

AN ABSTRACT OF THE THESIS OF

Raj E. Bastianpillai for the Master of Science Degree in Physical Sciences with a Chemistry Emphasis presented on July 25, 1988.

The Application of the Fuoss-Onsager Conductance Theory to Chlorides of Alkali Metals in Ethanol-Water Mixtures.

Abstract approved: Charles Grunberg

The conductance of three 1:1 electrolytes; NaCl, KCl, and CsCl were evaluated at 25°C in ethanol-water mixtures. The results were interpreted in terms of the Fuoss-Onsager equation:

$$A = A^{\circ} - S c^{1/2} + E c \ln c + J_1 c + J_2 c^{3/2}$$

The two adjustable parameters used in this equation were the ion-size and the limiting equivalent conductance. The ion association constants for these electrolytes in different solvent compositions were also calculated and compared.

THE APPLICATION OF THE FUOSS-ONSAGER CONDUCTANCE THEORY  
TO CHLORIDES OF ALKALI METALS IN ETHANOL-WATER MIXTURES

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by

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## I. Introduction

Electrolytic conductance is the ability of a liquid to carry an electric current. Conductance measurements constitute one of the most sensitive and widely used physical methods for investigating the properties of electrolyte solutions. In electrolytic solutions, the current is transported by ions, in contrast to electron flow in metallic conductors. The response of ions to an externally applied electrical field can be measured with high precision even at very low concentrations.<sup>1</sup> The conductance of an electrolyte solution depends upon the number of ions in solution, the ionic charge, and the rate of ion movement under the influence of an electromotive force. The ability of a solution to conduct electricity is expressed in terms of its equivalent conductance,  $\lambda$ , which is defined as the conductance of one gram equivalent of the solute when contained between two electrodes spaced one centimeter apart.

$$\lambda = A = 1000 L/c \quad (1.1)$$

where  $L$  is the specific conductance of the solution and  $c$  is the concentration in equivalents per liter.<sup>2</sup>

The mobility of an ion in solution is governed by four forces. An "electrical force", equal to the product



of the potential of the electrode and the charge of the ion, which tends to move the ion towards one of the electrodes. An opposing effect is the "frictional force". The viscous frictional force exerted by the solvent on the ions is proportional to the speed of the ions and opposes them.<sup>3</sup> Two other factors; the "electrophoretic effect" and the "relaxation effect", cause the equivalent conductance of an electrolyte to decrease as the ionic concentration increases.

The electrophoretic effect is caused by the motion of the oppositely charged ions surrounding the ion of interest. These ions carry with them molecules of solvent and the motion of the primary ion is thus retarded by the flow of solvent molecules in the opposite direction. This effect results in a decrease in the conductance of the solution. The electrophoretic effect is larger in solvents which are more polar, due to stronger ion - dipole interactions.

In the absence of an external electrical field, each ion is surrounded by a spherically shaped ionic atmosphere consisting of oppositely charged ions. When an electrical field is applied, the ions begin to move toward their respective electrodes. This movement distorts the ionic atmosphere and it loses its spherical shape. As the ions move through the solution the ionic

atmosphere is constantly being created and destroyed. This phenomena is called the relaxation effect and it also results in a decrease in the conductance of the solution.<sup>4</sup>

For strong electrolytes, in the dilute solution region, a linear relationship exists between the equivalent conductance and the square root of concentration. Extrapolation of this straight line relationship to zero concentration yields a value for the equivalent conductance at infinite dilution,  $\lambda(0)$ . A similar plot for weak electrolytes is non-linear, and direct evaluation of  $\lambda(0)$  is difficult.<sup>5</sup>

At infinite dilution, electrophoretic and relaxation effects become insignificant as the distance between nearest neighbor ions is large and only the effect of the applied electric field is felt by the individual ions. Kohlrausch's law of independent mobilities states the following:

$$\Lambda^0 = (\lambda^0_+) + (\lambda^0_-) \quad (1.2)$$

where  $\lambda(0)$  is designated as  $\Lambda^0$ , and  $\lambda^0_+$  and  $\lambda^0_-$  are the equivalent ionic conductances of the cation and the anion of the electrolyte at infinite dilution.<sup>6</sup>

The equivalent conductance of a given solution depends on the velocity and the concentration of the

ions. These quantities, in turn, are dependent upon the solvent, the temperature, the pressure, and the strength of the electrical field. The solvent affects the conductance primarily through its viscosity, its dielectric constant and its specific interaction with the ions. Solvent viscosity resists the motion of the ions. The dielectric properties of the solvent control the effective field strength and interionic potential. These affect not only ion velocities, but also the attraction between ions and consequently the extent of ion pairing. Specific solvation of ions does affect both mobility and association.

Variation of temperature or pressure changes the viscosity, the dielectric constant and the density of the solvent. Furthermore, the temperature is proportional to the thermal energy of the ions, and of the solvent molecules. Thus, the temperature affects the interactions between the electrolyte and the solvent. High pressure decreases free volume and forces the solution components closer together, also changing interactions among them.<sup>7</sup>

The conductance of three 1:1 electrolytes (NaCl, KCl and CsCl) were evaluated. The solvent system selected was ethanol-water. The dielectric constant of the system was varied by changing the weight percent ethanol in the

solvent. The dependence of the conductance of these electrolytes on the dielectric constant was evaluated and compared. The temperature was kept at 25° C and the pressure was assumed to be constant at one atmosphere. Determination of the equivalent conductance as a function of concentration of the electrolyte, followed by analysis using an appropriate equation gave a value for  $K_a$ , the association constant.

## II. Development of the Conductance Equation

Over the years a number of theoretical equations have been proposed for the dependence of mobilities or equivalent conductance on concentration. Arrhenius succeeded in describing the conductance of dilute solutions of weak acids and bases by expressing the degree of dissociation,  $r$ , as:

$$r = A/A^{\circ} \quad (2.1)$$

where  $A$  is the equivalent conductance. However, strong acids and bases and their salts failed completely even to approximate linearity when the data were plotted in accordance with Ostwald's dilution law. In 1923, Debye and Huckel assumed complete dissociation of aqueous solutions of strong electrolytes, and ascribed the change of the equivalent conductance with concentration to a change of mobility (rather than of the degree of dissociation) with concentration. Their theory led to the verification of the limiting result found empirically by Kohlrausch years earlier:

$$A = A^{\circ} - S c^{1/2} \quad (2.2)$$

Shortly thereafter, Onsager gave a theoretical derivation of the coefficient  $S$ , using the Debye-Huckel model of ion atmosphere and their processes of relaxation braking and electrophoretic counterflow. The Onsager

equation for the limiting tangent to the conductance curve is:

$$A = A^{\circ} - [\alpha (A^{\circ}) + \beta] c^{1/2} \quad (2.3)$$

where  $\alpha$  and  $\beta$  are completely determined given temperature, valence type of electrolyte, and dielectric constant and viscosity of the solvent.<sup>8</sup> This approach was based upon the Debye-Huckel theory for dilute solutions of electrolytes, where the ions were treated as point charges and the solvent as a continuum with a bulk dielectric constant and viscosity. This equation is of limited application for extrapolating equivalent conductance data to obtain the equivalent conductance at infinite dilution because it only yields the slope at infinite dilution and one is normally interested in analyzing data over a finite concentration range.<sup>9</sup> Several extensions of the crude model of the Debye-Huckel theory have taken into account ionic size, employing the model of the ion considered as a sphere, with its charge at the center of the sphere, moving in a continuum. The most widely used equation for unassociated 1:1 electrolytes is the Fuoss-Onsager equation:

$$A = A^{\circ} - S c^{1/2} + E c \ln c + J_1 c \quad (2.4)$$

where the symbols are defined in Appendix III.  $S$ ,  $E$ , and  $J_1$  contain contributions from both the electrophoretic and the relaxation effects and each

depends on the equivalent conductance at infinite dilution.  $J_1$  is also a function of "a", the ion-size parameter.<sup>10</sup> The coefficient E, like S, is made up of two terms, an electrostatic and a hydrodynamic one.<sup>11</sup>

Further development of the Fuoss-Onsager equation includes taking the occurrence of ion pairing or ion-association into consideration. If the magnitude of the electrostatic attraction energy is substantially greater than the thermal kinetic energy of species in the solution, then the pair of oppositely charged ions will form an entity with sufficient stability to exist over the course of several collisions with solvent molecules. Such an entity is called an "ion-pair". Ion-pairs are essentially neutral in solution and thus, they are non-conducting. However, an ion-pair does not remain stable indefinitely. If another ion should approach the pair close enough to exert its own coulombic force, a new ion-pair is formed.

The concept of ion-pairs was introduced by Bjerrum. He used a model similar to that of Debye and Huckel to find a theoretical expression for the degree of association for ion-pairs as a function of electrolyte concentration, ionic charge, temperature, dielectric constant, and ion-size parameter. His theory indicated

that ion association is usually negligible for 1:1 electrolytes in water. Nevertheless, for electrolytes with higher  $z^+ z^-$  values (2:2 electrolytes, for example), ion association can be quite substantial even at low concentrations.<sup>12</sup>

The solvent water has a high dielectric constant due to the polarity of the water molecule. In solvents with lower dielectric constant values (such as ethanol), the magnitude of the electrostatic attraction energy is greater than in aqueous solutions. Hence, ion-pair formation in these solvents is greater than in water. Even for 1:1 electrolytes such as NaCl, KCl, and CsCl, ion-pair formation is important in solvents with low dielectric constants.

One consequence of the Bjerrum hypothesis was the definition of a distance beyond which the ions were considered to be free entities, and within which the ions were considered to be non-conducting ion-pairs. This "Bjerrum's distance parameter",  $b$ , was expressed as:<sup>13</sup>

$$b = (z^+)(z^-) e^2 / D a k T \quad (2.5)$$

where "a" is the ion-size parameter, which in this case, is treated as an adjustable constant.

In order to determine the association constant  $K_a$ , Fuoss derived an equation which takes into account the



volumes excluded by paired ions:<sup>14</sup>

$$K_a = (4 \pi N a^3 / 3000) \times \exp(z^2 e^2 / D a k T) \quad (2.6)$$

According to the mass action equation,  $K_a$  can be determined as the ratio of non-conducting, associated pairs  $(1-r)$  to the number of free ions  $(c r^2 f^2)$ :

$$K_a = (1-r) / c r^2 f^2 \quad (2.7)$$

For associated electrolytes, the Fuoss-Onsager equation is then extended to include the association constant and the degree of association:<sup>15</sup>

$$A = A^0 - S (c r)^{1/2} + E c r \ln (c r) + J_1 (c r) - K_a c r f^2 A \quad (2.8)$$

By including terms of higher order in the mathematical treatment of the relaxation and electrophoretic effects, the Fuoss-Onsager equation becomes:<sup>16</sup>

$$A = A^0 - S c^{1/2} + E c \ln c + J_1 c + J_2 c^{3/2} \quad (2.9)$$

where  $J_2$  is also a function of the ion-size parameter. This term has not been widely used since its magnitude appeared to be small. However, the inclusion of terms in  $c^{3/2}$  improves the fit compared to the earlier versions of the equation.<sup>17</sup>

For associated electrolytes, the Fuoss-Onsager equation corresponding to Equation (2.9) is:

$$\begin{aligned} A = A^{\circ} - S (cr)^{1/2} + E (cr) \ln (cr) \\ + J_1 cr + J_2 (cr)^{3/2} \end{aligned} \quad (2.10)$$

### III. Equipment and Experimental Techniques

The requirements for precise conductance measurements can be summarized in terms of four main factors: accurately known concentrations; true conductance readings; good temperature control; and exact solvent composition.

#### A. Preparation of Solutions

The non-aqueous component of the mixed solvent used in this work is ethanol. The dielectric constant of the solvent was changed by varying the weight percent ethanol in the solvent mixture. Initially, methanol was chosen as the solvent system since alkali halides showed a slightly higher solubility in the more polar methanol. However, considerable difficulty was encountered in making measurements with anhydrous methanol as the solvent. The conductance readings showed an abnormal drift and it was difficult to obtain accurate measurements. This effect was attributed to an oxidation reaction of methanol at the platinized electrodes.<sup>18</sup>

The only way to eliminate this problem was to remove the dissolved oxygen in methanol by bubbling nitrogen through it. Furthermore, the methanol had to be prevented from

being contaminated by the atmosphere while the solutions were being prepared and while conductance measurements were being taken. As this process was to be time consuming and difficult, ethanol was substituted for methanol.

The electrolytes chosen for this research were NaCl, KCl, and CsCl. They were selected for the following reasons: trends in conductance and ion-association of group 1 electrolytes could be evaluated; they can be obtained at high purity levels (above 99.9%); they are among the least hygroscopic of the alkali chlorides; and application of the conductance equations are more feasible on 1:1 electrolytes.

ACS Reagent grade NaCl (Fisher Scientific Co.), KCl (MC&B Corp.), and CsCl (Fisher Scientific Co.) crystals were dried overnight in an oven at 110°C and left to cool in a dessicator containing the drying agent Anhydrone - anhydrous magnesium perchlorate. Anhydrone is an excellent drying agent with the capability of dessicating up to .002 mg residual water/liter of air at 30.5°C.<sup>19</sup> The crystals of each salt were weighed by difference using a balance with a precision of 0.00002 g. The balance was enclosed in a transparent glove-bag in order to minimize contact with moisture in the air during the weighing process. Also, several

containers of anhydrous were placed in the glove-bag in order to remove moisture from the air contained within the glove-bag.

U.S.D. 95% (by volume) ethanol was used in preparing the solvent mixtures. Conductivity water, of a specific conductance of about  $1.3 \times 10^6$  mho/cm was prepared by passing distilled water through a Sybron Barnstead BD-1 ion-exchange column. The ethanol-water mixtures were then made up by weight using 0.8100 and 0.99707 g/ml respectively, as densities for ethanol and water. The volumes of the liquids were measured using grade A Pyrex volumetric flasks.

The variation of conductance with concentration was measured for each salt at ten different solvent compositions. For example, conductance measurements for NaCl were taken in 0, 7.1, 16.0, 27.4, 33.2, 42.4, 51.9, 58.4, 72.0, and 83.7 weight percent ethanol mixtures. Each solvent composition was made fresh, the day of a particular conductance run.

## B. Conductance Cell

The conductance cell used in this work is the Yellow Springs Instruments (YSI) 3402 dip cell with a cell constant of 0.1/cm. The cell body is made of Pyrex and

the electrodes are a platinum-iridium alloy coated with platinum black. The electrodes are gold soldered to platinum lead wires. The conductance cell is attached to a conductance meter, YSI model 34, with a digital display. Cells with a cell constant of 0.1/cm give a meter reading that is higher by a factor of ten. YSI cells allow measurements in a range of 0.01 micromho to 200 millimho with an accuracy of 0.10%. These cells are calibrated using a reference solution of 0.01 mmol/kg KCl.<sup>20</sup>

The YSI model 34 conductance meter is powered by rechargable nickel-cadmium batteries. However, if direct current is applied, the current flow decreases rapidly with time; partially because of gas evolving at or on the electrodes, reducing their effective surface area. This effect is called "polarization", and must be circumvented before conductance measurements are taken. The degree of polarization depends upon the magnitude of the current density per unit area and the amount of time for which it flows. Practical conductance measurements use a very small alternating potential (sine wave or short pulses), giving a minute current flowing in each direction for a period insufficient to cause a significant polarization error. Also, electrode areas are kept as large as possible to reduce current density per unit area.<sup>21</sup>

The model YSI 34 conductance meter obtains a reading by varying the amplitude of a square wave current forced through the cell so that the time-averaged magnitude of the cell voltage over each half-cycle is constant and is equal to a reference voltage. Under these conditions, the current and the conductance are directly proportional. The direction of the current is switched every half cycle. The forced current method also minimizes the errors in measurement, from series capacitance at the conductance cell, introduced by the polarization effects.<sup>22</sup> However, since electrolytic conductance is strongly dependent on the temperature, the total current passing through the cell must be kept small so that no significant heating occurs.

The unforeseen oxidation of methanol at the electrodes affected the platinum black coating and resulted in an abnormal drift in the readings. After switching to ethanol, the electrode surfaces had to be cleaned before the cell could be used again. The cleaning solution used was a mixture of equal parts by volume of isopropyl alcohol and 10 normal HCl.

### C. Constant Temperature Bath

The conductance of a solution is related inversely

to its viscosity. Since viscosities change several percent per degree, the temperature of the bath must be controlled to at least  $\pm 0.005^{\circ}\text{C}$  if a precision of 0.1% is to be obtained. The constant temperature bath used in this work was the GCA / Precision Scientific circulating system Model 255. The bath has a temperature range of  $-24^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$ ; uniformity of  $\pm 0.03^{\circ}\text{C}$  (at  $25^{\circ}\text{C}$ ) ; and sensitivity of  $\pm 0.005^{\circ}\text{C}$  (at  $25^{\circ}\text{C}$ ).<sup>23</sup> The thermostatic medium in the bath was water, although an oil bath is generally preferred because a water bath could cause a capacitance coupling between the leads of electrodes, the solution, and the bath; which results in erroneous resistance readings.<sup>24</sup> The Model 255 circulating system contains solid state temperature controllers; a heating and refrigeration unit, two centrifugal pumps, and sensitive platinum probes which provide accurate temperature control.

#### D. Procedure

The first salt analyzed in this work was KCl. The conductance runs were done on the following nine solvent mixtures: 7.86, 16.01, 27.35, 35.81, 42.36, 49.10, 58.39,



72.01, and 83.73 weight % ethanol. Eighteen different KCl solution samples were prepared from each of the nine solvent mixtures. For example, from the 7.86 % solvent mixture, eighteen KCl solutions with concentrations ranging from 0.00200 N to 0.0200 N were prepared. Then the specific conductance of each solution was measured at 25°C. This process was repeated for the other eight solvent mixtures.

The solvent mixtures were prepared fresh every day with newly opened 95% ethanol and deionized water. Grade A Pyrex volumetric flasks were used. Since these were "to contain" glassware, a drainage time of three minutes was allowed after pouring a liquid from one flask to another. The flasks were stoppered so as to prevent the ethanol from evaporating from the solvent mixture.

The KCl crystals were dried overnight in an oven at 110°C and left to cool in the dessicator. Samples of KCl ranging from .00277 g to .19924 g were weighed using aluminum weighing dishes. The samples were then carefully transferred to eight-inch test tubes. The aluminum dishes were re-weighed and the actual weight of the samples were calculated. A 50 ml aliquot of the 7.86% solvent mixture was poured into each test tube. The test tubes were then stoppered and agitated until the KCl crystals dissolved in the solvent. The rubber

stoppers for the test tubes were covered with saran-wrap in order to prevent absorption of ethanol by the rubber. The test tubes were partially immersed in the constant temperature water bath. This was done by placing the test tubes in a specially designed wire cage which could be adjusted to a specific height in the water bath. The temperature of the bath was set at 25.0°C, and a ten minute time limit was allowed for the solutions to reach the constant temperature of 25.0°C. The solutions were then ready for conductance measurements.

Any conductance cell that has been stored dry has to be soaked in deionized water for 24 hours before use, to assure complete wetting of the electrode surfaces. The cell was then soaked in the prepared solvent (7.86% ethanol) for one hour. The conductance of the solutions are then measured by dipping the cell into each test tube, agitating it gently for 15 seconds, and waiting for another 15 seconds before taking a reading. A blank run (solvent only) was done before starting on the solutions. The specific conductance was read to a maximum of four significant figures. Air bubbles trapped between the electrodes were dislodged by gently tapping the outer wall of the cell. A temperature probe from the conductance meter was also used to confirm that the solutions were at 25.0°C. The conductance cell was

rinsed with the solvent and carefully dried with a paper towel after each measurement.

The above procedure was repeated with the next eight weight % ethanol solvents. It was noticed that as the solvents were getting more ethanol-rich, the harder it was to get the KCl crystals to dissolve. At 72.0% ethanol, even overnight agitation on a shaker-bath at 30°C did not result in complete solvation. However this problem was solved when a few glass beads were placed in each test tube. The constant grinding action of the glass beads speeded up the dissolution process significantly.

NaCl and CsCl solutions were prepared and their conductance values were measured in a similar manner. The solvent mixtures used for these two salts were as follows: 0, 7.13, 16.01, 27.35, 33.24, 42.36, 51.85, 58.39, 72.01, and 83.73 weight % ethanol. Experimental results are summarized in Appendix V.

#### IV. Analysis of Experimental Data.

##### A. Application of the conductance equation

Initially, the ion-size parameter "a", was set equal to the sum of the crystallographic radii of the cation and the anion (281, 314, 356 picometers for NaCl, KCl, and CsCl respectively).<sup>25</sup> Dielectric constant, viscosity, and density values for the solvent mixtures were calculated from the equations and coefficients shown in Table 1 (Appendix I). These values were derived from polynomial curves which were obtained from curve fitting literature data.<sup>26,27</sup> The temperature was set at a constant 298.15 K. As the three salts used were 1:1 electrolytes, the  $z$ ,  $K_h$ , and  $K_e$  values were all set equal to 1.0.

For each salt, the equivalent conductance at infinite dilution for every solvent composition was derived from a polynomial curve obtained from curve fitting literature data.<sup>28,29,30</sup> SuperCalc 3a, a spreadsheet, was used to organize and evaluate the data. The Bjerrum's distance parameter  $b$ , and the coefficients  $\alpha$ ,  $\beta$ ,  $E'_1$ ,  $E'_2$ , and  $kq/c^{1/2}$  were then calculated using equations shown in Appendix IV. Using the value derived for  $b$ , the three Q functions were

calculated (Equations 10, 11, and 12). The next step was to calculate the  $\sigma$  (sigma) functions (Equations 13, 14, 15, 16, and 17). Finally, the four coefficients of the Fuoss-Onsager equation;  $E$ ,  $S$ ,  $J_1$ , and  $J_2$ , were derived. CGS units were used in all calculations. A theoretical value of the equivalent conductance was calculated for each corresponding concentration by applying the Fuoss-Onsager Equation (Equation 2.9).

The equivalent conductance derived from experimental readings by applying Equation 1.1 will now be called the "experimental lambda" and the equivalent conductance derived from the Fuoss-Onsager equation will be called the "calculated lambda".

## B. Calculation of Ion-Size Parameters

The ion-size parameter "a" is one of the adjustable parameters used in this study. Figure 1 shows the methodology used in arriving at a best-fit value for "a". The difference between the experimental lambda and the calculated lambda for each measurement was squared. A total was then obtained by summing all the squared values together. The ion-size parameter was adjusted so that the total gives the minimum possible value. The best-fit "a" obtained from the curve, was used in the conductance

equation. Thus, each solvent composition has its own "a" value. Also, the variation of "a" with the solvent composition was evaluated for each salt (Figures 2,3). However, this method did not work well for CsCl. The "a" values obtained was off scale by a factor of  $10^{-6}$ . Therefore, the sum of its crystallographic radii was used in the calculations. Calculated values of "a" are shown in Table 2 (in Angstroms).

### C. Calculation of Association Constants

The form of the Debye-Huckel Equation used for calculating the activity coefficient is given as:

$$\ln f = -A' (z+z-) I^{1/2} / (1 + B' I^{1/2}) \quad (4.1)$$

where I is the ionic strength of the solution and B' is a constant that depends on the distance of closest approach of ions and the size of the solvent molecule. In order to minimize the number of adjustable parameters, B' has been set equal to one. A' is a constant which is given as:

$$A' = (2 \pi / 1000)^{1/2} N^2 e^3 \times d^{1/2} / (DRT)^{3/2} \quad (4.2)$$

This constant was derived from the equation for the Debye length, b', which takes the form:<sup>31</sup>

$$(b')^2 = I (2L^2 e^2 d / DRT) \quad (4.3)$$

when the Debye-Huckel equation is written as:

$$\ln f = -(z+z-)(e^2/8 \pi DRT)[b'/(1+b')] \quad (4.4)$$

Equation 4.1 is used in the calculation for association constants. Also, for 1:1 electrolytes, the ionic strength is equal to the molality of the solution.<sup>32</sup> Thus, it can be written as:

$$I = \text{moles solute/Kg solvent} \quad (4.5)$$

Three more equations used in these calculations are the ones for the function Z and its variable z\* which are as follows:<sup>33,34</sup>

$$Z = A/(A^0 r) \quad (4.6)$$

$$Z = 1 - z^* \{ 1 - z^* [ 1 - z^* (1 - z^*)^{-1/2} ]^{-1/2} \}^{-1/2} \quad (4.7)$$

$$z^* = S (c A)^{1/2} / (A^0)^{3/2} \quad (4.8)$$

Substitution of Equation 4.6 into the mass action equation (Equation 2.7) and rearrangement gives:

$$Z/A = 1/A^0 + K_a [c f^2 A/Z(A^0)^2] \quad (4.9)$$

Consequently, a graph is drawn where;

$$y = Z/A \quad (4.10)$$

$$x = [c f^2 A/Z (A^0)^2] \quad (4.11)$$

This figure allows the determination of  $K_a$  from the slope and  $1/\lambda(0)$  as the intercept. In order to apply this method, a literature value for  $\lambda(0)$  was

used in the calculation of the variable  $z^*$ . From the intercept, another approximation for  $\lambda(0)$  can be obtained.

As shown in Table 3 (Appendix I), calculations were done at every solvent composition for each salt. The slope was derived using a least-square analysis program. The variation of  $K_a$  with the dielectric constant is shown for each salt in Figures 4, 5, and 6.



## V. Interpretation of Conductance Parameters

### A. Ion-Size Parameter

According to Figures 2 and 3, the "a" value ranges were 200-480 and 600-1000 picometers for NaCl and KCl, respectively. Therefore, in comparison KCl seems to have higher "a" values than NaCl. This trend seems reasonable since the crystallographic radii of KCl (314 pm) is indeed bigger than that of NaCl (278 pm).<sup>35</sup> However, the proper physical interpretation of the ion-size parameter arising from the theoretical equations is not clear. The model used in which ions have a finite size but the solvent is a continuum is clearly unrealistic. The discrete molecular nature of the solvent in the vicinity of an ion strongly affects the distribution of neighboring ions. The preferential orientation of solvent molecules in the field of the ion makes questionable the use of the bulk viscosity and dielectric constant in its immediate vicinity. The magnitude of the ion-size parameter is affected by these factors as well as by all mathematical approximations involved in the theoretical equations.<sup>36</sup>

Unfortunately, the results for CsCl could not be compared with the results for NaCl and KCl because the

minimum best-fit method could not be applied to its values, possibly due to erroneous experimental data. The "a" values were off-scale by a factor of  $10^{-6}$ . Ion association could also be the reason for this problem. One must take note that while these ion-size parameter adjustments were being made, ion association was not taken into consideration, and the Fuoss-Onsager equation was set up according to Equation 2.9.

The important thing to remember is that "a" is a parameter of best-fit and its magnitude depends on the quality of the data and the choice of equations. Ideally, the smallest value possible for "a" should be the crystallographic radii. All other values should be higher because solvation increases the distance between ions. Results obtained in this work for NaCl and KCl are reasonable. However, no definite conclusions could be drawn from the plots regarding the variation of the ion-size parameter with the solvent composition.

#### B. Limiting Equivalent Conductance

The second adjustable parameter used in this work is the limiting equivalent conductance -  $\lambda(0)$ . Initially, literature values<sup>37</sup> of  $\lambda(0)$  were used as the trial value in the calculations. After adjusting

the ion-size parameter to its best value, the best-fit method was applied to  $\lambda(0)$  and it was adjusted accordingly. Figure 7 shows both the initial and the adjusted  $\lambda(0)$  values for NaCl, plotted against the solvent composition. The limiting equivalent conductance had to be decreased slightly for best-fit to occur. KCl and CsCl showed similar results. Table 2 shows these adjusted or best-fit values of  $\lambda(0)$ .

## VI. Evaluation of Association Constants

Table 3 shows an example of calculations for CsCl at a specific solvent composition. A similar analysis was performed for each salt at each solvent composition. The x-axis and the y-axis were calculated using Equations 4.11 and 4.10 respectively. A graph (Figure 8) was plotted using a least-squares program and the slope ( $K_a$ ) was derived from it. All three electrolytes showed considerable association, especially in ethanol-rich solvent systems. Figures 4, 5, and 6 demonstrate the increase of ion association as the dielectric constant decreases. The  $K_a$  vs.  $D$  plot for KCl did not produce a smooth curve unlike the plots for NaCl and CsCl. This is probably due to the quality of some of the experimental data for KCl.

Table 4 shows the  $K_a$  values calculated for the three salts. The  $K_a$  values for NaCl turned out to be much higher than expected. A possible reason could be that the ion-size and the  $\lambda(0)$  parameters were not properly adjusted. In general, all calculated  $K_a$  values were high when compared to literature values.<sup>38,39</sup> This was probably due to the fact that those association constants were calculated by other methods.

On comparing experimental values of  $K_a$  with values

calculated from theory, a wide divergence in behavior was observed with experimental values being either greater or less than calculated values. The difference between the observed values and those predicted by theory can be partially accounted for in terms of a high degree of ionic solvation, dispersion forces, which can stabilize the collision complex, dielectric saturation, which would reduce the effective macroscopic dielectric constant, solvent reorganization in the vicinity of the ion pair, which would also modify the dielectric constant and the existence of two or more kinds of ion pairs, which will produce larger values for  $K_a$ .<sup>40</sup>

In Figure 9,  $\ln K_a$  values for NaCl, KCl, and CsCl were plotted as a function of the reciprocal dielectric constant. The plots did not turn out to be as linear as they were expected to be. This meant that the association constants did not conform perfectly to Equation 2.6. Furthermore, NaCl showed higher association than CsCl and KCl. This was not in agreement with the order found by Kay<sup>41</sup> for alkali halides in various hydrogen-bonded solvents; namely, association increases:  $Na < K < Cs$ . Again, the main cause for these discrepancies could be that the parameters were not properly adjusted.

However, the plots for CsCl and KCl were in

agreement with the literature values, with CsCl showing higher association than KCl. Furthermore, as shown in Table 4, all three salts indicate significant ion association in solvent compositions which are 58% or greater in ethanol (dielectric constants of less than 44).

## VII. Discussion

The conductance of NaCl, KCl, and CsCl were measured over a range of ethanol-water solvent compositions at 25°C. The Fuoss-Onsager equation was applied to the data. The ion-size and  $\lambda(0)$  parameters were adjusted in order to provide a best-fit curve of the variation of electrolytic conductance with concentration (Figure 10). Finally, the phenomena of ion association for these salts in different solvent compositions was investigated.

The lack of precision in some of the experimental data affected the calculations. The scatter is due to a variety of experimental errors. Data at the lowest electrolyte are always the hardest to obtain, but are of the most use from a theoretical viewpoint. Although the salts were weighed by difference, some of the crystals could have been lost while they were transferred from the aluminum dishes to the test tubes. Also, the deliquescent crystals of CsCl could have absorbed some moisture from the air during the weighing process. In preparing the solutions, some of the glassware used were "to-contain" volumetric flasks. A fraction of the liquid would have been lost while being transferred from one flask to another. It is also possible that not all of

the crystals dissolved in the solvent. Furthermore, ethanol is quite volatile and some of it could have evaporated during the preparation of the solutions. Even after extensive cleaning of the electrodes, the readings on the conductance meter showed a slight drift. Also, bubbles forming between the electrodes could have given some erroneous readings. Another important fact to remember is that conductometric measurements suffer from a lack of selectivity, since any charged species contributes to the total conductance of the solution. The specific conductance of pure water is only about  $5 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ , and traces of ionic impurity will increase the conductance by an order of a magnitude or more.<sup>42</sup> This emphasizes the need for proper cleaning of all glassware. It is also possible that some atmospheric  $\text{CO}_2$  could have dissolved in the deionized water during storage and caused a slight increase in the conductance.

The dielectric constant of the solvent system decreases as the weight percent of ethanol increases. From the experimental data obtained, it was found that as the dielectric constant decreased, the conductance of an electrolytic solution decreased too. This is clearly demonstrated in Figure 11. The primary reason for this is that a lower dielectric constant favors ion-pair



formation. When strong electrolytes are dissolved in solvents of low dielectric constants, coulombic forces are sufficient to cause ion association at low ionic concentrations.<sup>43</sup>

It was also observed that CsCl was more associated than KCl. This is in agreement with literature values.<sup>44</sup> It is the larger solvation energy of potassium as compared to that for cesium ion which accounts for the lower  $K_a$  value and lower association of KCl. The high values for the association constants obtained for NaCl were explained in the previous chapter.

The values obtained for the ion-size parameters for NaCl and KCl are reasonable. A definite relationship between the ion-size parameter and the solvent composition could not be derived from analysis of the data. However, there are many factors that prevent a simple physical interpretation of "a" values.<sup>45</sup> Consequently, a comparison with the literature values is rarely fruitful. The main purpose of the ion-size and  $\lambda(0)$  parameter adjustments was to improve the fit of the Fuoss-Onsager equation to the experimental conductance data. The magnitude of the adjustments required, depends on the quality of the experimental results, the completeness of the equation which is applied, the type of solute-solvent system used, and the

extent of ion association.

One must note that the Fuoss-Onsager equation makes several assumptions which need to be considered while analyzing the results. The solvent is treated as a continuum, while the ions are assigned a finite size. That is, over a range of compositions involving mixtures of ethanol and water, the solvent is being treated as a continuous medium with assigned bulk dielectric constant and viscosity values for each composition. Specific ion-solvent molecule interactions are not taken into consideration. Furthermore, the viscosity values used in the calculations are those for the pure solvent compositions. When the electrolyte solutions are prepared by dissolving the salt in the solvent mixture, the viscosity changes. This change is not accounted for in the equation.

Furthermore, Kay and Dye<sup>46</sup> have shown that the electrophoretic contribution to conductance can be obtained independent of the relaxation effect from the concentration dependence of transference numbers. Their calculations show that the Fuoss-Onsager equation evaluates the electrophoretic effect correctly for water and methanol solutions but cannot correctly account for ethanol solutions. Also, in the Fuoss-Onsager series-expansion formulation (Appendix IV) the equations

chosen for the Q and s coefficients were those derived by Quint-Villiard.<sup>47</sup> Perhaps, one of the other sets of equations derived by Pitts, Fuoss-Chen, or Fuoss-Hsia could have produced better results.

An important conclusion derived from the experimental results is the comparison of the conductance shown by the three electrolytes. Figures 12 and 13 show that the order of electrolytic conductance increases: NaCl < KCl < CsCl. This order was the same at all equivalent solvent compositions. This result is somewhat surprising as one would expect cesium, the largest ion among the three, to be the least mobile and thus show the lowest conductance. In fact, the reverse order seemed more logical. Nevertheless, comparison with literature values confirmed that these results are indeed correct. The most plausible explanation for this phenomena is hydration, or in this case solvation, of cations. Sodium, being the smallest cation here, has the largest charge density. The solvent molecules, due to ion-dipole interactions, surround the cation, forming a cage-like structure. The sodium ion, with the largest charge density, retains the largest solvent sheath. This, in effect, results in sodium ion being the least mobile and showing the lowest conductance.

In conclusion, the analysis of the experimental

results show that in ethanol-water solvent systems, both conductance and ion association increase in the order: NaCl < KCl < CsCl, and that the Fuoss-Onsager equation can be successfully applied to 1:1 electrolytes, even in mixed solvent systems.

## BIBLIOGRAPHY

1. Warmoth, Denis, Chem. Eng., 18 , 18 (1984).
2. Skoog, Douglas A., "Principles of Instrumental Analysis", 3rd ed., p 705; Saunders University: New York, 1985.
3. Levine, I.N., "Physical Chemistry", 2nd ed., p 478; McGraw-Hill: New York, 1983.
4. Popovych, Orest, and R.P.T. Tomkins, "Nonaqueous Solution Chemistry", p 258; Wiley-Interscience: New York, 1981.
5. Skoog, p 705.
6. Bromberg, Philip, "Physical Chemistry", 2nd ed., p 308; Allyn and Bacon: Boston, 1984.
7. Evans D.F., and M.A. Matesich In "Techniques of Electrochemistry"; Yeager, E., and A.J. Salkind, Ed.; Wiley-Interscience: New York, 1973; Vol.2, Chapter 1.
8. Fuoss, Raymond M. In "Chemical Physics of Ionic Solutions"; Conway, B.E., and R.G. Barradas, Ed.; Wiley: New York, 1966; Chapter 20.
9. Popovych and Tomkins, p 256.
10. Evans and Matesich (1973)
11. Fuoss, "Chemical Physics of Ionic Solutions", Chapter 20.
12. Robinson, R.A., and R.H. Stokes, "Electrolyte Solutions", 2nd ed., p 392; Academic: New York, 1959.
13. Fuoss, R.M., and Lars Onsager, and J.F. Skinner, J. Phys. Chem., 69 , 2583 (1965).
14. Justice, Jean-Claude, Electrochim. Acta, 16 , 704 (1971).
15. Fernandez-Prini, R., Trans. Faraday Soc., 64 , 2146 (1968).
16. Justice, Jean-Claude In "Comprehensive Treatise of Electrochemistry"; Conway, B.E., and J.O'M. Bockris, and Ernest Yeager, Ed.; Plenum: New York, 1983.
17. Evans and Matesich (1973)
18. Kay, Robert L., J. Phys. Chem., 69 , 2787 (1965).
19. Bower, J.H., Natl. Bur. Stds. J. Res., 12 , 241 (1934).
20. Yellow Springs Instruments Model 34 Conductance-Resistance Meter Instruction Manual.
21. Warmoth (1984).
22. Yellow Springs Model 34 Manual.
23. GCA/Precision Operating Instructions for Constant Temperature Circulating Systems Model 255.
24. Jones, G., and R.C. Josephs, J. Am. Chem. Soc., 50 , 1049 (1928).

25. Huheey, James E., "Inorganic Chemistry", 2nd ed., p 66; Harper and Row: New York, 1978.
26. Spivey, H.O., and T. Shedlovsky, J. Phys. Chem., 71 , 2165 (1967).
27. "Nonaqueous Electrolytes Handbook"; Janz, G.J., and R.P.T. Tomkins, Ed.; Academic: New York, 1972.
28. Haws, J.L., and R.L. Kay, J. Phys. Chem., 69 , 2420 (1965).
29. Spivey and Shedlovsky, (1967).
30. Pedersen, L.G., and E.S. Amis, Z. Physik. Chem. (NF), 36 , 199 (1963).
31. Bromberg, p 331.
32. Bromberg, p 325.
33. Fuoss, Raymond, and Phillip Accascina, "Electrolytic Conductance", p 229; Interscience: New York, 1959.
34. Fuoss, R., J. Am. Chem. Soc., 57 , 489 (1935).
35. Huheey, p 66.
36. Evans and Matesich (1973).
37. Spivey and Shedlovsky, (1967).
38. Haws and Kay, (1965).
39. Spivey and Shedlovsky, (1967).
40. Popovych and Tomkins, p 263.
41. Kay, R.L., J. Am. Chem. Soc., 82 , 2099 (1960).
42. Skoog, p 711.
43. Harned, H.S., and B.B. Owen, "The Physical Chemistry of Electrolytic Solutions", 3rd ed., p 283; Reinhold: New York, 1958.
44. Haws and Kay, (1965).
45. Evans and Matesich, (1973).
46. Kay, R.L., and J.L. Dye, Proc. Natl. Acad. Sci. U.S., 49 , 5 (1963).
47. Justice, Jean-Claude In "Comprehensive Treatise of Electrochemistry".
48. Justice, Jean-Claude In "Comprehensive Treatise of Electrochemistry".

TABLE 1

Polynomial Curve-Fit Analysis of Literature Values for  
Density, Dielectric Constant, and Viscosity of  
Ethanol-Water Mixtures at 25°C.

$$Y = m + mX + mX^2 + mX^3 + mX^4 + mX^5 + \dots$$

Polynomial Coefficient	D	V	d
0	78.815	8.954	0.9966
1	-0.5398	0.3193	$-1.4 \times 10^{-4}$
2	$-3.3 \times 10^{-3}$	0.0164	$-6.6 \times 10^{-6}$
3	$7.5 \times 10^{-5}$	$-5.9 \times 10^{-4}$	
4	$-7.5 \times 10^{-7}$	$6.1 \times 10^{-6}$	
5	$3.2 \times 10^{-9}$	$-2.1 \times 10^{-8}$	
std. error	0.13340	0.03914	$4.5 \times 10^{-3}$

TABLE 2

A(0), a, S, E, and J(1) values as a function of the solvent composition for NaCl, KCl, and CsCl at 25C

wt% EtOH	A(0)	KCl (25C)			
		a	S	E	J(1)
7.86	113.69	6.40	73.84	16.48	179.25
16.01	89.16	6.30	59.99	17.25	137.71
27.35	68.88	6.15	51.02	19.49	96.73
35.81	59.89	6.70	49.19	22.43	95.83
42.36	54.99	6.68	49.76	25.64	75.43
49.10	51.16	2.28	51.88	30.03	-170.29
58.39	47.35	7.85	57.38	38.71	55.62
72.01	44.39	13.00	72.04	62.03	271.17
83.73	44.24	8.65	93.60	103.75	-365.14
100.00	45.42	16.50	148.46	201.45	-197.17
		NaCl (25C)			
.00	122.80	2.20	88.55	10.64	-4.91
7.13	100.50	.60	71.53	12.17	-98.89
16.01	76.80	4.25	56.57	13.12	45.85
27.35	58.72	4.80	47.74	14.86	37.77
33.24	54.00	2.00	46.51	16.93	-82.44
42.36	47.72	3.05	46.79	20.36	-75.28
51.85	44.20	3.15	50.47	26.52	-129.12
58.39	42.72	2.95	54.88	32.78	-203.56
72.01	41.92	1.95	70.28	56.53	-561.44
83.73	42.80	3.95	92.27	98.36	-867.63
100.00	45.42	2.81	148.46	201.45	-2781.09
		CsCl (25C)			
.00	153.75	3.56	95.67	17.80	71.63
7.13	125.01	3.56	77.60	18.74	48.65
16.01	97.47	3.56	62.28	20.02	22.99
27.35	73.51	3.56	52.51	21.60	-8.21
33.24	65.10	3.56	50.42	22.96	-26.54
42.36	56.21	3.56	50.25	26.53	-63.50
51.85	50.79	3.56	53.63	33.15	-124.23
58.39	48.53	3.56	58.03	40.24	-190.13
72.01	45.91	3.56	73.13	65.41	-452.48
83.73	45.10	3.56	94.40	106.99	-958.44
100.00	48.00	3.56	151.89	221.41	-2727.51



TABLE 3

Analysis of the Association Constant for CsCl in 27% Ethanol at 25°C.

c	A	I	f	z*	Z	"x" (10 <sup>6</sup> )	"y"
.00014	72.87	.0001	.9809	.0083	.9917	1.79	.01361
.00024	72.65	.0003	.9750	.0109	.9890	3.07	.01361
.00029	72.57	.0003	.9727	.0120	.9879	3.67	.01361
.00033	72.50	.0003	.9709	.0128	.9871	4.19	.01362
.00041	72.37	.0004	.9675	.0144	.9855	5.21	.01362
.00053	72.20	.0006	.9631	.0164	.9835	6.74	.01362
.00066	72.05	.0007	.9592	.0182	.9817	8.24	.01363
.00074	71.96	.0008	.9569	.0192	.9806	9.16	.01363
.00082	71.87	.0009	.9547	.0202	.9796	10.14	.01363
.00086	71.83	.0009	.9538	.0207	.9791	10.56	.01363
.00094	71.74	.0010	.9517	.0216	.9871	11.54	.01363
.00099	71.70	.0011	.9506	.0222	.9776	12.09	.01364
.00113	71.56	.0012	.9473	.0237	.9760	13.74	.01364
.00121	71.49	.0013	.9456	.0245	.9752	14.63	.01364
.00128	71.42	.0014	.9440	.0252	.9744	15.51	.01364
.00147	71.26	.0016	.9403	.0270	.9726	17.66	.01365
.00190	70.93	.0020	.9328	.0306	.9689	22.41	.01366
.00239	70.58	.0025	.9254	.0342	.9652	27.67	.01367

Table 4

Association Constants as a Function of the Solvent  
Composition for NaCl, KCl, and CsCl at 25°C.

wt. %	NaCl	KCl	CsCl
0.00	1.08 +/- .01	-----	0.37 +/- .01
7.13	4.88 +/- .08	-----	0.72 +/- .01
16.01	3.07 +/- .11	-----	1.32 +/- .01
27.35	4.72 +/- .07	1.18 +/- .09	2.50 +/- .01
33.24	9.11 +/- .07	-----	3.39 +/- .01
35.81	-----	1.73 +/- .07	-----
42.36	11.59 +/- .06	3.19 +/- .13	5.42 +/- .02
49.10	-----	9.78 +/- .28	-----
51.85	17.24 +/- .29	-----	8.77 +/- .04
58.39	25.23 +/- 1.05	10.94 +/- .86	13.12 +/- .26
72.01	53.52 +/- 3.26	15.22 +/- 9.13	32.87 +/- 1.97
83.73	93.32 +/- 5.34	48.05 +/- 2.26	62.57 +/- 2.48

Figure 1. Analysis of ion-size parameter by minimum best-fit method for  $\text{KCl}_2$  in 16% ethanol at  $25^\circ\text{C}$ :  $\text{Sum}(\Lambda_{\text{exp}} - \Lambda_{\text{cal}})^2$  vs.  $a$ .

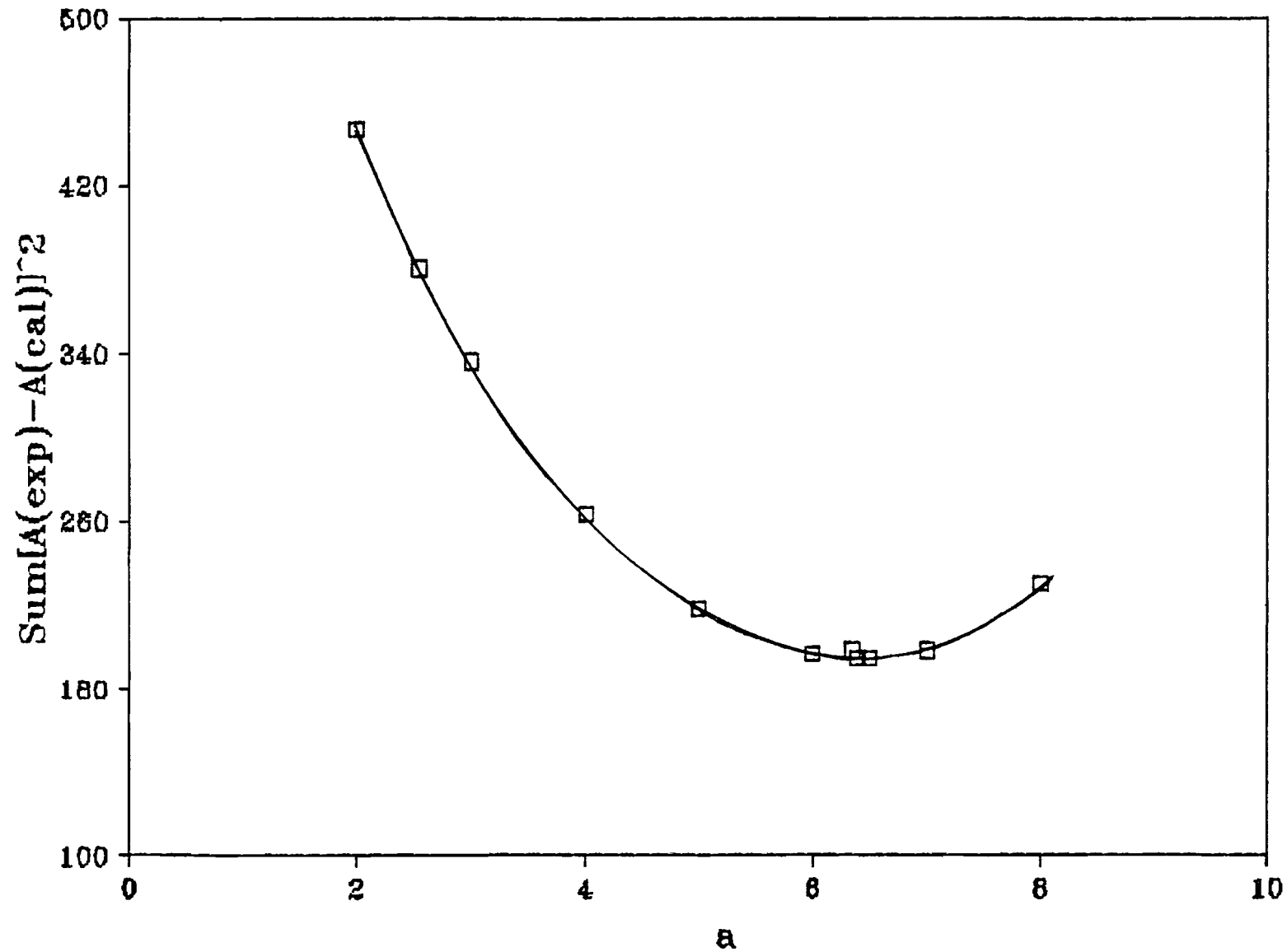


Figure 2. Plot of ion-size parameter as a function of solvent composition for KCl at 25<sup>o</sup>C.

# KCl

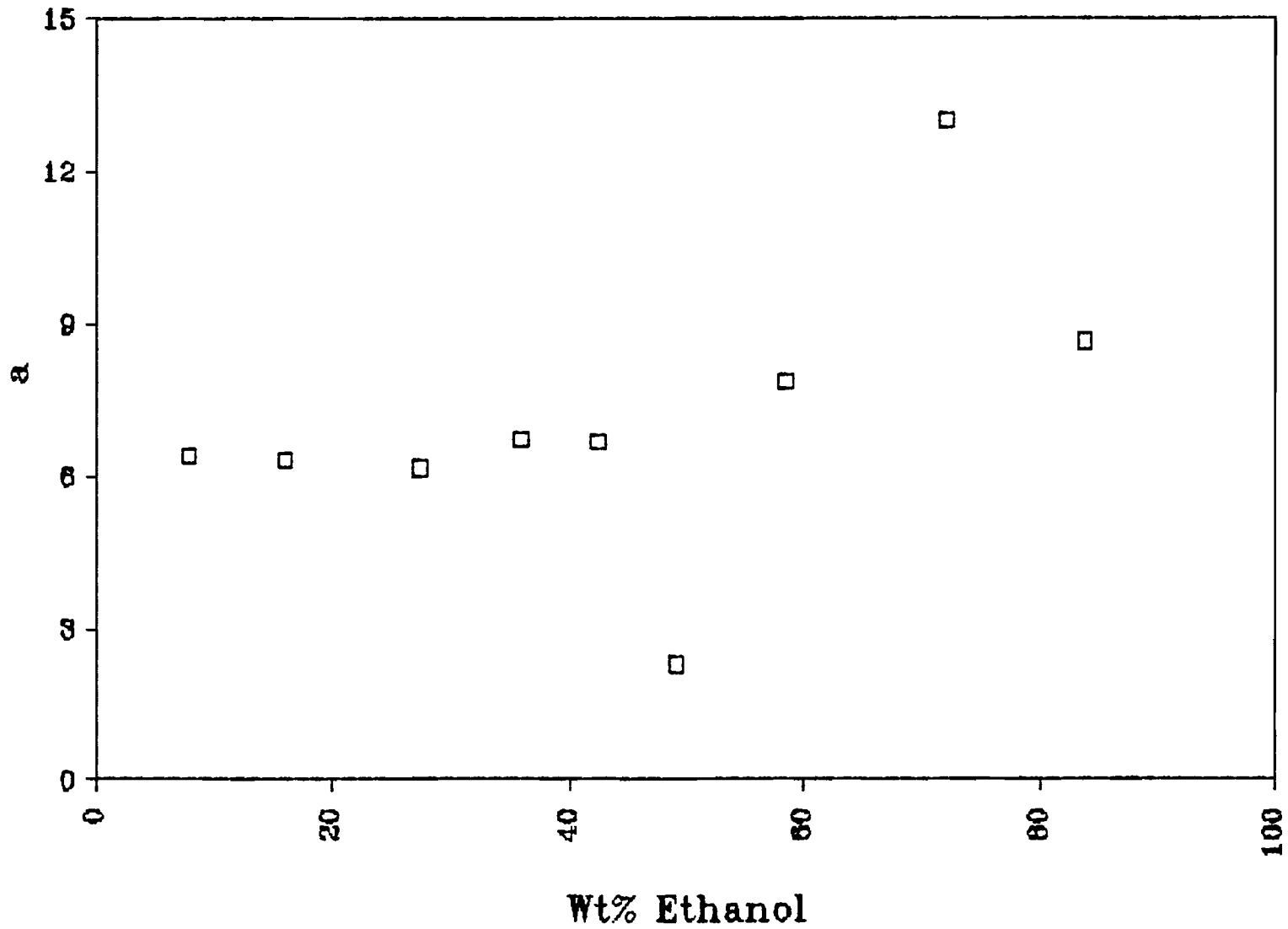


Figure 3. Plot of ion-size parameter as a function of solvent composition for NaCl at 25°C.

# NaCl

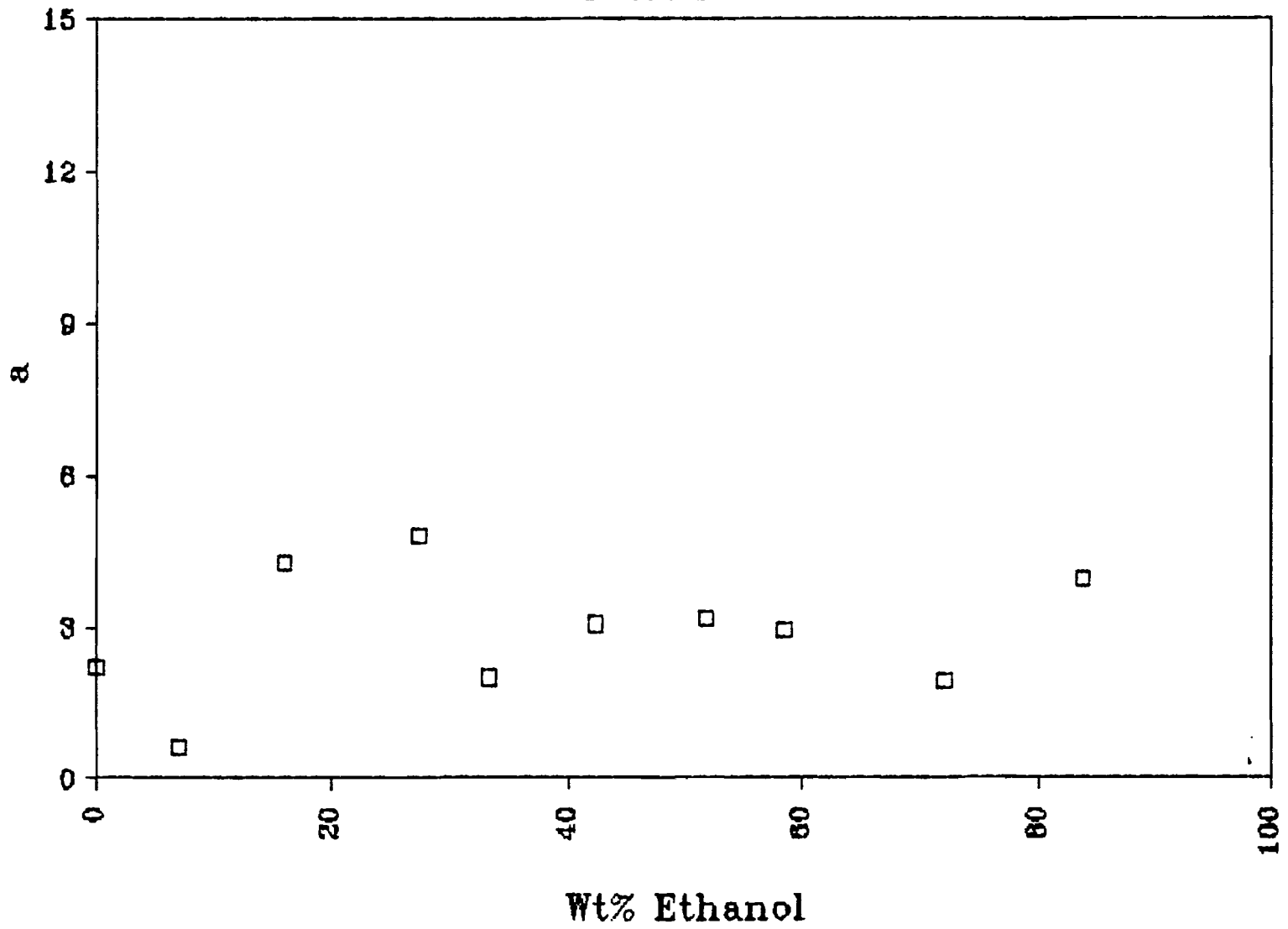




Figure 4. Plot of association constant as a function of dielectric constant for NaCl at 25°C.

# NaCl

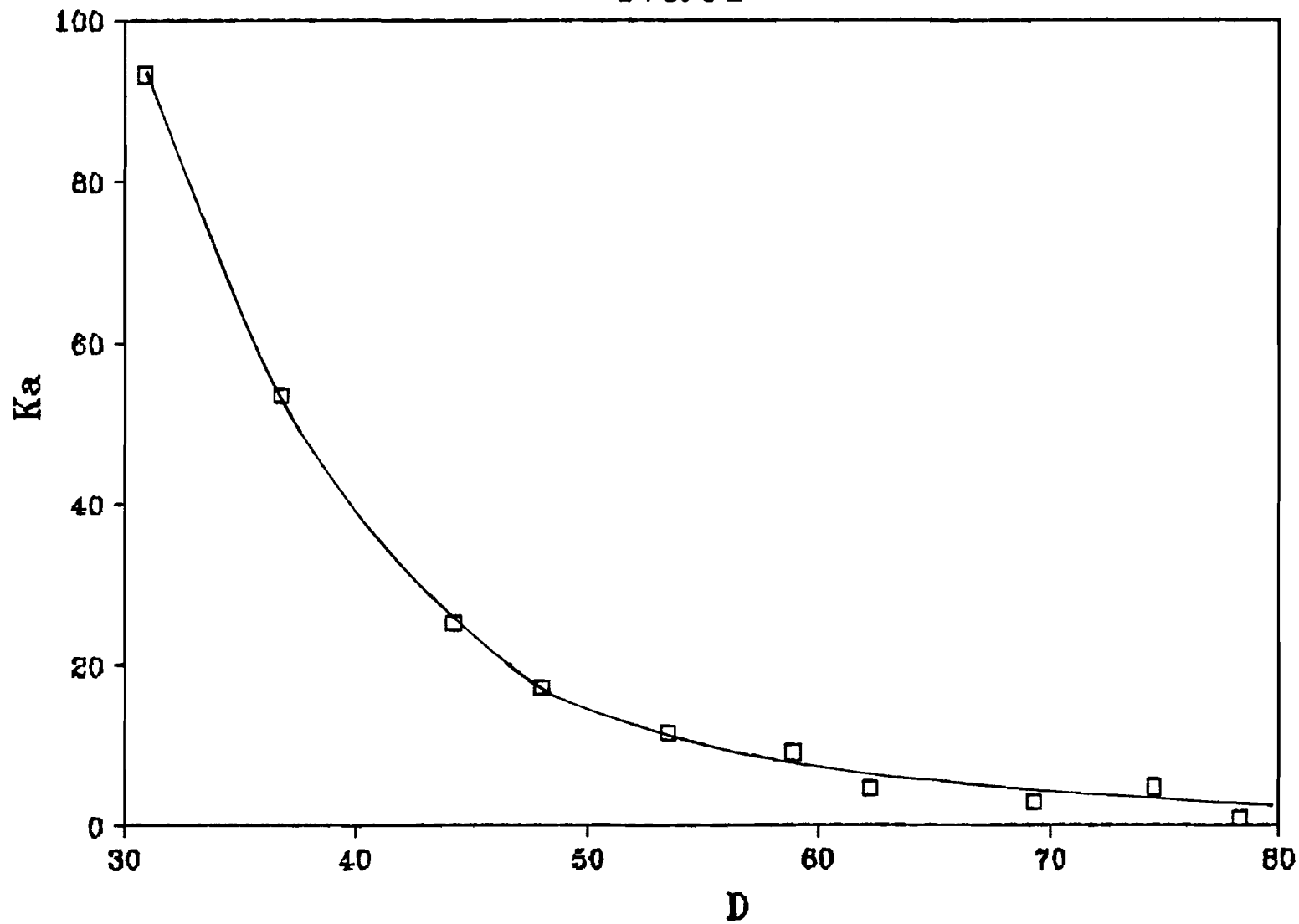


Figure 5. Plot of association constant as a function of dielectric constant for KCl at 25°C.

# KCl

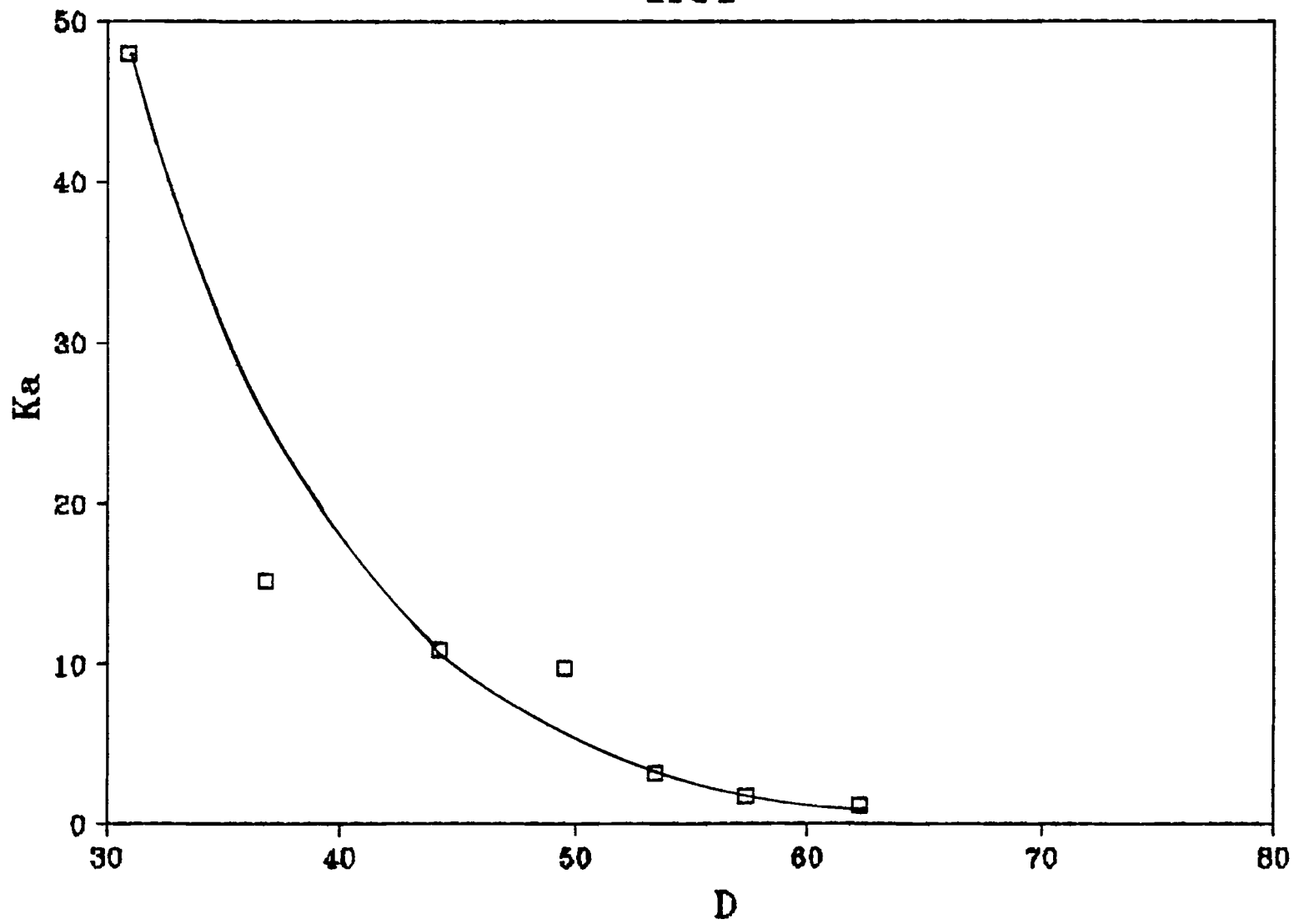


Figure 6. Plot of association constant as a function of dielectric constant for CsCl at 25°C.

# CsCl

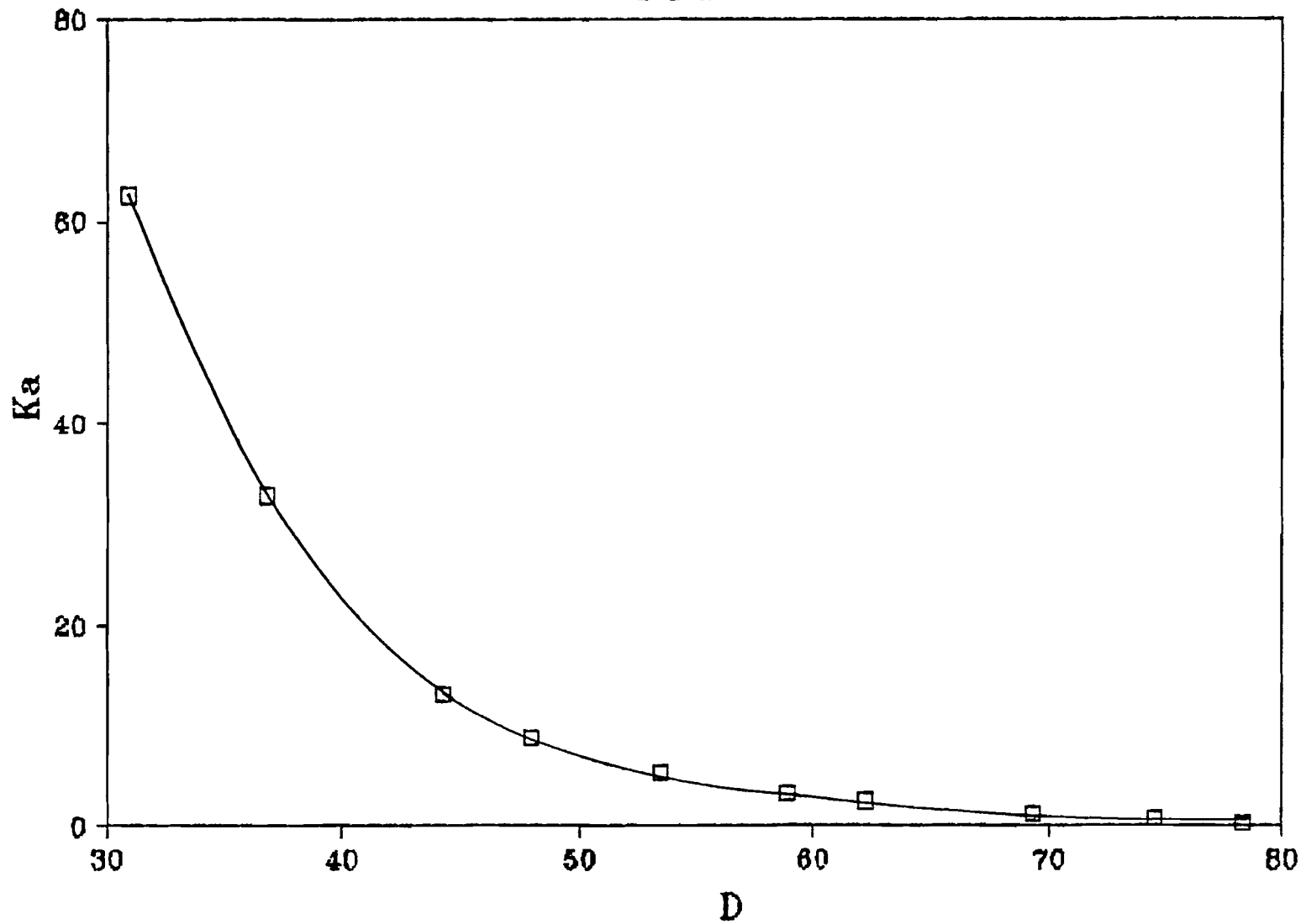


Figure 7. Plot of literature and calculated  $\lambda(0)$  values as a function of solvent composition for NaCl at 25°C.

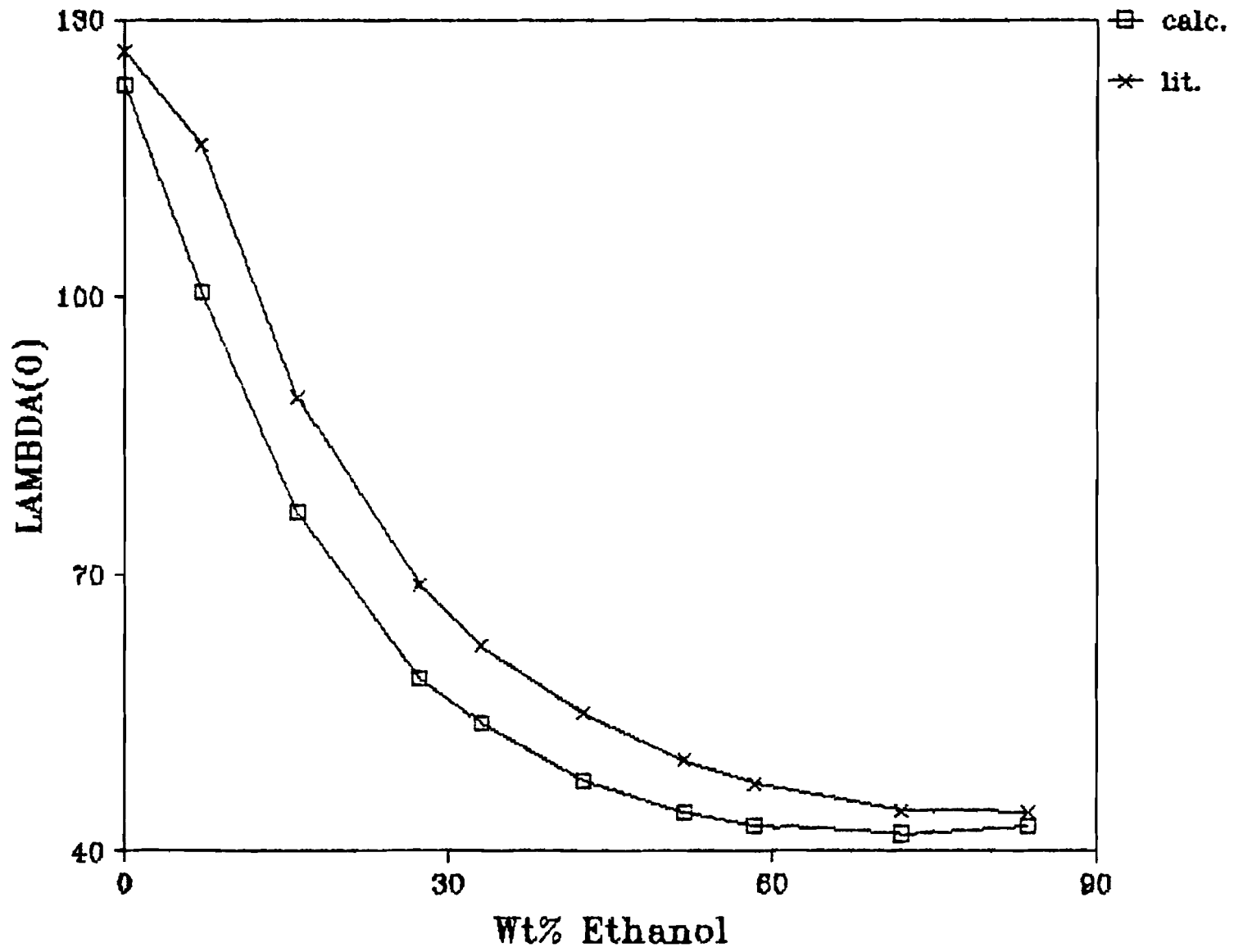




Figure 8. Analysis of association constant for CsCl in 27% ethanol at 25°C : plot of "x" (Equation 4.11) vs. "y" (Equation 4.10).

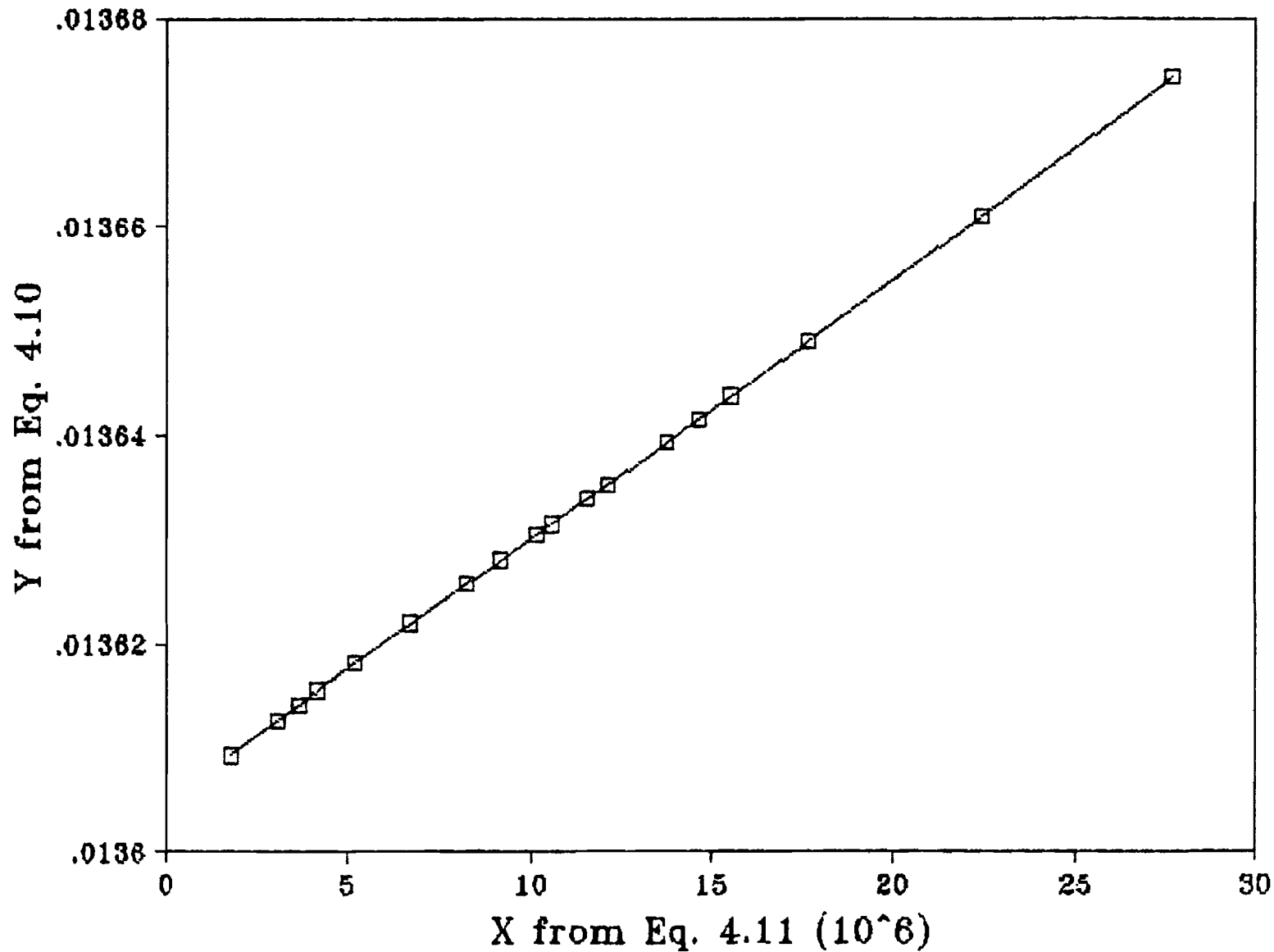


Figure 9. Plot of  $\ln K_a$  as a function of reciprocal of the dielectric constant for NaCl, KCl, and CsCl at 25°C.

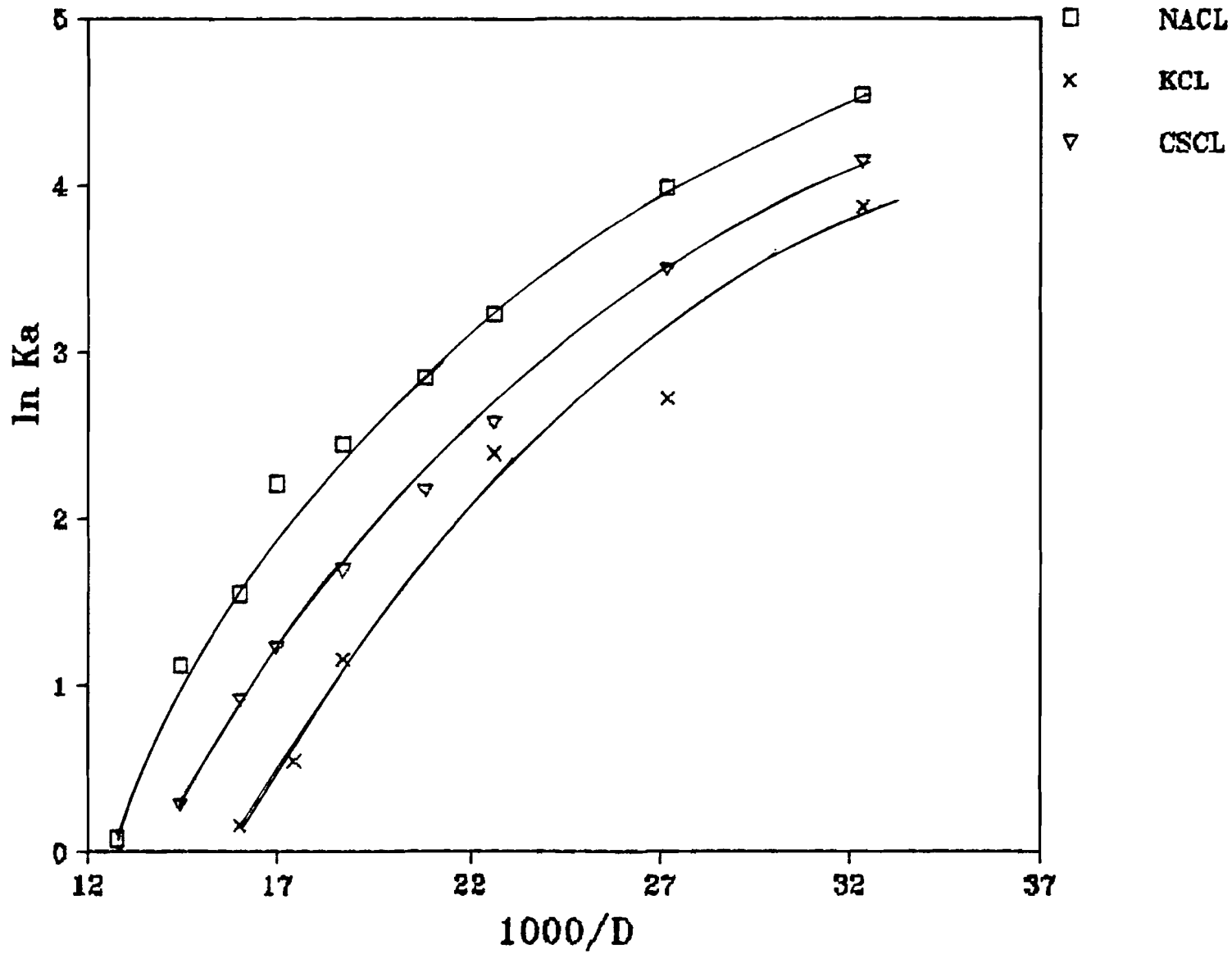


Figure 10. Plot of the Fuoss-Onsager equation for KCl in 7.86% ethanol at 25°C.

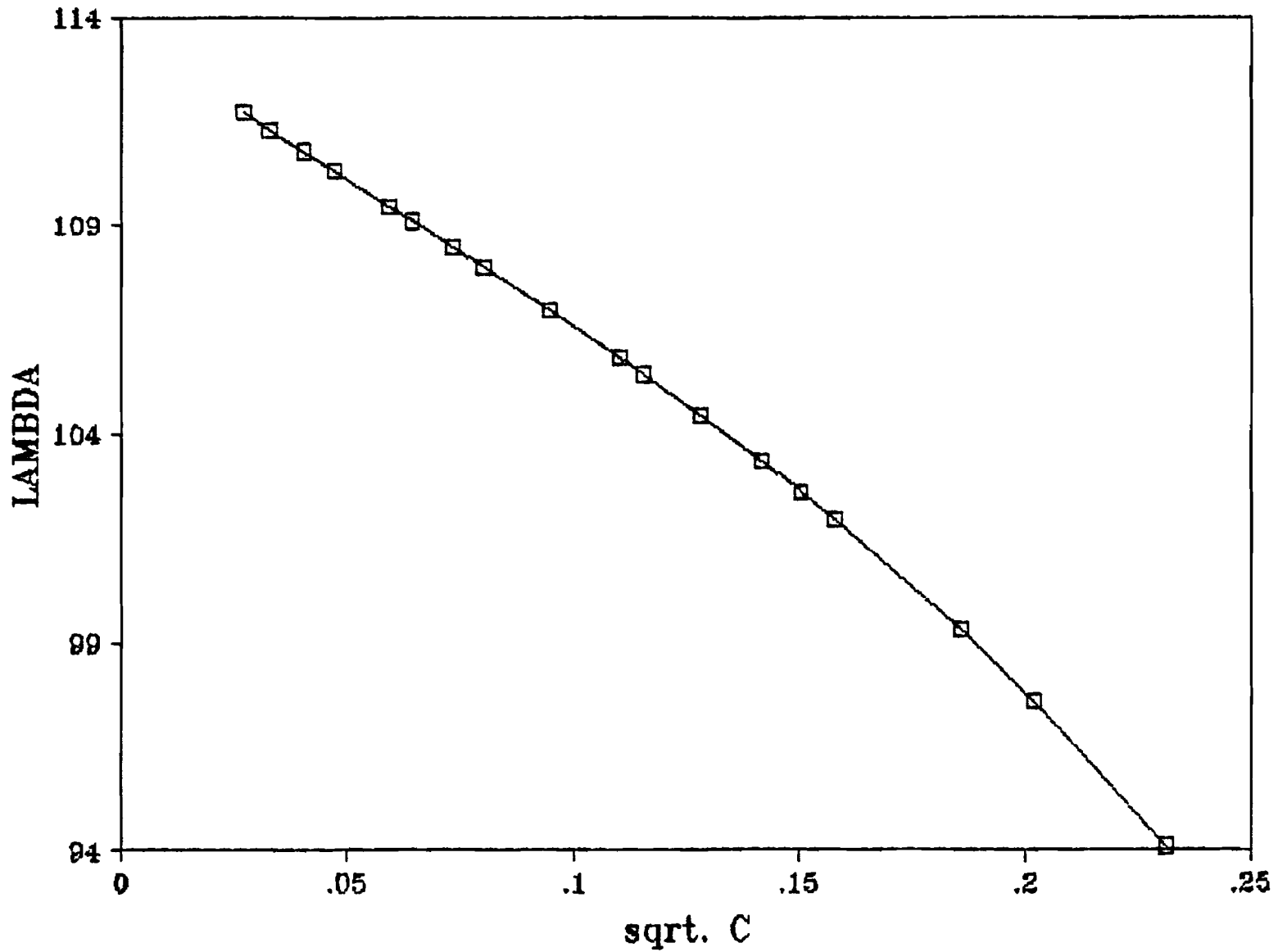


Figure 11. Plot of the Fuoss-Onsager equation for KCl in 7.86%, 27.35%, 42.36%, and 83.73% ethanol at 25°C.

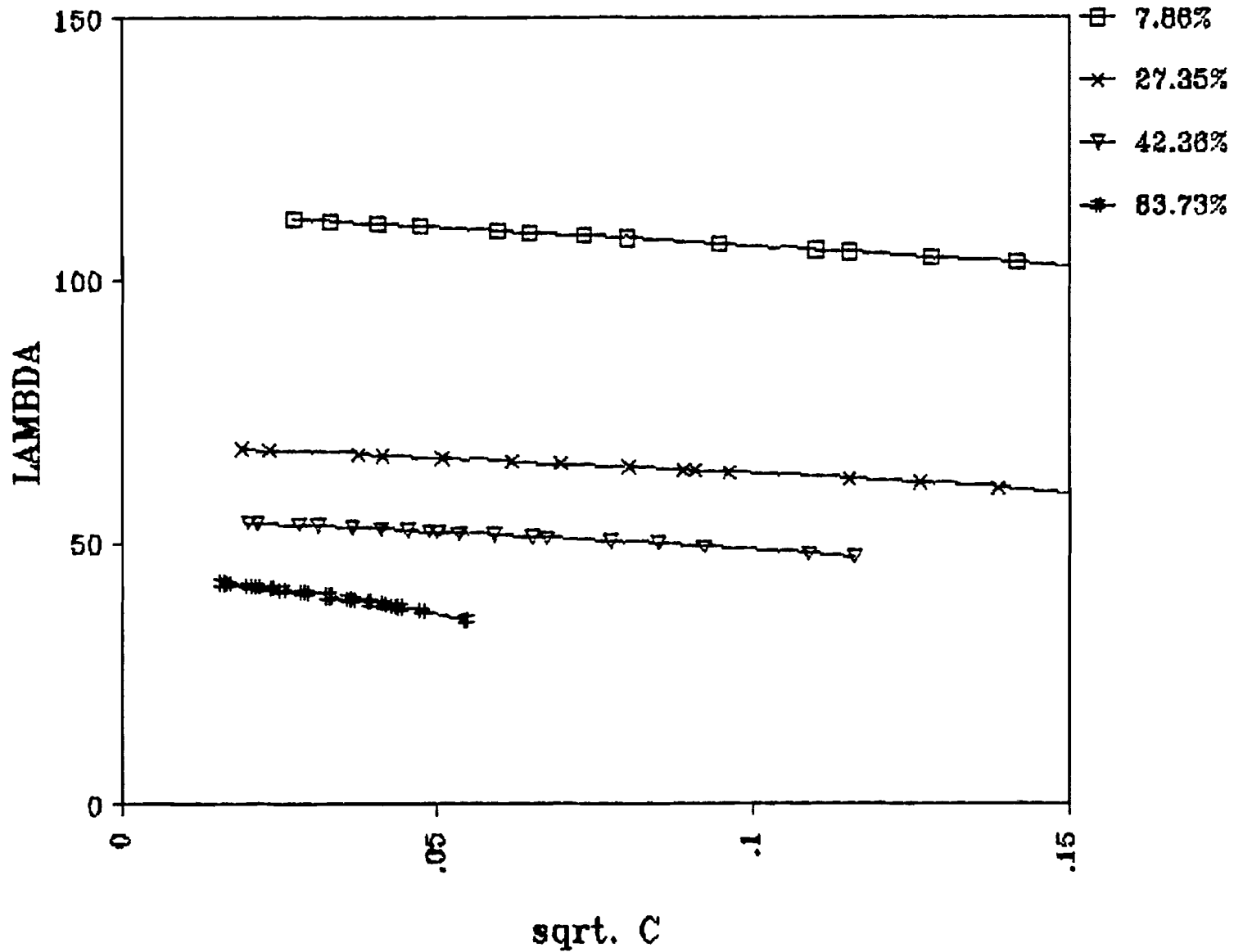




Figure 12. Plot of the Fuoss-Onsager equation for NaCl, KCl, and CsCl in 16.0% ethanol at 25°C.

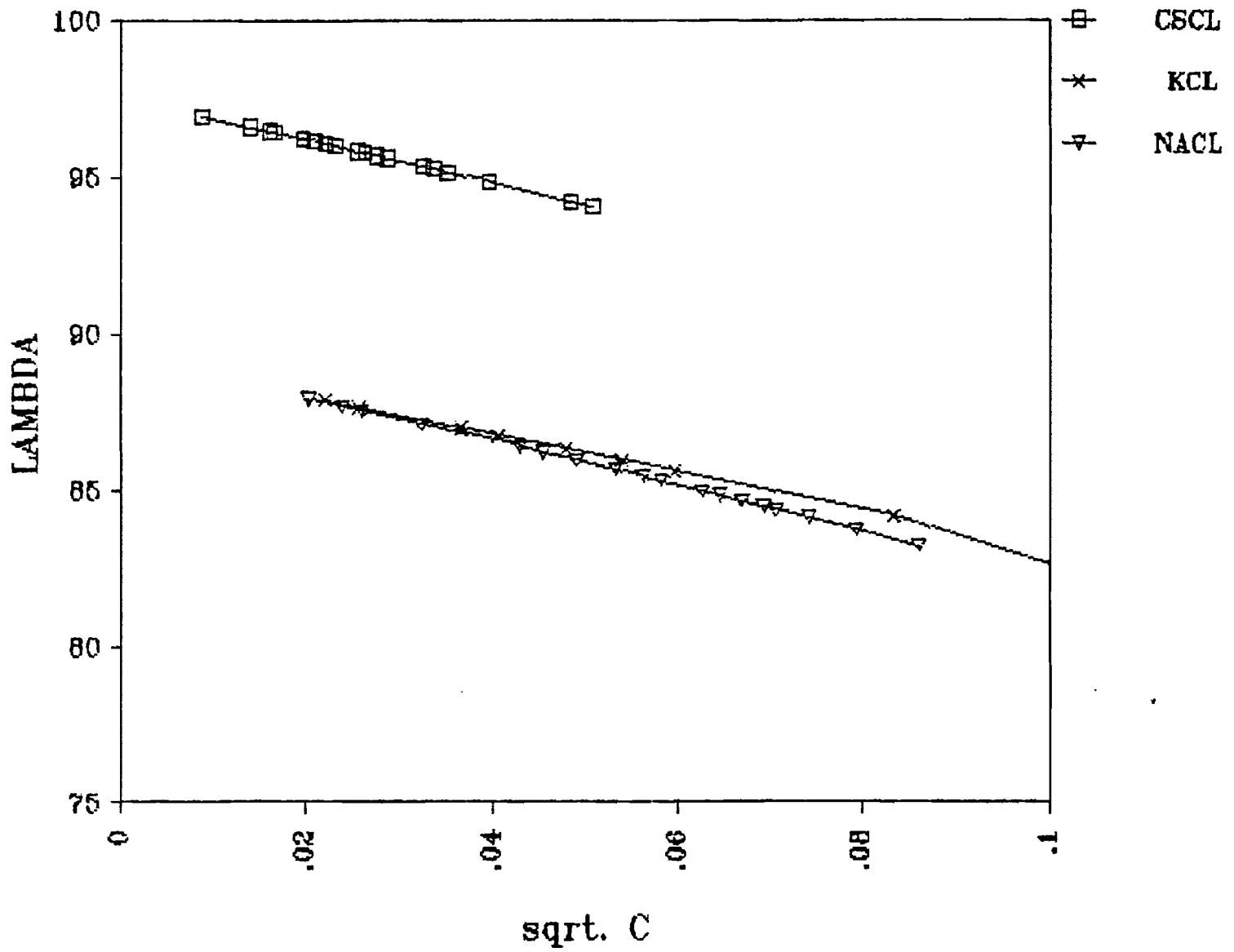
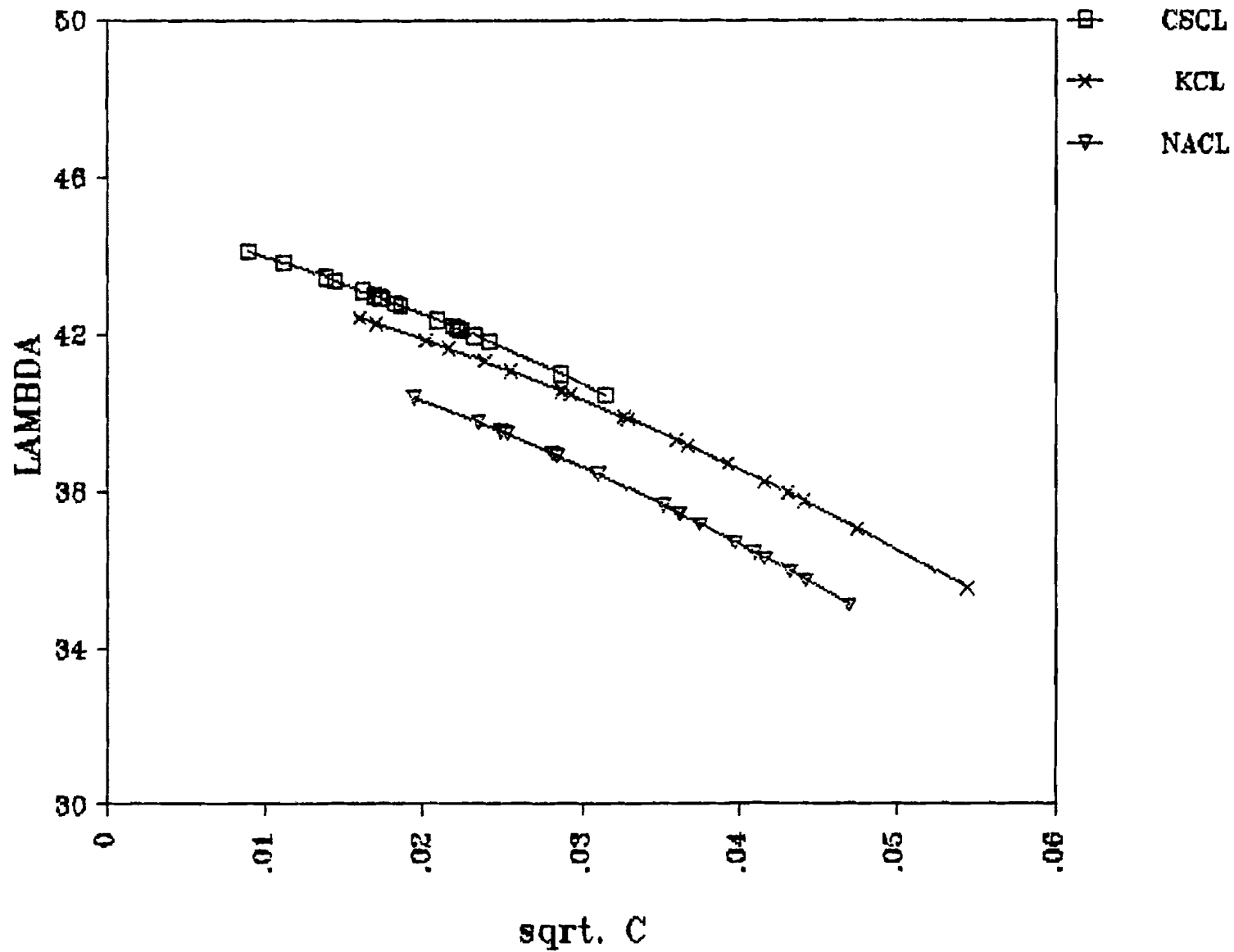


Figure 13. Plot of the Fuoss-Onsager equation for NaCl, KCl, and CsCl in 83.7% ethanol at 25°C.



## APPENDIX III

## Glossary of Symbols

A	equivalent conductance
A'	a constant in the Debye-Huckel equation for activity coefficients
A <sup>o</sup>	limiting equivalent conductance
a	ion-size parameter (Tabulated values are in Angstroms.)
a <sup>o</sup>	single ion limiting conductance
alpha	relaxation coefficient of the Onsager limiting law
B'	a constant in the Debye-Huckel equation for activity coefficients
b	Bjerrum's distance parameter
b'	Debye length
beta	electrophoretic coefficient of the Onsager limiting law
c	concentration in equivalents per liter
D	dielectric constant
d	density at 25°C
E	logarithmic term in Fuoss-Onsager equation
E' <sub>1</sub>	evaluation of the first electrophoretic contribution to conductance
E' <sub>2</sub>	evaluation of the second electrophoretic contribution to conductance
e	charge on electron
f	mean ionic activity coefficient
I	Ionic strength
J <sub>1</sub>	first term of the relaxation effect
J <sub>2</sub>	second term of the relaxation effect
K <sub>a</sub>	association constant
k	Boltzmann's constant
k <sup>e</sup>	electrophoresis numerical constant
k <sup>h</sup>	hydrodynamic numerical constant
L <sup>h</sup>	specific conductance
N	normality of solution
N <sup>o</sup>	Avogadro's number
Q <sup>o</sup>	coefficient of the s (sigma) functions
q	Bjerrum's "closest approach" parameter
R	gas constant
r	degree of dissociation
S	Onsager limiting slope
s	sigma function or coefficient of the J <sub>1</sub> and J <sub>2</sub> functions
T	absolute temperature
V	viscosity of solvent
Z	function used in ion-association calculations
z*	variable for the Z function
z	absolute charge number on ion

APPENDIX IV

The Fuoss-Onsager Series-Expansion Formulation  
of Conductance for Symmetrical Electrolytes\*

1.  $A = A^0 - Sc^{1/2} + Ec \ln c + J_1c + J_2c^{3/2}$
2.  $S = \alpha A^0 + \beta$
3.  $E = E'_1 A^0 - (K_e + K_h)E'_2$
4.  $J_1 = s_1 A^0 + s_2$
5.  $J_2 = s_3 A^0 + s_{4e} + s_{4h}$
6.  $E'_1 = 2.9422 \times 10^{12} z^6 / (DT)^3$
7.  $E'_2 = 0.4333 \times 10^8 z^5 / (DT)^2 \text{ v}$
8.  $\alpha = 0.8204 \times 10^6 z^3 / (DT)^{3/2}$
9.  $\beta = 82.501 z^2 / (DT)^{1/2} \text{ v}$
10.  $Q^{\text{rel}} = -(1/b^3) + (2/b^2) + (2/b) + 0.9074 - \ln b$
11.  $Q_h = -(2/3b) - 1.0168 + \ln b$
12.  $Q_e = (1/b^2) + (6.5/b) - 0.6596 + \ln b$
13.  $s_1 = 2E'_1 [Q^{\text{rel}} - \ln 2kq/c^{1/2}]$
14.  $s_2 = 2E'_2 [Q_h + Q_e - (k_h + k_e) \ln 2kq/c^{1/2}]$
15.  $s_3 = -(2kq/c^{1/2})E'_1 (3.8048/b^3 + 4.4296/b^2 + 1.6094/b)$
16.  $s_{4e} = -(2kq/c^{1/2})E'_2 (13.60947/b^2 - 1.3904/b)$
17.  $s_{4h} = -(2kq/c^{1/2})E'_2 (2.2761/b^2 + 2.3940/b)$

$$18. b = 16.708 \times 10^{-4} z^2 / (aDT)$$

$$19. kq/c^{1/2} = 4.20155 \times 10^6 z / (DT)^{3/2}$$

$$20. k_h = k_e = 1$$

\* The set of equations given above were taken from  
Jean-Claude Justice's "Conductance of Electrolyte  
Solutions".<sup>48</sup>

APPENDIX V

Experimental Data

NaCl (25C)

0 % EtOH

c	A	c	A
.00037	119.86	.00339	117.77
.00069	124.15	.00434	117.85
.00110	121.60	.00500	113.33
.00138	119.63	.00566	104.53
.00169	121.02	.00674	115.46
.00216	119.67	.00802	113.62
.00244	119.43	.00885	115.53
.00286	119.33	.01020	114.98
.00319	114.25	.01202	114.16

7.13 % EtOH

.00068	100.67	.00363	94.65
.00101	100.14	.00429	95.00
.00150	98.30	.00469	94.28
.00215	97.09	.00500	94.87
.00243	95.48	.00520	94.45
.00335	94.02	.00654	94.40
.00337	96.71		

16.0 % EtOH

.00041	74.27	.00337	73.28
.00057	76.99	.00392	72.73
.00068	74.53	.00416	73.11
.00105	72.05	.00447	73.22
.00183	73.14	.00479	72.64
.00205	75.39	.00498	73.10
.00240	74.05	.00549	73.01
.00282	72.96	.00628	71.66
.00315	73.69	.00738	71.66

27.3 % EtOH

.00053	58.44	.00339	55.90
.00067	56.04	.00378	55.22
.00092	56.82	.00406	54.74
.00145	56.86	.00443	55.73
.00177	53.86	.00488	55.37
.00204	56.09	.00598	55.06
.00243	56.22	.00640	54.38
.00274	56.10	.00676	54.89
.00330	55.51	.00724	54.44



Experimental Data

NaCl (25C)

33.2 % EtOH

c	A
.00025	50.15
.00036	54.27
.00084	53.31
.00104	53.08
.00130	51.81
.00143	52.38
.00193	51.10
.00233	51.35
.00301	50.94

c	A
.00303	50.06
.00308	50.13
.00337	49.63
.00346	50.52
.00388	50.13
.00414	53.85
.00455	50.09
.00510	50.01
.00518	50.15

42.4 % EtOH

.00062	46.10
.00068	46.02
.00089	45.52
.00111	46.84
.00165	45.31
.00207	45.93
.00218	45.48
.00247	44.78

.00275	44.47
.00288	45.10
.00300	44.12
.00318	42.87
.00337	44.47
.00344	44.40
.00375	44.75
.00407	43.95

51.8 % EtOH

.00034	44.12
.00062	42.70
.00072	42.58
.00091	41.68
.00120	41.66
.00142	42.25
.00163	41.40
.00183	41.48
.00202	40.71

.00228	40.87
.00250	40.19
.00274	40.87
.00313	40.24
.00342	40.53
.00351	40.62
.00370	40.53
.00409	39.88

58.4 % EtOH

.00039	41.38
.00089	40.80
.00128	40.75
.00139	39.83
.00164	39.57
.00205	39.35
.00233	39.45
.00240	39.11

.00262	38.81
.00294	38.46
.00323	37.20
.00339	38.11
.00388	38.26
.00426	37.30
.00471	37.40

Experimental Data

NaCl (25C)

72.0 % EtOH

c	A	c	A
.00022	42.71	.00151	37.99
.00046	39.18	.00169	37.78
.00060	39.24	.00173	37.84
.00071	40.04	.00202	37.05
.00099	39.20	.00216	36.74
.00116	38.21	.00267	36.98
.00125	38.27	.00287	34.96
.00139	37.23	.00308	34.25

83.7 % EtOH

.00038	39.05	.00131	37.46
.00055	41.28	.00140	36.35
.00062	37.83	.00157	36.65
.00063	40.28	.00168	36.26
.00079	37.61	.00173	36.80
.00080	38.17	.00187	36.19
.00096	37.78	.00195	36.45
.00123	37.26	.00221	36.06
.00130	37.22		

Experimental Data

KCl (25C)

7.86 % EtOH

c	A	c	A
.00074	114.79	.01211	107.66
.00109	113.65	.01331	107.63
.00165	115.64	.01644	107.01
.00224	111.51	.02209	106.42
.00352	111.80	.02266	105.85
.00415	110.86	.02498	105.21
.00536	109.72	.03455	102.99
.00640	110.06	.04075	103.26
.00895	109.41	.05345	100.62

16.0 % EtOH

.00049	83.61	.01383	84.96
.00066	90.46	.01999	83.50
.00134	87.47	.02004	83.57
.00164	86.39	.02070	83.68
.00228	87.65	.02376	82.72
.00289	88.27	.02980	82.16
.00355	89.82	.03528	81.29
.00692	86.34	.04422	82.71
.01150	85.60	.05361	80.17

27.3 % EtOH

.00036	68.75	.00825	64.13
.00055	68.73	.00926	63.93
.00141	67.10	.01332	62.85
.00171	66.49	.01602	62.49
.00258	65.86	.01926	61.67
.00380	65.88	.02287	61.26
.00482	65.41	.02689	61.25
.00644	64.58	.03198	60.29
.00792	63.79	.05014	59.05

35.8 % EtOH

.00035	55.77	.00371	56.10
.00046	59.73	.00542	54.78
.00082	55.97	.00846	53.99
.00109	56.70	.01063	53.22
.00131	57.18	.01473	53.21
.00154	56.72	.01771	52.69
.00180	55.39	.02007	52.07
.00208	56.61	.02334	51.71
.00301	56.79	.02576	51.44

Experimental Data

KCl (25C)

42.4 % EtOH

c	A
.00041	52.83
.00046	53.22
.00079	52.56
.00097	53.44
.00134	52.74
.00169	51.57
.00205	52.02
.00237	51.33
.00250	51.05

c	A
.00285	51.19
.00346	50.76
.00421	50.54
.00451	51.19
.00600	50.05
.00722	49.43
.00852	49.07
.01187	48.44
.01350	50.75

49.1 % EtOH

.00029	51.91
.00067	47.82
.00094	48.74
.00119	48.58
.00156	49.00
.00198	46.38
.00202	48.36
.00226	48.27
.00256	47.38

.00285	47.36
.00306	46.85
.00358	47.22
.00403	46.22
.00452	46.04
.00472	46.14
.00505	45.90
.00540	46.11

58.4 % EtOH

.00030	45.85
.00074	45.03
.00100	44.61
.00108	43.97
.00134	44.57
.00169	44.96
.00191	42.89
.00224	43.79

.00283	43.04
.00285	42.97
.00313	44.27
.00396	42.84
.00427	42.66
.00454	42.43
.00568	42.06
.00621	41.86

72.0 % EtOH

.00017	42.60
.00036	43.90
.00057	42.93
.00066	45.03
.00100	42.10
.00124	40.35
.00145	41.75
.00178	40.09
.00182	40.47

.00226	38.07
.00242	39.43
.00287	39.26
.00301	38.97
.00338	39.76
.00365	38.70
.00393	38.47
.00413	38.41
.00433	38.85

Experimental Data

KCl (25C)

83.7 % EtOH

c	A	c	A
.00025	40.02	.00108	39.23
.00029	41.42	.00129	38.82
.00041	43.69	.00134	39.36
.00046	40.08	.00154	39.16
.00057	40.81	.00173	38.55
.00065	40.37	.00185	37.92
.00082	39.72	.00194	37.94
.00085	38.10	.00226	37.76
.00106	39.26	.00296	37.17

Experimental Data

CsCl (25C)

0 % EtOH

C	A	C	A
.00011	146.85	.00083	147.16
.00021	149.65	.00085	143.28
.00031	153.52	.00105	147.91
.00032	151.90	.00109	146.31
.00041	150.06	.00119	144.54
.00045	151.07	.00120	141.35
.00049	150.50	.00128	146.35
.00058	152.04	.00148	148.75
.00070	152.57	.00206	141.67

7.86 % EtOH

.00008	139.50	.00074	118.12
.00012	124.26	.00082	117.97
.00021	123.93	.00094	118.92
.00029	125.08	.00114	117.27
.00036	122.62	.00126	118.01
.00040	123.05	.00145	118.26
.00046	121.09	.00160	116.98
.00065	118.93	.00174	117.79
.00068	117.70	.00191	116.60

16.0 % EtOH

.00008	110.08	.00069	92.24
.00020	99.48	.00077	88.88
.00026	96.42	.00083	92.48
.00027	94.06	.00107	92.04
.00039	93.67	.00113	90.35
.00044	94.64	.00124	90.33
.00049	94.03	.00157	89.15
.00053	93.91	.00233	89.53
.00066	92.11	.00257	89.82

27.3 % EtOH

.00014	68.81	.00086	68.28
.00024	68.61	.00094	68.41
.00029	71.55	.00099	68.26
.00033	71.63	.00113	69.03
.00041	69.54	.00121	68.75
.00053	71.27	.00128	68.04
.00066	69.62	.00147	68.63
.00074	69.11	.00190	68.08
.00082	70.39	.00239	68.22

Experimental Data

CsCl (25C)

33.2 % EtOH

c	A
.00007	54.72
.00013	68.11
.00015	68.02
.00025	63.33
.00029	63.22
.00036	64.03
.00039	64.03
.00045	60.92
.00049	62.01

c	A
.00056	61.14
.00057	62.08
.00060	62.01
.00081	62.43
.00089	61.84
.00096	61.68
.00103	61.80
.00115	62.05
.00147	61.35

42.4 % EtOH

.00010	52.61
.00012	56.12
.00023	54.05
.00026	55.10
.00035	55.07
.00037	56.12
.00043	55.42
.00045	55.82
.00049	55.38

.00055	55.08
.00061	54.63
.00066	55.21
.00070	54.50
.00080	55.28
.00083	54.50
.00090	54.19
.00104	55.22
.00143	54.51

51.8 % EtOH

.00008	53.10
.00009	50.51
.00010	56.45
.00010	52.49
.00017	52.31
.00026	52.42
.00027	48.31
.00028	50.15
.00033	48.40

.00037	49.69
.00044	50.28
.00045	46.52
.00048	47.56
.00048	49.88
.00051	48.16
.00055	50.14
.00073	49.41
.00083	47.48

58.4 % EtOH

.00016	41.15
.00017	46.30
.00021	44.25
.00026	50.89
.00027	46.12
.00030	46.55
.00039	44.13
.00052	45.28

.00072	45.82
.00078	42.03
.00079	46.08
.00080	41.65
.00084	46.69
.00103	45.35
.00105	44.96
.00162	44.16

Experimental Data

CsCl (25C)

72.0 % EtOH

c	A
.00009	42.65
.00013	43.62
.00017	42.69
.00023	42.53
.00026	44.00
.00036	41.81
.00048	41.04
.00058	42.52
.00061	42.33

c	A
.00066	41.41
.00078	41.20
.00086	40.45
.00091	41.32
.00102	40.91
.00108	40.80
.00119	41.29
.00235	39.26

83.7 % EtOH

.00008	49.00
.00012	41.69
.00019	40.51
.00021	44.74
.00026	43.24
.00029	44.19
.00030	41.25
.00030	42.25
.00033	41.19

.00034	41.80
.00043	41.51
.00048	41.67
.00049	41.27
.00050	41.49
.00054	40.23
.00058	41.57
.00081	40.92
.00099	40.26