that no solvent correction was employed.

At 80 and 100 mole percent ethylene carbonate at 40 °C, the slope has increased further to a value of -0.84. A negative value of the slope of this magnitude (theoretically -0.833) corresponds to trimer formation, coupled with simple association.

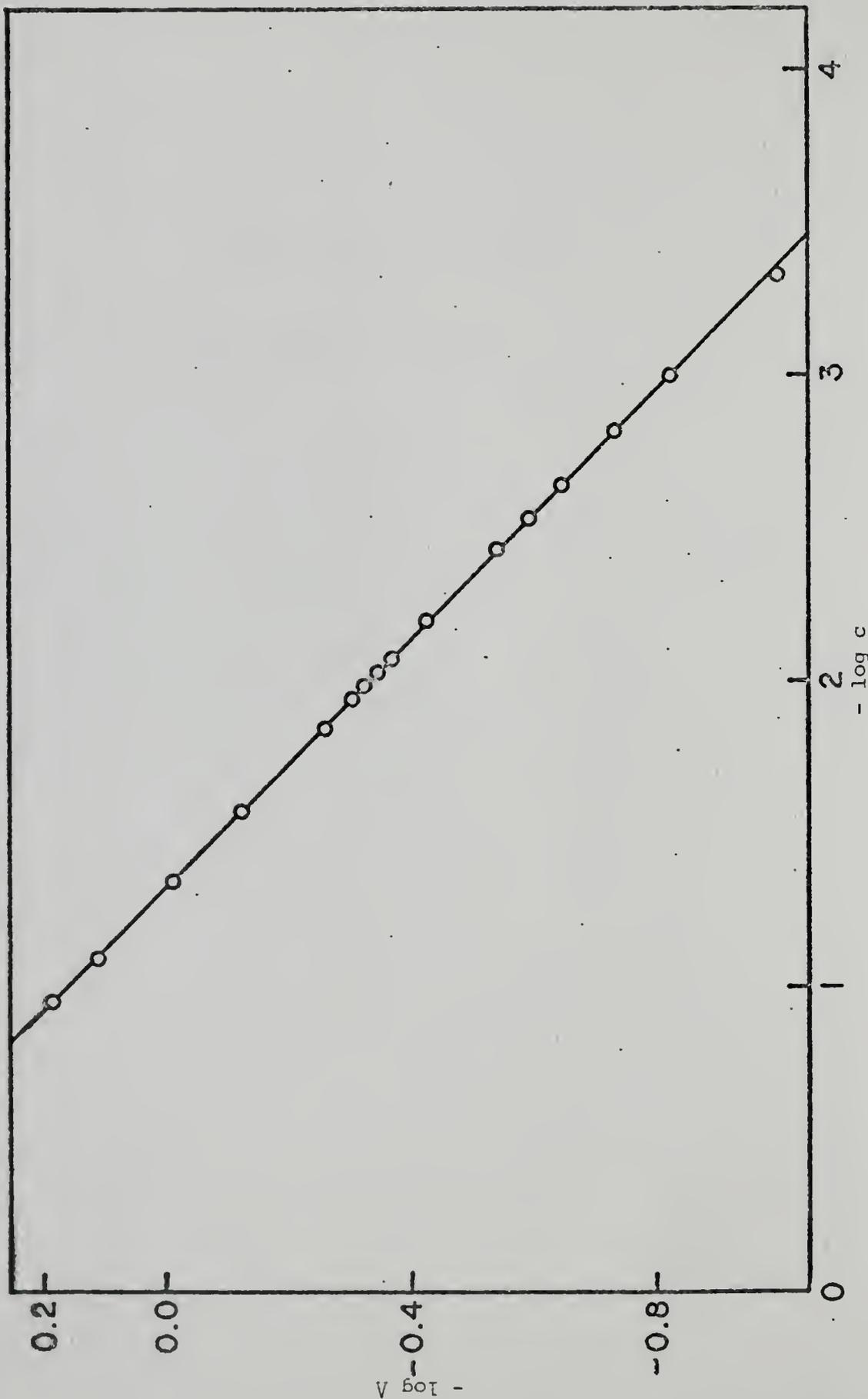


Figure 30. Plot of the negative log of the equivalent conductance vs. the negative log of concentration for HAc in 20 mole percent ethylene carbonate at 25 °C.

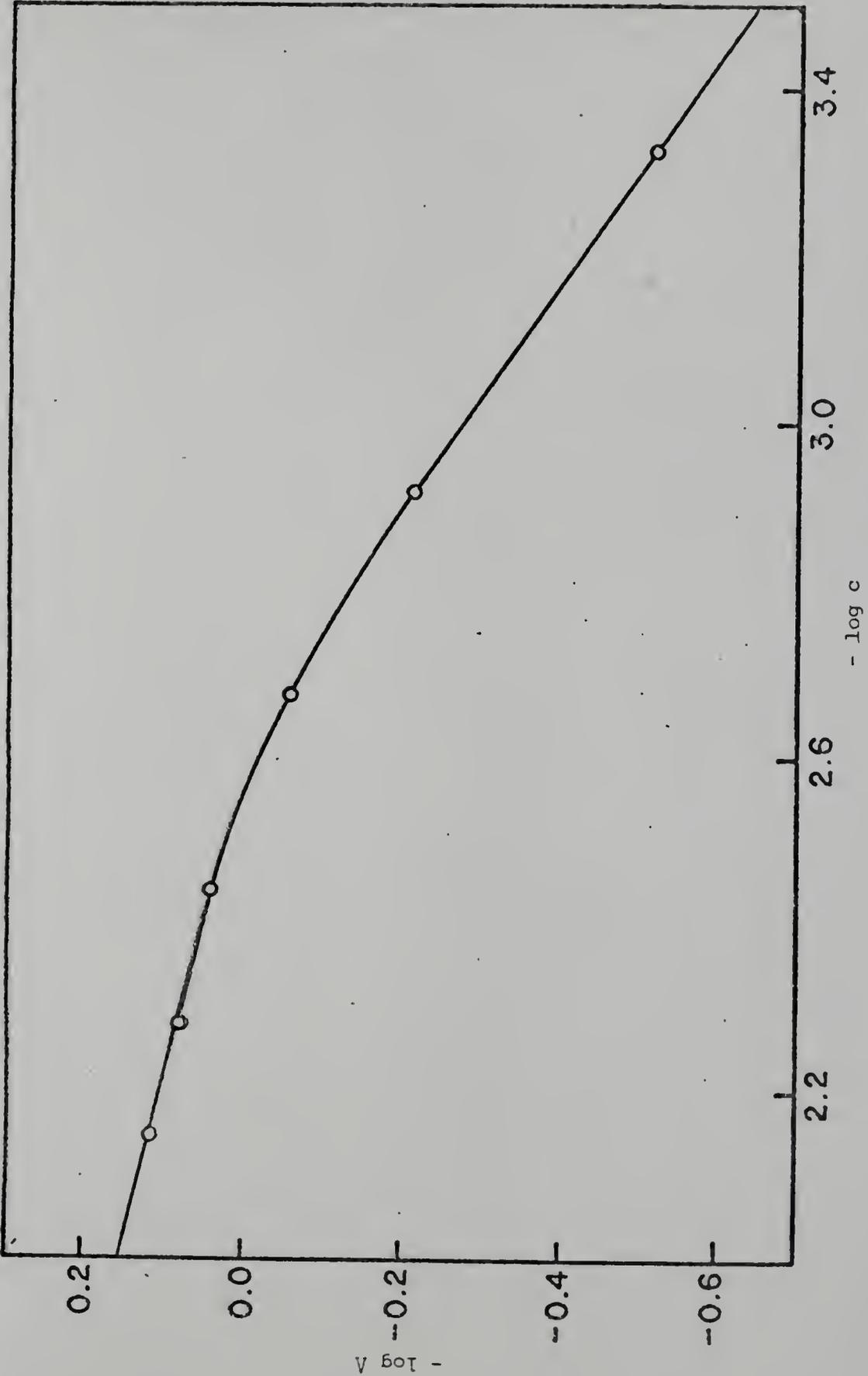
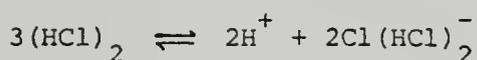


Figure 31. Plot of the negative log of the equivalent conductance vs. the negative log of concentration for HCl in 100 mole percent ethylene carbonate at 40 °C.

For hydrogen chloride in 100 mole percent ethylene carbonate at 40 °C, the picture is more complex, as shown in Figure 31. There appear to be two linear regions present. At the lower concentrations of hydrogen chloride, the slope is again around -0.75, consistent with dimerization and simple dissociation. At higher concentrations, the slope lessens to a value approximating -0.25. This behavior corresponds to dimer formation, but now coupled with the more complex dissociation:



The difference in behavior between the two acids is probably due to the presence of the carbonyl group in acetic acid. This permits more extensive solvation for acetate ion than for chloride ion by a dipole - dipole interaction.

As the values of the intercepts are combinations of the magnitudes of  $\Lambda^\infty$  and  $K_a$ , some idea of the magnitude of these parameters can be gained. If we assume that Kohlrausch's law of independent migration holds,  $\Lambda^\infty$  for acetic acid can be determined from the values for the other electrolytes by the simple relation:

$$\Lambda_{\text{HAc}}^\infty = \Lambda_{\text{HCl}}^\infty - \Lambda_{\text{NaCl}}^\infty + \Lambda_{\text{NaAc}}^\infty \quad (52)$$

The data at 20 mole percent confirm that this relationship holds at this solvent composition. Thus, we now have a means of extracting  $K_a$  from the log-log plots. Table 6 summarizes the results of such calculations.

Halle<sup>91</sup> has determined the value of  $K_a$  for acetic acid in 50 weight percent ethylene carbonate at 25 and 40 °C by EMF measurements. 50 weight percent is approximately 20 mole percent, and his value for the pK, 5.65, is in good agreement with the experimental value determined in this work (5.84).

TABLE 6

Summary of calculated conductance parameters for HAc at 25 and 40 °C.

	M	$\Lambda^\infty$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	Slope	$K_a$ (liter $\text{mol}^{-1}$ )
25 °C	20	181.77	-0.50	$6.9 \times 10^5$
	40	91.71	-0.51	$6.4 \times 10^6$
	50	67.30	-0.50	$2.0 \times 10^7$
	60	51.83	-0.52	$9.8 \times 10^7$
40 °C	20	226.62	-0.50	$7.8 \times 10^5$
	40	117.58	-0.50	$7.7 \times 10^6$
	50	86.90	-0.51	$2.5 \times 10^7$
	60	67.54	-0.75	$2.4 \times 10^8$
	80	-	-0.84	-
	100	-	-0.84	-

## CHAPTER VI

### CONCLUSIONS

In general, ethylene carbonate can be considered to be a dipolar aprotic solvent of high dielectric constant with minimal self-association. It may be that ethylene carbonate has a better claim to being a nearly ideal solvent for ions than has propylene carbonate, as discussed by Friedman.<sup>94</sup> When mixed with water, solvent mixtures result which have solvating powers intermediate between the two pure solvents. Experimental results from this study and others<sup>1, 70</sup> support the idea that the water structure is broken down by the addition of ethylene carbonate.

Based on the general behavior of the  $\Lambda$  vs.  $\sqrt{c}$  plots and the discussions of Fuoss and Accascina,<sup>78</sup> it appears that ion association becomes evident for the stronger electrolytes (sodium chloride, sodium acetate, and hydrogen chloride) at solvent compositions about 40 mole percent ethylene carbonate. Problems associated with the computer fit at 20 mole percent ethylene carbonate, assuming  $K_a = 0$  and  $\alpha = 1$ , indicate that ion association was important even at this composition, except perhaps at concentrations below 0.01 molar.

Hydrogen chloride was the least associated of these three stronger electrolytes, followed by sodium chloride and finally by sodium acetate. However, hydrogen chloride became more associated than sodium chloride at a solvent composition of approximately 50 mole percent ethylene carbonate. This was probably due to the higher polarizability of the sodium ion, which resulted in the sodium ion becoming more solvated than the smaller hydrogen ion.

Some workers<sup>95</sup> consider salts yielding  $K_a$  values less than 10 to be unassociated. Based on this criterion, sodium acetate begins to associate at approximately 50 mole percent ethylene carbonate. Hydrogen chloride begins to experience association around 60 mole percent ethylene carbonate, and sodium chloride would have probably started about 70-80 mole percent ethylene carbonate.

Acetic acid is strongly associated at all solvent compositions. When the solvent composition was less than 50 mole percent ethylene carbonate, the association process common to water apparently predominated up to the maximum concentration range studied (about 0.1 M). However, as the concentration of ethylene carbonate in the solvent was raised, dimer and trimer formation appeared to become increasingly important.

The dissociation of acetic acid could be studied by conductance over the entire concentration range of the mixed solvents using the method described by Caruso et al.<sup>92</sup> However, an independent determination of  $\Lambda^\infty$  was required for quantitative results. Problems of solubility of the salts needed to determine  $\Lambda^\infty$  limited quantitative results to solvent compositions of 60 mole percent ethylene carbonate and below. More conventional studies based on the Pitts conductance expression were reasonably successful only at solvent compositions of 20 mole percent ethylene carbonate.

The behavior of hydrogen chloride at compositions approaching pure ethylene carbonate probably reflects dimer formation and combinations of simple dissociation into single ions and the more complex association resulting in the formation of  $\text{Cl}(\text{HCl})_2^-$ . A quantitative estimate of the magnitudes of the various association constants, and of  $\Lambda^\infty$  was impossible under the experimental conditions of this study.

In general, the results of this study indicate that the addition of ethylene carbonate to water increases ion association despite an increase in dielectric constant. This increase in ion association was probably primarily the result of the reduced anion solvation by dipolar aprotic solvents. The interactions of these solvents with ions are the result of induction forces superimposed upon ion-dipole forces.<sup>96</sup> Hence, solvation is expected to be greater for larger, more polarizable ions, and this behavior was supported by the experimental results.

Cations are most probably solvated by interaction with the negative end of the dipole, the carbonyl oxygen. However, the electron pair donating power of this group in ethylene carbonate is somewhat low,<sup>97</sup> and hence solvation of cations is probably lower than is the usual case with carbonyl groups.

Anion solvation is poor, and this is probably the result of the fact that the positive charge is spread over all three carbon atoms of the ring, as evidenced by molecular orbital calculations.<sup>98</sup> This makes it difficult for the negatively charged anions to interact strongly enough with the solvent to form a solvation sheath. Indeed, work in water-propylene carbonate indicates that most anions are preferentially solvated by water in this mixed solvent system.<sup>80</sup> This behavior is expected for water-ethylene carbonate as well.

The dimer and trimer formation of the acids can perhaps be explained in terms of poor ion solvation coupled with favored interaction with the neutral molecules. With hydrogen chloride, the poorer solvation of the hydrogen ion and the increased chance of hydrogen bonding via the fairly electronegative chlorine atom result in degrees of ion association greater than for sodium chloride, as well as dimer formation

and other complex ion associations. Acetic acid is similar in structure to ethylene carbonate, and this fact may favor interaction with the neutral molecule rather than with an ion. Hydrogen bonding with the carboxyl group of the acetic acid is responsible for the dimer and trimer formation.

In general, solvation of cations in the water-ethylene carbonate solvent system is expected to be moderate, while solvation of anions is probably minimal. The low solvation probably favors interaction with a neutral species when these non-ionic interactions are possible. Exceptions to these general trends (such as with perchlorate) are most likely due to a favorable positioning of charges, thus favoring interactions with the charge density of the heterocyclic ring.

Studies have also been done in propylene carbonate with the pH glass electrode.<sup>99</sup> A linear response over the range  $10^{-2}$  -  $10^{-5}$  M was reported, with a slope slightly less than Nernstian. The deficient slope and the almost complete lack of selectivity for the alkali metals have been attributed to the dehydration of the glass. Obviously, dehydration would be much less of a problem in water-ethylene carbonate mixtures. This technique would provide an alternative method of studying ion pairing.

Studies also show that propylene carbonate is essentially non-toxic, and only moderately irritating to the mucous membranes of the eyes.<sup>100</sup> Similar results have been reported for ethylene carbonate as well.<sup>101</sup> Propylene carbonate is also a widely used solvent for synthetic polymers, and ethylene carbonate is expected to behave similarly. Hence, water-ethylene carbonate mixtures constitute a potentially useful solvent system for biological studies as well. They should find many and varied uses in theoretical and practical studies.

APPENDIX A  
KEQIVES PROGRAM

```

0001  DIMENSION EC(25),EL(25),XL(25),AL(25),Y(25),G(25),QL(25),X(
125),CL(25),DEL(25),RCI(25),YP(25),D(25),YK(25),DSQ(25),FACT(25),BL(25),E
2P2(25),TP(25),SP(25),RL(25),D(25),YK(25),DSQ(25),FACT(25),BL(25)
0002  DOUBLE PRECISION AI,EC,EL,D,OL,XL,AL,CI,Y,G,QL,X,SY,SY2,SYX
1,AB,F,SL,ECK,SO,SOL,SSL,SSECK,CL,DEL,BA,RCI,YP,YPI,YP2,EP,EP1,EP2,
2TP,SP,RL,RT,AP,GP,BP,HP,AD,DC,T,V,OK,SO,SDSQ,SDCL,FACT,MSOL,DEN,BL
3,MSLU
J=0
1 J=J+1
2 READ(5,2) DC,T,V,DEN,MSOL,MSLU
81 READ(5,81) N,OL
81 FORMAT(I10,E12.5)
4 DO 3 I=1,N
81 READ(5,4) EC(I),EL(I)
81 FORMAT(2E12.5)
3 EL(I)=0.999505D0*EL(I)
85 WRITE(6,85) N,DC,T,V,DEN,MSOL,MSLU
85 FORMAT('0',I2.6E14.5)
AI=(3.643252D6)/((DC*T)**1.5)
AD=0.0D0
AP=1.158266D6/((DC*T)**1.5)
BP=2.345787D13/((DC*T)**3)
GP=82.34164D0/(V*((DC*T)**0.5))
HP=2.795299D6/((DC*T)**1.5)
RT=DSORT(2.0D0)
V=C
11 M=M+1
AC=AD+1.0D-8
35 WRITE(6,35) AC
35 FORMAT('0',T1,IPE12.5)
BA=5.020330D9*AD/((DC*T)**0.5)
K=0
5 K=K+1
DO 8 I=1,N
33 XL(I)=OL
AL(I)=EL(I)/QL(I)
CI(I)=AL(I)*EC(I)
RCI(I)=DSORT(CI(I))
YP(I)=BA*RCI(I)
YP2(I)=1.707107D0*YP(I)
SYP=YP(I)
SYP1=YP1(I)
SYP2=YP2(I)

```

```

0042 CALL EXP1(SYP,SEP,AUX)
0043 CALL EXP1(SYPI,SEPI,AUX)
0044 CALL EXP1(SYP2,SEP2,AUX)
0045 EP(I)=SEP
0046 EP1(I)=SEPI
0047 EP2(I)=SEP2
0048
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0082

CALL EXP1(SYP,SEP,AUX)
CALL EXP1(SYPI,SEPI,AUX)
CALL EXP1(SYP2,SEP2,AUX)
EP(I)=SEP
EP1(I)=SEPI
EP2(I)=SEP2
QTP(I)=0.75D0/(RT+YP(I))+(3.0D0/8.0D0)*(3.0D0*RT*DEXP(YPI(I))*EP1(I)
I)/(RT+YP(I))-2.0D0*DEXP(YPI(I))*EP(I)
OSP(I)=(9.0D0*RT-10.0D0+YP(I))*3.0D0*RT+1.0D0+2.0D0*(YP(I)**2)/(8
1.0D0*(1.0D0+YP(I))*RT+YP(I)**2)-DEXP(YPI(I))/(4.0D0*(1.0D
20+YP(I)))+(7.0D0*RT*DEXP(YP2(I))*EP2(I))/(16.0D0*(1.0D0+YP(I)**2
3)*(RT+YP(I)))+(RT*DEXP(YPI(I))*EP1(I))/(16.0D0*(1.0D0+YP(I))*(RT+Y
4P(I)))
OKL(I)=-OL*(AP*RCI(I)/(1.0D0+YP(I))*(RT+YP(I))+BP*CI(I)*SP(I))-GP
1*RCI(I)*(1.0D0/(1.0D0+YP(I))-AP*RCI(I)/((1.0D0+YP(I))**2)*(RT+YP(
2I))-HP*RCI(I)*TP(I)/(1.0D0+YP(I)))
XL(I)=DL+RL(I)
D(I)=DABS(XL(I))-GL(I)
IF(D(I).GT.0.0001) GO TO 33
34 Y(I)=EL(I)-RL(I)
G(I)=(1.0D1)**((-AI*DSQRT(CI(I))/(1.0D0+BA*DSQRT(CI(I))))
FACT(I)=(DEN/(DEN+1.0D-3*EC(I))*(2.0D0*MSDL)-MSLU))**2
G(I)=G(I)*FACT(I)
GK(I)=(1.0D0-AL(I))/(AL(I)**2)*EC(I)*G(I)
8 X(I)=((EL(I)**2)*EC(I)*G(I))/XL(I)
SX=0.
SY=0.
SX2=0.
SY2=0.
SXY=0.
DO 6 L=1,N
SX=SX+X(L)
SY=SY+Y(L)
SXY=SXY+X(L)*Y(L)
SX2=SX2+(X(L)**2)
SY2=SY2+(Y(L)**2)
6 AB=(FLOAT(N)*SX2)-(SX**2)
OL=((SX2*SY)-(SXY**2))/AB
SL=((FLOAT(N)*SXY)-(SX*SY))/AB
EQK=-SL
F=((SXY-(SX*SY)/FLOAT(N))**2)/(SX2-(SX**2)/FLOAT(N))
SO=DSQRT((SY2-(Y**2)/FLOAT(N))-F)/(FLOAT(N)-2.0D0)
SOL=SO*DSQRT(SX2/AB)
SSL=SO*DSQRT(FLOAT(N)/AB)
SSEQK=SSL
WRITE(6,7) OL,SDL,EQK,SSEQK,SO
7 FORMAT(12,1P5E14.5)
IF(K.LT.5) GO TO 5

```

```

0083 DO 10 I=1,N
0084   OCL(I)=OL-OL*(AP*RCI(I)/(1.0D0+YP(I))*RT+YP(I))+BP*CI(I)*SP(I))-
0085   IGP*RCI(I)*(1.0D0/(1.0D0+YP(I))-AP*RCI(I)/(1.0D0+YP(I))*2)*(RT+Y
0086   2P(I))-HP*RCI(I)*TP(I)/(1.0D0+YP(I))
0087   OAL(I)=DABS((DSQR(1.0D0+4.0D0*EC(I)*G(I)*EQK)-1.0D0)/(2.0D0*EC(I)*
0088   1G(I)*EQK))
0089   CL(I)=AL(I)*CL(I)
0090   DEL(I)=EL(I)-CL(I)
0091   90   DSQ(I)=(DEL(I)*1.0D2/EL(I))*2
0092   DC 52 L=1,N
0093   62   SDSQ=SDSQ+DSQ(L)
0094   10   SDCL=DSQR(SDSQ/(FLOAT(N)-1.0D0))
0095   9   WRITE(6,9) EC(I),EL(I),CL(I),DEL(I),XL(I),CI(I),AL(I),G(I),GK(I)
0096   61   FORMAT(T2.1P9E14.5)
0097   WRITE(6,61) SDCL
0098   IF(M.LT.24) GO TO 11
0099   IF(J.LT.6) GO TO 1
0100   END

```

APPENDIX B  
RAW CONDUCTANCE DATA

## NaCl

25 °C40 °C20 mole percent

$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
$3.84714 \times 10^{-3}$	69.9157	$1.06238 \times 10^{-3}$	96.3157
$5.15477 \times 10^{-3}$	69.3857	$1.59654 \times 10^{-3}$	95.7401
$6.18638 \times 10^{-3}$	69.0127	$2.63144 \times 10^{-3}$	95.0051
$7.17859 \times 10^{-3}$	68.6882	$3.53211 \times 10^{-3}$	94.3534
$8.32640 \times 10^{-3}$	68.3446	$4.33181 \times 10^{-3}$	93.8676
$9.34287 \times 10^{-3}$	68.0686	$5.29032 \times 10^{-3}$	93.3690
$1.08059 \times 10^{-2}$	67.5894	$6.58058 \times 10^{-3}$	92.7596
$1.21463 \times 10^{-2}$	67.2850	$7.58834 \times 10^{-3}$	92.3504
$1.37742 \times 10^{-2}$	66.9339	$9.70683 \times 10^{-3}$	91.5290
$1.48534 \times 10^{-2}$	66.8131	$1.12092 \times 10^{-2}$	91.0132
$1.62089 \times 10^{-2}$	66.5492	$1.29511 \times 10^{-2}$	90.4529
$1.77249 \times 10^{-2}$	66.2750	$1.65281 \times 10^{-2}$	89.4819
$1.84825 \times 10^{-2}$	66.1385	$2.09688 \times 10^{-2}$	88.4498
$1.99139 \times 10^{-2}$	65.8740		

40 mole percent

$2.20611 \times 10^{-3}$	49.6662	$2.42733 \times 10^{-3}$	68.3017
$2.98560 \times 10^{-3}$	49.2580	$3.51511 \times 10^{-3}$	67.6018
$4.26083 \times 10^{-3}$	48.7166	$4.60282 \times 10^{-3}$	66.9853
$5.41297 \times 10^{-3}$	48.2912	$6.13632 \times 10^{-3}$	66.2295
$6.81548 \times 10^{-3}$	47.8248	$8.14800 \times 10^{-3}$	65.3884
$8.23681 \times 10^{-3}$	47.4006	$9.62367 \times 10^{-3}$	64.8448
$9.78572 \times 10^{-3}$	46.9758	$1.10581 \times 10^{-2}$	64.3528
$1.20954 \times 10^{-2}$	46.4017	$1.28484 \times 10^{-2}$	63.7794
$1.40700 \times 10^{-2}$	45.9541	$1.47824 \times 10^{-2}$	63.2080
$1.72859 \times 10^{-2}$	45.2941	$1.77688 \times 10^{-2}$	62.4011
$2.07594 \times 10^{-2}$	44.6553	$2.30170 \times 10^{-2}$	61.1482
$2.55262 \times 10^{-2}$	43.8662	$1.40086 \times 10^{-1}$	47.9598
$6.41155 \times 10^{-2}$	39.4290		

## NaCl

25 °C40 °C50 mole percent

$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
$2.72587 \times 10^{-3}$	44.1198	$3.97845 \times 10^{-3}$	59.4500
$3.64349 \times 10^{-3}$	43.7139	$5.17939 \times 10^{-3}$	58.8091
$4.71154 \times 10^{-3}$	43.2802	$7.40547 \times 10^{-3}$	57.8080
$5.86274 \times 10^{-3}$	42.8631	$8.84042 \times 10^{-3}$	57.3219
$7.56620 \times 10^{-3}$	42.2984	$1.08147 \times 10^{-2}$	56.5142
$9.72261 \times 10^{-3}$	41.6681	$1.35550 \times 10^{-2}$	55.6275
$1.11335 \times 10^{-2}$	41.2896	$1.67882 \times 10^{-2}$	54.6878
$1.29683 \times 10^{-2}$	40.8471	$2.01797 \times 10^{-2}$	53.7939
$1.46892 \times 10^{-2}$	40.4449	$2.66537 \times 10^{-2}$	52.3059
$1.68184 \times 10^{-2}$	39.9896	$3.44418 \times 10^{-2}$	50.7651
$1.89462 \times 10^{-2}$	39.5513	$7.14310 \times 10^{-2}$	45.3602
$2.11268 \times 10^{-2}$	39.1370	$1.41182 \times 10^{-1}$	38.9206

60 mole percent

$5.06366 \times 10^{-4}$	42.0038	$1.58878 \times 10^{-3}$	55.9639
$1.24686 \times 10^{-3}$	41.4083	$2.45133 \times 10^{-3}$	55.2620
$1.95180 \times 10^{-3}$	40.9867	$3.46869 \times 10^{-3}$	54.6395
$2.69735 \times 10^{-3}$	40.5485	$4.42897 \times 10^{-3}$	54.1135
$3.49306 \times 10^{-3}$	40.1825	$5.72449 \times 10^{-3}$	53.4348
$4.97385 \times 10^{-3}$	39.5885	$6.85161 \times 10^{-3}$	52.9255
$7.08575 \times 10^{-3}$	38.8452	$7.98415 \times 10^{-3}$	52.4543
$9.02211 \times 10^{-3}$	38.2473	$9.22755 \times 10^{-3}$	51.9702
$1.13843 \times 10^{-2}$	37.5870	$1.10278 \times 10^{-2}$	51.3108
$1.38157 \times 10^{-2}$	36.9715	$1.30938 \times 10^{-2}$	50.6061
$1.61404 \times 10^{-2}$	36.4264	$1.50679 \times 10^{-2}$	49.9727
$1.89477 \times 10^{-2}$	35.8205	$1.72170 \times 10^{-2}$	49.3436
$2.09918 \times 10^{-2}$	35.4084	$2.02913 \times 10^{-2}$	48.4864
$2.53227 \times 10^{-2}$	34.5970	$2.70992 \times 10^{-2}$	46.8445
		$4.86602 \times 10^{-2}$	42.6914

## NaAc

25 °C40 °C20 mole percent

$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
$4.15756 \times 10^{-4}$	54.9843	$1.49955 \times 10^{-3}$	74.5087
$6.32413 \times 10^{-4}$	54.7091	$2.55479 \times 10^{-3}$	73.7143
$1.01766 \times 10^{-3}$	54.3735	$3.37779 \times 10^{-3}$	73.1798
$1.43314 \times 10^{-3}$	54.0909	$4.52031 \times 10^{-3}$	72.5248
$1.93121 \times 10^{-3}$	53.7889	$5.86054 \times 10^{-3}$	71.8788
$2.50133 \times 10^{-3}$	53.4877	$6.75309 \times 10^{-3}$	71.4230
$3.07830 \times 10^{-3}$	53.1770	$7.95945 \times 10^{-3}$	70.8833
$3.61073 \times 10^{-3}$	53.0521		
$4.11305 \times 10^{-3}$	52.8403		
$4.81601 \times 10^{-3}$	52.5603		
$5.54163 \times 10^{-3}$	52.3023		
$6.57112 \times 10^{-3}$	51.9554		
$7.88330 \times 10^{-3}$	51.5504		
$9.11888 \times 10^{-3}$	51.2211		
$1.03201 \times 10^{-2}$	50.8981		
$1.18426 \times 10^{-2}$	50.5208		
$1.38490 \times 10^{-2}$	50.0683		
$1.61447 \times 10^{-2}$	49.6005		

40 mole percent

$1.78830 \times 10^{-3}$	39.4918	$1.01474 \times 10^{-3}$	56.2658
$2.24048 \times 10^{-3}$	39.2040	$1.81976 \times 10^{-3}$	55.5011
$3.08418 \times 10^{-3}$	38.7612	$2.49127 \times 10^{-3}$	54.9772
$3.53907 \times 10^{-3}$	38.5654	$3.48102 \times 10^{-3}$	54.2689
$4.74283 \times 10^{-3}$	38.0223	$4.62297 \times 10^{-3}$	53.5887
$5.97389 \times 10^{-3}$	37.5208	$6.68979 \times 10^{-3}$	52.4509
$7.41172 \times 10^{-3}$	36.9872	$7.46237 \times 10^{-3}$	52.0716
$8.78698 \times 10^{-3}$	36.5213	$8.46565 \times 10^{-3}$	51.6097
$1.09730 \times 10^{-2}$	35.8483	$1.02972 \times 10^{-2}$	50.8224
$1.28855 \times 10^{-2}$	35.3091	$1.19296 \times 10^{-2}$	50.1837
$1.61078 \times 10^{-2}$	34.4848	$1.48473 \times 10^{-2}$	49.1435
$2.24362 \times 10^{-2}$	33.0874	$1.99969 \times 10^{-2}$	47.5418
		$8.96989 \times 10^{-2}$	35.9412

## NaAc

25 °C40 °C50 mole percent

$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
$7.53854 \times 10^{-4}$	36.6420	$1.56937 \times 10^{-3}$	50.4227
$1.15079 \times 10^{-3}$	36.3009	$2.66724 \times 10^{-3}$	49.4296
$1.54895 \times 10^{-3}$	36.0616	$3.96365 \times 10^{-3}$	48.4606
$2.17423 \times 10^{-3}$	35.6581	$5.93674 \times 10^{-3}$	47.2203
$2.58970 \times 10^{-3}$	35.4259	$7.45455 \times 10^{-3}$	46.3925
$3.14531 \times 10^{-3}$	35.1208	$8.96446 \times 10^{-3}$	45.6411
$3.84670 \times 10^{-3}$	34.7600	$1.09991 \times 10^{-2}$	44.6945
$4.56152 \times 10^{-3}$	34.4226	$1.27163 \times 10^{-2}$	43.9656
$5.29751 \times 10^{-3}$	34.0901	$1.43515 \times 10^{-2}$	43.3302
$5.84068 \times 10^{-3}$	33.8544	$1.59724 \times 10^{-2}$	42.7386
$6.48254 \times 10^{-3}$	33.5864	$1.74999 \times 10^{-2}$	42.2137
$7.22434 \times 10^{-3}$	33.2872	$1.90285 \times 10^{-2}$	41.7029
$8.07526 \times 10^{-3}$	32.9715		
$8.87640 \times 10^{-3}$	32.6791		
$9.83720 \times 10^{-3}$	32.3469		

60 mole percent

$8.29576 \times 10^{-4}$	34.6137	$2.18717 \times 10^{-3}$	46.1162
$1.13155 \times 10^{-3}$	34.3523	$2.90841 \times 10^{-3}$	45.4906
$1.62920 \times 10^{-3}$	33.9573	$3.86528 \times 10^{-3}$	44.7384
$2.22556 \times 10^{-3}$	33.5297	$4.60981 \times 10^{-3}$	44.1960
$3.24839 \times 10^{-3}$	32.8960	$5.29357 \times 10^{-3}$	43.7284
$4.27202 \times 10^{-3}$	32.2576	$6.07711 \times 10^{-3}$	43.2278
$5.65698 \times 10^{-3}$	31.5213	$7.19192 \times 10^{-3}$	42.5598
$7.03265 \times 10^{-3}$	30.8780	$8.03131 \times 10^{-3}$	42.0654
$8.10247 \times 10^{-3}$	30.4136	$9.02460 \times 10^{-3}$	41.5269
$9.24205 \times 10^{-3}$	29.9498	$1.02169 \times 10^{-2}$	40.9105
$1.05366 \times 10^{-2}$	29.4581		
$1.14780 \times 10^{-2}$	29.1592		
$1.23746 \times 10^{-2}$	28.8832		

## HCl

25 °C40 °C20 mole percent

$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
$1.77675 \times 10^{-3}$	195.551	$1.07956 \times 10^{-3}$	244.823
$2.12747 \times 10^{-3}$	195.291	$1.73870 \times 10^{-3}$	243.788
$2.59927 \times 10^{-3}$	194.956	$2.55356 \times 10^{-3}$	242.728
$3.07378 \times 10^{-3}$	194.587	$3.30475 \times 10^{-3}$	242.012
$3.43622 \times 10^{-3}$	194.378	$4.78442 \times 10^{-3}$	240.566
$3.86989 \times 10^{-3}$	194.108	$5.34495 \times 10^{-3}$	240.149
$4.40138 \times 10^{-3}$	193.780	$6.08951 \times 10^{-3}$	239.664
$5.40053 \times 10^{-3}$	193.278	$7.03674 \times 10^{-3}$	239.071
$7.23095 \times 10^{-3}$	192.437	$7.95130 \times 10^{-3}$	238.542
$9.93031 \times 10^{-3}$	191.382	$8.81425 \times 10^{-3}$	238.002
		$9.77677 \times 10^{-3}$	237.510
		$1.08047 \times 10^{-2}$	237.026
		$1.21898 \times 10^{-2}$	236.406

40 mole percent

$1.52112 \times 10^{-3}$	99.7174	$2.12419 \times 10^{-3}$	127.519
$1.95878 \times 10^{-3}$	99.4321	$3.01712 \times 10^{-3}$	126.503
$2.90896 \times 10^{-3}$	98.8563	$3.70665 \times 10^{-3}$	125.929
$3.92282 \times 10^{-3}$	98.2592	$4.37885 \times 10^{-3}$	125.388
$5.04751 \times 10^{-3}$	97.6477	$5.39848 \times 10^{-3}$	124.719
$6.17736 \times 10^{-3}$	97.1223	$6.61574 \times 10^{-3}$	123.962
$7.94009 \times 10^{-3}$	96.3854	$7.91579 \times 10^{-3}$	123.217
$9.42031 \times 10^{-3}$	95.8277	$1.06868 \times 10^{-2}$	121.823
$1.15423 \times 10^{-2}$	95.0819	$5.95950 \times 10^{-2}$	109.297
$2.35371 \times 10^{-2}$	91.7503		

## HCl

25 °C40 °C50 mole percent

$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
$4.00605 \times 10^{-4}$	74.9242	$9.97067 \times 10^{-4}$	95.1069
$5.14002 \times 10^{-4}$	74.8081	$2.03113 \times 10^{-3}$	94.0032
$6.48676 \times 10^{-4}$	74.6374	$2.74854 \times 10^{-3}$	93.3072
$7.55771 \times 10^{-4}$	74.5256	$3.42204 \times 10^{-3}$	92.7384
$8.71755 \times 10^{-4}$	74.4053	$4.05298 \times 10^{-3}$	92.2325
$9.72576 \times 10^{-4}$	74.2148	$4.91402 \times 10^{-3}$	91.5473
$1.12153 \times 10^{-3}$	74.0874	$5.81214 \times 10^{-3}$	90.9440
$1.28942 \times 10^{-3}$	73.8900	$6.76002 \times 10^{-3}$	90.3412
$1.45923 \times 10^{-3}$	73.7424	$7.73856 \times 10^{-3}$	89.7534
$1.77018 \times 10^{-3}$	73.4825	$9.19380 \times 10^{-3}$	88.9469
$2.09338 \times 10^{-3}$	73.2428	$1.09574 \times 10^{-2}$	88.0395
$2.59527 \times 10^{-3}$	72.8846	$4.05909 \times 10^{-2}$	78.3115
$3.08176 \times 10^{-3}$	72.5535		
$3.57660 \times 10^{-3}$	72.2422		
$4.09293 \times 10^{-3}$	71.9034		

60 mole percent

$4.51278 \times 10^{-4}$	57.8123	$2.75068 \times 10^{-3}$	72.4716
$7.23942 \times 10^{-4}$	57.4397	$3.60593 \times 10^{-3}$	71.7063
$1.08942 \times 10^{-3}$	57.0197	$4.53253 \times 10^{-3}$	70.9638
$1.56687 \times 10^{-3}$	56.5190	$5.58808 \times 10^{-3}$	70.1951
$2.15608 \times 10^{-3}$	56.0190	$6.45962 \times 10^{-3}$	69.5977
$2.72780 \times 10^{-3}$	55.5477	$7.34160 \times 10^{-3}$	69.0347
$3.37647 \times 10^{-3}$	55.0593	$8.38651 \times 10^{-3}$	68.4082
$4.20177 \times 10^{-3}$	54.4957	$9.12236 \times 10^{-3}$	68.0296
$5.09842 \times 10^{-3}$	53.9249	$1.09784 \times 10^{-2}$	67.1102
$6.40766 \times 10^{-3}$	53.1658		
$7.33463 \times 10^{-3}$	52.6657		
$8.48906 \times 10^{-3}$	52.0877		
$9.98672 \times 10^{-3}$	51.3934		
$2.46355 \times 10^{-2}$	46.6291		

HCl

40°C

80 mole percent100 mole percent

$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^1 \text{ mol}^{-1})$	$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
$1.46163 \times 10^{-3}$	45.2686	$4.72572 \times 10^{-4}$	$3.27884 \times 10^{-0}$
$2.30806 \times 10^{-3}$	43.4810	$1.20780 \times 10^{-3}$	$1.62809 \times 10^{-0}$
$3.13662 \times 10^{-3}$	42.0696	$2.10771 \times 10^{-3}$	$1.13997 \times 10^{-0}$
$4.28583 \times 10^{-3}$	40.5495	$3.62593 \times 10^{-3}$	$9.08222 \times 10^{-1}$
$5.58384 \times 10^{-3}$	38.9731	$5.24780 \times 10^{-3}$	$8.32738 \times 10^{-1}$
$7.08731 \times 10^{-3}$	37.4571	$7.11328 \times 10^{-3}$	$7.66498 \times 10^{-1}$
$8.87239 \times 10^{-3}$	35.9674		
$1.09969 \times 10^{-2}$	34.4221		

## HAc

25 °C40 °C

20 mole percent

$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
$2.28881 \times 10^{-3}$	4.44324	$3.79737 \times 10^{-3}$	4.07723
$2.94273 \times 10^{-3}$	3.92226	$5.16488 \times 10^{-3}$	3.49837
$3.71594 \times 10^{-3}$	3.49460	$6.56903 \times 10^{-3}$	3.10847
$4.35080 \times 10^{-3}$	3.23355	$8.87513 \times 10^{-3}$	2.67597
$5.26418 \times 10^{-3}$	2.94248	$1.10299 \times 10^{-2}$	2.40174
$6.36175 \times 10^{-3}$	2.67914	$1.36230 \times 10^{-2}$	2.16260
$7.37100 \times 10^{-3}$	2.49074	$1.64595 \times 10^{-2}$	1.96886
$8.47833 \times 10^{-3}$	2.32508	$1.94823 \times 10^{-2}$	1.81045
$9.32320 \times 10^{-3}$	2.21803	$2.32272 \times 10^{-2}$	1.65882
$1.03619 \times 10^{-2}$	2.10470	$2.92834 \times 10^{-2}$	1.47804
$1.13285 \times 10^{-2}$	2.01385	$3.81937 \times 10^{-2}$	1.29595
$1.39270 \times 10^{-2}$	1.81790	$8.06264 \times 10^{-2}$	8.94817 *
$2.66580 \times 10^{-2}$	1.31902		
$4.43029 \times 10^{-2}$	1.02538		
$7.94855 \times 10^{-2}$	7.66440 *		
$1.11242 \times 10^{-1}$	6.47739 *		

40 mole percent

$7.44079 \times 10^{-4}$	1.58924	$1.01086 \times 10^{-3}$	1.50251
$1.50317 \times 10^{-3}$	1.05748	$2.40156 \times 10^{-3}$	9.16085 *
$2.45388 \times 10^{-3}$	8.06100 *	$3.41902 \times 10^{-3}$	7.56012 *
$3.79655 \times 10^{-3}$	6.37440 *	$5.85270 \times 10^{-3}$	5.69026 *
$5.21096 \times 10^{-3}$	5.38835 *	$8.10190 \times 10^{-3}$	4.80604 *
$7.20606 \times 10^{-3}$	4.54716 *	$1.16214 \times 10^{-2}$	3.99198 *
$8.88154 \times 10^{-3}$	4.07901 *	$1.44164 \times 10^{-2}$	3.57650 *
$1.18138 \times 10^{-2}$	3.52120 *	$1.68774 \times 10^{-2}$	3.30060 *
$1.40892 \times 10^{-2}$	3.21624 *	$1.97111 \times 10^{-2}$	3.05162 *
$1.86753 \times 10^{-2}$	2.78417 *	$2.33807 \times 10^{-2}$	2.80011 *
$2.20716 \times 10^{-2}$	2.55682 *	$2.80217 \times 10^{-2}$	2.55577 *
$2.77982 \times 10^{-2}$	2.27415 *	$3.57408 \times 10^{-2}$	2.26282 *
$3.70483 \times 10^{-2}$	1.95610 *	$4.72081 \times 10^{-2}$	1.97078 *
$7.14853 \times 10^{-2}$	1.40007 *	$9.90940 \times 10^{-2}$	1.36610 *
$1.39484 \times 10^{-1}$	1.00721 *	$1.85885 \times 10^{-1}$	1.00688 *

\*Should be  $\times 10^{-1}$

## HAc

25 °C40 °C

50 mole percent

$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
$3.30593 \times 10^{-4}$	$1.19603 \times 10^0$	$5.38923 \times 10^{-4}$	$1.15028 \times 10^0$
$1.34786 \times 10^{-3}$	$4.74256 \times 10^{-1}$	$1.54190 \times 10^{-3}$	$5.59835 \times 10^{-1}$
$2.65167 \times 10^{-3}$	$3.19284 \times 10^{-1}$	$2.29627 \times 10^{-3}$	$4.35689 \times 10^{-1}$
$3.71694 \times 10^{-3}$	$2.63758 \times 10^{-1}$	$3.54486 \times 10^{-3}$	$3.36440 \times 10^{-1}$
$4.8688 \times 10^{-3}$	$2.27488 \times 10^{-1}$	$5.72555 \times 10^{-3}$	$2.55470 \times 10^{-1}$
$6.63294 \times 10^{-3}$	$1.91173 \times 10^{-1}$	$7.54456 \times 10^{-3}$	$2.19124 \times 10^{-1}$
$7.69520 \times 10^{-3}$	$1.76796 \times 10^{-1}$	$9.61264 \times 10^{-3}$	$1.92254 \times 10^{-1}$
$8.58906 \times 10^{-3}$	$1.66079 \times 10^{-1}$	$1.15337 \times 10^{-2}$	$1.74435 \times 10^{-1}$
$1.00173 \times 10^{-2}$	$1.52921 \times 10^{-1}$	$1.33674 \times 10^{-2}$	$1.61222 \times 10^{-1}$
$1.12527 \times 10^{-2}$	$1.44120 \times 10^{-1}$	$1.49052 \times 10^{-2}$	$1.52264 \times 10^{-1}$
$1.24679 \times 10^{-2}$	$1.36318 \times 10^{-1}$	$1.75722 \times 10^{-2}$	$1.39870 \times 10^{-1}$
$1.39232 \times 10^{-2}$	$1.28582 \times 10^{-1}$	$2.03878 \times 10^{-2}$	$1.29641 \times 10^{-1}$
$1.55191 \times 10^{-2}$	$1.31312 \times 10^{-1}$	$2.63738 \times 10^{-2}$	$1.13903 \times 10^{-1}$
$1.67642 \times 10^{-2}$	$1.16767 \times 10^{-1}$	$6.49942 \times 10^{-2}$	$6.99997 \times 10^{-2}$
		$1.27358 \times 10^{-1}$	$4.97627 \times 10^{-2}$

60 mole percent

$6.75407 \times 10^{-4}$	$3.29234 \times 10^{-1}$	$6.69642 \times 10^{-4}$	$1.83586 \times 10^0$
$1.50808 \times 10^{-3}$	$1.86035 \times 10^{-1}$	$2.30470 \times 10^{-3}$	$5.72693 \times 10^{-1}$
$2.83407 \times 10^{-3}$	$1.23054 \times 10^{-1}$	$4.39060 \times 10^{-3}$	$3.16117 \times 10^{-1}$
$5.04332 \times 10^{-3}$	$8.63331 \times 10^{-2}$	$6.30100 \times 10^{-3}$	$2.27772 \times 10^{-1}$
$7.69816 \times 10^{-3}$	$6.74824 \times 10^{-2}$	$8.92969 \times 10^{-3}$	$1.67198 \times 10^{-1}$
$1.07533 \times 10^{-2}$	$5.57879 \times 10^{-2}$	$1.27427 \times 10^{-2}$	$1.23351 \times 10^{-1}$
$1.45604 \times 10^{-2}$	$4.71431 \times 10^{-2}$	$1.58972 \times 10^{-2}$	$1.02510 \times 10^{-1}$
$1.77469 \times 10^{-2}$	$4.23184 \times 10^{-2}$	$1.90374 \times 10^{-2}$	$8.85163 \times 10^{-2}$
$2.02129 \times 10^{-2}$	$3.94767 \times 10^{-2}$	$2.28422 \times 10^{-2}$	$7.65179 \times 10^{-2}$
$2.27507 \times 10^{-2}$	$3.70703 \times 10^{-2}$	$2.56762 \times 10^{-2}$	$6.98229 \times 10^{-2}$
$2.59021 \times 10^{-2}$	$3.46104 \times 10^{-2}$	$2.91705 \times 10^{-2}$	$6.32885 \times 10^{-2}$
$2.80266 \times 10^{-2}$	$3.32087 \times 10^{-2}$	$3.20754 \times 10^{-2}$	$5.89370 \times 10^{-2}$
$3.07483 \times 10^{-2}$	$3.16461 \times 10^{-2}$	$3.60200 \times 10^{-2}$	$5.40603 \times 10^{-2}$
$3.48990 \times 10^{-2}$	$2.96410 \times 10^{-2}$		
$7.31627 \times 10^{-2}$	$2.03914 \times 10^{-2}$		
$1.39450 \times 10^{-1}$	$1.50755 \times 10^{-2}$		

## HAc

80 mole percent

100 mole percent

40 °C

$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	$c(\text{mol liter}^{-1})$	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
$8.64884 \times 10^{-4}$	$1.25946 \times 10^0$	$2.65808 \times 10^{-3}$	$2.77935 \times 10^{-1}$
$2.15032 \times 10^{-3}$	$5.51964 \times 10^{-1}$	$5.34690 \times 10^{-3}$	$1.44078 \times 10^{-1}$
$3.92199 \times 10^{-3}$	$3.19532 \times 10^{-1}$	$9.95671 \times 10^{-3}$	$8.11524 \times 10^{-2}$
$6.52947 \times 10^{-3}$	$1.97784 \times 10^{-1}$	$1.42550 \times 10^{-2}$	$6.00186 \times 10^{-2}$
$9.17074 \times 10^{-3}$	$1.44126 \times 10^{-1}$	$1.95505 \times 10^{-2}$	$4.62127 \times 10^{-2}$
$1.21443 \times 10^{-2}$	$1.10434 \times 10^{-1}$	$2.42864 \times 10^{-2}$	$3.86022 \times 10^{-2}$
$1.56610 \times 10^{-2}$	$8.66024 \times 10^{-2}$	$2.97389 \times 10^{-2}$	$3.25710 \times 10^{-2}$
$2.06805 \times 10^{-2}$	$6.62662 \times 10^{-2}$	$4.02934 \times 10^{-2}$	$2.49500 \times 10^{-2}$
$2.60575 \times 10^{-2}$	$5.30353 \times 10^{-2}$	$9.86488 \times 10^{-2}$	$1.11903 \times 10^{-2}$
$3.25305 \times 10^{-2}$	$4.27996 \times 10^{-2}$		

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## BIOGRAPHICAL SKETCH

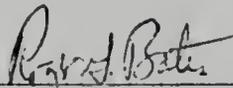
Barry Richard Boerner was born in Miami Beach, Florida, on September 10, 1945. After attending various schools in the Miami area, he was graduated from Miami-Palmetto Senior High in 1963. He obtained a Bachelor of Science degree from the University of Florida in August, 1967.

Graduate work was started immediately afterward under Dr. Stuart P. Cram. However, this work was not completed before Dr. Cram left the University of Florida. Subsequently, after a brief interim period, graduate work was started under Professor Roger G. Bates in 1972, and continued until the present time.

He was married to the former Gaylia Anne Morgan on March 17, 1970. They have one child, Benjamin Richard.

He is a member of the Analytical Division of the American Chemical Society.

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Roger G. Bates, Chairman  
Professor of Chemistry

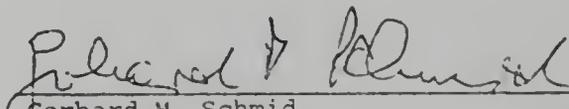
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Assistant Professor of Chemistry

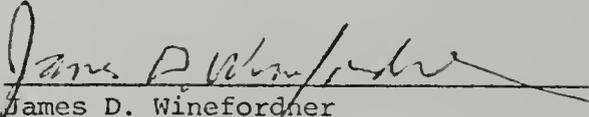
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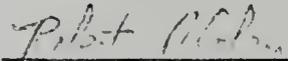
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Robert J. Cohen  
Assistant Professor of Biochemistry

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1975

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Dean, Graduate School