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A Test of the Theoretical Equation.

Abstract approved:

The application of the Fuoss-Onsager equation for the conductance is tested for a set of literature-source studies of the conductance of the alkali-chlorides: LiCl, NaCl, KCl, and CsCl in different solvent systems of pure water, methanol, and ethanol, as well as for systems which are composed of the salts in aqueous alcohol mixtures. The best fit of the data was accomplished, and the best-fit values for the ion-size parameter, the equivalent conductance at infinite dilution, and the association constant are interpreted.

THE FUOSS-ONSAGER TRUNCATED SERIES-EXPANSION FORMULATION OF CONDUCTANCE FOR SYMMETRICAL ELECTROLYTES: A TEST OF THE THEORETICAL EQUATION

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PREFACE

This paper is intended to be both as informative and as concise as is possible. The development of the electrostatic theory of electrolytes is meant to provide a basis for understanding the concepts which are introduced in the Analysis and the Results and Discussion sections. It is felt that the content of this work should include a short treatise on Experimental Considerations, so named to show that it contains aspects of the actual measurement-taking process, as well as methods which are employed to minimize experimental errors.

Due to the number of variables, parameters, and constants which are presented within the conductance equations, a list of the symbols and their definitions has been placed at the beginning of Appendix A. The second section of Appendix A is allocated to the enumeration of the full equation of Fuoss and Onsager. Appendix B contains the literature and the new experimental data, with references cited. The data are tabulated in the appendicies to improve the overall readability of the paper. The graphical analysis of the data is in Appendix C.

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I. THE DEVELOPMENT OF THE ELECTROSTATIC THEORY OF ELECTROLYTES IN SOLUTION

The early years of the electrostatic theory of electrolytes were trying times. In the laboratory, experimentalists would make electrical measurements of the conductivity of solutions. Theoreticians then tried to evaluate the results in terms of the kind and amount of ions which were present in the solution, since any electrochemical process is based on the movement and interactions of these ions.

Much of the credit for the early characterization of ionic behavior must be given to Clausius, who first suggested that ions were produced when an electrolyte such as NaCl was dissolved in water. We now know that the ions exist in the solid crystals even before being dissolved, but at that time, this was a revelation. It seemed to explain why certain compounds were electrolytes while others were non-electrolytes. Clausius also recognized that an equilibrium could exist between free ions and unbroken molecules of solute, which he characterized as electrolytic dissociation. This concept was further refined by Arrhenius, who concluded that an electrolyte can vary in the extent to which it supplies ions, and that this extent was dependent on concentration.[1]

One way to measure the extent to which ions are supplied by an electrolyte in a solution is to measure the conductivity of the solution. The conductivity (formerly called the specific conductance) of a solution is the ratio of the current density which results when an electrical field is applied to the solution, to the strength of the applied field.[2] The current density is given by the sum of the products of the number of ions per unit volume, the charge of the ion, and the velocity with which the ions move. Therefore, a measurement of the conductivity will be indicative of the number of ions which are present in the solution. The conductivity can then be normalized with respect to concentration by introducing the equivalent conductance, A:

$$A = 1000\ L/c, \qquad (1)$$

where L is the conductivity, and c is the concentration in units of normality. (Of course, if the concentration is in moles per liter, the quantity which results is the molar conductance.)

Using conductance data, Arrhenius calculated the degree of dissociation for the electrolyte:

$$r = A/A_{\infty}. \qquad (2)$$

As the concentration approaches zero, the equivalent conductance approaches its maximum value, A_{∞}, the equivalent conductance at infinite dilution. This linear variation with concentration was ascribed by Arrhenius to an increase in the degree of dissociation as zero concentration was approached. Arrhenius then used the law of mass-action to assign to each electrolyte an equilibrium constant, termed the concentration dissociation constant:

$$K' = [M+][L-]/[ML] \tag{3}$$

$$= (r^2)c/(1-r). \tag{4}$$

Ostwald then combined these two important concepts of Arrhenius to formulate his famous dilution law:

$$K' = (A^2)c/A_o(A_o-A), \tag{5}$$

which is also written as:

$$1/A = 1/A_o + cA/K(A_o^2). \tag{6}$$

A plot of cA against 1/A gave straight lines for many electrolytic systems and so seemed to follow Arrhenius' theory of dissociation. Ostwald's law facilitated the classification of electrolytes as strong (largely dissociated) or weak (minimally dissociated) on the basis of conductance measurements of aqueous solutions of the substance. This designation served well, until precise measurements on non-aqueous solvent systems were made. Conflicting results were then found. "Strong" electrolytes in aqueous solution behaved as "weak" (partially dissociated) electrolytes in non-aqueous solutions, but "weak" electrolytes in aqueous solutions were still "weak" electrolytes in non-aqueous solutions.

The inability of the researchers to explain this behavior was due to a lack of understanding of the basic structure of electrolytes. As we now know, some compounds exist as ions in a crystal lattice (strong electrolytes), while other compounds are neutral molecules which can produce ions by a dissociation process (weak electrolytes). On the other hand, the behavior of strong electrolytes in non-aqueous solutions indicates that these compounds can produce neutral molecules, or some non-conducting structures in solution.[3]

About this time, very precise conductance data were compiled for a number of electrolytes in aqueous solutions by Kohlrausch which showed that at low concentrations the conductance varied not linearly with concentration, but as some fractional power of the concentration.[4] His data led him to believe that A varied as the square root of c at low concentrations.

Advanced by the precise data compiled by Kohlrausch on ion-containing substances was the conclusion that it was the mobility of free ions in solution that was reduced as the concentration was increased. This is evident when we refer back to the basic definition of the current density and the specific conductance in terms of the velocity of the ions present in the solution.

For almost fifty years, the Ostwald dilution law was not seriously challenged. Then, Debye and Huckel[5] brought electrostatic theory into the realm of differential equations by considering the system of an electrolytic solution in terms of an appointed reference ion, with all other ions, said to be discrete sites of charge, replaced by a continuous space-charge, whose density was a function of the distance from the reference ion. They then used the Poisson equation to relate the total chemical potential of the solution to the distribution of the ions which it contains. The Poisson statistical equation[2,6] is a one-parameter discrete frequency distribution giving the probability that n points (or events) will be (or will occur) in an interval, x, provided that these points are individually independent and that the number occurring in a subinterval does not influence the number occurring in any other non-overlapping subinterval. The equation has the form:

$$f(n,x) =(e^{-rx})(rx^{n})/n!, \qquad (7)$$

where rx is both the mean and the variance, and r is the average density (or rate) with which the events occur. By this method, they were able to relate the electrostatic potential around the reference ion to the charge density and the dielectric constant, D, (the ability of the medium to hold or carry a charge). Using the Boltzmann statistical distribution to describe local concentrations, they replaced the charge density with the stoichiometric concentration and the charges and potentials of the ions. Debye and Huckel then applied the result to the conductance problem, and arrived at a good first approximation which showed that the equivalent conductance at low concentration did, indeed vary linearly with the square root of the concentration. The Debye-Huckel Limiting Law arises from the fact that at low concentrations their treatment is exact. The deviations which begin to show themselves as the concentration is increased are because of the ion-size effect.[7]

Before proceeding further, it will be best served to define two of the main negative contributions to the conductance of ions in solution, the relaxation effect and the electrophoretic effect.[8] To define the relaxation effect, what is meant by the ionic atmosphere must be explained. The presence of one ion tends to exclude ions of like charge, and attract ions of opposite charge. The result is that an ion is surrounded by ions of opposite charge. In an undisturbed state (in the absence of an external electrical field), the ionic atmosphere of a mono-atomic ion is spherical, as the surrounding electrical field due to the electrons of the ion is spherical. When an electrical current is applied to the solution, there results a disturbed state wherein the ions begin to move toward the oppositely-charged electrodes. This movement disturbs the ionic atmosphere, which becomes non-spherical. As the ion zig-zags from point to point in the non-continuous medium of the solution, the atmosphere is constantly being created and destroyed. The re-establishment of the ionic atmosphere, which requires approximately 10-7 seconds in a 0.01 molal solution at twenty-five degrees Celsius, contributes negatively to the ionic velocity, and results in a decrease in the conductivity of the solution.

The electrophoretic effect is the negative contribution to the ionic velocity which arises from the tendency of the ion to drag solvent molecules with it as it moves. Since ions of opposite charge are moving in opposite directions in the solution when an electrical field is applied, each ion is not moving through a stationary medium, but, rather, against a stream of solvent molecules which are moving in the opposite direction. Again, this effect results in a decrease in the conductivity of the solution. (This effect is certainly larger in solvents which are more polar, since stronger ion-dipole interactions will occur.)

The work of Onsager, including the thermal motion of the reference ion, and using a more complete evaluation of the relaxation effect and electrophoretic effect, resulted in a more accurate mathematical expression for the conductance:[9]

$$A = A_{o} - (@A_{o} - B)c^{1/2} \qquad (8)$$

@ and B are determined by the absolute temperature, in kelvins, the dielectric constant and the viscosity of the solvent, the valence type of the solute, and universal constants. (The reader is referred to Appendix A for a complete enumeration of @ and B.)

This equation, then, only includes one arbitrary constant, A_{∞}, the equivalent conductance at infinite dilution. The application of this equation to a large body of experimental data showed that it was the exact expression for the limiting tangent to the conductance curves at zero concentration. It was, however, based inaccurately on the representation of ions as point charges in a continuous solvent medium. We now know that this is not entirely correct, as the ions do have a definite non-zero ionic radius, and that there exist in a solution discontinuities in the dielectric constant of the solvent in the vicinity of an ion which result from ion-dipole interactions which tends to form a more stable "cage-like" structure of solvent molecules which surrounds the ion.[10]

Using a different, more accurate model for the electrolytic system which incorporated these facts, Fuoss and Onsager[2] arrived at a more complete expression for the shape of the conductance curves, particularly for lower concentrations:

$$A = A_{\infty} - Sc^{1/2} + Eclnc + Jc, \qquad (9)$$

where S is the Onsager coefficient of the limiting law,

$S=(@A_\infty + B)$, E is a constant defined by the same variables as S, and J is a function of ion size. This form of the conductance equation is the result of a series expansion[11] of the functional form which facilitates easier calculations of the conductance, but does not introduce serious errors. (It is interesting to note that R.A.Robinson and R.H.Stokes at one time concluded that[12]..."For symmetrical electrolytes, the valence factor in the second-order term of the electrophoretic function vanishes; hence, there can be no term in clnc in this case".)

The concepts of ion-association and ion-pairs must now be explained before further advancements of the theory are included. As was stated earlier, the behavior of electrolytes, such as NaCl, in non-aqueous solutions indicates that there arises some non-conducting species which are not present in aqueous solutions. For a species to be non-conducting, it must be neutral in solution. There must be, then, some re-combination of the charged ions which are present. Such a re-combining is said to be ion association. Bjerrum was the first to suggest that free ions in solution could associate to form ion-pairs. If the Coulomb potential energy resulting from the attraction of opposite charges in contact is large compared to kT, the average thermal energy, then the ion-pair is not broken apart merely by the local perturbations of neighboring solvent molecules. This is not to say that the ion-pair remains stable indefinitely, but, rather, that it is stable until another ion approaches the pair closely enough to exert its' Coulombic influence on the ions. One consequence of the Bjerrum hypothesis was the definition of a critical distance beyond which the ions were considered to be free entities and inside of which ions were considered to be non-conducting ion-pairs. This "distance of closest approach" was determined by Bjerrum to be dependent on ion size and the dielectric constant of the solvent medium, such that this distance, b, was expressed as:[1]

$$b = e^2 /DakT. \tag{10}$$

The use of Bjerrum's critical value and its relationship to the dissociation constant of electrolytes has now been found inadequate, as the treatment was determined to be mathematically unsound, since numerical values of b and k were found to behave in a non-physical way.[1](When b=2, no association occurs abruptly.) Bjerrum's work did, however, serve to help to further characterize electrolytic solutions, as the concept of ion-pairs was established. It should be stated that there also exist higher combinations than pair-wise when the charges on one of the ions is greater than +1 or -1, as in 1-2 or 2-1 electrolytes. (Only 1-1 symmetrical electrolytes will be considered here, for simplicity.)

If we begin with Arrhenius' value for the fraction of free, unassociated ions, $r=A/A_o$, the mass-action equation indicates that an association constant, K_a, can be determined as the ratio of non-conducting, associated ion-pairs (1-r) to the number of free ions (cr^2f^2):

$$K_a = (1-r)/ cr^2f^2. \qquad (11)$$

The Fuoss-Onsager equation then is extended to include the association constant:

$$A = Ao - Sc^{1/2} + Eclnc + Jc - K_acf^2A. \quad (12)$$

In solvents of high dielectric constant, the K_a term becomes small.

If we then extend the Fuoss-Onsager equation to those systems where ion association occurs, we arrive at:

$$A = A_o - S(cr)^{1/2} + Ecrlncr + Jcr - K_acrf^2A. \qquad (13)$$

(cr is the concentration of free ions.) This equation can then be used to evaluate the association constant.

By including terms of higher order in the mathematical treatment of the relaxation and electrophoretic effects and cross terms, the Fuoss-Onsager equation becomes:[13]

$$A = A_o - Sc^{1/2} + Eclnc + J_1c + J_2c^{3/2}, \qquad (14)$$

or, where ion association occurs:

$$A = A_o - S(cr)^{1/2} + E(cr)\ln(cr) + J_1 cr + J_2(cr)^{3/2}, \qquad (15)$$

where the J_2 term is dependent on the same variables as J_1: ion size, dielectric constant, and absolute temperature. We are now very close to expressing the shape of conductance curves in a useful mathematical form. One should note that no association constant term appears in these last two equations. This can be justified by stating that any value for K_a is dependent on the assigned (chosen) value for the radius of the solvated ion, "a" and upon which form of the equation is used.

II.EXPERIMENTAL CONSIDERATIONS

It should be apparent from looking at the pertinent equations that conductance is a function of the absolute temperature, the nature of the solvent, and the concentration and identity of the solute.

As was stated earlier, the conductance at lower concentrations, less than 0.001N in water (N is the normality, in equivalents of solute per liter of sloution.), follows closely the values given by the Ostwald Dilution Law. However, as the concentration increases, the conductance begins to deviate negatively from the predicted values. Therefore, it is at higher concentrations (greater than 0.001N in water) that conductance measurements are of interest.[10, 14-20] The best way to prepare these solutions is gravimetrically, to eliminate the errors due to the uncertainty of the volume measurements required in volumetric methods. Also, preparing a larger portion of the desired solution will result in a more accurate value for the concentration, as the number of significant figures in the mass determination increases.

For precise analytical work, the solute must first be purified. This can be accomplished by recrystallization from conductivity water (Conductivity water is water with a very low solvent conductivity.) and then dried in an oven at 50-60$_{o}$ C, or fused under a dry, purified nitrogen stream, to ensure its purity. The purity of the solvent used is also important. If water is the solvent, it can be purified by distillation to a conductivity of around 1.0 $*10^{-3}$ Seimen (1Seimen = $1ohm_{-1}$), but since lower concentrations of solute result in conductivities of the order of 1.0 $*10^{-4}$Seimen, the water must be further purified to enable more accurate measurements to be made. The water is further purified using a column de-ionizer, or an ion-exchange resin,and this reduces the conductivity to about 1.3 $*10^{-6}$ Seimen, which is of sufficient purity for all but very low values of concentration (below approximately 1.0 $*10^{-4}$ N). The main concern in water purification is the exclusion of CO_2, which forms H^+ and HCO_3^- ions when allowed to come in contact with water. Non-aqueous solvents must be similarly purified, usually by treatment using a molecular sieve which allows only solvent molecules to pass through. Here, the main concern is the exclusion of water, as ions will accompany water into the system, and to ensure that the solutions are prepared as a known weight percent of alcohol to water.

For precise analytical work, the CO_2 from the air must be excluded from the system. This is accomplished by placing the system in a closed environment over which some inert gas, such as argon or helium is circulated. In this manner atmospheric air, and thus CO_2 and other trace impurities, is excluded.

Since the conductivity is also temperature dependent, (The conductivity increases with increasing temperature.) care must be taken to ensure that the temperature at which the measurements are taken is constant. A thermostatically-controlled water bath can be used to keep the solutions at a specific temperature. It has been found, however, that if a substance such as kerosene or mobile transfer oil is used, the errors due to induced fields in the water were greatly reduced.[21] (In water, the conductivity varies considerably with the frequency of the applied signal.) Stirring is also recommended so that the temperature is uniform, and to ensure that the contents of the cell are thoroughly mixed.

Alternating Current Methods

The majority of conductivity measurements have thus far been obtained by using some form of alternating current Wheatstone bridge arrangement[22]. This bridge consists of a double-armed circuit to which an oscillator and a phone are connected to act as a source of current and a detector, respectively. On one side of the circuit, a variable resistance is connected. On the other side, an electrolytic cell is located. As a current from the oscillator is applied to the circuit, the phone will ring if the resistance of the cell is different from the resistance which is set on the variable resistance box. Therefore, the resistance is varied until the phone no longer produces a sound. At this point the resistance of the cell which is being measured is equal to the setting on the variable resistance box. The oscillator signal is in the audio-frequency range (550-5000Hz). Since the conductivity of the solution is effected by the frequency of the applied signal, this range is small enough so that frequency effects are minimal.

The resistance and the conductivity are related by:

$$L = (1/a_o)\ R \qquad (16)$$

by Ohms law. By determining the resistance of a solution of known conductivity, the cell constant, $(1/a_o)$, can be calculated. This value is then used to determine the conductivity of other solutions, once their resistance is known.

The main problems early instruments such as these suffered were polarization effects which were due to the proximity and construction of the connections and components of the circuits. One flowing current would induce a field in another, closely-placed component. Also, the old cathode-ray tubes operated inefficiently. Many of these problems were eliminated with the advent and use of transistors. This also resulted in less bulky instruments.

Referring back to Equation (16), in order to find the conductivity, the quantity $(1/a_o)$, termed the cell constant, k, must first be determined. By definition, l refers to the length and a_o is the cross-sectional area of the body of solution which is being measured. The conductivity cell is designed so that l equals the distance between two similar electrodes of the cell, which are of equal area, a_o. The electrodes are metal plates which are covered with "platinum black" or some other coating which inhibits the adsorption of solution components, as this will cause errors due to a changing effective concentration in the solution. Using a standard solution of electrolyte in the appropriate solvent, usually 0.02000 N KCl for aqueous solutions (The conductivity of this concentration of KCl in water is known with some certainty to be: $L = 0.002768$ mhos at 25_oC.), the cell constant must be determined for each conductivity cell.

Modern instruments are equipped with a detector, in place of the phone, and an amplifier for increasing the sensitivity of the instrument.

Direct Current Methods

A direct current meter for measuring conductivities consists of some constant current device, such as a transformer ratio-arm bridge, which is deflected an amount which is proportional to the resistance of the solution, and a reversible electrode cell.[1] The type of electrode which is used depends on the type of system which is being considered. The electrodes must be reversible with respect to the solution or the concentration of ions will decrease as a function of time, as the electrolyte is "plated out" at the electrodes. A second set of readings is usually taken with the current reversed to eliminate any static bias potential between the electrodes. Then, using the equation:

$$R_{k}/R_{\bullet} = G/L, \qquad (17)$$

where R_{k} is some known resistance, $R_{\bullet}$ is the resistance of the cell, and G is the cell constant, after G has been determined from measurements on a standard solution, L, the conductivity, can be evaluated in the same manner as in A.C. measurements.

In either method of analysis, the solvent conductivity must be determined and subtracted from the values for the solutions. Also, if the cell is not a dilution-type cell, like the one which is described below, care must be taken to see that the cell is rinsed and dried between readings so that contamination of solutions does not occur.

Some cells are designed so that errors which are due to contamination are avoided.[23] In these cases, the cells are "dilution" cells, where the analysis begins with the most concentrated solution, and solvent is added during the analysis so that the only errors are dilution errors. There are also cells designed so that the pure solute is added to the solvent through a port in the side of the cell.

The solutions which were used in the determination of the equivalent conductance of chlorides of lithium, sodium, potassium, and cesium in water were prepared by dissolving an amount of the solute (the range was approximately 100-400 mg.) which was weighed on the Mettler B6 balance, in a known volume (250 ml) of the solvent. Also, the salts were procured from new, unopened containers of analytical grade Fisher Scientific chemicals, A.C.S. grade and so were considered pure, although the actual lot analysis was slightly less than 100% purity. The de-ionized water which was used to prepare the solutions was prepared from distilled water which was purified by circulation through a Barnstead Bantam Still which was equipped with a Fisher Scientific ultrapure de-ionizing column. The salts were weighed out on the balance, and the solutions were prepared by a dilution method in which an initial concentration of each salt was diluted by volume to successive lesser concentrations. It was necessary to do this to avoid having to weigh out extremely small quantities of the solutes. The procedure did not include methods for excluding atmospheric contaminants, except that the solutions, once they were prepared, were kept in test tubes stoppered with parafilm-covered rubber stoppers. The analysis was done the same day that the solutions were prepared, as the atmospheric carbon dioxide caused the conductivity to increase with time at the rate of around $5.0X10^{-5}$ per day if two or three readings were taken, and a larger variation was observed if readings were taken slowly, or repetitively. Steps for maintaining a constant temperature were attempted by immersing the test tubes in a water bath, equipped with a thermometer, while the readings were taken. This was done to check the temperature-compensating mode of the meter, and it was found that the readings did show some deviation with temperature, even while the compensating mode was on.

The conductivity was measured with an Amber Science Model 1052B digital conductivity meter equipped with a P/N 1125 platinum conductivity dip cell. The meter, which was equipped with an automatic temperature-compensating mode, was accurate to three significant figures. It was standardized with 0.02000N KCl which had a conductivity of 0.00277 Seimen. This solution was used to calibrate the meter before and after the readings were taken on the experimental solutions to maintain the accuracy of the readings.

Although the above steps were taken to ensure the accuracy of the readings which were taken, the experimental points show a large deviation from a plot of literature values for the same systems versus concentration, and so further attempts at experimentally determining the conductivity were considered fruitless, as the precision with which this quantity is measured would certainly get worse as the weight per cent of alcohol in the solvent system is increased, due to the necessity of mixing the two solvents in differing quantities in addition to the measurement of the quantity of solute which is added.

III. THE ANALYSIS OF CONDUCTANCE DATA

A. The variation of conductance with concentration

If the conductivity of strong electrolytes in solution follows the Ostwald dilution law, Equation (5), a plot of the equivalent conductance versus the square root of the concentration will give a straight line, with the slope equal to the Onsager coefficient, -S, and the y-intercept will be the equivalent conductance at infinite dilution, Λ_o. Since Equation (5) holds only at smaller concentrations, ($c< 0.001N$) the line which results is not linear, but is slightly curved. However, the plot is a smooth function of concentration, and so this plot will give the value at infinite dilution, corresponding to zero concentration, but the slope is some value which is slightly different from the Onsager coefficient. (This is due to the electrophoretic and relaxation effects which must be included to more accurately describe the systems.) This method of analysis was used to compare literature data with values of the equivalent conductance which were calculated from the full equation. The final results of the calculations are listed, along with the square root of the concentration, in Appendix B. The graphs which correspond to each data set are found in Appendix C. Fuoss[24] describes a method by which the value at infinite dilution is found by iterative calculations where the value which is found in each step is inserted back in the original equation and the process is repeated, until the value becomes constant. This A_o value is then used to determine S, E and J. The J-term is then plotted versus "a" and the ion size is interpolated. This treatment is used when the coefficients of the equation are not known. When S, E and J are known, the usual method is the one which has been used here. Other methods of analysis,[25] for solutions of slightly-associated electrolytes, include assuming that the solute is completely dissociated, or that the ion-size parameter is some physically reasonable quantity, either of which makes the equations two-parameter equations, instead of three-parameter equations, and as such, they result in different values for Ka and "a", but they are easier to fit to the data and yield reasonable results.

The values which were calculated from the full equation are meant to be similar to those listed in the literature in that the parameters for each system which were used in the calculations were the same as those listed in the literature, when they were given. When the viscosity and the dielectric constant for each system were not given in the text, it was stated that the values which were used were those of Alkeroff.[26] The values which were used in the computer analysis, however, were read from a plot of the values given in the Non-aqueous Electrolytes Handbook[27] versus the weight per cent of alcohol.
When the values of the ion size parameter were not given, an estimation of the value was ascertained from the sum of

the crystallographic radii of the ions, and from the fluctuations which were reported in comparable studies. A list of these, in angstroms (1 angstrom=10^{-8} cm.), is found in Table I for the data from Werblan, et. al. for CsCl in methanol. (Cesium chloride has a crystallographic radius of 3.47 angstroms). In all cases, the temperature and the conductance at infinite dilution were given. When ion-pairing was suspected, the mean activity coefficient was evaluated according to the extended Debye-Huckel equation:[28]

$$\log f+- = [-1.824 \times 10^{6}/(DT)^{3/2}] \text{ X } [I^{1/2} / (1+I^{1/2})], \qquad (18)$$

with the approximation that the Ba term, which is usually present in the denominator of the second bracketed quantity has been set equal to unity.

TABLE I. A COMPARISON OF THE ION-SIZE PARAMETER*

LITERATURE VALUE	VALUE OF BEST FIT
2.13	1.80
2.36	2.57
2.52	2.98
2.82	3.40
3.81	6.30
4.25	5.52

* Werblan, et. al.[10]

B. CHOOSING THE PARAMETERS: a, Ka, and Ao.

The choice of the value of "a", the ion-size parameter is by no means a cut-and-dried subject. Not only does the parameter need to reflect the size of the actual ion, but there are also such things as "solvent-separated" ion-pairs and the effects of the solvent-solute electrostatic interactions on the electron density of the ions. Also, associated with the ions in solution is a certain amount of "dead space" around it which is due to the open structure of water (assuming that the density of the water is the same around the ion as it is in the bulk of the solution).[29] This suggests that the ion acquires its size from its radius and its environment. It has been found that the value of "a" increases with decreasing dielectric constant.[10] That this is true is evident from a comparison of the various literature values. Also evident is the fact that the value which is chosen for "a" is dependent on which form of the conductance equation is used.[25] From Table I it can be seen that there is actually a range of "a" values which satisfy any equation. The value which is chosen is dependent on the value of A_o. When computer analysis are done, the value of "a" is varied until the calculated values approached the listed values for the conductance, using the listed values of A_o. When the best-fitting "a" was found, the value of A_o was decreased slightly, which enabled different, larger values for "a" to fit the data. If A_o is increased slightly, the values of "a" which closely fit the data decreased. Hence, there is a range of A_o-"a" pairs which closely fit the data.

The association constant, K_a, depends on both of the forementioned parameters, and so, K_a can only be unambiguously determined when the other two parameters are known with some certainty. From Equation (11) it can be seen that K_a is calculated from the degree of dissociation and the activity of the solute in solution. It was once thought that K_a had a value of zero in very dilute solutions. Fuoss,et.al.[8] have found, however, that even in dilute solutions the ions are not completely dissociated, and so K_a has a non-zero value for a great number of aqueous solutions. The value of K_a in very dilute solutions is very small, though (K_a=0.0261 l/mole for KCl in aqueous solution at 25°C). Even when the other parameters of the equation are known, the value of K_a is dependent on the form of the Debye-Huckel equation which is used for the evaluation of the activity coefficient.[23] Carman[11] has found that there is a wide range of ("a",K_a) pairs which result in an almost constant standard deviation.

C. Viscosity Corrections

One quantity which is frequently used to quantitatively describe electrolytic solutions is the Walden product. This quantity, the equivalent conductance at infinite dilution multiplied by the viscosity of the solvent system, was said by Walden to be a constant value for a particular solvent system. That this relationship does not hold true[30,31a,31b] can be ascribed to the solvent in that there exist certain fluctuations around the vicinity of the ion in the dielectric medium due to the mixing of the solvents and to the presence of the solute in the solution which cause the viscosity of the system to be slightly different than the viscosity of the pure solvent. Viscosity corrections which try to explain this deviation of the Walden product have been presented,[30] and, indeed, there is evidence that this type of correction should be included in the treatment of conductance(32).

IV. RESULTS AND DISCUSSION

The treatment of the transport properties of an electrolytic solution, and in particular the process of conductance, relies heavily on the nature of the model which is used to describe the system. The representation of ions in a solution as point charges in a continuous dielectric medium is limited as to its accuracy by the fact that the ions do have some non-zero radius, and by the fact that there are ion-solvent interactions which cannot be ignored. Any time there are charges in the solution, there exists some intrinsic electrostatic interactions which not only inhibit the mobility of the ions, but must also inhibit the motion of the solvent molecules. Added to this is the phenomenon that when solvated electrons are introduced into a solution, as they are when the resistance is being measured, absorption spectra indicate that the solvated electrons ion-pair with cations in the solution[26].

From the graphs of the calculated data, it can be seen that the values which are calculated using equation (14) are quite close to those reported for these salts in water, and in methanol. For the ethanol-water systems, they are consistently low, when compared to the literature. This can be attributed in part to the fact that different forms of the conductance equation were used (The literature sources, almost invariably use equation (12) in the analysis, whereas the present research includes the

$c^{3/2}$ term in the electrophoretic and relaxation effects given by Equation (14).) However, this suggests that the equation is less accurate as the dielectric constant of the solvent decreases. This is not surprising, since the occurrence of ion-association increases similarly. Also, the agreement is worse as the concentration increases, which is expected because of the similar behavior of the Debye-Huckel treatment on which conductance is based. The values of Λ_o and "a" are comparable to those found by the literature sources, but, again, these depend on the equation which is used.

No analysis or comparison of the values for the association constant was attempted, primarily because of the difficulties which were reported[7,11,23,28] in assigning some physical significance to this parameter. For instance, Panda,et.al. found,[34] 1n 1962, that KCl and NaCl in 76.24% methanol have non-zero values of K_a, but the literature values[27] are zero. There are accepted values for this quantity[35] for these salts in the solvents studied, and those values which are listed in the literature[10,14-19] do not differ considerably from these. The focus of this study was on the ion-size parameter and the fit of the data to Equation (14).

An empirical correction to Equation (14) was found for application when the dielectric constant of the solvent becomes small enough so that the fit of the data is poor. This consists of replacing the effective concentrations of the solute in the solution with the "effective activity" of the salt. This is to say that the concentration, whenever encountered in the full equation, was multiplied by Arrhenius' degree of dissociation, as in Equation (15), and also by the mean activity coefficient for the particular concentration as calculated above, using Equation (18). A plot of the equivalent conductance calculated in this way is shown in Figure 45, Appendix C. This treatment of the conductance values is purely an empirical result of an attempt to better fit the calculated values to the literature values, but this aspect appears to have some basis in the definition of the activity as the chemically active portion of the salt which is present, since the chemically active portion would be that part which is dissociated to its ions, and as such would exist as charged, current-carrying particles. As this research involves those systems where only one symmetrical uni-valent salt is present, it remains to be seen if the treatment is applicable to salts of higher valence, or to non-symmetrical electrolytes.

Recently, researchers have worked toward the inclusion of specific ion-solvent interactions in the treatment[36,37,38] of the electrostatic theories. Padova[36] has found from solubility studies that cations are larger in methanol than in water solutions, whereas anions tend to be smaller. Friedman,et.al.[37] have investigated volume changes in alcohol-water systems as being related to the hydrocarbon size.

Krestov, et. al.[38] have attributed the decrease in the enthalpies of solution of sodium iodide in methanol, ethanol, acetone, and in aqueous mixtures of the two alcohols, respectively, below 298 K, to changes in the solvent structure as the temperature is decreased.

In light of the inability of researchers to significantly improve the theory of electrostatic interactions over the last few years, it seems reasonable to assume that the specific short-range and more general long-range ion-solvent interactions need to be included in the treatment.

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APPENDIX A: SYMBOLS AND EQUATIONS

There follows a list of the symbols which are presented in the text, particularly within the pertinent equations. The complete enumeration of the equation for the conductance is found immediately after the Glossary. The functions were evaluated according to the Fuoss-Chen treatment[13].

I. GLOSSARY OF SYMBOLS

Symbol	Definition
@	alpha-function of the Onsager coefficient of the limiting law
a, "a"	the ion-size parameter
A	the equivalent conductance
A_{∞}	the equivalent conductance at infinite dilution
b	Bjerrum's distance of closest approach
B	beta-function of the Onsager coefficient of the limiting law
c	the concentration, in equivalents per liter
D	the dielectric constant (the ability of the solvent to hold a charge
E	includes like terms of the electrophoretic and relaxation effects (of the order clnc)
f	the mean activity coefficient of the solute
J_1	like terms in the relaxation and electrophoretic effects (of the order1.5)
J_2	like terms in the relaxation and electrophoretic effects (of the order 1)
k	the Boltzmann constant
K',Ka	the association constant
L	the specific conductivity
n	the number of events from the Poisson equation
N	normality (equivalents per liter)
q	Bjerrum's closest-approach parameter
r	the average density from the Poisson equation; also, the degree of dissociation
R	the resistance of an electrolytic solution
S	the Onsager limiting slope
T	temperature
x	the time interval in the Poisson equation

II. A COMPLETE EVALUATION OF THE FULL FUOSS-ONSAGER EQUATION

1. $A=A_o - Sc^{1/2} + E'c\ln c + J(a)c + J_{3/2}(a)c^{3/2} +$
...

2. $S=@A_o + B$

3. $E' = [E'_1 A_o - (k_e + k_h)E'_2]$

4. $J(a) = s_1(a)A_o + s_2(a)$

5. $s_1(a) = 2E'_1[\ Q^{rel}(b) + \ln 2kq/c^{1/2}]$

6. $s_2(a) = 2E'_2[Q_h(b) + Q_e -$

$(k_h + k_e)\ln 2kq/c^{1/2}$

7. $J_{3/2}(a) = (s_3(a)A_o + s_{4e}(a) +$

$s_{4h}(a))$

8. $@ = 0.8204 \times 10^6 z^{3/2}/(DT)^{3/2}$

9. $B = 82.501 \times z^{3/2}/(DT)^{1/2}n$

10. $E'_1 = 2.9422 \times 10^{12} \times z^3/(DT)^3$

11. $E'_2 = 0.43329 \times 10^8 \times z^3/n(DT)^2$

12. $b = 16.708 \times 10^{-4} \times z/aDT$

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

14. $Q^{rel} = -1/b^3+2/b^2+2/b+0.9074-\ln b$

15. $Q^h = -2/3b \times 0.76685 + \ln b$

16. $Q^e = 1/b^2+6.5/b-0.2676 + \ln b$

17. $k_h=k_e=1$

18. $s_3 = -2kq/c^{1/2} \times E'_1(3..8284/b^3 +$

$4.4748/b^2 + 0.6094/b)$

19. $s_{4e} = -2kq/c^{1/2}E'_2(13.60944/b^2 +$

$0.1712/b)$

20. $s_{4h} = 2kq/c^{1/2}E'_2(2.2761/b^2 + 1.5405/b)$

APPENDIX B: THE EQUIVALENT CONDUCTANCE OF SOME ALKALI-METAL CHLORIDES IN WATER, METHANOL AND ETHANOL, AND IN AQUEOUS ALCOHOL MIXTURES

A= Data calculated by Equation 15

B= Literature or experimental data reported in this research

C= The square root of the concentration

Jervis,et.al. (14)

LiCl in Water

A	B	C
109.39	109.34	.07071
110.57	110.56	.05477
111.34	111.33	.04472
112.39	112.39	.03162
113.13	113.13	.02236

Harned-Owen (8)

NaCl in Water

A	B	C
99.82	106.74	.31623
107.35	111.76	.22361
114.19	115.76	.14142
117.68	118.51	.10001
120.19	120.65	.07071
123.62	123.74	.03162
124.45	124.50	.02236

Foster-Amis (15)

KCl in Water

A	B	C
128.47	133.52	.21571
139.79	141.17	.10161
139.82	140.92	.10135
142.82	142.57	.07102
144.94	145.29	.04962
145.61	146.00	.04301
147.29	147.54	.02596
147.74	148.39	.02145
148.68	149.14	.01194

Stimatze (20)

LiCl in Water

A	B	C
109.24	105.70	.06581
111.90	108.90	.03808
112.89	117.30	.02511
113.78	119.60	.01449
114.21	120.80	.00949
114.42	127.40	.00707

Stimatze (20)

NaCl in Water

A	B	C
120.68	119.30	.07099
122.14	115.80	.05273
123.73	120.10	.03194
125.19	143.10	.01414
125.52	132.10	.01049
125.82	137.50	.00707

Stimatze (20)

KCl in Water

A	B	C
136.24	139.50	.14142
140.26	144.10	.10001
142.04	146.90	.08167
143.09	149.40	.07071
143.82	148.10	.06325
144.77	150.30	.05348
147.34	149.10	.02704

Werblan,et.al. (10)

CsCl in Water

A	B	C
144.92	144.84	.07076
145.90	145.93	.06004
146.99	146.93	.05004
147.52	146.46	.04475
147.99	147.94	.04003
148.52	148.48	.03467
148.98	148.94	.03001
149.52	149.50	.02452
149.58	149.96	.02001

Jervis,et.al. (14)

LiCl in Methanol

A	B	C
77.64	76.73	.07071
80.43	79.73	.05477
82.33	81.74	.04472
84.97	84.52	.03162
86.95	86.65	.02236
88.78	88.70	.01414
89.72	89.74	.01001

Evers-Knox (16)

KCl in Methanol

A	B	C
78.39	89.25	.06383
85.81	92.40	.05004
89.87	94.35	.04165
93.07	96.08	.03451
95.64	97.67	.02835
97.67	99.02	.02310
98.79	99.85	.02004
99.94	100.70	.01676
100.75	101.34	.01435
101.44	101.89	.01224
102.11	102.44	.01009
102.49	102.74	.00880

Stimatze (20)

CsCl in Water

A	B	C
144.86	136.20	.08654
146.61	145.50	.06099
148.72	246.10	.02721
150.12	138.00	.02001
150.45	332.70	.01049
151.18	127.20	.00837

Evers-Knox (16)

NaCl in Methanol

A	B	C
69.79	82.18	.06775
79.84	85.99	.04841
84.92	88.44	.03711
88.27	90.33	.02888
90.05	91.39	.02413
91.71	92.51	.01943
92.66	93.19	.01661
94.14	94.30	.01194
94.85	94.86	.00957
95.39	95.31	.00767
73.75	82.94	.06319
81.17	86.19	.04729
83.62	87.42	.04153
87.37	89.55	.03211
89.33	90.77	.02679
90.77	91.73	.02267
92.12	92.74	.01861
93.11	93.51	.01551
93.84	94.09	.01313
94.37	94.52	.01133
95.03	95.07	.00907
95.41	95.41	.00769
95.73	95.71	.00654

Evers-Knox (16)

KCl in Methanol

A	B	C
74.93	87.64	.07176
81.36	90.11	.06008
86.39	92.34	.05011
91.46	94.97	.03904
94.90	96.99	.03077
96.55	99.08	.02652
98.50	99.45	.02121
99.44	100.14	.01847
100.22	100.75	.01617
101.24	101.60	.01301
101.87	102.11	.01097
102.41	102.60	.00918
102.72	102.88	.00811

Werblan,et.al. (10)

CsCl in Methanol

A	B	C
94.16	96.51	.04998
96.38	98.20	.04470
98.33	99.67	.03999
100.47	101.37	.03460
102.25	102.83	.02998
104.27	104.60	.02449
105.87	106.03	.01998
107.80	107.89	.01416

Foster-Amis (15)

KCl in 60.7% Methanol

A	B	C
61.88	59.72	.22473
63.27	62.02	.17643
68.77	68.60	.06951
71.13	71.45	.03732

Foster-Amis (15)

KCl in 20.2% Methanol

A	B	C
83.93	87.57	.22805
92.29	93.87	.08154
94.37	95.53	.05468
96.01	96.79	.03501
96.19	97.07	.03302
96.87	97.38	.02522
97.21	97.69	.02151
98.01	97.83	.01274

Foster-Amis (15)

KCl in 40.2% Methanol

A	B	C
67.36	66.84	.21374
69.27	69.38	.15738
72.61	72.69	.08644
74.76	74.83	.05017
75.77	75.96	.03483
75.98	75.79	.03299
76.64	76.58	.02199
76.99	77.18	.01689
77.49	77.35	.00981

Foster-Amis (15)

KCl in 60.7% Methanol

A	B	C
71.78	71.84	.02921
72.29	72.34	.02276
72.81	72.77	.01652
73.34	72.64	.01026
73.68	73.85	.00612

Foster-Amis (15)

KCl in 80.7% Methanol

A	B	C
72.84	56.87	.26316
79.93	78.76	.09021
84.31	83.94	.05042
85.05	84.74	.04449
85.95	85.90	.03741
86.93	86.86	.02991
87.39	87.66	.02645
88.49	88.86	.01833

Werblan,et.al. (10)

CsCl in 16.49% Methanol

A	B	C
99.55	99.82	.07087
100.40	100.60	.06005
101.19	101.32	.05004
101.59	101.70	.04478
101.94	102.02	.04026
102.73	102.76	.02998
103.14	103.16	.02454
103.48	103.48	.02004

Werblan,et.al. (10)

CsCl in 54.24% Methanol

A	B	C
69.55	69.58	.07078
70.59	70.55	.06005
72.01	71.93	.04477
72.44	72.36	.04005
72.92	72.85	.03467
73.33	73.26	.03006
73.81	73.77	.02452
74.19	74.18	.02003
74.68	74.71	.01415

Foster-Amis (15)

KCl in Methanol

A	B	C
76.11	65.37	.22917
87.02	80.22	.11414
92.57	89.83	.06378
96.65	96.60	.03505
98.58	99.67	.02186

Werblan,et.al. (10

CsCl in 30.77% Methanol

A	B	C
79.99	80.32	.07087
80.80	81.04	.06006
81.54	81.71	.05004
81.93	82.06	.04477
82.23	82.37	.04003
82.65	82.72	.03470
82.98	83.03	.03006
83.37	83.39	.02457
83.69	83.70	.02000

Werblan,et.al. (10

CsCl in 80.58% Methanol

A	B	C
74.90	76.26	.06007
76.70	77.62	.05005
77.62	78.34	.04478
78.43	78.99	.04004
79.32	79.71	.03469
80.08	80.36	.03003
80.95	81.11	.02453
81.64	81.74	.02003

Werblan,et.al. (10)

CsCl in 94.12% Methanol

A	B	C
83.35	86.50	.05993
86.83	88.50	.04994
87.92	89.55	.04467
89.26	90.47	.03995
90.73	91.50	.03460
91.97	92.48	.02990
93.34	93.60	.02447
94.42	94.49	.02000

Kay-Broadwater(17)

KCl in 5.09% Ethanol

A	B	C
121.36	121.93	.07696
122.20	122.61	.06801
122.86	123.16	.06077
123.56	123.77	.05313
124.37	124.48	.04423
125.19	125.24	.03500
126.21	126.39	.02344

Kay-Broadwater(17)

KCl in 10.10% Ethanol

A	B	C
105.59	106.30	.07713
106.18	106.73	.07020
106.81	107.24	.06279
107.44	107.77	.05519
108.09	108.30	.04724
108.81	108.95	.03841
109.73	109.89	.02692

Kay-Broadwater(17)

KCl in 15.77% Ethanol

A	B	C
90.77	92.12	.09621
91.55	92.68	.08670
92.20	93.18	.07871
92.81	93.60	.07115
93.37	94.01	.06404
94.06	94.53	.05513
94.82	95.13	.04527
95.90	96.08	.03080

Kay-Broadwater(17)

KCl in 18.21% Ethanol

A	B	C
87.48	88.31	.07501
88.05	88.73	.06789
88.56	89.12	.06141
89.13	89.55	.05420
89.71	90.02	.04655
90.39	90.58	.03755
91.20	91.38	.02639

Kay-Broadwater(17)

KCl in 23.23% Ethanol

A	B	C
80.03	80.08	.07655
80.47	80.45	.06949
80.87	80.79	.06294
81.31	81.21	.05568
81.81	81.67	.04750
82.37	82.23	.03805
83.03	83.02	.02674

Kay-Broadwater(17)

KCl in 26.84% Ethanol

A	B	C
72.28	74.35	.10094
72.82	74.65	.09437
73.60	75.13	.08459
74.34	75.57	.07514
74.92	75.95	.06748
75.73	76.49	.05661
76.60	77.12	.04470
77.67	77.91	.02920

Hawes-Kay (18)

KCl in 38.37% Ethanol

A	B	C
49.66	52.249	.11571
50.39	52.603	.10718
51.04	52.933	.09942
51.66	53.260	.09185
52.54	53.763	.08083
53.32	54.240	.07058
54.28	54.870	.05745
55.70	55.895	.03731

Hawes-Kay (18)

KCl in 39.91% Ethanol

A	B	C
49.32	51.241	.11112
49.98	51.609	.10250
50.55	51.942	.09492
51.21	52.345	.08599
51.95	52.826	.07575
52.68	53.325	.06533
53.62	54.010	.05137
54.74	54.889	.03386

Kay-Broadwater(17)

KCl in 37.93% Ethanol

A	B	C
61.61	64.46	.09563
62.06	64.68	.09090
62.81	65.03	.08282
63.62	65.44	.07389
64.42	65.88	.06468
65.27	66.37	.04347
66.15	66.92	.04354
67.16	67.62	.02998

Hawes-Kay (18)

KCl in 60.25% Ethanol

A	B	C
36.77	40.164	.10249
38.17	40.832	.09082
38.95	41.235	.08405
39.83	41.711	.07634
40.48	42.125	.06968
41.71	42.828	.05895
42.83	43.577	.04788
44.01	44.421	.03552

Hawes-Kay (18)

KCl in 79.29% Ethanol

A	B	C
27.47	34.330	.09584
29.18	35.019	.08789
30.44	35.558	.08193
31.98	36.255	.07448
33.40	36.938	.06749
35.10	37.820	.05883
36.72	38.737	.05023
38.63	39.919	.03955

Hawes-Kay (18)

KCl in 87.92% Ethanol

A	B	C
20.03	33.115	.08634
22.04	33.734	.08072
24.39	34.501	.07403
26.69	35.308	.06736
28.78	36.093	.06117
31.36	37.137	.05335
34.02	38.315	.04495
36.65	39.600	.03612

Hawes-Kay (18)

CsCl in 40.38% Ethanol

A	B	C
51.95	53.111	.08328
52.41	53.413	.07754
52.95	53.778	.07066
53.39	54.09	.06494
53.92	54.46	.05806
54.44	54.862	.05100
55.10	55.377	.04184
55.94	56.075	.02964

Hawes-Kay (18)

CsCl in 60.13% Ethanol

A	B	C
39.36	41.652	.08309
40.08	42.057	.07720
40.82	42.522	.07099
41.61	42.989	.06433
42.27	43.408	.05863
43.22	44.057	.05011
44.34	44.867	.03960
45.44	45.712	.02864

Hawes-Kay (18)

CsCl in 73.90% Ethanol

A	B	C
33.43	36.394	.08363
34.36	36.912	.07805
35.37	37.498	.07195
36.34	38.094	.06591
37.39	38.774	.05924
38.51	39.536	.05198
39.87	40.529	.04276
41.74	42.023	.02914

Hawes-Kay (18)

CsCl in 84.33% Ethanol

A	B	C
28.03	33.752	.07964
29.64	34.553	.07312
31.13	35.334	.06706
32.44	36.059	.06166
33.81	36.847	.05601
35.43	37.83	.04922
37.54	39.191	.04019
40.35	41.174	.02749

Hawes-Kay (18)

CsCl in 91.25% Ethanol

A	B	C
25.40	32.429	.07509
27.18	33.301	.06929
28.87	34.177	.06378
30.63	35.137	.05803
32.75	36.357	.05114
34.92	37.692	.04403
37.68	39.514	.03487
40.16	41.282	.02633

Haves-Kay (18)

CsCl in 93.24% Ethanol

A	B	C
24.04	31.642	.07632
26.14	32.665	.06975
28.16	33.709	.06348
30.20	34.833	.05715
32.25	36.027	.05082
34.43	37.38	.04408
36.84	38.968	.03661
39.97	41.2	.02662

Pedersen-Amis (19)

CsCl in Water

A	B	C
137.65	145.88	.08322
140.60	146.77	.07246
143.09	147.51	.06258
145.52	148.80	.05191
147.91	150.12	.04019
149.38	150.92	.03217
152.12	152.6	.01427

Pedersen-Amis (19)

CsCl in 58.3% Ethanol

A	B	C
40.86	42.888	.07989
42.70	44.004	.06386
44.37	45.169	.04844
45.06	45.621	.04179
46.21	46.26	.03013
47.39	47.41	.01653

Haves-Kay (18)

CsCl in 100% Ethanol

A	B	C
25.30	31.777	.06200
27.93	33.270	.05507
30.66	34.936	.04805
33.64	36.887	.04059
37.55	39.687	.03088

Pedersen-Amis (19)

CsCl in 22.4% Ethanol

A	B	C
72.55	78.190	.07015
74.68	78.864	.06011
76.28	79.316	.05184
78.04	80.045	.04156
79.38	80.358	.03261
81.08	81.43	.01860

Pedersen-Amis (19)

CsCl in 42.7% Ethanol

A	B	C
49.49	51.268	.08993
50.66	52.043	.07595
51.16	52.239	.06984
53.17	53.787	.04376
54.19	54.40	.02941
54.94	55.05	.01787

Kay-Broadwater (17)

CsCl in 15.74% Ethanol

A	B	C
93.88	95.00	.08637
94.43	95.39	.07979
95.07	95.86	.07213
95.62	96.29	.06546
96.43	96.92	.05330
97.11	97.47	.04670
97.88	98.13	.03693
98.98	99.06	.02215

Kay-Broadwater (17

CsCl in 26.74% Ethanol

A	B	C
74.80	76.62	.09187
75.48	77.03	.08398
76.20	77.49	.07544
76.93	77.97	.06664
77.74	78.53	.05639
78.41	79.02	.04775
79.30	79.69	.03584
80.24	80.40	.02570

Kay-Broadwater (17)

CsCl in 26.87% Ethanol

A	B	C
76.57	77.67	.06726
77.25	78.21	.05923
78.36	78.98	.04539
79.27	79.75	.03356
80.18	80.31	.02095

Kay-Broadwater (17

CsCl in 38.07% Ethanol

A	B	C
64.51	66.14	.08708
65.21	66.58	.07818
65.92	67.05	.06882
66.59	67.51	.05984
67.32	68.04	.04968
68.11	68.61	.03849
69.21	69.38	.02191

APPENDIX C:Graphical Results*

Dark Squares	The literature values
Crosses	The values calculated via Equation 15
Diamonds	Experimental values
Circles	The values which were calculated using the activity of the solute, instead of the concentration.

* The graphs are in much the same order as the data in Appendix B.

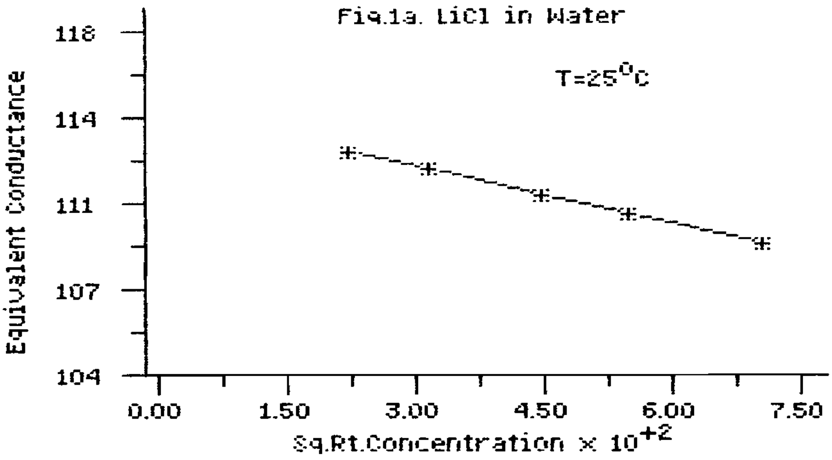

Fig.1a. LiCl in Water

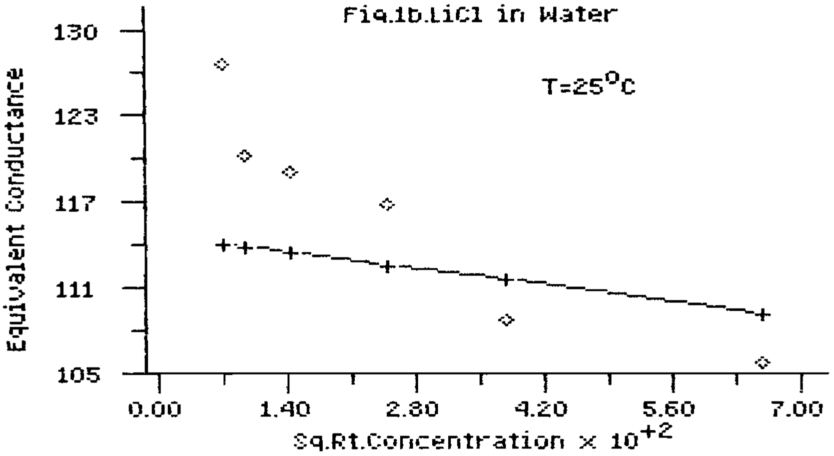

Fig.1b.LiCl in Water

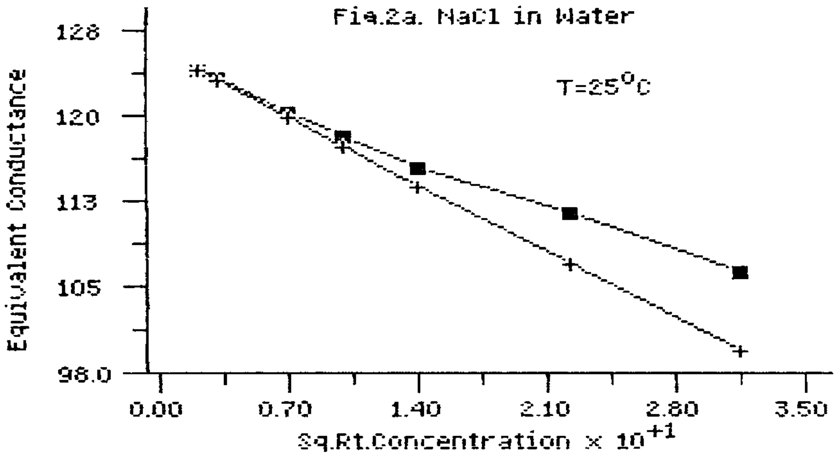

Fig.2a. NaCl in Water

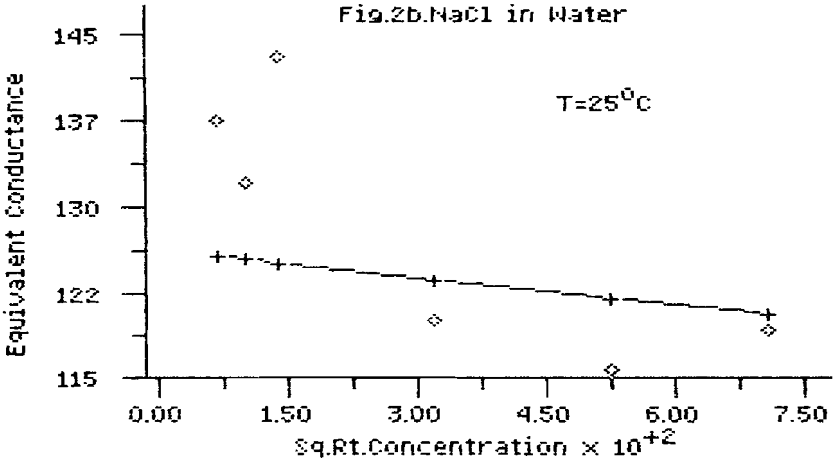

Fig.2b.NaCl in Water

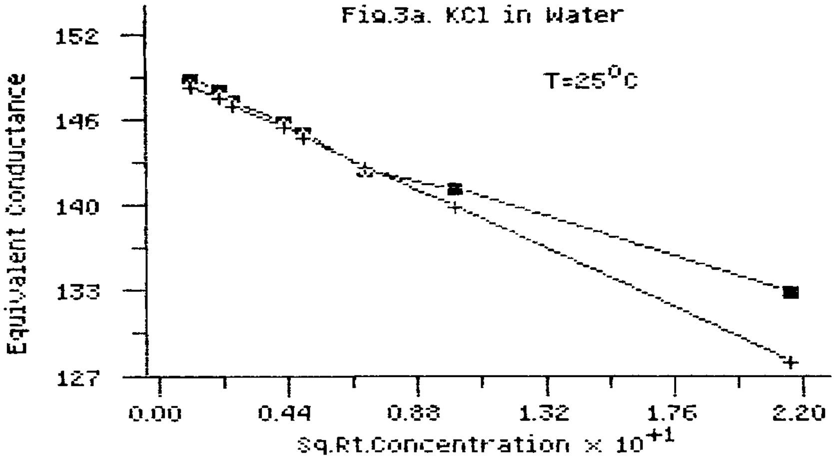
Fig.3a. KCl in Water
T=25°C
Equivalent Conductance
152
146
140
133
127
0.00
0.44
0.88
1.32
1.76
2.20
Sq.Rt.Concentration × 10^{+1}

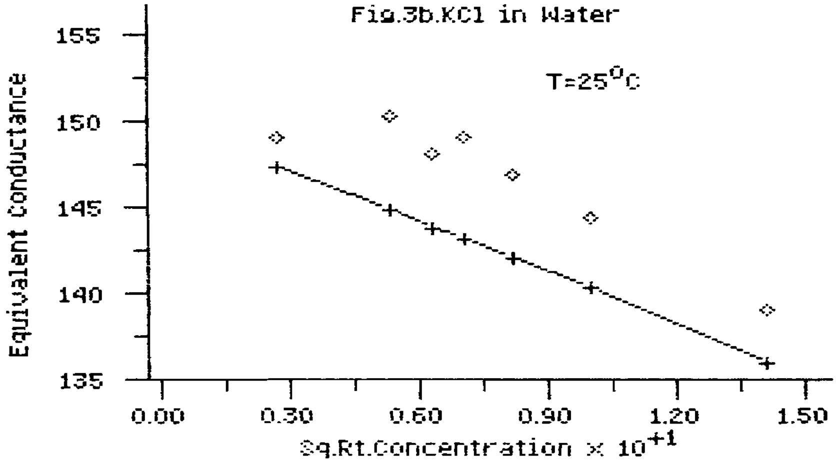
Fig.3b.KCl in Water
T=25°C
Equivalent Conductance
155
150
145
140
135
0.00
0.30
0.60
0.90
1.20
1.50
Sq.Rt.Concentration × 10^{+1}

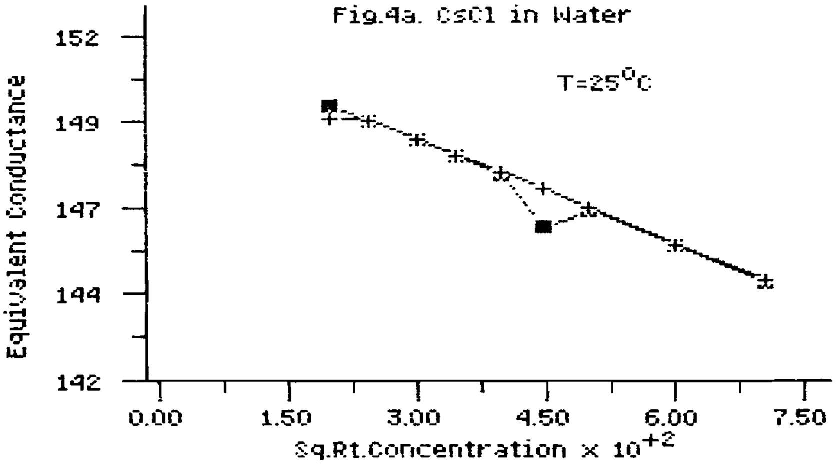
Fig.4a. CsCl in Water
T=25°C
Equivalent Conductance
152
149
147
144
142
0.00
1.50
3.00
4.50
6.00
7.50
Sq.Rt.Concentration × 10+2

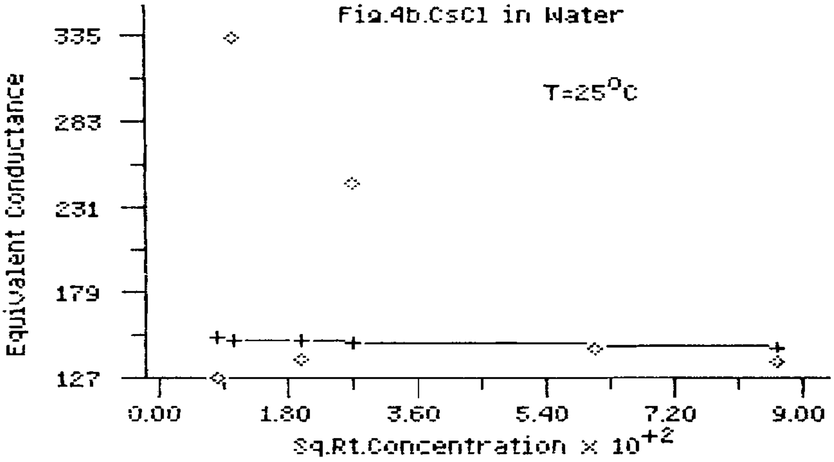
Fig.4b.CsCl in Water
T=25°C
Equivalent Conductance
335
283
231
179
127
0.00
1.80
3.60
5.40
7.20
9.00
Sq.Rt.Concentration × 10+2

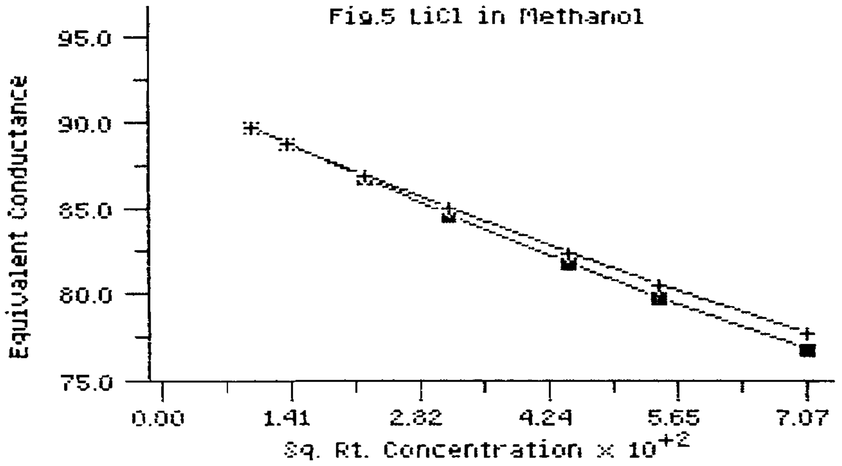
Fig.5 LiCl in Methanol

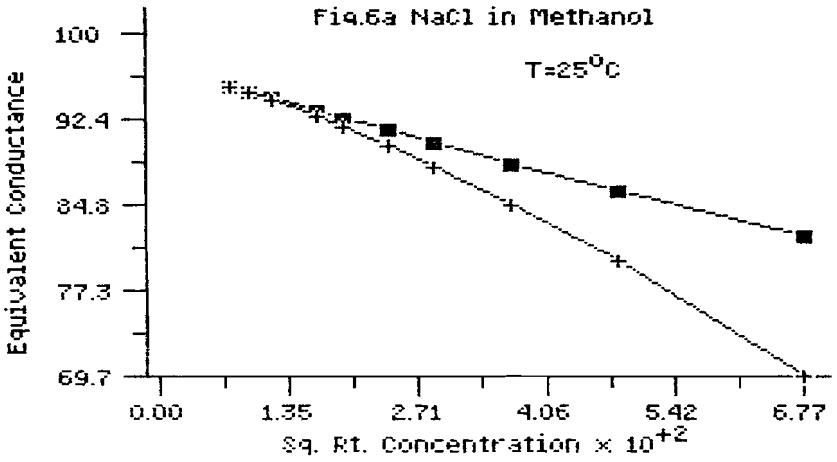
Fig.6a NaCl in Methanol

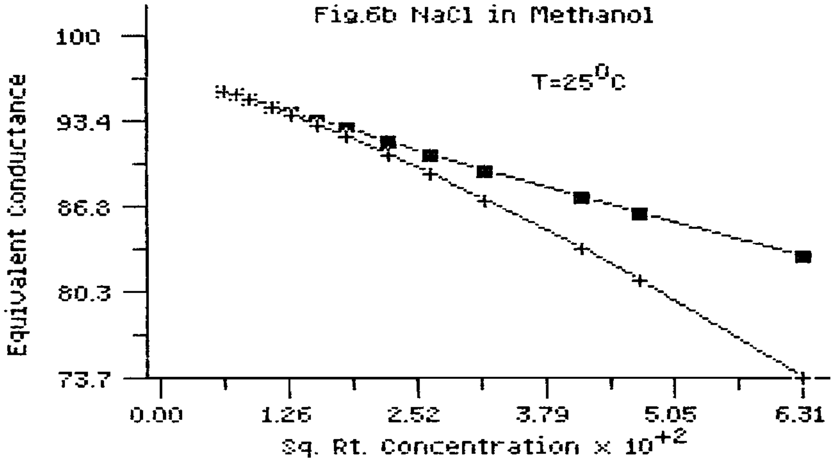

Fig.6b NaCl in Methanol

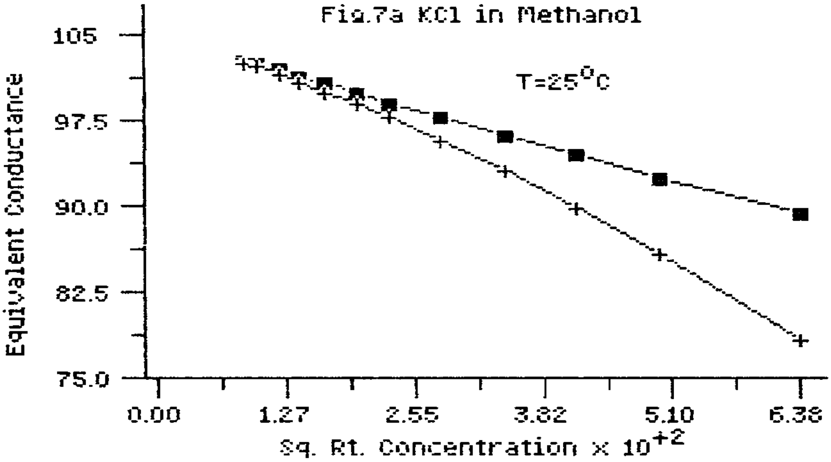

Fig.7a KCl in Methanol

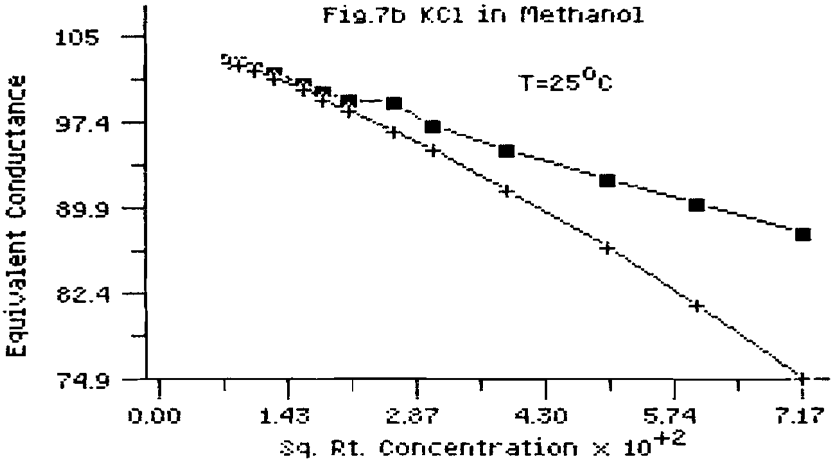
Fig.7b KCl in Methanol
T=25°C
Equivalent Conductance
105
97.4
89.9
82.4
74.9
0.00
1.43
2.87
4.30
5.74
7.17
Sq. Rt. Concentration × 10+2

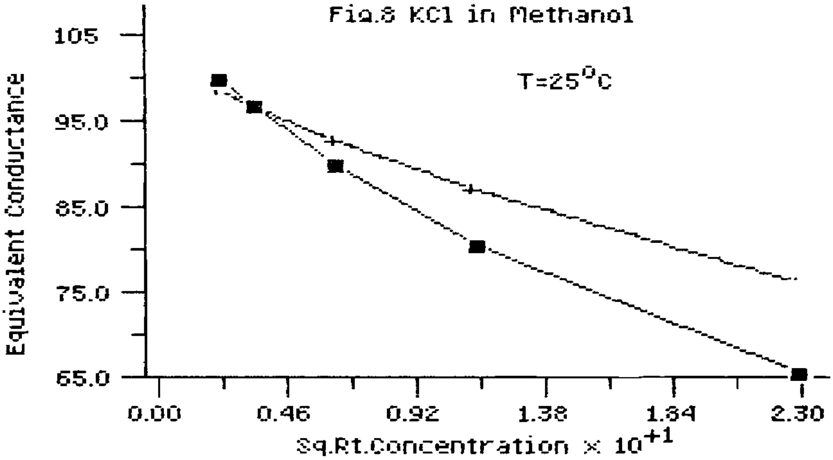
Fig.8 KCl in Methanol
T=25°C
Equivalent Conductance
105
95.0
85.0
75.0
65.0
0.00
0.46
0.92
1.38
1.84
2.30
Sq.Rt.Concentration × 10+1

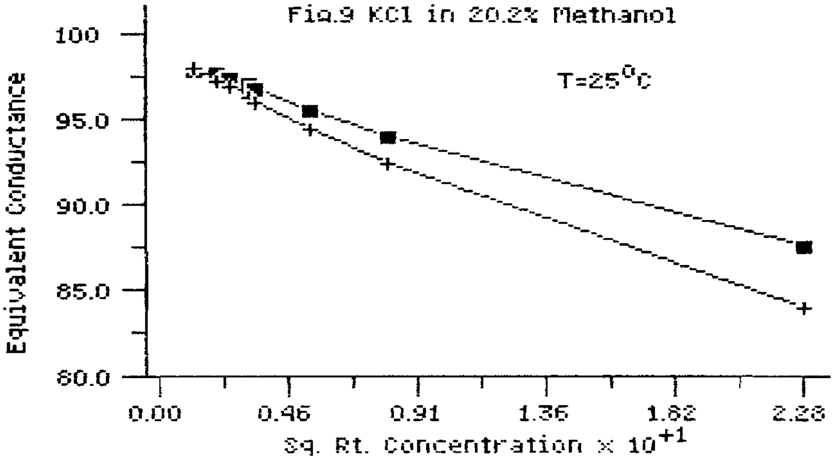
Fig.9 KCl in 20.2% Methanol
T=25⁰C
Equivalent Conductance
100
95.0
90.0
85.0
80.0
0.00
0.46
0.91
1.36
1.82
2.28
Sq. Rt. Concentration x 10+1

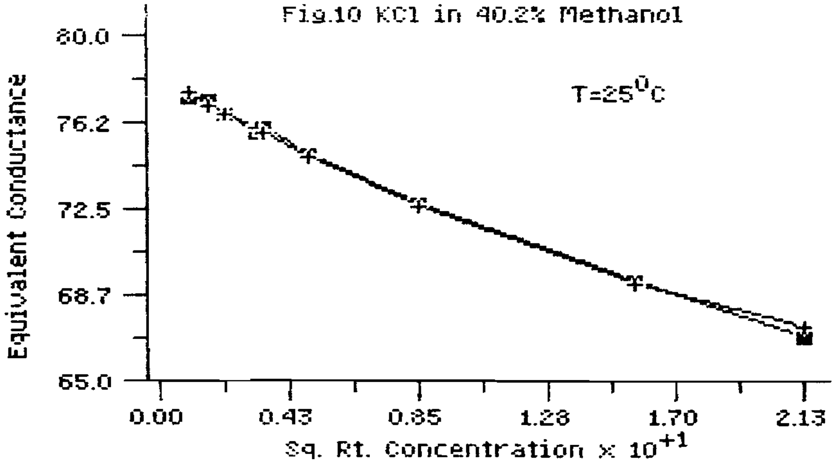
Fig.10 KCl in 40.2% Methanol
T=25⁰C
Equivalent Conductance
80.0
76.2
72.5
68.7
65.0
0.00
0.43
0.85
1.28
1.70
2.13
Sq. Rt. Concentration x 10+1

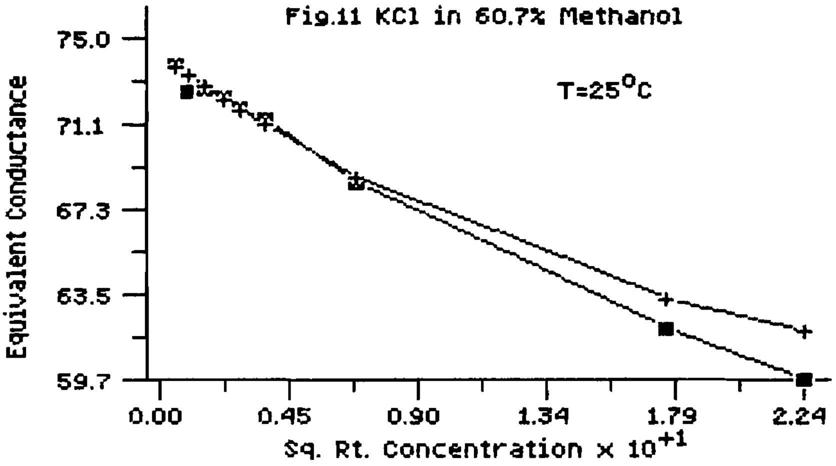
Fig.11 KCl in 60.7% Methanol

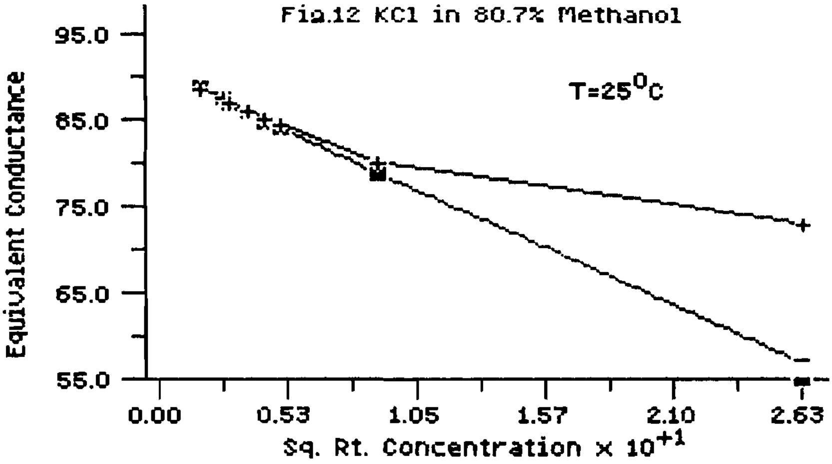
Fig.12 KCl in 80.7% Methanol

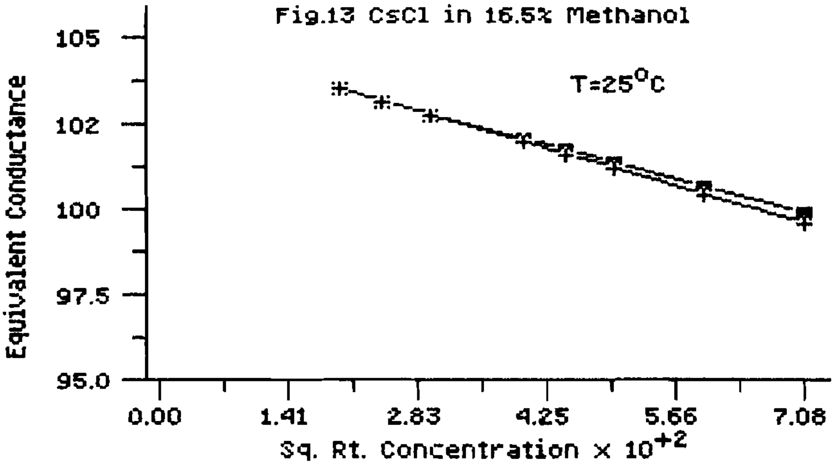

Fig.13 CsCl in 16.5% Methanol

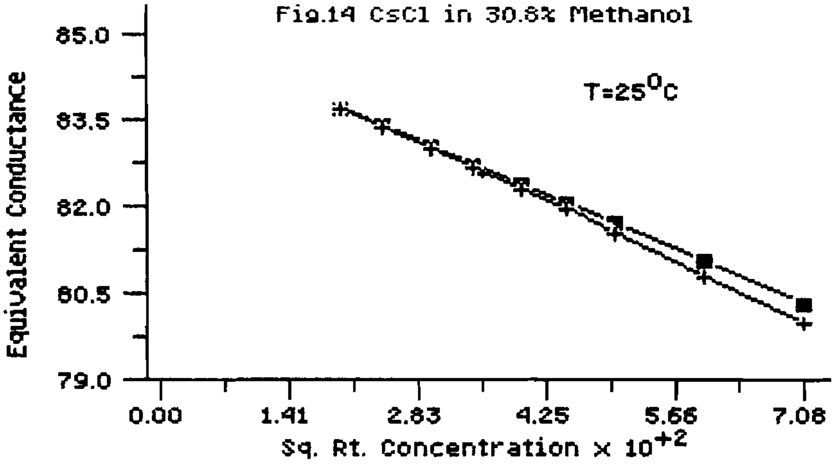

Fig.14 CsCl in 30.8% Methanol

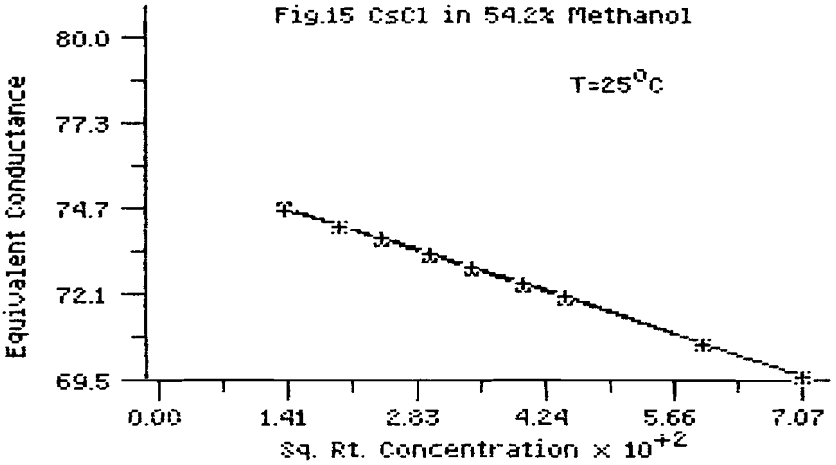

Fig.15 CsCl in 54.2% Methanol

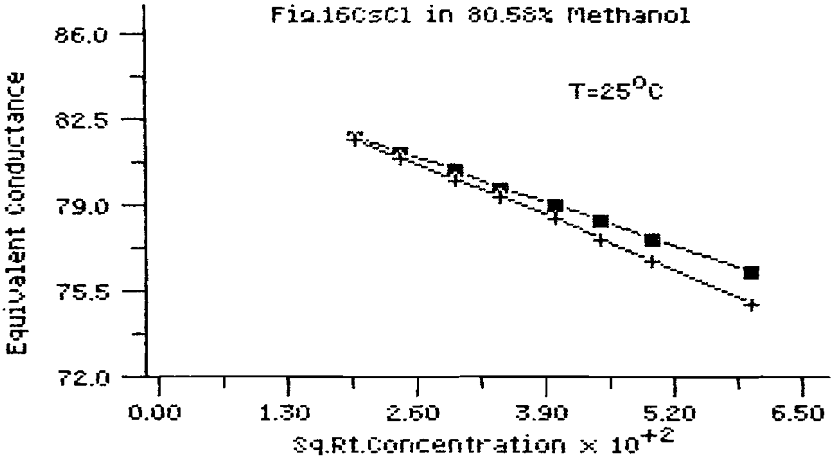

Fig.16CsCl in 80.58% Methanol

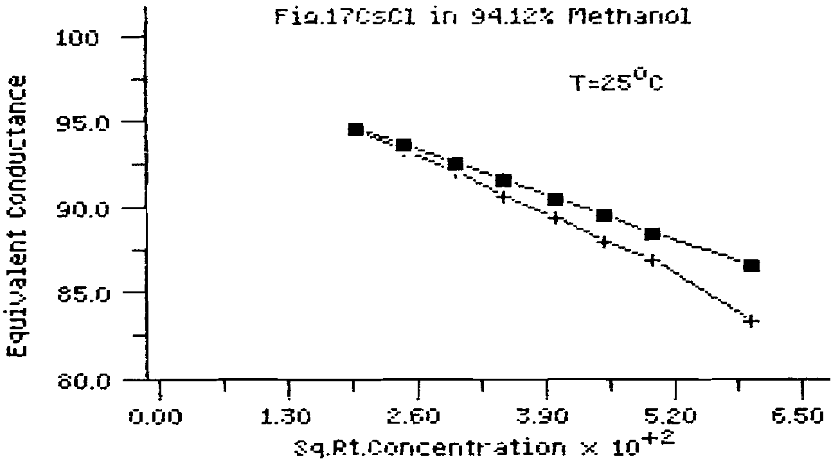

Fig.17CsCl in 94.12% Methanol

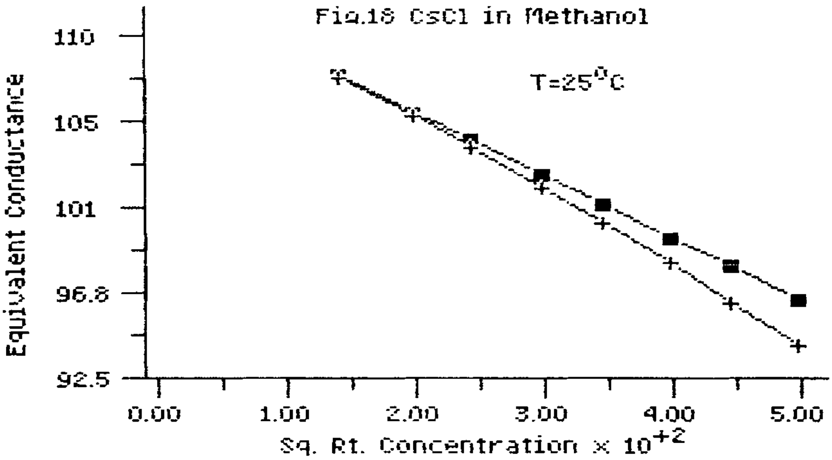

Fig.18 CsCl in Methanol

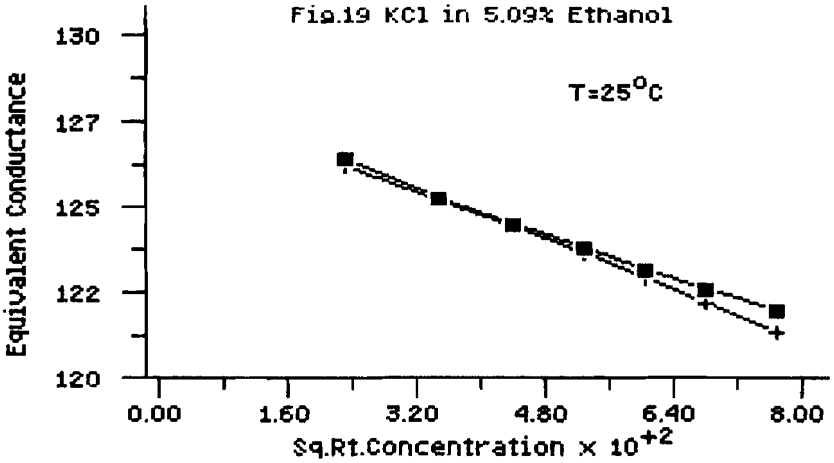

Fig.19 KCl in 5.09% Ethanol

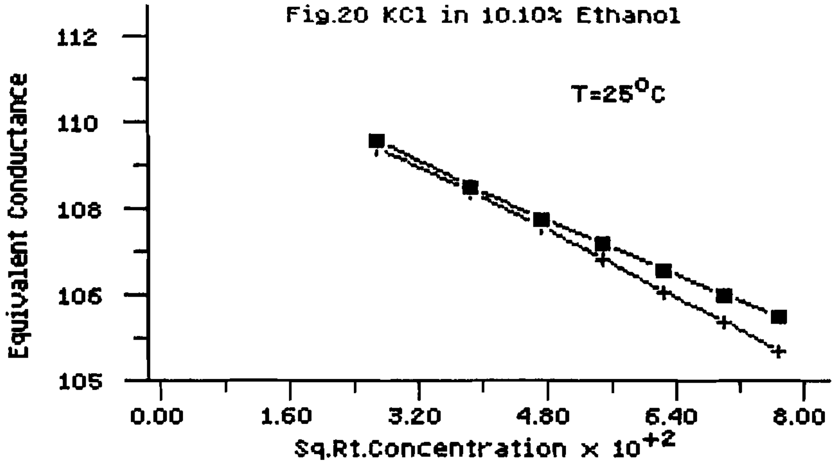

Fig.20 KCl in 10.10% Ethanol

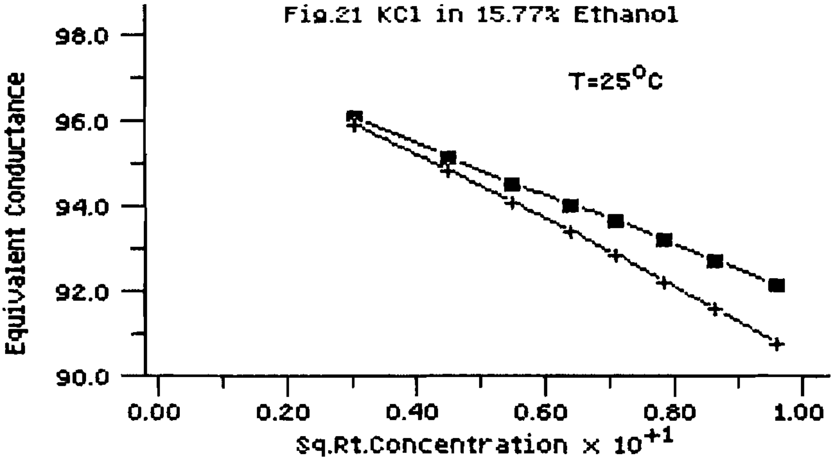

Fig.21 KCl in 15.77% Ethanol

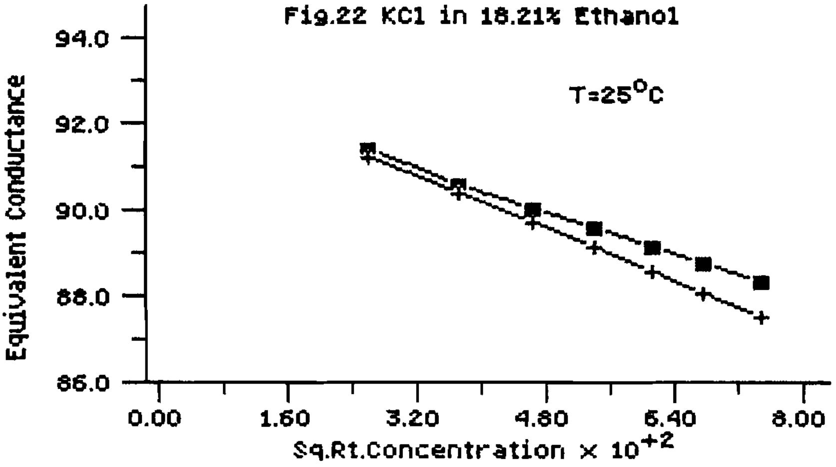

Fig.22 KCl in 18.21% Ethanol

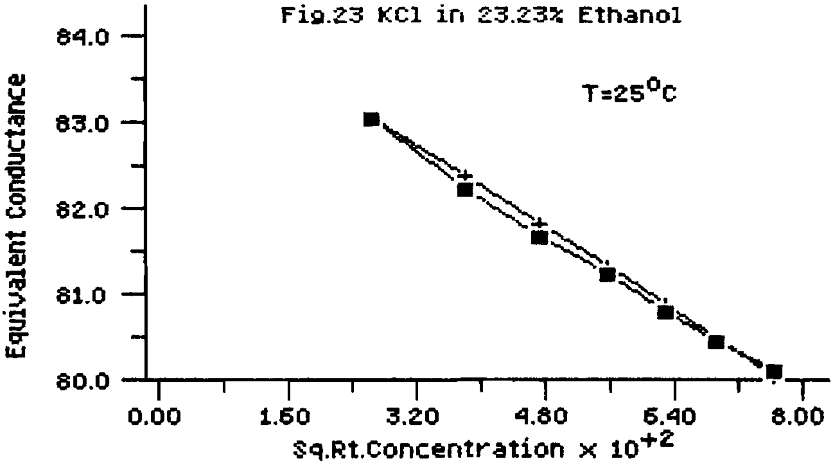
Fig.23 KCl in 23.23% Ethanol
T=25°C
Equivalent Conductance
84.0
83.0
82.0
81.0
80.0
0.00
1.60
3.20
4.80
6.40
8.00
Sq.Rt.Concentration × 10+2

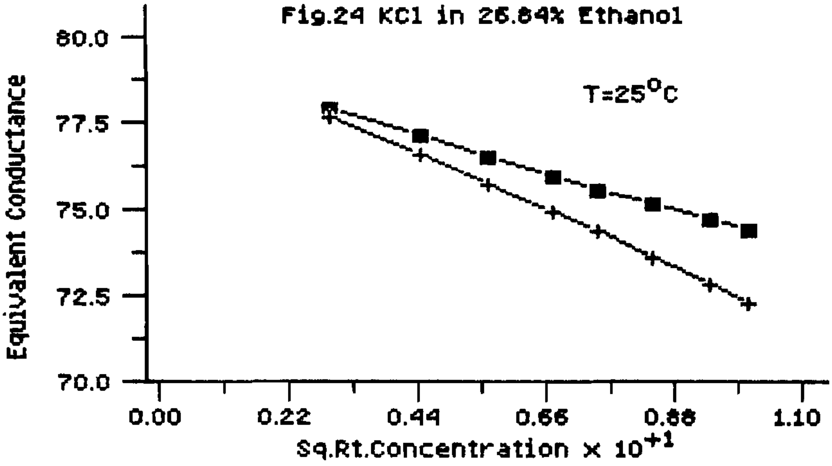
Fig.24 KCl in 26.84% Ethanol
T=25°C
Equivalent Conductance
80.0
77.5
75.0
72.5
70.0
0.00
0.22
0.44
0.66
0.88
1.10
Sq.Rt.Concentration × 10+1

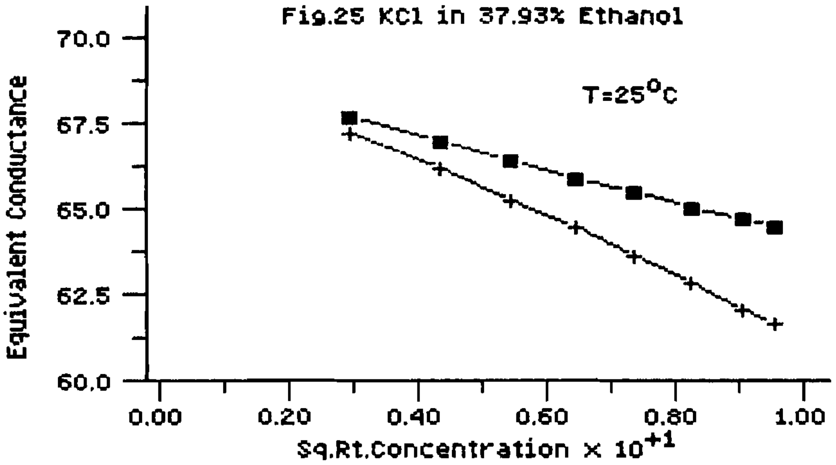
Fig.25 KCl in 37.93% Ethanol

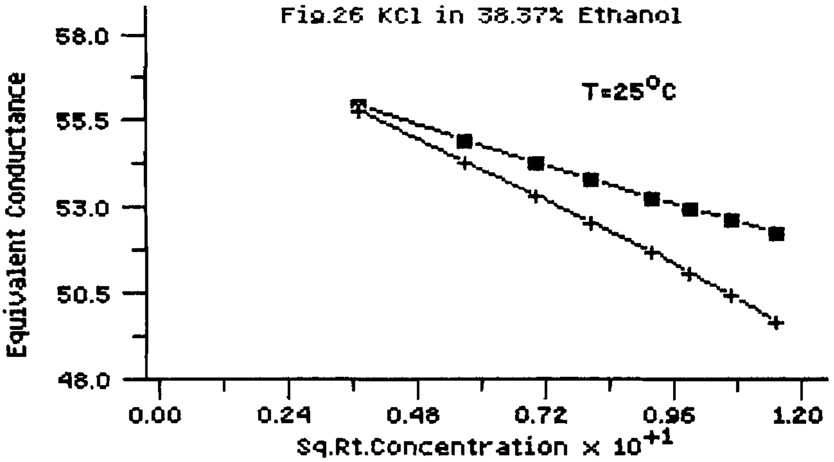
Fig.26 KCl in 38.37% Ethanol

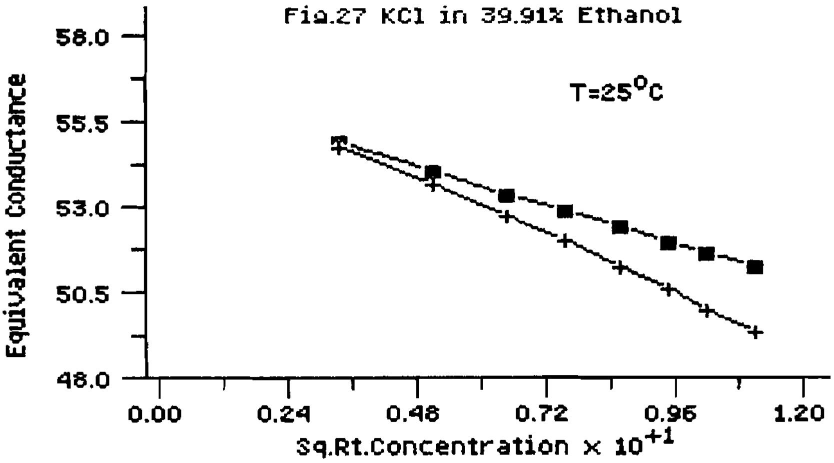

Fig.27 KCl in 39.91% Ethanol

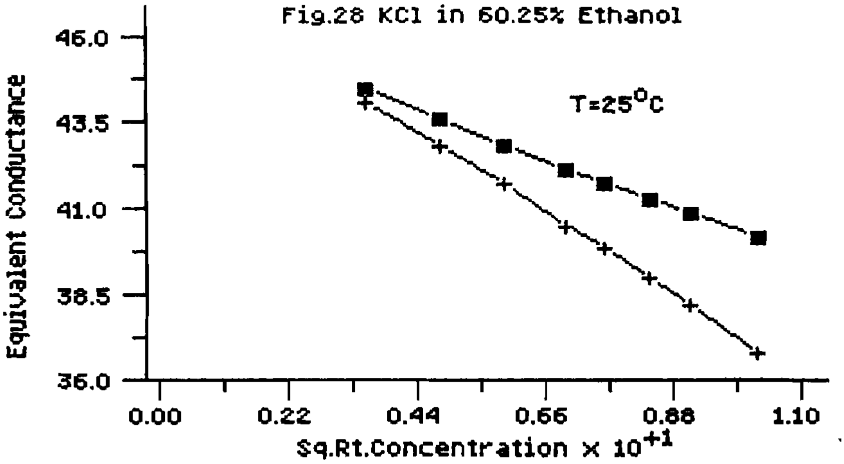

Fig.28 KCl in 60.25% Ethanol

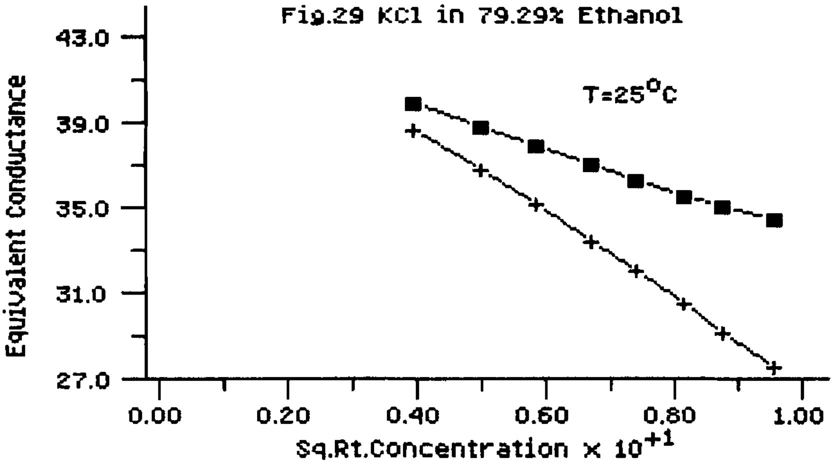

Fig.29 KCl in 79.29% Ethanol

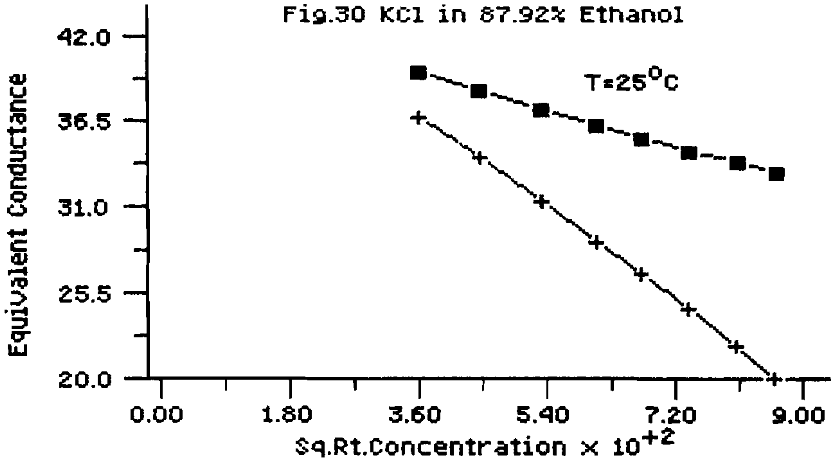

Fig.30 KCl in 87.92% Ethanol

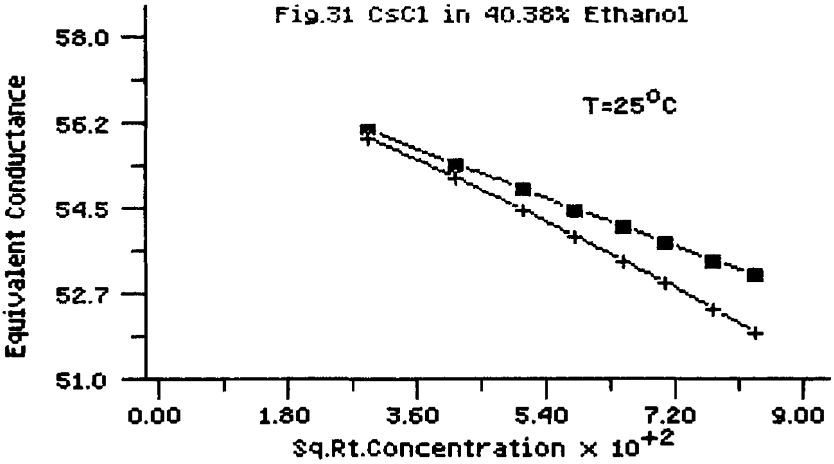
Fig.31 CsCl in 40.38% Ethanol

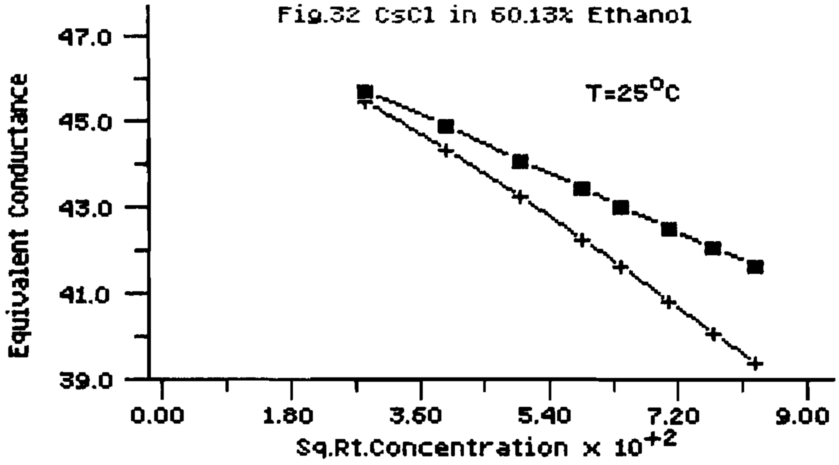
Fig.32 CsCl in 60.13% Ethanol

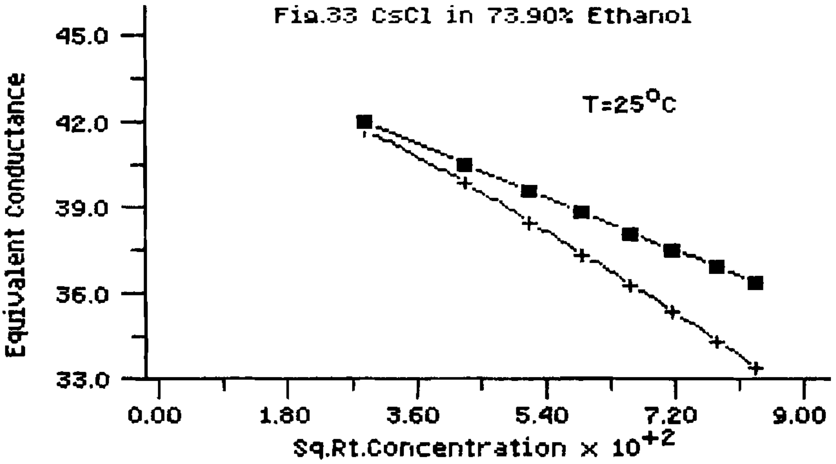

Fig.33 CsCl in 73.90% Ethanol

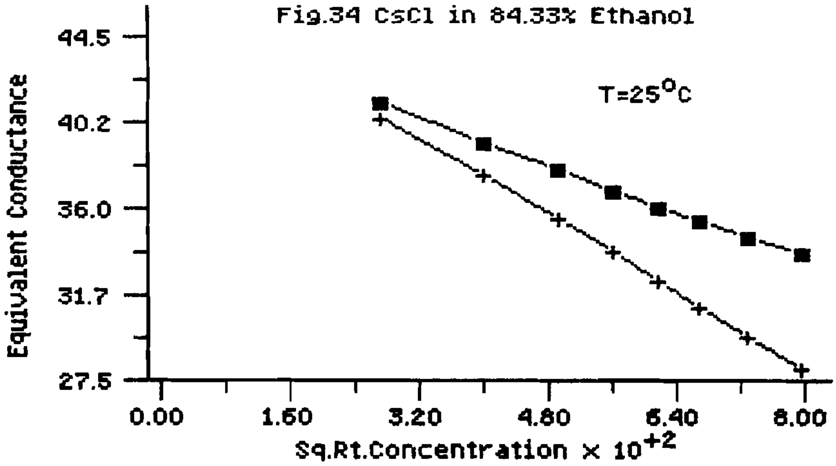

Fig.34 CsCl in 84.33% Ethanol

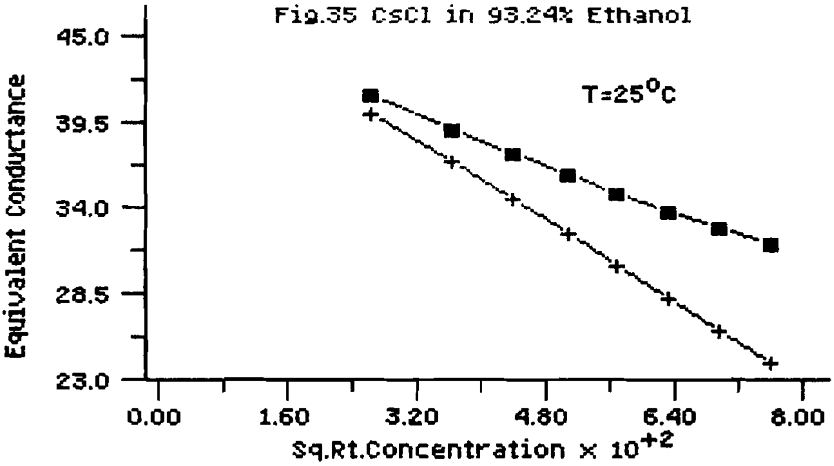
Fig.35 CsCl in 93.24% Ethanol
T=25°C
Equivalent Conductance
45.0
39.5
34.0
28.5
23.0
0.00
1.60
3.20
4.80
6.40
8.00
Sq.Rt.Concentration × 10+2

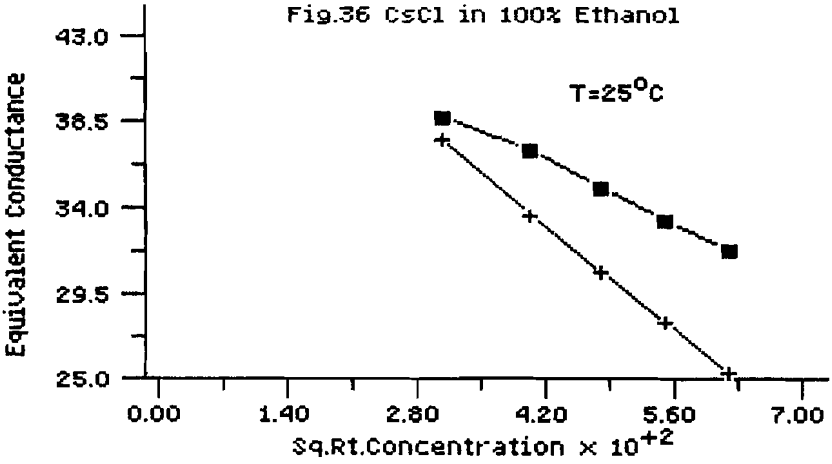
Fig.36 CsCl in 100% Ethanol
T=25°C
Equivalent Conductance
43.0
38.5
34.0
29.5
25.0
0.00
1.40
2.80
4.20
5.60
7.00
Sq.Rt.Concentration × 10+2

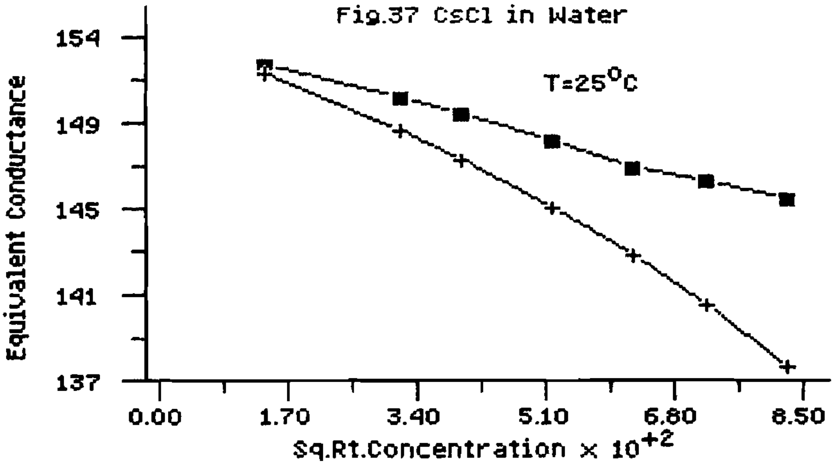

Fig.37 CsCl in Water

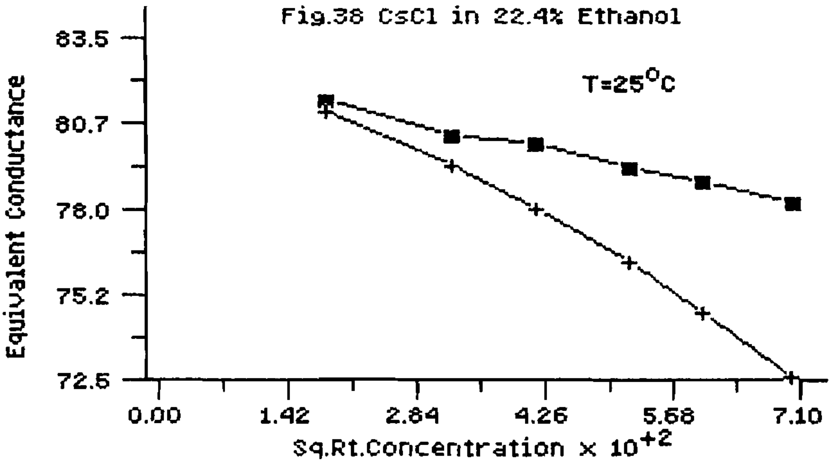

Fig.38 CsCl in 22.4% Ethanol

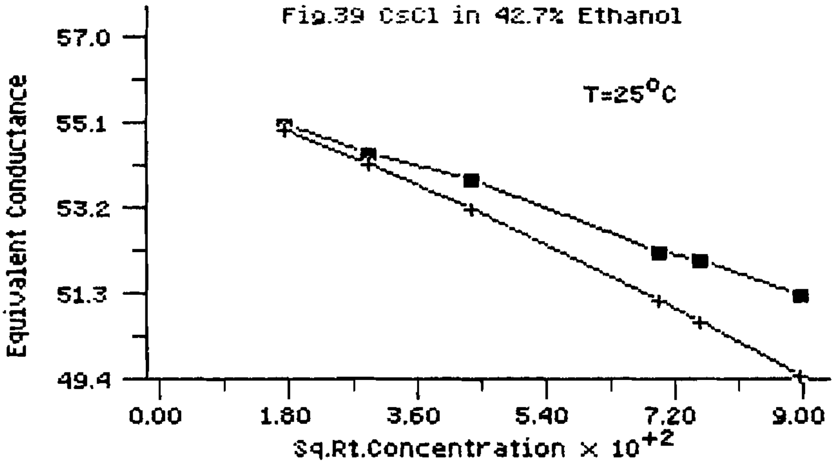
Fig.39 CsCl in 42.7% Ethanol

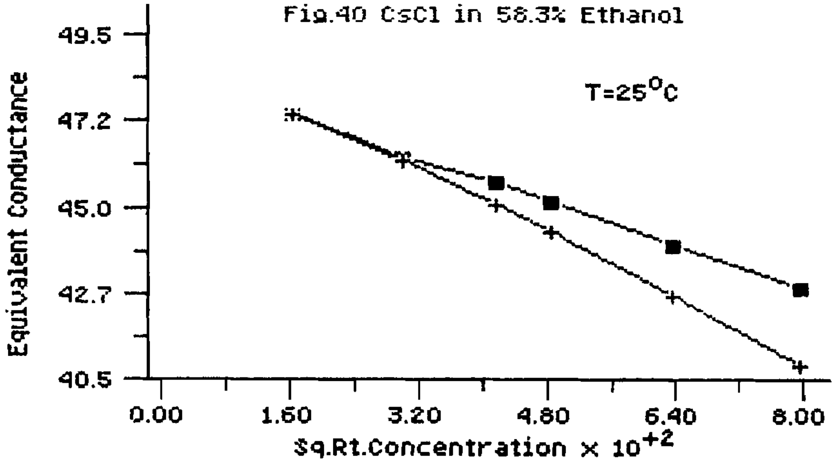
Fig.40 CsCl in 58.3% Ethanol

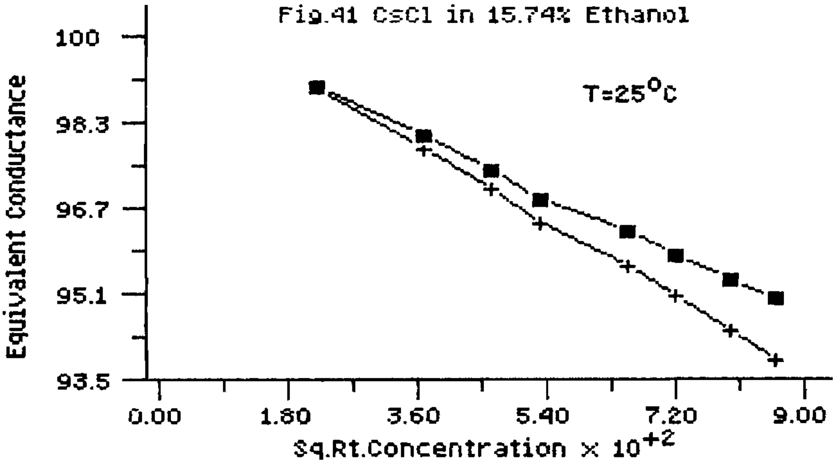
Fig.41 CsCl in 15.74% Ethanol

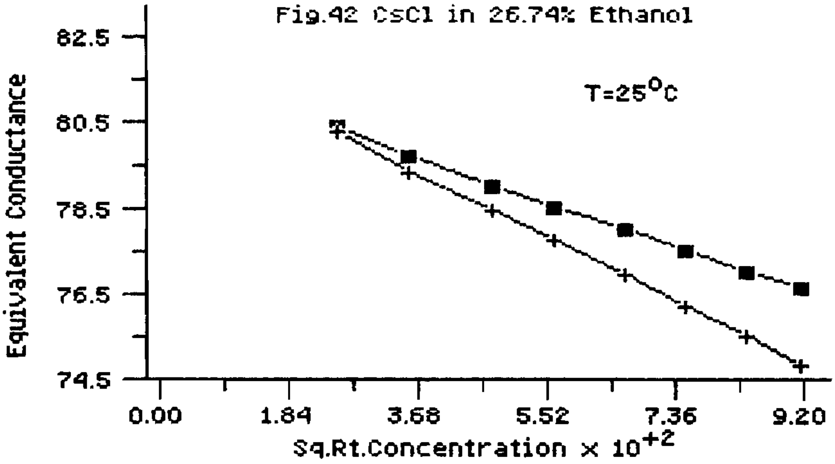
Fig.42 CsCl in 26.74% Ethanol

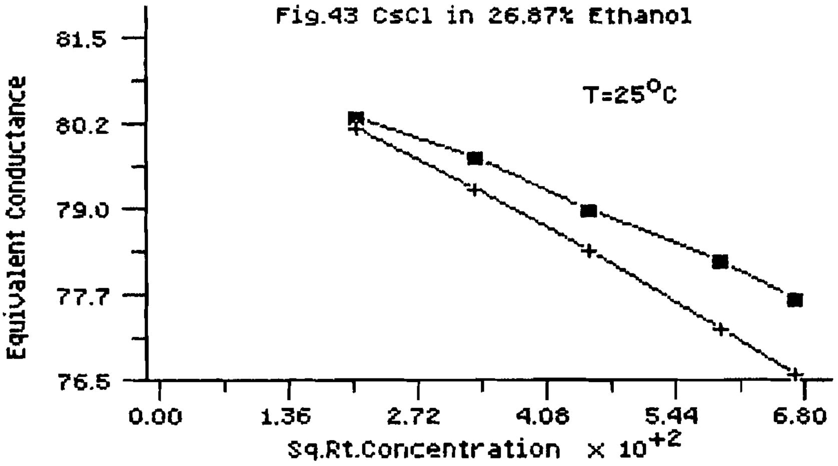
Fig.43 CsCl in 26.87% Ethanol

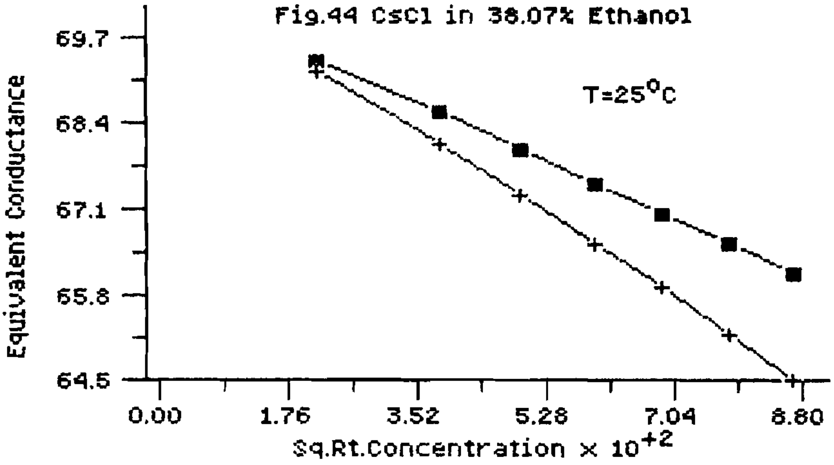
Fig.44 CsCl in 38.07% Ethanol

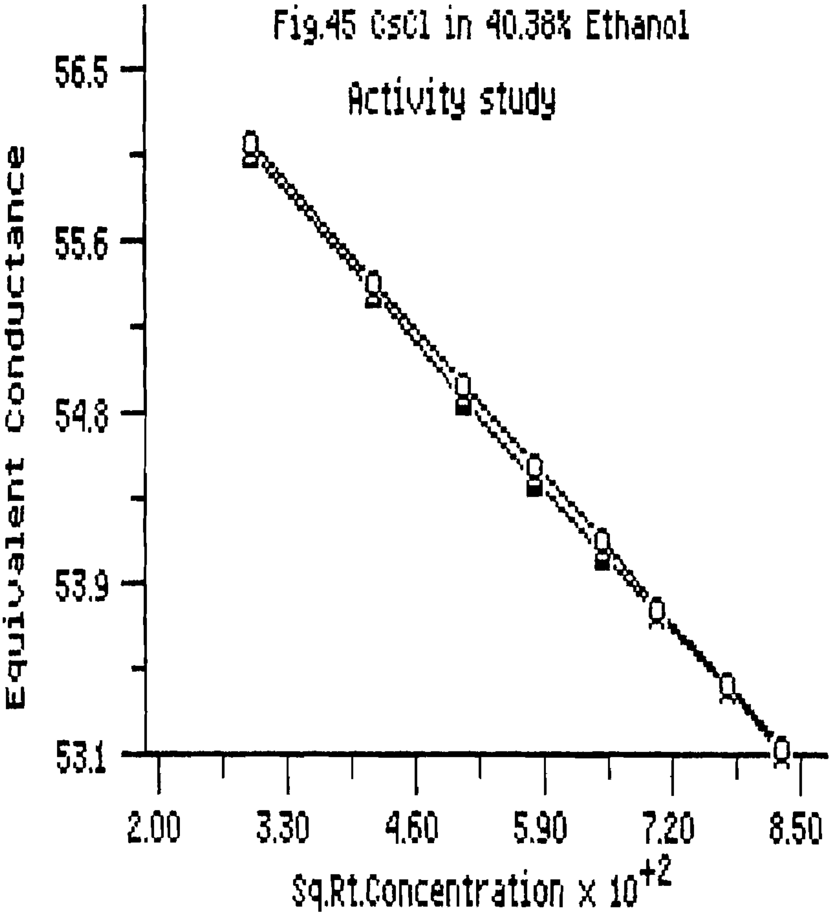
Fig.45 CsCl in 40.38% Ethanol
Activity study
Equivalent Conductance
56.5
55.6
54.8
53.9
53.1
2.00
3.30
4.60
5.90
7.20
8.50
Sq.Rt.Concentration x 10^{+2}