THE ELECTRICAL CONDUCTANCE
OF
TETRAETHYLAMMONIUM BROMIDE AND CHLORIDE
IN
NITROMETHANE

A thesis

by

Roland Robert Tink MSc. (U. of Sask.)

Submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy

McGill University

September 1953

ACKNOWLEDGEMENTS

The author would like to acknowledge the advice and criticism of Dr. H. I. Schiff during the course of this work and the financial assistance of International Nickel Company and the Consolidated Mining and Smelting Company.

CONTENTS

THE ELECTRICAL CONDUCTANCE OF TETRAETHYLAMMONIUM BROMIDE AND CHLORIDE IN NITROMETHANE

The Arrhenius Theory

The first major contribution to the theory of electrolytic conductivity was made by Kohlrausch(11) who found that molar conductivity could be expressed as the sum of two quantities - the individual conductances of the anions and cations. He called this the "Law of Independent Movement of Ions".

The next advance to the theory was made by Arrhenius (13). He assumed that a solution is composed of ions and neutral molecules and that the proportion of ions increased with increasing dilution. From this he concluded that the degree of dissociation of the solute in a given solution was equal to the ratio of the equivalent conductance of that solution to the equivalent conductance of an infinitely dilute solution.

Arrhenius had also developed an expression for osmotic pressure resembling Boyle's Law on the basis of the analogy between the processes of vaporization and solution. He was able then to compare the values of the degree of dissociation as obtained from the colligitive properties of the solution with those obtained from the conductivity measurements and found good agreement.

Further tests of these ideas were carried out using the relation between conductance and the equilibrium constant as deduced by Ostwald(14). Weak acids and bases were found to obey this law(15). However the law failed completely at high concentration(17) and for strong electrolytes(109). Various corrections have been used in an attempt to fit fact and theory i.e. solvent correction (18) and G. N. Lewis's empirical conception of the activity coefficient (125). None have had success in explaining the conductances of all solutions (59). However, the theory has been used until quite recently and still has some adherents (88).

One of the implicit assumptions of the Arrhenius Theory (one that was not realized until long after the theory had been accepted) was that the mobility of the ions was the same in concentrated as well as in dilute solutions. This is contrary to transport data. (36)

The Interionic Attraction Theory

Although the Arrhenius Theory continued to be dominant for almost forty years attempts had been made to consider the possibility of complete dissociation(20). The first successful quantitative treatment of this concept was made by Debye and Huckel in 1923.(33)

The qualitative mechanical picture used in this theory involved the consideration of a central ion and the field due to this ion in relation to the rest of the solution. The solvent was considered only as an inert medium and of no consequence except for its viscosity (to calculate the hydrodynamic resistence of the ions to movement) and its dielectric constant (for its effect on the electric fields). The other ions were considered to distribute themselves so that on the average more ions of the opposite charge would be in the neighborhood of the central ion than ions of like charge. These ions thus formed an "ionic atmosphere" around the central ion. This ionic atmosphere was considered to be symmetrical with respect to the central ion except when an external force (such as an electric field) was applied. In an electric field, the ions tend to travel in one direction and the atmosphere in the other because of their opposite charges. The atmosphere must then form continuously in front of the central ion and dissipate behind the ion in an effort to remain symmetrical around the ion. This assymetry of the atmosphere retards the movement of the ion. The Debye-Huckel Theory comprised the mathematical calculations based on this qualitative picture.

The assumptions made in this theory were: (1) complete dissociation of the salt (2) Coulomb's law of electrostatic forces may be applied to the ions and all other forces between the ions may be neglected (3) the distribution of the ions in that given by the Boltzman Distribution Law, (4) the resistance to movement of the ionic atmosphere is given by Stokes Law (5) the macro-dielectric constant and viscosity are applicable to the system even in the neighborhood of the ions (6) the solutions were considered so dilute that ions are at large distances from one another. The resultant general equation indicated that the conductance of the electrolytes should vary as the square root of the concentration in agreement with what Kohlrausch had found empirically earlier(38). L. Onsager made calculations correcting the result for the effect of Brownian Movement(35). The same general form of equation remained.

The validity of the Debye-Huckel-Onsager theory was supported by the effects found at high field strengths and at high frequencies. Wein found that the conductance of an electrolytic solution increased with increasing applied potential in violation of Ohm's Law(76). The explanation offered is that the ion moves so rapidly that the ion atmosphere does not form or if it does the ion is rapidly removed from its influence.

The effect increases with increasing concentration, increasing valence type, decrease in dielectric constant and temperature as predicted by the theory. The fact that the equivalent conductance does not extrapolate to the value at infinite dilution with increasing field strength indicates that the effect of the ionic atmosphere is never completely removed.

Another success of the interionic attraction theory was the prediction(78) of the action of high frequencies of the applied field upon the conductance of electrolytes. If the frequency of the applied electric field becomes so great that the period of oscillation of the ion due to this field is of the order of or greater than the time of relaxation of the atmosphere around the ion, then the asymmetric ionic atmosphere has less chance to form and thus the conductance of the solution increases. The influence of concentration, valence type, dielectric constant and temperature on this effect was likewise in the direction indicated by the theory(79).

With few exceptions, the Debye-Huckel-Onsager Theory predicts the conductance of strong electrolytes in water. In non-aqueous solvents, the usefulness of this theory decreases with the decrease of the dielectric constant of the solvent. In solvents of low dielectric constants, conductance changes previously thought to be characteristic of concentrated solutions (as long as water was used as the solvent) have been found to occur in dilute solutions. In media with a low dielectric constant or in concentrated solutions, the short range interactions between ions, ions and ion dipoles, need to be accounted for (113). Moreover specific reactions with the solvent must be considered. For example, in acetone, anion conductances were found to be markedly greater than cation conductances suggesting a specific solvent interaction with cations(68). Also ions of small atomic dimensions have lower conductance than would be expected from larger members of the series(66,67) suggesting that the smaller ions solvated to a greater degree.

Attempts have been made to account for the effects of the increased electrical attractions in media of lower dielectric constant by evaluating the higher terms in the various mathematical series arising in the Debye-Huckel-Onsager treatment. Such calculations are quite complicated and a more general practice is to evaluate extended terms to the Debye-Huckel-Onsager expansion empirically. Such terms can be shown to have the general form required by the more complete treatment. However, for non-aqueous solvents the assumptions made by Debye and Huckel may be quite inapplicable.

A somewhat different theoretical approach was made by N. Bjerrum. N. Bjerrum postulated that ions could be treated as rigid unpolarizable spheres that obeyed the Maxwell-Boltzmann distribution law and Coulomb's Law. The dielectric constant used was again the macroscopic dielectric constant. At a certain distance of separation, ions of opposite charge associate to give ion pairs(70). Confirmation and elaboration of this ion pair concept was carried out by R. M. Fuoss and C. A. Kraus(71), and by J. G. Kirkwood(72). Fuoss and Kraus postulated the formation of triple ions , quadrupoles, and ionic clusters to account for the minimum and inflection points observed in the curves obtained by plotting equivalent conductance versus concentration (73)(74)(75). In solvents of low dielectric constant (less than 10), ion pairs and triple ions were both required to account for the conductance change with concentration. In these solvents, minima were observed in graphs of equivalent conductance curves. With solvents of lower dielectric constant, the minimum becomes more distinct and shifts to the direction indicating increased dilution. The increase with increasing concentration after the minimum is believed to be due to the triple ions. However the Bjerrum concept has been found to be in error when applied quantitatively.

In an attempt to aid in the search for a more general theory of electrical conductance, a decision was made to measure the conductance of tetra ethylammonium bromide and tetra ethylammonium chloride in nitromethane.

Although considerable attention has been given to solvents of very low dielectric constant few reliable measurements have been made with solvents of intermediate dielectric constant. Nitromethane was chosen because although it has a dielectric constant about the same as methanol, for which accurate data has recently been obtained, it differs from methanol in various respects. For example, since it does not contain a hydroxyl group it may solvate preferrentially with the cation, whereas methanol should solvate with both ions(45). The salts were chosen both because of their solubility and large degree of dissociation.

The direct current method of Gordon and Gunning was used because of the simplicity of the apparatus compared to that required for the use of alternating current. The use of alternating current is complicated by capacitance effects of the cell and various parts of the bridge network. Inductance of various parts of the network also interferes. The proper design of the cell and electrical network is very important. The use of shielding has been advocated and condemned(80).

The use of direct current was for a long time considered to be impractical due to the decomposition of the solution and the resultant polarization. The first accurate measurements using direct current were made by E. Newbury. Reversible electrodes were used and a 0.6% discrepancy was found between these measurements and values obtained using alternating current(83). Later the two methods were again compared with a discrepancy of only 0.02%(84). Both of these studies were made using relatively concentrated solutions, although agreement has also been found with very dilute solutions.(85) Apparently the conditions required for the use of direct current measurements to give accurate results are: 1) reversible electrodes to eliminate polarization. 2) small current so that only small changes occur in the solution(36). Measurements have been subsequently made using direct current(86,87) with a precision as great as that obtained by the use of the more complex alternating current techniques.

Experimental

Purification of Nitromethane

Methods described in the literature for the purification of nitromethane usually consisted of chemical dehydration followed by distillation. Walden has reported the use of sodium sulphate, phosphorus pentoxide, and potassium carbonate either individually or in succession(62,89,91). Lattey and Gatty used calcium chloride followed by phosphorus pentoxide since it was found that calcium chloride alone would not remove the last traces of water(91,92). Distillation over mercuric oxide and freshly sublimed phosphorous pentoxide was also used(93). One of the difficulties connected with using these drying agents was their subsequent removal. For example, even after five distillations traces of phosphorous pentoxide, after its use as a drying agent, remained in the distillate(62). Another difficulty arose from the action of the drying agent upon the nitromethane. Potassium carbonate reacted to give a yellow product(91).

Hartley et al. avoided the difficulties produced by chemical purification by refluxing the nitromethane for several hours while bubbling dry air through it, followed by distillation. In all instances the conductance of the solvent was taken as a measure of purity.

The thermal decomposition of nitromethane was reviewed to obtain information on possible impurities that may be formed by distillation. The main reaction at 350°C appeared to be a homogeneous unimolecular decomposition into nitrosomethane and oxygen(94,95). The final products were carbon dioxide, water, nitrogen, nitrogen oxide, hydrogen cyanide, ethane, and methane. Liquid nitromethane at its boiling point produced isolatable amounts of formaldoxime after 48 hours(94). Nitrosomethane re-arranges readily into formaldoxime.

The nitromethane was obtained from Commercial Solvents in five gallon cans. Upon arrival, the nitromethane had a deep yellow color and was cloudy. Its specific conductance was about 5×10^{-4} mhos.

Preliminary distillations were carried out with a small apparatus. It was found that the color and conductance of the nitromethane reduced by distillation. Also the lower the temperature (and pressure) of the distillation the more the product improved. The conductance of the various fractions showed that there was present material some of which was slightly more volatile than nitromethane and some of which was much less volatile; both of which had higher conductivity than nitromethane. Some yellow material present seemed to be almost inseparable from nitromethane by distillation. Also as the distillation proceeded the residue in the pot darkened with time. Thus it was obvious that although distillation improved the quality of the nitromethane, other methods of purification had to be used also.

Washing the nitromethane with aqueous solutions (5%) of sulfuric acid, nitric acid, sodium hydroxide, and sodium bicarbonate, and water was tested. The acids removed little or none of the colored material. The sodium compounds removed large quantities of the yellow material. Both treatments produced gas evolution. This yellow material in the aqueous layer soon turned red and then black. The water wash removed some yellow material but not nearly as much as did the sodium salts. More of the yellow color was removed by a second washing with sodium bicarbonate or sodium hydroxide. However further washings did not seem to make any further improvement although the wash was colored. It seemed that the color was generated as fast as it was removed.

It was also noticed that the volume decrease of the nitromethane was greatest during the first washing with the sodium hydroxide or sodium bicarbonate than during subsequent washes or during the washing by the water or acid solutions.

It seemed possible that the yellow material inseparable by distillation from the nitromethane was dinitromethane. Dinitromethane is an acid, yellow, and boils at 100°C. (nitromethane boils at 102°C). When the nitromethane was washed with water a material was extracted that was yellow and a strong acid.

Another possible impurity was methazonic acid. Nitromethane in the presence of sodium bicarbonate produces the sodium salt of this acid(129). Upon standing, this material turns to a dark red, just as the wash water with the bicarbonate did.

The following procedure was therefore adopted. Nitromethane was washed twice with aqueous 5% sodium carbonate, once with aqueous 5% sulfuric acid, and three times with conductance water. It then was a light yellow in color, and had a conductance of about 5×10^{-5}. If left wet, the conductance would rise to about 5×10^{-4} in one day, indicating that decomposition occured. It was found that the faster the water was removed by distillation (without use of high temperature) the better the conductance of the product. The water formed an azeotrope with nitromethane, boiling point of the azeotrope being about 17° lower than either pure substance. The nitromethane produced had a low conductance and was water white. Redistillation of this material gave a product with a higher conductance indicating that during distillation some decomposition occurs. However repetition of the washing and distillation gave a better product.

The distillation apparatus was all pyrex glass of usual vacuum type design. See Figure 1. Specific details of important parts are as follows. The pot had a five litre capacity and was heated by a Glas-col heating mantle. The fractionation column was 3.6 cm in diameter and 167 cm long. The column packing was glass helices of 1/8" inside diameter. These helices were dropped into the column individually to insure close even packing. This tedious task was facilitated by the use of a three necked flask fitted with a blowing tube from a nitrogen cylinder on one side neck, a cork on the middle large neck, and an outlet tube just large enough to emit one helix at a time. A few helices were placed into the flask through the centre neck. Then nitrogen was blown into the flask at such a rate that the helices did not plug the outlet or were not broken but left the flask through the outlet singly.

The head of the distillation apparatus was a conventional magnetic take-off type actuated by a switch with a one half minute cycle.

A cartesian manostat was used to regulate the pressure.

DISTILLATION APPARATUS

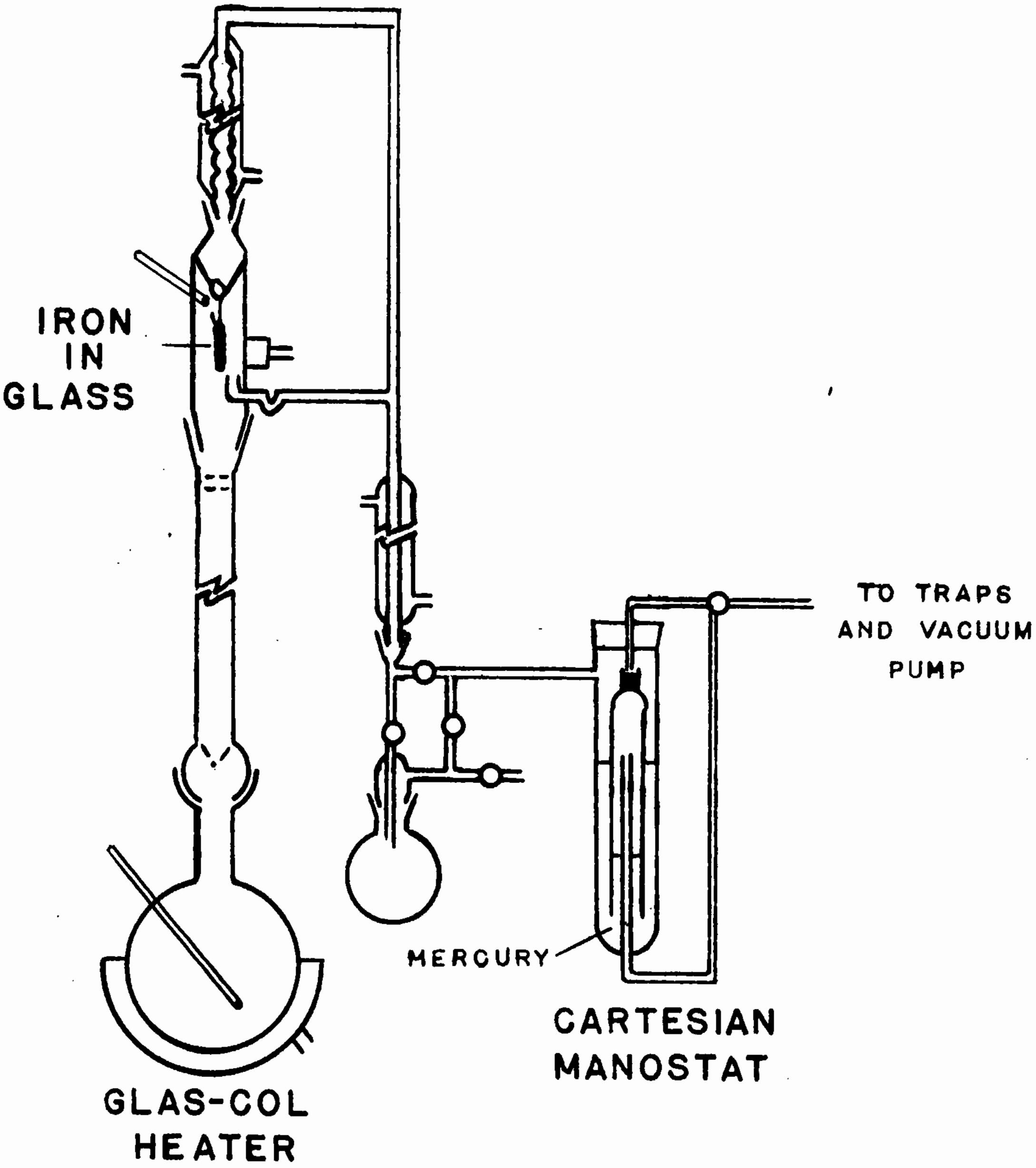


Figure 1

The usual dry ice-acetone cold traps and vacuum oil pump were used.

After washing, the nitromethane was immediately distilled; the water was removed as quickly as possible but the temperature of the nitromethane was kept below 40°C at all times. At the beginning no reflux was allowed. The reflux was gradually increased so that the azeotropic fraction had some excess of nitromethane due to incomplete fractionation. All water was removed from the still in about two hours.

After the water appeared to be gone, about 500 ml of nitromethane was distilled off and discarded. This acted to flush out the condensers and insure that no water went into the product. About two litres of nitromethane was collected leaving something over 500 ml as residue. The fractions were all collected near 30°C. The nitromethane fraction was collected at a pressure of 45 mm of mercury with a reflux of 75%.

This procedure was completely repeated on the purified nitromethane. After the repetition of the procedure, the nitromethane was at least 99.8 mole% pure (as measured by the cryometer) and had a conductance of 10^{-8} mhos.

The nitromethane was finally purified by fractional crystallization using the apparatus shown in Figure 2. The two litre flask was filled with the nitromethane, the thermistor put in place, and the whole apparatus placed in a copper box (insulated with cork 2 inches thick) containing dry ice. The copper facilitated the even distribution of the temperature. The rate of freezing of the nitromethane was kept at about one litre in 24 hours by regulating the amount of insulation separating the nitromethane and the dry ice. The temperature of the liquid was measured at various times so that its purity could be estimated.

FRACTIONAL CRYSTALLIZATION APPARATUS

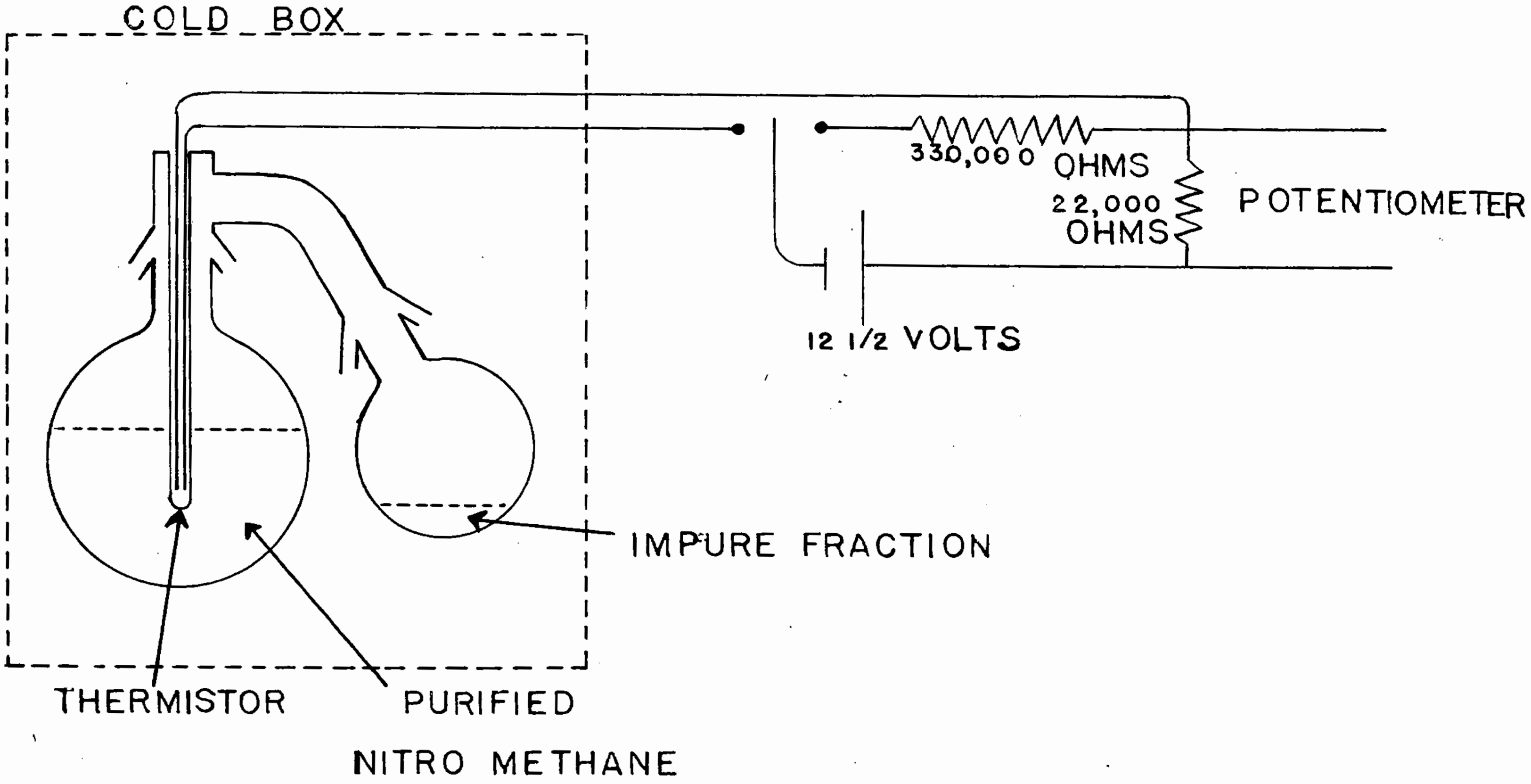


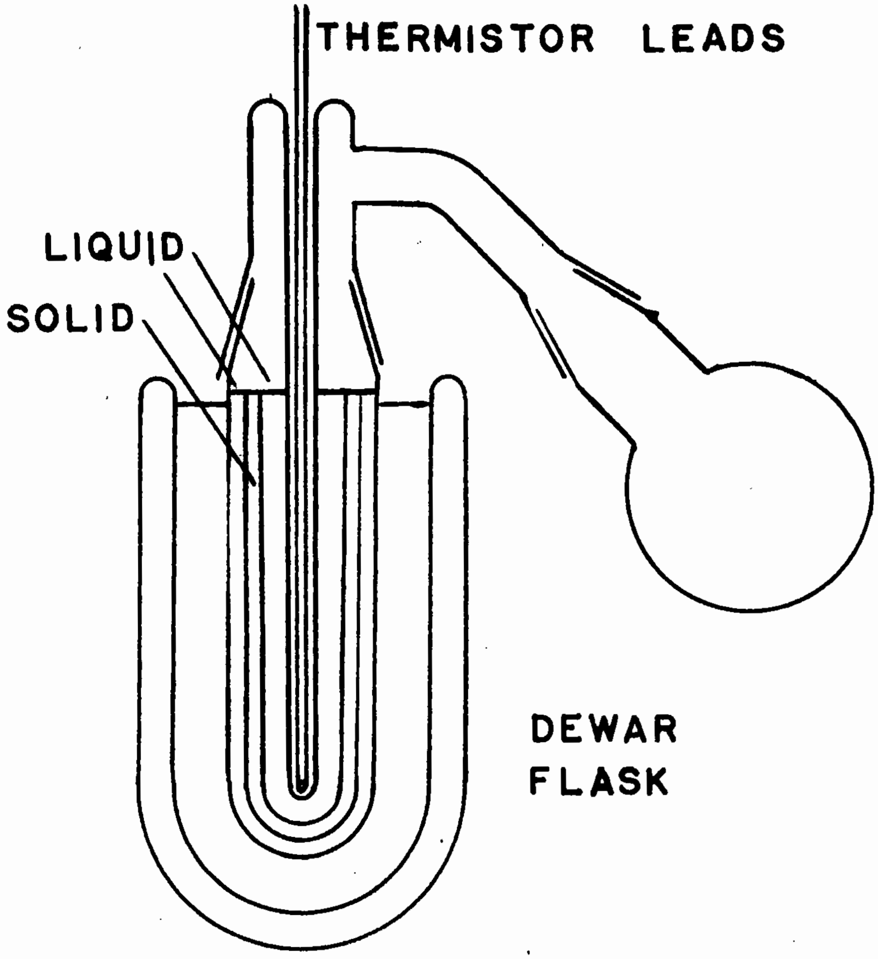
Figure 2

When all but approximately 100 millilitres of the nitromethane was frozen, the liquid was poured into the side flask. The solid nitromethane was melted except for a very small crystal which acted as a seed. When pure, the nitromethane could be easily supercooled 20°C and would not freeze even with violent shaking. After about five crystallizations, the freezing point would not change either during crystallization or with further fractional crystallization. This indicated that the nitromethane was at least 99.99 mole percent pure.

The nitromethane used in the conductance determinations was at least 99.99 mole percent pure, had less than $1x10^{-4}$ weight percent water as determined by the Karl Fischer reagent, and a specific conductance of 1 to $2x10^{-8}$ mhos.

Before assembling the crystallization apparatus, the thermistor, obtained from the Western Electric Company, was connected to a 600 volts direct current from batteries in series for 15 seconds at -30°C to aid in its stabilization. The tip was covered with aluminum paint to minimize radiation effects.

To standardize the apparatus, the resistance of the thermistor was determined at the freezing point of mercury, carbon tetrachloride, and chlorobenzene, by the following method. The liquid was placed in the apparatus shown in Figure 3. This apparatus is similar in design to the cryometer of Streiff and Rossini(39). A thin shell of frozen material was made and then partly melted so that from the outside to the center there is a shell of liquid, a layer of solid, and then the main body of liquid at its freezing point. This is kept in a Dewar flask with acetone near this temperature. The resistance of the thermistor was measured. The shell of frozen material was melted (except



STANDARDIZATION
OF
THERMISTOR

Figure 3

for a small seed). The liquid was slowly frozen to fractionally crystallize the liquid. When only a small amount of liquid remained, this liquid was poured into the side reservoir. The frozen material was melted and the shells reformed as before. The resistance of the thermistor was measured. When the resistance of the thermistor did not change after two fractionations, the material remaining was considered pure. Nitromethane was found to freeze at -28.2°C.

Naphthalene was added to nitromethane to determine the molal freezing point lowering which was found to be 12 $\Delta \ln \frac{V}{V_T}$. That calculated from the heat of fusion of nitromethane(40) was 11.4 $\Delta \ln \frac{V}{V_T}$. The calculations concerning estimation of impurity were as follows:

Let V be the potential across R_1 when the current is going through the thermistor, V_T when the current is going through the resistor R_2.

Then $V(R_1 + R_3) = V_T(R_1 + R_2)$

However R_3 varies with temperature of the thermistor

$$R_3 = R_o e^{b/T}$$

where Ro, b are constants and T is the absolute temperature

$$\therefore \ln\left(\frac{V_T}{V} - \frac{R_1}{R_1 + R_2}\right) = \ln \frac{R_o}{R_1 - R_2} + \frac{b}{T}$$

With this apparatus and at the temperature it was used at

$$\frac{V_T}{V} = 6.5 \quad \text{and} \quad \frac{R_1}{R_1 + R_2} = 0.06$$

Therefore a plot of $\ln \frac{V_T}{V}$ vs $\frac{1}{T}$ should be nearly linear and it was.

For equation

$$\ln \frac{\sqrt{1}}{\sqrt{\ }} = K + \frac{b}{T}$$

it was found that $b = -1656$

$\therefore$ mole per cent impurity$^{(m)}$ for the solution was

$$m = 69.5\,\Delta \ln \frac{\sqrt{1}}{\sqrt{\ }}$$

Now $\ln \frac{\sqrt{1}}{\sqrt{\ }}$ could be determined to five figures. Therefore m could be estimated to ± 0.005%.

The Preparation of Conductance Water

The distillation apparatus for the production of conductance water from distilled water consisted of a copper pot of ten litres capacity fitted at the top with several copper baffle plates to stop entrained droplets. The pot contained a thousand watt Calrod heater. A quartz tube was bent to lead the water vapor down to the receiver. The downward position of the tube was cooled by a pyrex water jacket. The receiver was a five litre flask fitted with appropriate glass outlets for blowing the conductance water into the storage bottles using purified nitrogen.

These storage bottles, when new, were treated in the following manner (as was all glassware which came in contact with materials used in the conductance cell). They were cleaned with chromic acid solution, left to stand filled with hot hydrochloric acid for 2 days to remove surface alkalinity. They were then flushed continuously for several days with tap water, rinsed several times with distilled water and finally with conductance water.

To prepare the conductance water, distilled water was placed with a small quantity of potassium hydroxide and potassium permanganate in the pot of the still. When the water vapor produced was only partially condensed, conductance water with conductance below 1x10^{-6} mhos at 25.0°C was obtained.

Tetraethylammonium Bromide

Equimolecular quantities of distilled, water-white, triethylamine and ethyl bromide were mixed in a long pyrex tube (50 cm x 8 cm) attached to a reflux condenser by a standard tapered joint. The solution turned cloudy immediately. It was heated slightly near the top of the solution and refluxed for two days. A white solid, tetraethylammonium bromide, formed and dropped to the lower and cooler part of the tube. In this manner, the salt was protected from thermal decomposition(44). The solid was removed from the liquid by filtration and recrystallized several times from dry distilled chloroform.

The salt was dried at 80°C in a vacuum oven over phosphorous pentoxide for several days(45). Before using, the salt was dried to constant weight.

The salt was analyzed for bromide by titration with silver nitrate solution using potassium chromate as indicator(2). The number equivalents of silver nitrate to titrate 4.647 x 10^{-3} equivalents of the salt was 4.649 x 10^{-3}.

Tetraethylammonium Chloride

The tetraethylammonium chloride was prepared from tetraethylammonium iodide by the reaction of silver oxide to give tetraethylammonium hydroxide which was neutralized by hydrochloric acid.

The tetraethylammonium iodide was prepared in a similar manner as the tetraethylammonium bromide. The time of reaction required was much less. Some chloroform was added to the mixture to keep the salt from caking in the tube. The tetraethylammonium iodide produced was slightly yellow but after crystallization from chloroform, the salt was white.

The tetraethylammonium iodide was treated five times with moist freshly precipitated silver oxide in ethanol(46). The total amount of silver oxide was three times the theoretical requirement for the reaction. However some iodide did not react and dissolved with the hydroxide. After being treated with excess hydrogen chloride, the solution was evaporated and dried. The salt was re-crystallized from chloroform four times in the following manner. The salt was dissolved in excess chloroform and the solution was allowed to stand for several days. The chloride which was very hygroscopic precipitated as the hydrate. The iodide remained in solution. The precipitate was thoroughly dried and the process was repeated. The salt was re-crystallized in this manner twice after no iodide could be detected by the starch test following oxidation with nitric acid.

The drying of this salt was carried out in the same manner as the bromide but seemed to require more time to attain constant weight.

The chloride was also titrated with silver nitrate, 4.718×10^{-3} moles requiring 4.715×10^{-3} equivalents of silver nitrate.

Purification of Potassium Chloride

The potassium chloride was the "Analar" grade of the British Drug House. It was recrystallized from conductance water twice. Immediately before using the salts was heated to 630°C for 30 minutes in a platinum boat in an electrically heated silica tube under a blanket of nitrogen from which oxygen was carefully removed (as described in the following section). The salt was allowed to cool in a dessicator for one hour and then weighed.

Purification of Nitrogen

The nitrogen used to dry the potassium chloride was treated with Fieser solution containing zinc amalgam to remove oxygen(107), water, dried by calcium chloride and phosphorous pentoxide, and then filtered through a column of glass wool. The oxygen was not removed (i.e. the Fieser solution was not used) when the nitrogen was used to transfer solutions.

Karl Fischer Apparatus for the Determination of Water

The nitromethane was analyzed for water using the electromeric apparatus of McKinney and Hall(105), pyridine, sulphur dioxide, and iodine reagent(106); and the usual apparatus set up to keep all moisture in the air from the reagents and titration flask. Sodium acetate trihydrate was used as a water standard(108).

The Conductance Apparatus

The Cell

Figure 4 shows the front and side view of the conductance cell used. The drawing is one half the actual size. The cell was built to the specifications of Gunning and Gordon(41). The large volume of the cell (approximately 400 ml) tended to minimize errors due to contamination. Etched lines on the ground glass joints aided in placing the electrodes in exactly the same position each time they were used.

The cell was cleaned with chromic acid, treated with hot hydrochloric acid and rinsed with water just as the other glassware before using. In addition, when not in use, it was kept full of conductance water. Thereafter it was periodically cleaned using chromic acid. After a determination, the cell was rinsed continuously with tap water, and then eight times with conductivity water. Before a determination, the cell was dried using the purified nitrogen.

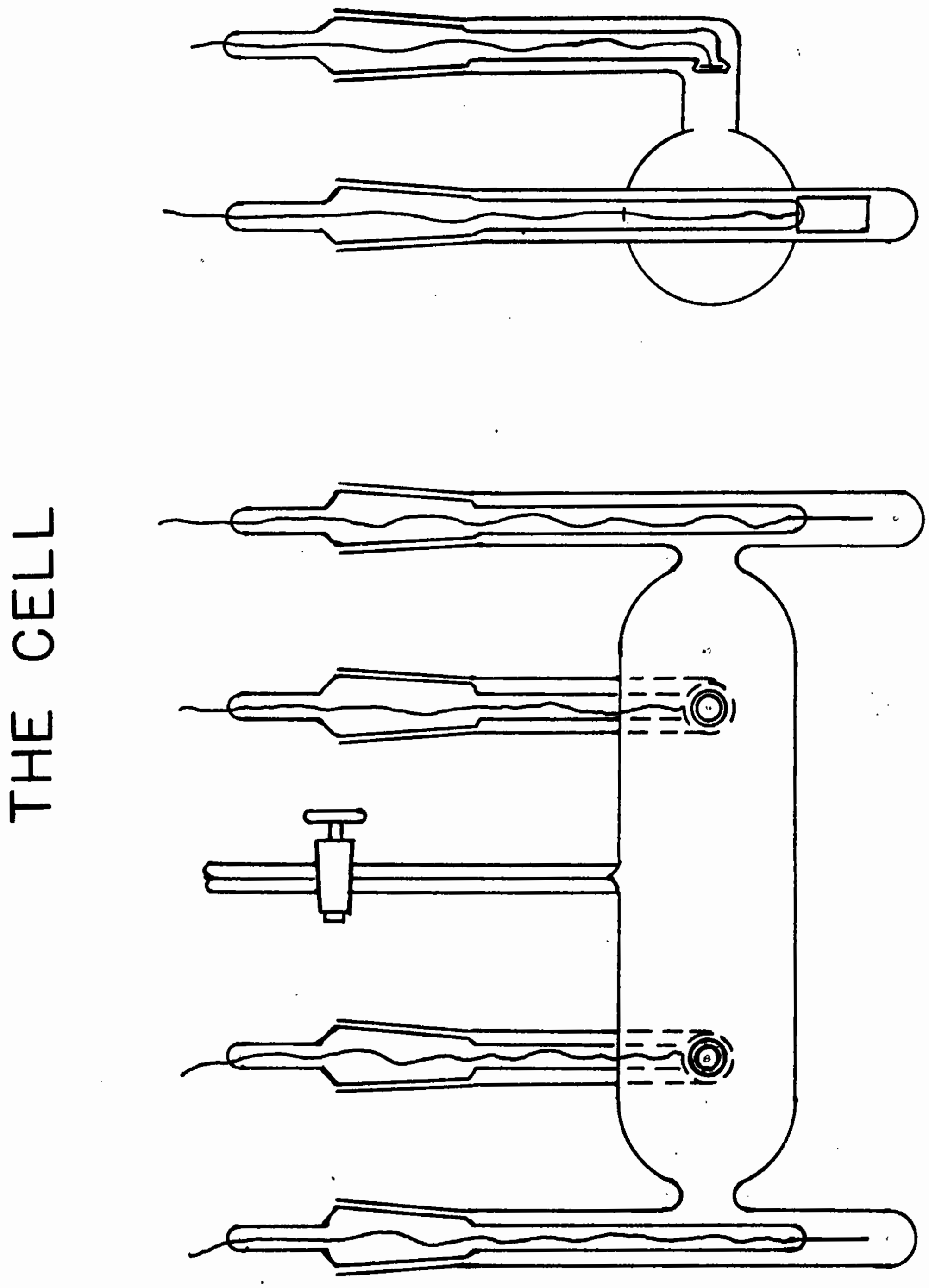


Figure 4

Each of the probe electrodes (as in Figure 4) was a platinum disk 8 mm. in diameter with all the exterior of disk covered with glass except for a vertical strip 1 mm wide and 6 mm high. The back of the platinum was connected to a wire which led to the potentiometer. The main electrodes were heavy platinum foil held in place by being embedded in the glass. The probe and main electrodes were plated with silver and then silver chloride (or bromide as required) according to the method of Brown and MacInnes(102). The probes were replated as soon as the determination became erratic. Sometimes as many as six determinations could be made before replating, other times only one or two. The main electrodes were replated as soon as the top part of the electrodes lost all of the halide. The top was the first part to lose all of the halide.

The cell was standardized using a 0.01 Demal solution of potassium chloride and the results of Jones and Bradshaw(103). The cell constant was 0.545199.

Electrical Circuit

The conductance was measured using direct current. A constant current device similar to that of LeRoy and Gordon(42), (See Figure 5) delivered a constant current to the mains of the cell. The potential drop between the probes due to this current in the cell was compared with the potential drop in a standard resistance due to the same current by means of a Leeds and Northrup Type K2 potentiometer and a ballistic galavanometer which had a sensitivity of 2 x 10^{-10} amperes per scale division at one meter.

Constant Temperature Bath

The constant temperature bath used to control the temperature of the conducting liquid was twelve gallons of light transformer oil,

ELECTRICAL CIRCUIT FOR CONDUCTANCE

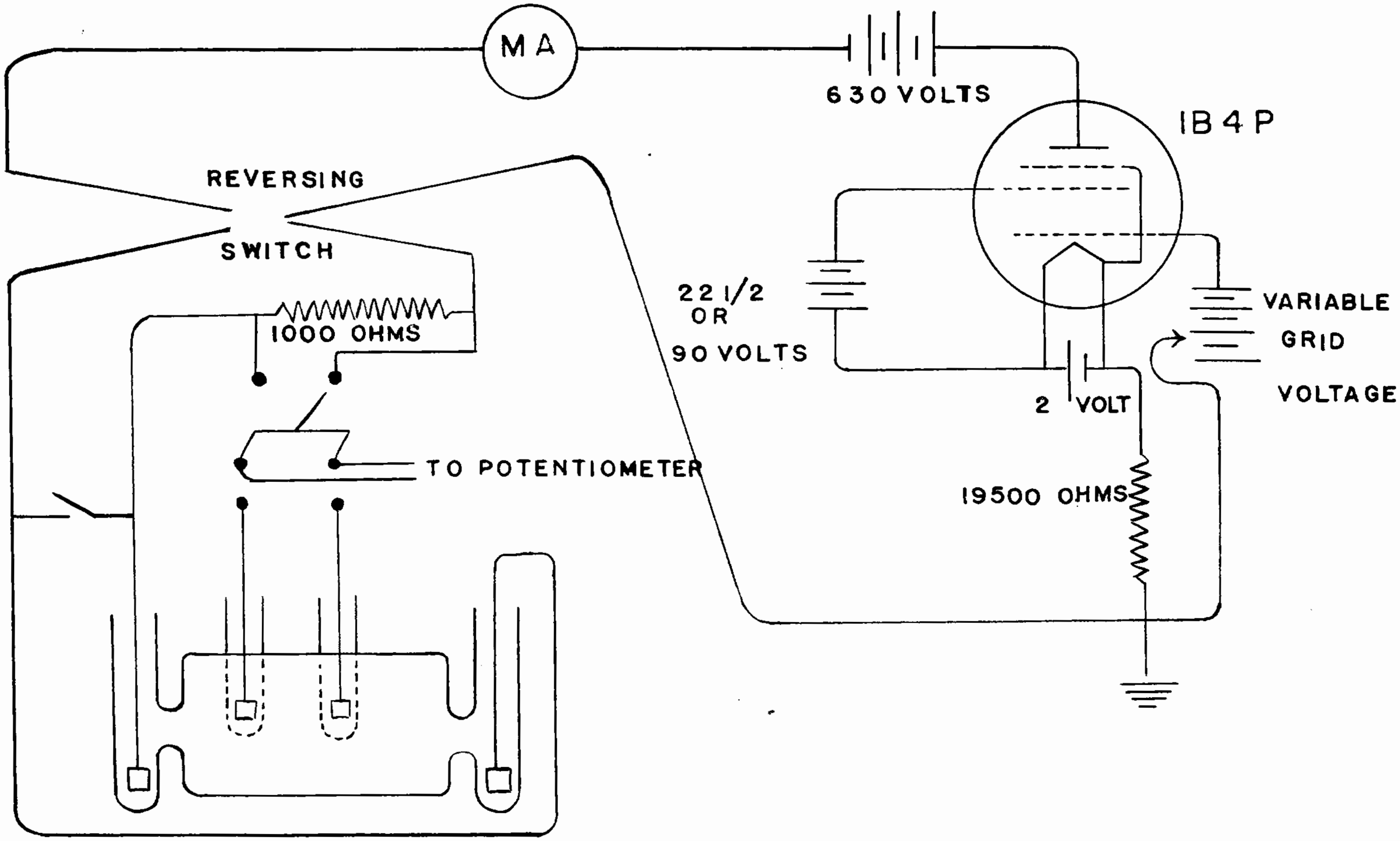


Figure 5

vigorously stirred by a large ten bladed stirrer. The container was insulated by cork two inches thick. The bath was heated by two blade heaters of 250 watts each and was cooled by water passing through a copper coil in it. The temperature was regulated by the movement of mercury in an eight millimetre diameter pyrex tube bent to occupy a similar amount of space as the cell. The copper cooling coil circled the shaft driving the stirrer at the bottom in the center. The regulator was placed at one end of the bath, the cell was placed at the other. The maximum temperature fluctuation in the bath was ± 0.002°C.

The temperature was measured with a mercury in glass thermometer calibrated against a standard platinum resistance thermometer at the National Research Council Ottawa.

Preparation of Solutions

All glassware was cleaned with chromic acid, treated with hot hydrochloric acid and rinsed with water as described previously. The salt was dried until constant weight and weighed in a platinum boat inside a small glass container with a standard taper joint that fitted the solution flasks. The purified nitromethane was weighed in the flask that was to contain the solution. All weights were corrected to vacuum. The salt was transferred to this flask by 1) removing the cap of the flask and the salt container, 2) tilting the flask so that the container fitted onto it without spilling the salt out of the platinum boat. The boat was eased into the flask by gentle tapping. Then the regular delivery top was placed on the flask, as in Figure 6. During all cap removals etc. exposure of salt or solution to the air was kept to a minimum to hold contamination by water vapor in the air to a minimum.

SOLUTION FLASK

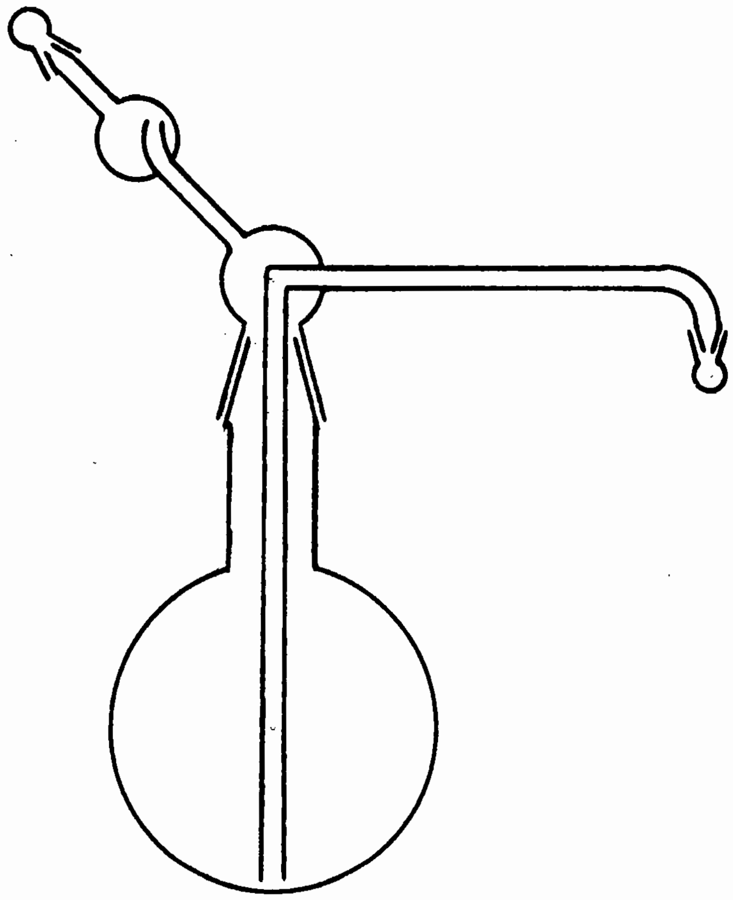


Figure 6

Dilutions were made from the stock solutions by adding weighed quantities of purified nitromethane to weighed amounts of salt solution using nitrogen for transferring the liquids.

The accuracy of the dilution technique was checked by measuring the conductivity of solutions of the same concentration made by diluting stock solutions of concentration varying by a factor of 2. The conductances of these solutions checked within the accuracy of the measurement.

Density Measurements

The pycnometer used to determine the density of the solutions was similar to that of Shedlovsky and Brown(104). The only difference was that it was made of "Exax" glass and the two ends were part of a seriological pipette with thousandths of a millilitre graduations. This pycometer was calibrated by weighing it, filling it with conductance water using a syringe, re-weighing with the water in it, bringing it to 25.00°C and noting the positions of the meniscus using a magnifying glass. The weight of the water was corrected to vacuum.

The Conductance Measurement

The probe electrodes were rinsed with the nitromethane solution and then allowed to stand in fresh solution in a closed container. The main electrodes were also soaked in the nitromethane solution. The probe electrodes and one of the main electrodes were placed in the dried cell and a filling tube connected the fourth position to the solution flask. The solution was forced into the cell using nitrogen pressure and leaving the air vent of the cell open. After being filled, the cell was fitted with the fourth electrode. After carefully placing the electrodes in their proper position, the cell was put into the bath. After at least an hour the conductance was measured. The shorting switch was opened

PYCNOMETER

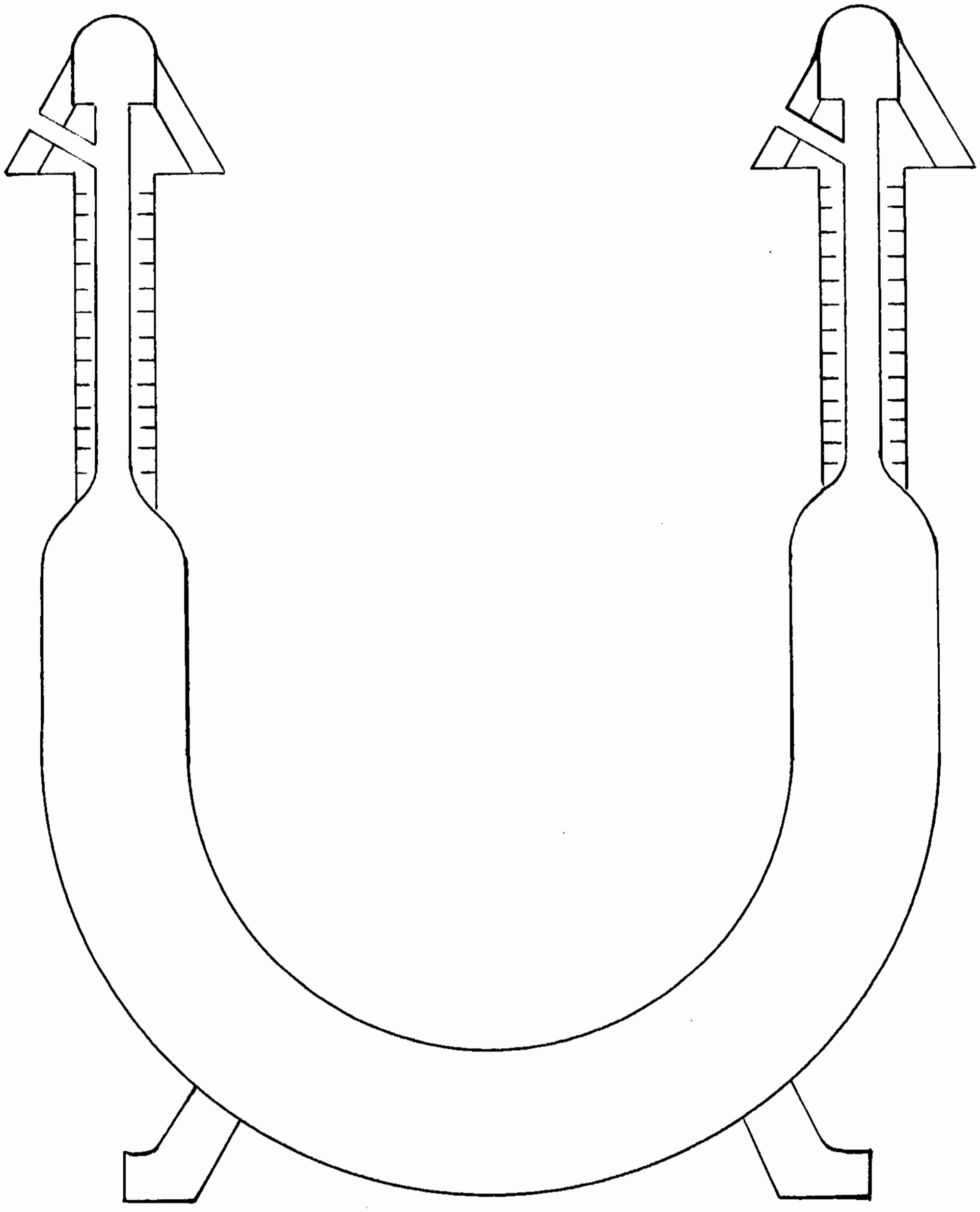


Figure 7

so that the current passed through the cell and the standard resistance. The potential across the proke electrodes E and the standard resistance E_s was measured. After closing the shorting switch, reversing the current, opening the switch, the potentials were again measured. These values were averages to eliminate the static bias between the prokes.

Results

The density of the nitromethane was found to be 1.13136 gms/ml. The density of the solutions of tetraethylammonium chloride (density = 1.11) in nitromethane at 25.00°C to concentration of 0.02 moles/litre was also 1.13136.

The density of the solutions of tetraethylammonium bromide in nitromethane at 25.00°C could be expressed by the equation

$$d = 1.13136 + 2.55 \times 10^{-2} m + 0.8^{m2}$$

where d is density in grams per millilitre and m is the molality. This equation has error of less than one in thirty thousand up to molality of 1.4×10^{-2}.

The conductances of tetraethylammonium bromide and chloride in nitromethane at 25.00°C are given in Table I and II respectively. The symbols: C, Λ , and Λ_0', represent the concentration in moles per litre, the equivalent conductance, and the Shedlovsky function respectively. The valves of the Shedlovsky function are given here for convenience. Their definition and significance will be discussed further on.

Discussion of Results

Density

Numerous density measurements have been made upon nitromethane.

Table I

CONDUCTANCE OF TETRAETHYLAMMONIUM BROMIDE SOLUTIONS

C x 10^4	C x 100	Λ	Λ'_0
95,090	9.7514	90.631	110.46
94.874	9.7403	90.697	110.51
94.470	9.7196	90.676	110.44
93.422	9.6655	90.884	110.54
70.381	8.3894	93.017	110.06
69.627	8.3443	92.966	109.90
69.530	8.3384	93.157	110.10
50.076	7.0764	95.481	109.84
49.399	7.0285	95.482	109.74
26.708	5.1680	99.162	109.64
26.614	5.1585	99.139	109.59
15.972	3.9965	101.50	109.61
15.961	3.9951	101.57	109.68
15.922	3.9903	101.62	109.72
15.794	3.9741	101.85	109.92
8.9153	2.9858	103.90	109.97
8.6813	2.9464	103.99	109.99
5.1882	2.2778	105.71	110.34
4.8346	2.1988	105.82	110.29
4.5255	2.1273	106.00	110.32
1.8012	1.3421	108.18	110.92
1.7943	1.3395	108.67	111.41

Table II

CONDUCTANCE OF TETRAETHYLAMMONIUM CHLORIDE SOLUTIONS

C x 10^4	C x 100	Λ	Λ'
100.726	10.036	90.031	110.44
100.432	10.022	90.137	110.53
70.982	8.4250	92.827	109.93
69.647	8.3455	92.922	109.86
55.858	7.4738	94.535	109.69
50.483	7.1051	95.277	109.68
49.115	7.0082	95.431	109.63
29.920	5.4699	98.432	109.52
29.834	5.4620	98.438	109.51
19.633	4.4309	100.510	109.49
19.617	4.4291	100.514	109.49
9.9911	3.1609	103.27	109.70
9.9749	3.1583	103.25	109.66
5.0074	2.3377	105.50	110.04
4.8883	2.2110	105.58	110.06
2.0142	1.4192	107.39	110.27
1.9968	1.4131	107.39	110.26

The recorded results are: 1.1300(119); 1.13015(90); 1.1306(81); 1.1311, 1.1312, 1.13125(64); 1.1311(120); 1.1314(62); and 1.1325(58). The density found (1.13136) was slightly less than the most recent recorded figure 1.1314(62) and greater than the figure recorded two years earlier 1.1312(64).

Apparently the tetraethylammonium chloride upon dissolving in the nitromethane occupied less volume than when solid for the density of the solutions were the same as the pure solvent even though the salt had a lower density (1.11) than the solvent 1.13136.

The ease with which these density measurements were duplicated indicated that the accuracy was better than one part in fifty thousand.

Conductance Treatment of nitromethane solutions as strong electrolytes

Since tetraalkylammonium salts have appeared as strong electrolytes in nitrobenzene, etc.(64,31), it was suspected that these salts would act like strong electrolytes in nitromethane in view of its relatively high dielectric constant.

Kohlrausch(11) had found empirically that the equivalent conductance of strong electrolytes obeyed the equation

$$\Lambda = \Lambda_o - K\sqrt{C}$$

where Λ is the equivalent conductance at concentration C, Λ_o is the conductance at infinite dilution, and K is a constant.

More recently, Debye, Huckel and Onsager have shown that such a relationship would apply to strong electrolytes if the assumptions previously mentioned were correct. Moreover their treatment provided a theoretical evaluation of the constant K.

Thus their equation had the form

$$\Lambda = \Lambda_0 - (A\Lambda_0 + B)\sqrt{C}$$

where A and B can be evaluated from the following equations:

$$A = \frac{\epsilon^2}{3\pi(2+\sqrt{2})}\left(\frac{8\pi\epsilon^2 N}{1000\,k}\right)\left(\frac{1}{DT}\right)^{3/2}$$

$$B = \frac{N\epsilon^2}{90\pi\, v\, \eta}\left(\frac{1}{DT}\right)^{1/2}\left(\frac{8\pi\epsilon^2 N}{1000\,k}\right)^{1/2}$$

where ϵ is the electrostatic charge, k the Boltzmann constant, N the Avogadio number, v the velocity of light, η the viscosity of the solvent, D the dielectric constant of the solution, and T the absolute temperature. The values of the universal constants used were taken from Manov et al(130). Few values of the dielectric constant of nitromethane at 25.0°C were available. These were 40.4(115), 39(90), both reported by Walden and 37(92) reported by Lattey and Gatty. The last value was the most recent and was considered to be probably the most accurate. It was the one used here.

The viscosity of nitromethane at 25.0°C has been reported by several authors. The reported values (in milli poises) were 6.11(117) 6.19(119) 6.19 and 6.25(116) 6.203(90) 6.27(64) 6.31(118). Again the most recent value (6.27) was used here.

Using these values, the theoretical constants for a uni-univalent electrolyte in nitromethane at 25.00°C become

$$A = 0.7080$$

$$B = 125.16$$

The equivalent conductances at infinite dilution were estimated to be 111.00 for tetraethylammonium bromide and 110.82 for tetraethylammonium chloride, from consideration of the square root plot and

and the Shedlovsky plot although neither plot was entirely satisfactory for this extrapolation due to the curvature of the curve. Walden and Birr reported the equivalent conductance at infinite dilution for tetraethylammonium bromide and chloride in nitromethane to be 107.6 and 88.6 respectively(62).

However in nitrobenzene the difference in equivalent conductance at infinite dilution of the bromide and chloride ions was calculated to be -0.6(54). This is much less than that found by Walden and Birr and is more in agreement with the results reported here.

From the limiting conductance the theoretical slopes of the square root plot become 203.75 for the tetraethylammonium bromide and 203.62 for tetraethylammonium chloride. These are shown with the experimental values in Figure 8 and 9.

Walden and Birr obtained slopes of 200 and 193 for the square root plot for the bromide and chloride respectfully, here the slopes were 223.9 and 236.7. Their slopes were less than predicted by the Debye-Huckel-Onsager theory while the present ones are larger.

In a further attempt to fit the data to theory, the extended form of the Debye-Huckel-Onsager was considered. The following extension of the Debye-Huckel Onsager equation

$$\Lambda = \Lambda_0 - (A\Lambda_0 + B)\sqrt{C} + EC\log C + FC$$

was justified theoretically by inclusion of neglected terms but E and F have not been theoretically evaluated. Thus E and F remain semi-empirical constants.

The inclusion of the C log C term may account for a curvature concave upwards of the conductance curve.

These constants E and F were evaluated by plotting the left hand side of the following equation versus log C.

$$\frac{\Lambda - \Lambda_0 + (A\Lambda_0 + B)\sqrt{C}}{C} = E \log C + F$$

This plot did not give a straight line. The section representing the lower concentrations gave a fairly flat curve. E and F were evaluated using this section for this reason and for the reason that the above equation does assume that the solution was dilute.

E = 1256 F = 2712 tetraethylammonium bromide

E = 1448 F = 3211 tetraethylammonium chloride

The large values of these constants indicate that the fit of such an analytical expression would be poor as can be seen in Table III and IV. The limits of accuracy of the measurements are considerably less than the discrepancies shown, particularly with the more concentrated solutions.

The Shedlovsky Function

Rearrangement of the Debye-Huckel-Onsager equation gives

$$\Lambda_0 = \frac{\Lambda + B\sqrt{C}}{1 - A\sqrt{C}}$$

The equivalent conductance at infinite dilution is a constant. therefore a plot of the right hand side of this equation versus concentration should be a horizontal straight line. However Shedlovsky found that the resulting plot was not a horizontal straight line but frequently one with a definite slope. He designated $\frac{\Lambda + B\sqrt{C}}{1 - A\sqrt{C}}$ as Λ_0' to differentiate this from the true equivalent conductance at infinite dilution. He represented the behavior of Λ_0' by the equation $\Lambda_0' = \Lambda_0 + HC$ where H is a constant. Sometimes the curve showed a slight curvature in the dilute solution range thus requiring an additional empirical term such as $MC \log C$

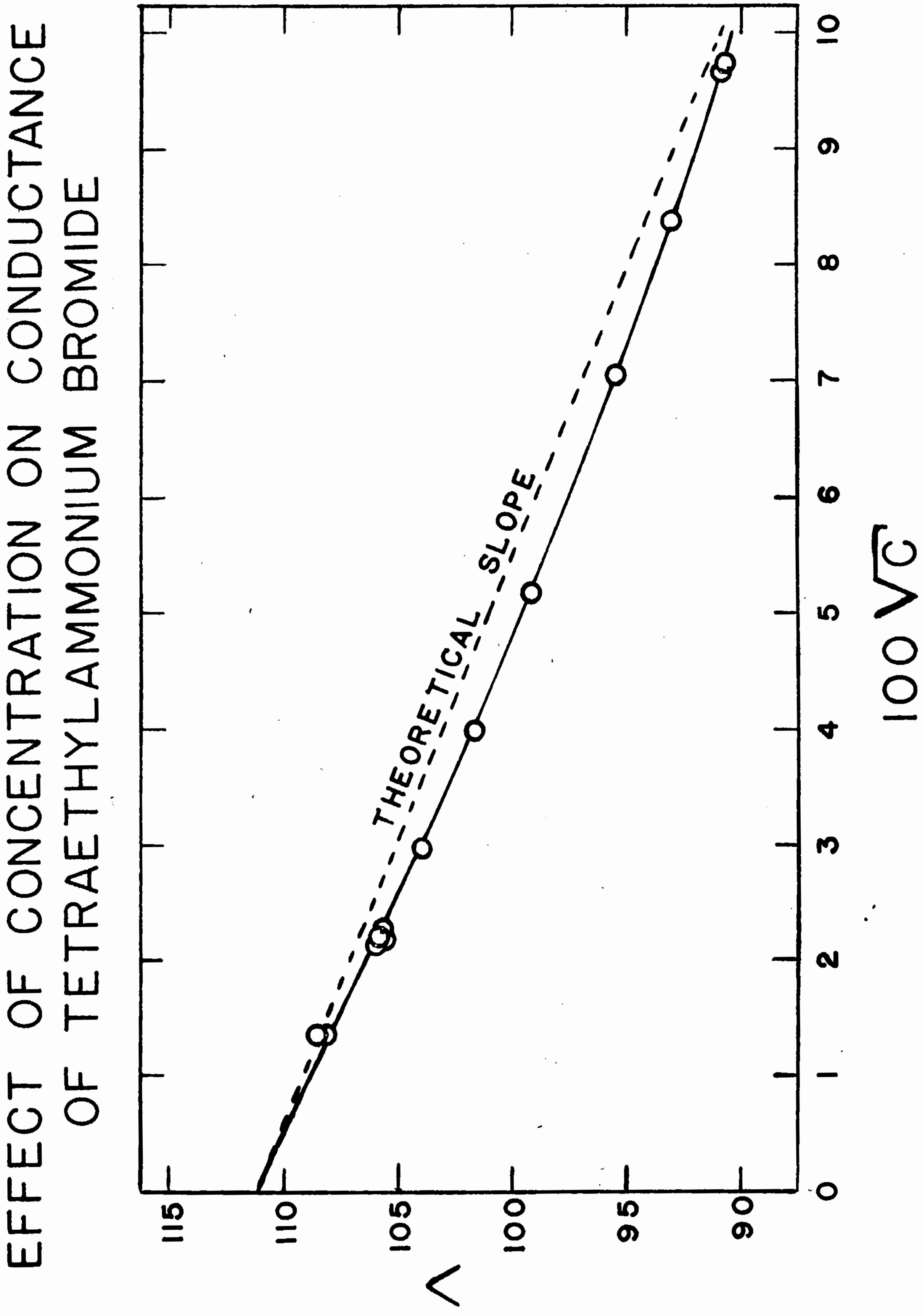

EFFECT OF CONCENTRATION ON CONDUCTANCE
OF TETRAETHYLAMMONIUM BROMIDE
THEORETICAL SLOPE
Λ
115
110
105
100
95
90
0
1
2
3
4
5
6
7
8
9
10
$100\sqrt{C}$

Figure 8

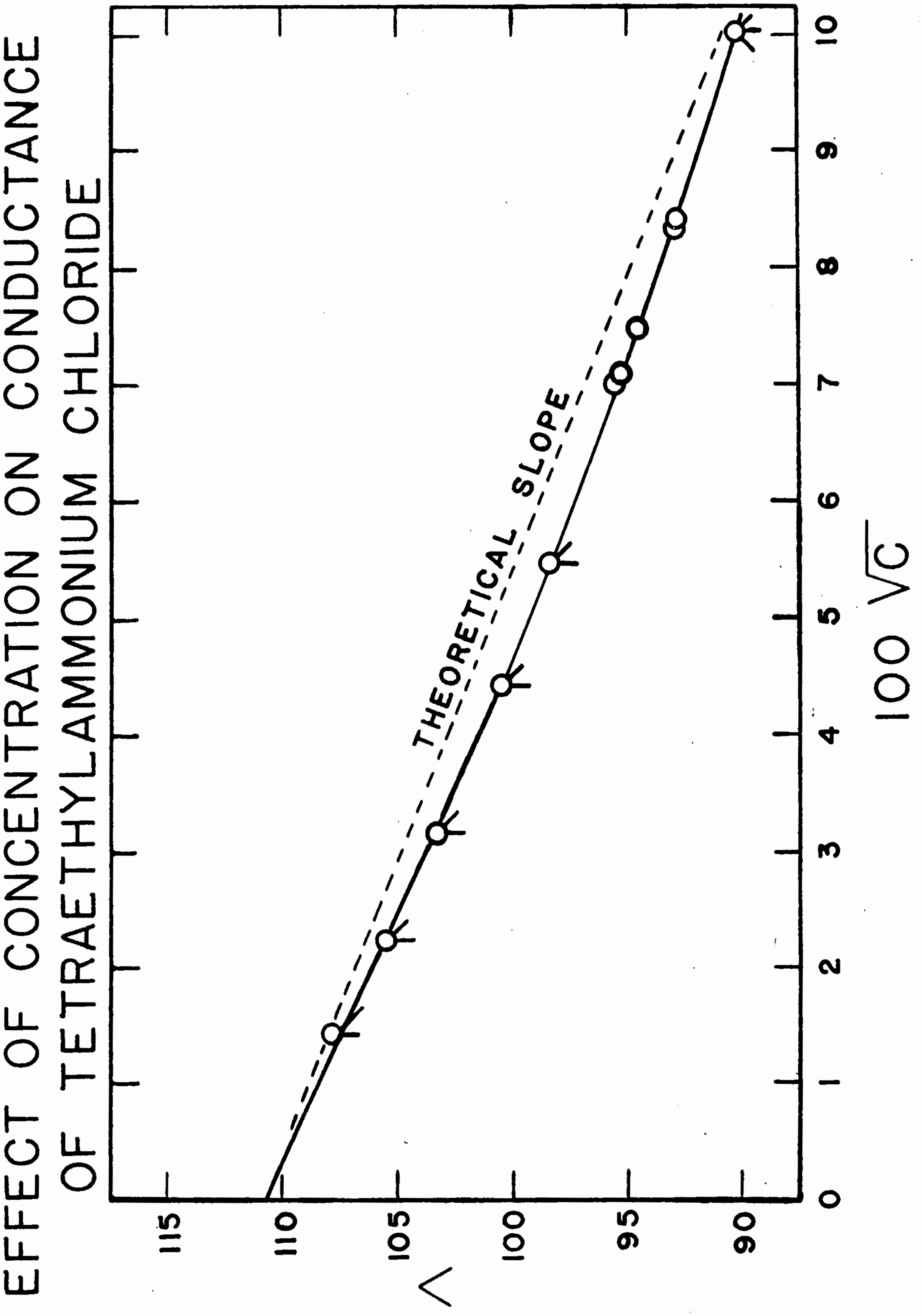

EFFECT OF CONCENTRATION ON CONDUCTANCE
OF TETRAETHYLAMMONIUM CHLORIDE
Λ
115
110
105
100
95
90
0
1
2
3
4
5
6
7
8
9
10
100 √C
THEORETICAL SLOPE

Figure 9

where L and M are constants.

Shedlovsky found that this equation represented the data for strong electrolytes in aqueous solution to a high degree of accuracy, It not only provided a very sensitive test of the data but provided a useful means of extrapolation to zero concentration although it gave preferential weight to the values at low concentration.

The value of the Shedlovsky function at different concentrations given in Tables I and II are plotted in Figures 10 and 11. As can be seen the curve has extreme curvature at the dilute portion, thus making the Shedlovsky function of little use in the determination of the equivalent conductance at infinite dilution. At the lower concentrations, the Shedlovsky function decreases rapidly, goes through a minimum, and then rises again. This initial decrease can be explained theoretically by differentiating Λ_0' with respect to C. It may be shown that

$$\frac{d\Lambda_0'}{dC} = -\infty$$

when C approaches zero as a limit(121). Generally the slope found in other research was not as great as found here. Such a behavior has been interpreted as indicating that the solutions behave somewhat as weak electrolytes.

The best fit to the data was obtained from the equations

$$\Lambda_0' = 111.00 + 2811C + 1302C\log C$$

for tetraethylammonium bromide

$$\Lambda_0' = 110.82 + 3327C + 1500C\log C$$

for tetraethylammonium chloride. These constants were found by plotting

$$\frac{\Lambda_0' - \Lambda_0}{C} \quad vs \quad \log C$$

Table III

COMPARISON OF Λ AND $\Lambda_{calc.}$ FOR TETRAETHYLAMMONIUM BROMIDE

C x 10^4	Λ	Λ calc.	Difference
95.090	90.63	92.75	2.14
94.874	90.70	92.77	2.07
94.470	90.68	92.79	2.11
93.422	90.88	92.83	1.95
70.381	93.02	93.96	0.94
69.627	92.97	94.02	1.05
69.530	93.16	94.02	0.86
50.076	95.48	95.70	0.22
49.400	95.48	95.77	0.29
26.708	99.16	99.08	-0.08
26.614	99.14	99.10	-0.04
15.972	101.50	101.58	0.08
15.961	101.57	101.58	0.01
15.922	101.62	101.59	-0.03
15.794	101.85	101.64	-0.21
8.9153	103.90	103.92	0.02
8.6813	103.99	104.01	0.02
5.1882	105.71	104.22	-0.49
4.8346	105.82	105.82	0.00
4.5255	106.00	105.99	-0.01
1.8012	108.18	107.91	-0.27
1.7943	108.67	108.59	0.08

Table IV

COMPARISON OF Λ AND Λcalc. FOR TETRAETHYLAMMONIUM CHLORIDE

C x 10^4	Λ	Λcalc.	Difference
100.73	90.03	93.60	3.57
100.43	90.14	93.61	3.47
70.982	92.83	94.37	1.54
69.647	92.92	94.44	1.52
55.858	94.54	95.31	0.77
50.483	95.28	95.77	0.49
49.115	95.43	95.90	0.47
29.920	98.43	98.35	-0.08
29.834	98.44	98.37	-0.07
19.922	100.49	100.34	-0.15
19.633	100.51	100.41	-0.10
19.617	100.51	100.41	-0.10
9.9911	103.27	103.25	-0.02
9.9749	103.25	103.26	0.01
5.0074	105.50	105.48	-0.02
4.8883	105.58	105.54	-0.04
2.0142	107.39	107.50	0.11
1.9968	107.39	107.52	0.13
1.9407	108.24	107.57	-1.67

which if the equation were strictly valid would give a straight line of slope and intercepts equal to the constants L and M respectively. Again no straight line was found except towards the dilute region of the curve. Since this is the region where the equation is more likely to be valid, this region was used preferentially. Tables V and VI show the comparison of values calculated from the equations and those obtained experimentally. Many of the differences are far greater than the limit of accuracy of the experimental work.

Ion Pair Formation

The postulation of the presence of ion pairs by Bjerrum in 1926 was further elaborated by Fuoss and Kraus(71) and Kirkwood(72).

According to the Boltzman equation, the time average number of ions, dn, in a small element, dv, at a distance r from a selected ion will be

$$dn = n e^{-\epsilon^2/DrkT} dV$$

If the volume element is a spherical shell of thickness dv then

$$\frac{dn}{dr} = 4\pi n r^2 e^{-\epsilon^2/DrkT}$$

For two spherical ions of opposite charge, the value of is a minimum for a certain value of r . This value can be calculated by differentiation of the preceding equation giving

$$r_{min.} = \frac{\epsilon^2}{2DkT}$$

Bjerrum assumed that two ions will form a non-conducting ion pair if they approach one another within this critical distance. Combining this idea with the law of mass action an equation for calculating the equilibrium constant was obtained, involving the so called distance of closest approach of the ions. However the ionic diameters of these salts have not been measured in nitromethane, thus this equation cannot be used.

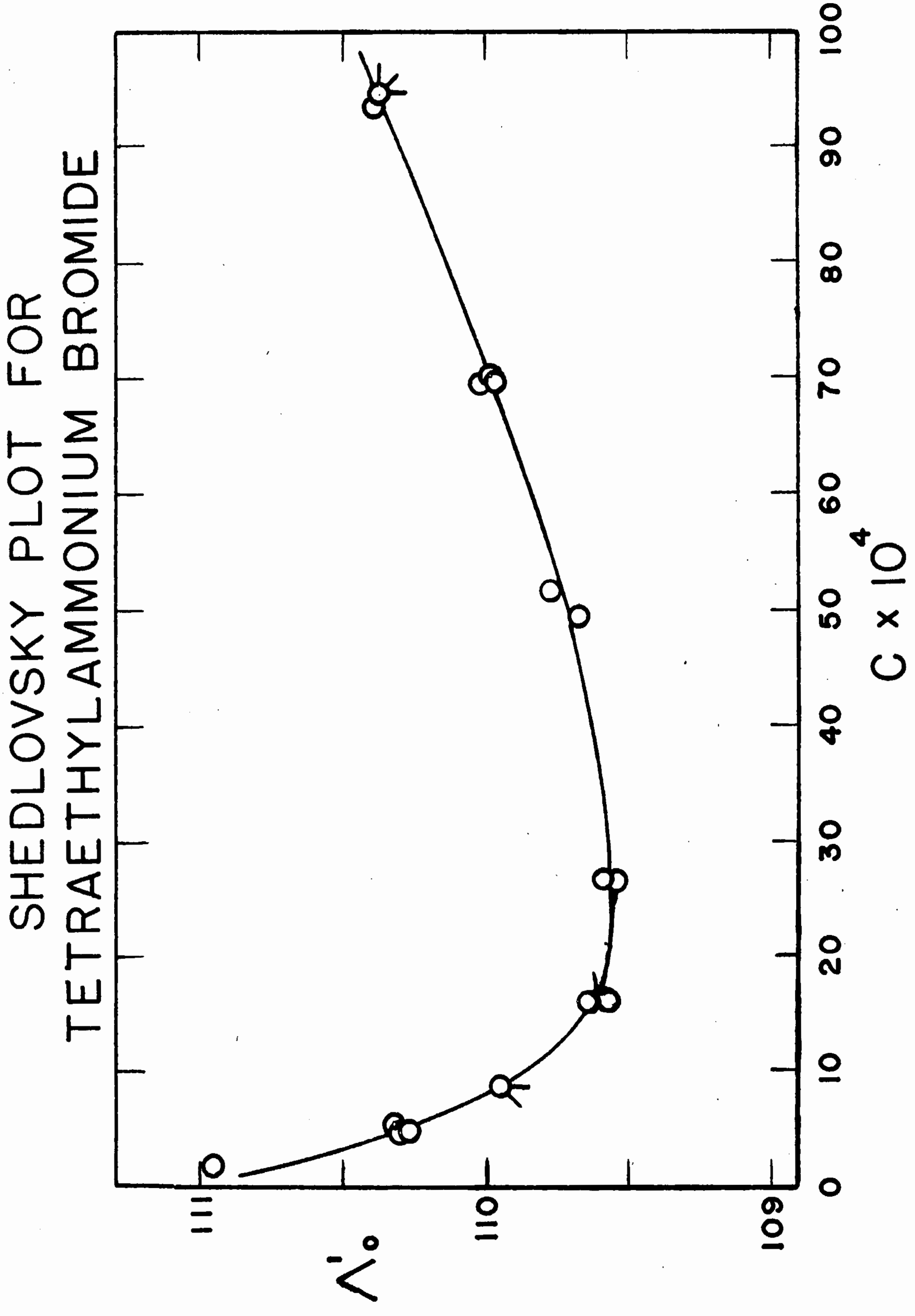

SHEDLOVSKY PLOT FOR
TETRAETHYLAMMONIUM BROMIDE
C x 10^4
0
10
20
30
40
50
60
70
80
90
100
Λ°'
111
110
109

Figure 10

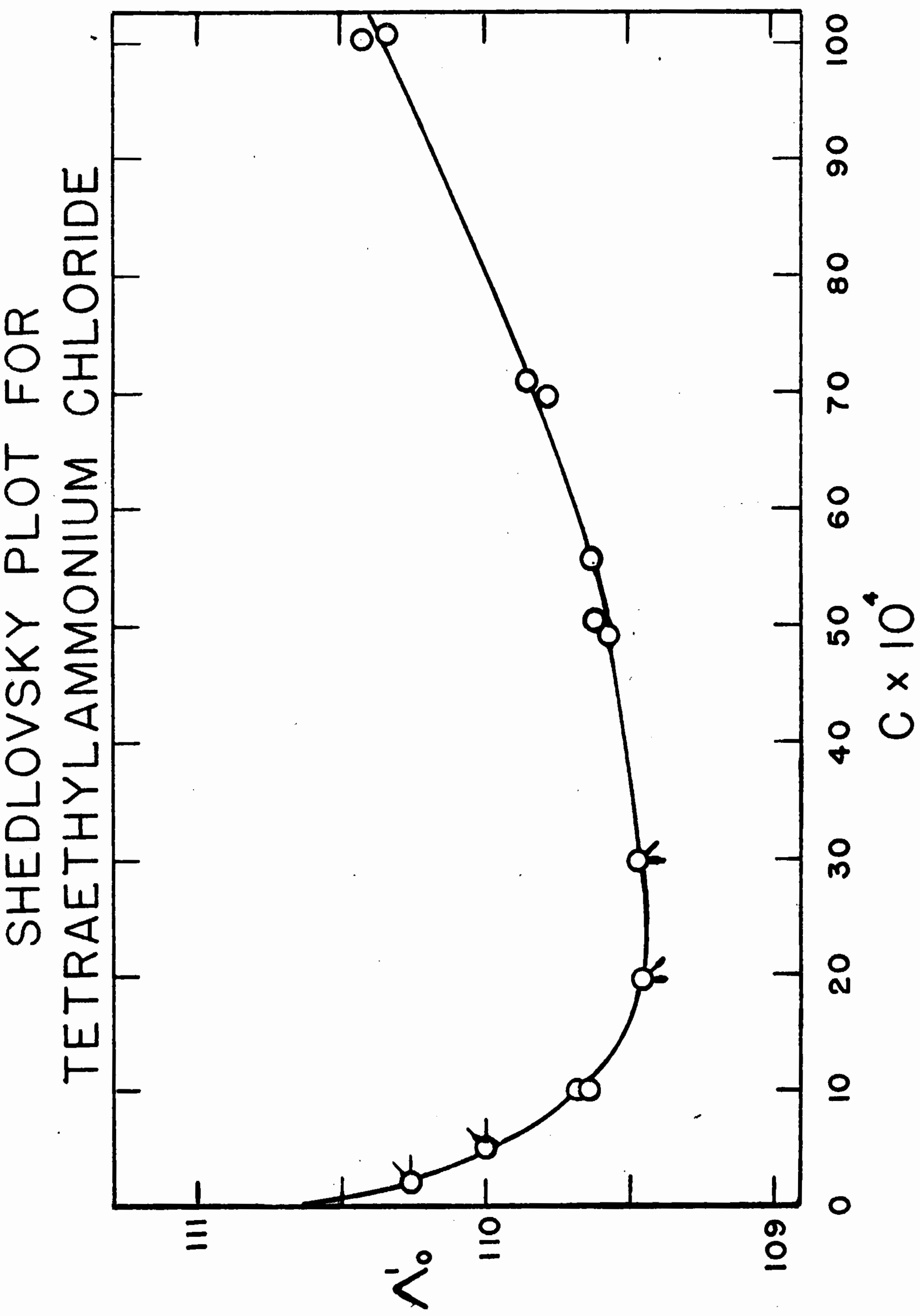

SHEDLOVSKY PLOT FOR
TETRAETHYLAMMONIUM CHLORIDE
Λ_o
111
110
109
0
10
20
30
40
50
60
70
80
90
100
$C \times 10^4$

Figure 11

The value of r min in nitromethane was calculated to be 7.82 Å. By analogy with other electrolytes the distance of closest-approach would be expected to be less than this. This would indicate that these salts should be associated. However similar calculations made for alkali halides in methanol lead to the same prediction but were discredited by experiment(132).

Treatment of nitromethane solutions as weak electrolytes

Since the results do not fit the Debye-Huckel-Onsager Theory where the salts are assumed to be strong electrolytes, the results will be considered with the assumption that the salts are weak electrolytes. A method of treating weak electrolytes which combines the Arrhenius Theory and the Debye-Huckel-Onsager Theory was suggested by Fuoss and Kraus(110,111,112).

It was assumed that

$$\Lambda = \alpha\left(\Lambda_0 - [A\Lambda_0 + B]\sqrt{C}\right)$$

where α is the fraction of electrolyte present as ions. This αC is the concentration of the ions. By rearranging

$$\alpha = \frac{\Lambda}{\Lambda_0\left(1 - [A\Lambda_0 + B]\dfrac{\sqrt{\alpha C}}{\Lambda_0}\right)}$$

In the limit this equation reduced to

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

as suggested by Arrhenius.

This equation was solved by successive substitution back into the correction term

$$1 - [A\Lambda_0 + B]\frac{\sqrt{\alpha C}}{\Lambda_0}$$

This term may be represented by

$$F(z) = 1 - z\left\{1 - z\left[1 - z(+c)^{-\frac{1}{2}}\right]^{-\frac{1}{2}}\right\}^{-\frac{1}{2}}$$

where

$$z = [A\Lambda_0 + B]\frac{\sqrt{C\Lambda}}{\Lambda_0^{3/2}}$$

Table V

COMPARISON OF Λ_0 WITH $\Lambda_0$calc. FOR TETRAETHYLAMMONIUM BROMIDE

C x 10^4	Λ_0' c	Λ_0 calc.	Difference
95.090	110.46	108.78	-2.24
94.874	110.51	108.83	-2.17
93.422	110.54	108.97	-2.03
70.381	110.06	109.30	-1.70
69.627	109.90	109.88	-1.12
69.530	110.10	110.09	-0.91
50.076	109.84	110.76	-0.14
49.399	109.74	110.69	-0.31
26.708	109.64	111.08	0.08
26.614	109.59	111.03	0.03
15.972	109.61	110.94	-0.06
15.961	109.68	111.01	0.01
15.922	109.72	111.04	0.04
15.794	109.92	111.24	0.24
8.9153	109.97	111.00	0.00
8.6813	109.99	111.01	0.01
5.1882	110.34	111.10	0.10
4.8346	110.29	111.02	0.02
4.5255	110.32	111.07	0.07
1.8012	110.92	111.34	0.34
1.7943	111.41	111.83	0.83

Table VI

COMPARISON OF Λ_o WITH $\Lambda_o$calc. FOR TETRAETHYLAMMONIUM CHLORIDE

C x 10^4	Λ_o'	$\Lambda_o$calc.	Difference
100.73	110.44	107.10	-3.72
1oo.43	110.53	107.22	_3.71
70.982	109.93	109.19	-1.63
69.647	109.86	109.22	-1.60
55.858	109.69	109.87	-0.83
50.483	109.68	110.28	-0.54
49.115	109.63	110.30	-0.52
29.920	109.52	110.89	0.o7
29.834	109.51	110.89	0.07
19.635	109.49	110.93	0.11
19.617	109.49	110.93	0.11
9.9911	109.70	110.87	0.05
9.9749	109.66	110.83	0.01
5.0074	110.04	110.85	0.03
4.8883	110.06	110.85	0.03
2.0142	110.27	110.72	-o.06
1.9968	110.26	110.70	-0.12

Thus

$$\alpha = \frac{\Lambda}{\Lambda_0 F(z)}$$

The value of α used to estimate the activity coefficient, $f\pm$, by the limiting law

$$\log f_\pm = \frac{1.283 \times 10^6}{(DT)^{3/2}} \sqrt{\alpha C}$$

Substituting these into the mass action law,

$$\frac{F(z)}{\Lambda} = \frac{1}{\Lambda_0} + \frac{C\Lambda f_\pm^2 / F(z)}{K(\Lambda_0)^2}$$

This equation is reported to be valid to a concentration of 3 x $0^{-7}D^3$ (111) or for nitromethane 2 x 10^{-2} moler.

Thus when $\frac{F(z)}{\Lambda}$ was plotted against $\frac{C\Lambda f_\pm^2}{F(z)}$ from the values given in Tables VII and VIII a straight line was obtained for a number of weak electrolytes. A plot of this type for the tetraethylammonium bromide and chloride is shown in Figure 12 and 13 respectively. Tables VII and VIII give the numerical values. Obviously a straight line was not obtained and these salts do not appear to be weak electrolytes especially when the values calculated for the degree of dissociation are noted.

Walden's Rule

For purposes of comparing the limiting conductance of salts in various solvents Walden's Rule has been widely used and will now be discussed in some detail.

Although Walden's Rule was discovered experimentally(126), it has been developed theoretically by combining Coulomb's Law, and Stokes Law in the following manner:

According to Stokes Law a sphere of radius, r, moving through a medium of viscosity, η, under the influence of a force, f, reaches a terminal velocity v given by

$$v = \frac{f}{6\pi\eta r}$$

TETRAETHYLAMMONIUM BROMIDE
AS A WEAK ELECTROLYTE

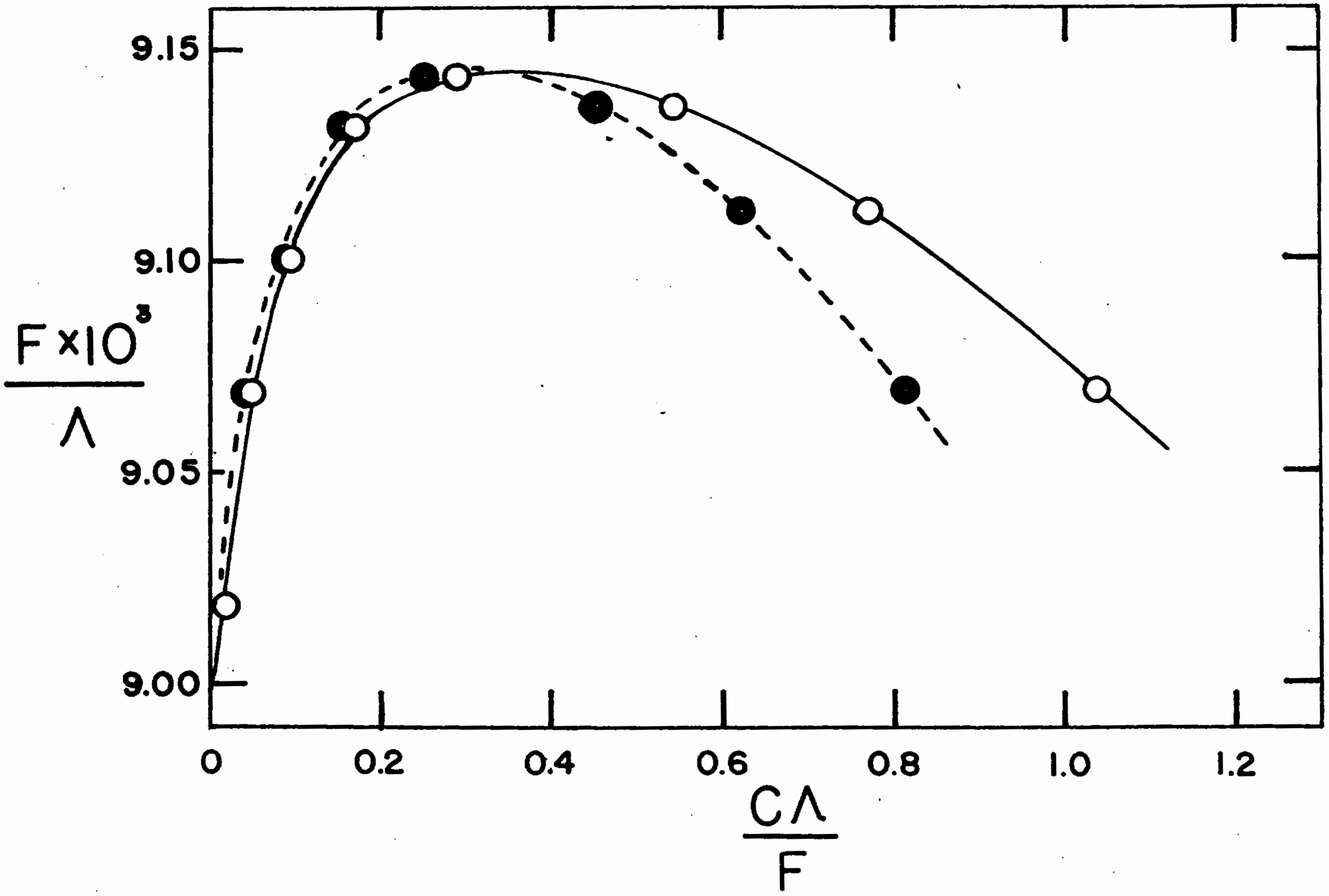


Figure 12

Figure 13

TETRAETHYLAMMONIUM CHLORIDE AS A WEAK ELECTROLYTE

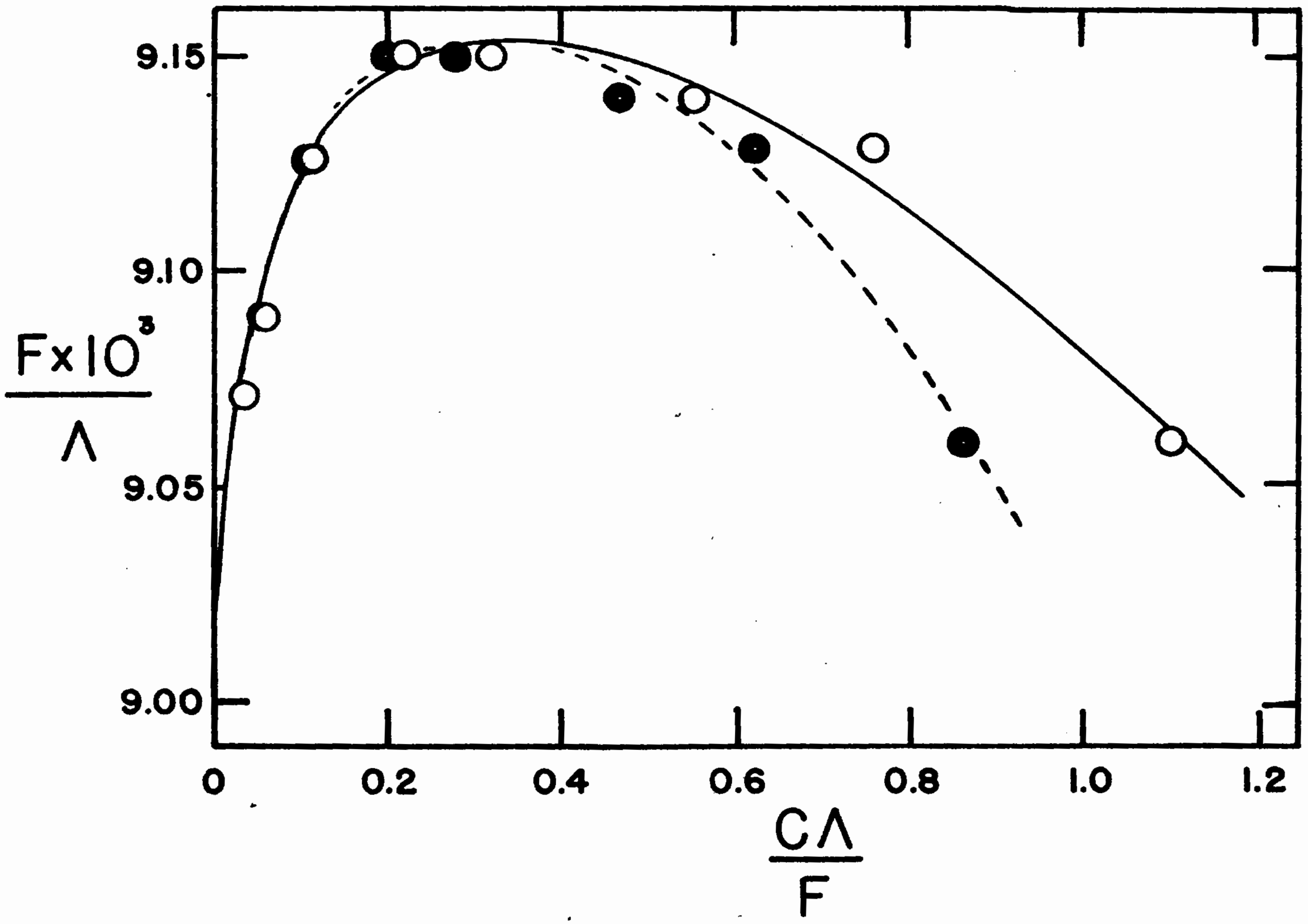


Table VII

TREATMENT OF TRTRAETHYLAMMONIUM BROMIDE
AS A WEAK ELECTROLYTE

F/Λ x 10^3	$\frac{C\Lambda}{F}$	$\frac{C\Lambda f^2}{F}$	α
9.06	1.05	0.816	0.993
9.11	0.773	0.624	0.989
9.13	0.549	0.459	0.987
9.14	0.291	0.255	0.985
9.13	0.174	0.158	0.987
9.10	0.098	0.0908	0.990
9.07	0.050	0.047	0.993
9.02	0.020	0.020	0.999

Table VIII

TREATMENT OF TETRAETHYLAMMONIUM CHLORIDE AS A WEAK ELECTROLYTE

$\frac{F/\Lambda}{x\ 10^3}$	$\frac{C\Lambda}{F}$	$\frac{C\Lambda f^2}{F}$	α
9.06	1.11	0.858	0.995
9.12	0.763	0.617	0.988
9.14	0.552	0.461	0.987
9.15	0.312	0.272	0.986
9.15	0.215	0.192	0.986
9.12	0.110	0.101	0.989
9.09	0.054	0.051	0.992
9.07	0.022	0.022	0.995

Under the influence of an applied electrical potential E the terminal velocity will also be equal

$$\upsilon = \frac{\lambda_\pm E}{F}$$

where $\lambda_\pm$ is the ionic conductance F is the Faraday constant equaling E times the electronic charge, ϵ, equating these values of υ one obtains the relationship

$$\eta\lambda_\pm = \frac{\epsilon F}{6\pi r_\pm \eta}$$

Hence the product of the ionic conductance times the viscosity will be a constant regardless of the solvent provided that (a) the radius of the ion does not change from solvent to solvent or (b) that the ions behave as spheres in a continuous medium.

Since the equation required ionic conductances, transference numbers are needed in order to test the validity of these assumptions. However transference data in non-aqueous media is almost entirely lacking.

However Fowler and Kraus have developed a method of obviating this limitation(47). Fowler and Kraus observed that the mobility of ions containing large number of carbon atoms decreased with increased number of carbon atoms. The decrease per carbon atom decreases with increasing number of atoms. In other words, the mobility of large ions asymptotically approaches a limiting value with increase in size. Thus with a salt of a large cation and anion, it may be assumed that the ionic conductances of the two ions were equal to one half that of the salt. They used tetra-n-butylammonium triphenyl borofluoride as a standard.

On the basis this method values of $\eta\lambda_0$ for the tetraethylammonium ions have been obtained. The agreement is remarkably good in view of the questionable assumption mentioned above. See Table IX.

To test the necessity of the requirements of Stokes Law, it was decided to ascertain whether other shaped particles would also provide a constant value for $\eta\lambda_0$ if the particle was an ion.

Table X shows the calculated values of $\eta\lambda_0$ for various shaped particle on the assumption that the hydrodynamic relationships can be applied to an ionic system.

If the dimensions of the ions were known it would be possible to discover whether any of these relationships would apply.

Since no measurements have been made on the sizes of these ions except in the crystalline form, a very approximate estimate was made using atomic radii and bond angles reported by Pauling and Huggins$^{(101)}$. The atomic radii used were: 0.70 A for nitrogen, 0.77 A for carbon, 0.28 A for hydrogen. The bond angle used was 109 28". The sizes adopted for this calculation are the maximum obtained when the ions are spread out. The actual size will tend to be less than this the longer the carbon chain. Tetrahedral models of the ions were used and half the distance from the apex to the opposite face was called the ionic "thickness". These values were calculated on the arbitrary assumption that the ions are not solvated. For the calculated values see Table XI.

Figure 14 shows the relationship between the ionic "thickness" and the inverse product.

Although a linear plot was obtained for these salts in water$^{(48)}$, the values were more sporadic in the other solvents.

The slope obtained in water was 1.2 showing good agreement with theory for a sphere.

Table IX

APPLICATION OF WALDEN'S RULE
TO
TETRAETHYLAMMONIUM IONS

Solvent		
Water	(127)	0.295
Methanol	(127)	0.294
Ethanol	(127)	o.295
Acetone	(127)	0.294
Furfural	(127)	0.293
Acetonitrile	(127)	0.294
Pyridine	(127)	0.294
Nitrobenzene	(52)	0.293
Nitromethane	(64)	0.310

Table X

DEPENDANCE OF WALDEN'S RULE UPON SIZE AND SHAPE

Theoretical Value of $\frac{1}{\eta\lambda}$	Shape and Motion
1.220 r	Sphere
1.036 r	Disk with face in direction of motion (97,98)
0.682 r	Disk moving edgewise (97)
0.906 r	Square with face in direction of motion (99)
0.158 L + 1.102 r	Cylinder of length L radius r (99)

Table XI

CALCULATED IONIC "THICKNESS"

Ion	"Thickness" A°
Ammonium	
Tetramethylammonium	1.50
Tetraethylammonium	2.30
Tetra-n-propylammonium	3.98
Tetra-n-butylammonium	5.00
Tetra-i-butylammonium	3.98
Tetra-n-amylammonium	6.00
Tetra-i-amylammonium	5.00

Table XII

THE PRODUCT $\eta\lambda_0^-$ FOR HALOGENS IN VARIOUS SOLVENTS

Solvent	Chloride	Bromide	Iodide
Water (128)	0.665	0.695	0.683
(127)	0.682	0.698	0.686
Methanol (128)	0.289	0.323	0.333
(127)	0.284	0.305	0.332
Ethanol (128)	0.263	0.278	0.310
Acetonitrile (128)	0.306	0.330	0.347
Acetone (128)	0.342	0.348	0.339
(127)	0.332	0.370	0.366
Nitrobenzene (52)	0.402	0.391	0.369
Nitromethane (128)			0.389

VARIATION OF CONDUCTANCE WITH SIZE OF TETRALKYLAMMONIUM IONS

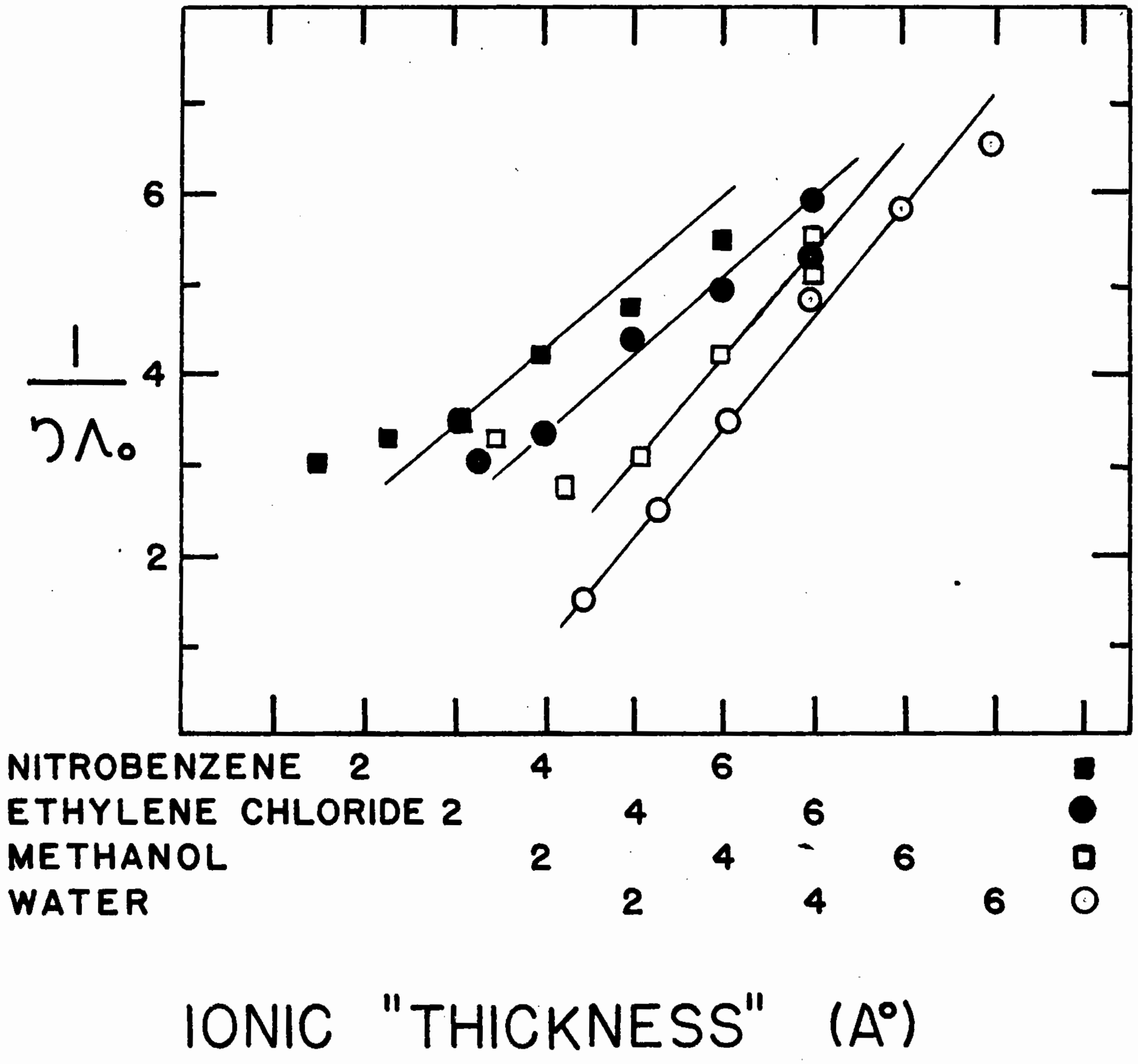


Figure 14

In the methanol(50), the line through the points representing the tetraethylammonium tetra-n-propylammonium and tetra-iso-amylammonium ions had the same slope as that for water. the tetramethylammonium ion had too low a conductance to fit the curve and the tetra-n-butylammonium ion had too high a conductance to fit.

The former may be explained by solvation, the latter by chain coiling to give a smaller size than was calculated. Small ions have been suspected of solvating more than larger ions because of their greater charge density.

Ethylene chloride(49,53,54,55,56) and nitrobenzene(51,52) had lower slopes (1.0 and 0.66 respectively) and more poorly defined lines. Again the small ions, amonnium, and tetramethylammonium, indicated a solvation effect and the larger ions a coiling effect.

All of the lines passed close to the origin of the plot which was also required by theory.

Walden's Rule when applied to chloride, bromide, and iodide ions was found to be rather inaccurate as can be seen in Table XII. Presumably such factors as solvation have a large effect upon the conductances of these ions.

This made this check of the present work of little value. Using the value of $\eta \lambda_0 = 0.40$ for the halogen and 0.295 for tetraethylammonium ion and 0.00627 for the viscosity, the conductance of the salts should be 110.7. This evidence would further indicate that the value of 88.60 for tetraethylammonium chloride reported by Walden(62) to be very low. Since the conductances of the bromide and chloride were so similar in nitrobenzene(52), it was expected that they should be very similar in nitromethane as was found.

Summary

The equivalent conductance of tetraethylammonium bromide and chloride in nitromethane measured from 1 x 10^{-4} to 1 x 10^{-2} molar was found to be verysimilar. The conductances at infinite dilution were 111.0 and 110.8 respectively. The plot of the equivalent conductance versus the square root of the concentration gave a slightly curved line instead of the straight line obtained for strong electrolytes. The data did not fit the short or extended forms of the Debye-Huckel-Onsager equation or the Shedlovsky equation. Also the data did not fit with the equation generally applicable to weak electrolytes.

The use of Walden's Rule was found to be fairly accurate for the tetraethylammonium ions but not so for the halogen ions. However in spite of this, work in other solvents indicate that the values found were correct.

BIBLIOGRAPHY

(1) Davy, Sir Humphry Phil. Trans. Roy. Soc. 96 1, 333 (1807)

(2) Berzelius Jour. Phys. 68 142 (1809) 69 1 (1810) 73 58(1811)

(3) Von Grothus, C. J. Ann. Chem. Phys. 63 20 (1811)

(4) Faraday, Michel Experimental Researches 1834

(5) Clausius, R. Pogg. Ann. 101 347 (1857)

(6) Williamson, Al Lieb. Ann. 77 37 (1851)

(7) Valson, M. C. Ann. Chim. Phys. IV 20 361 (1870) Compt. Rendu 73 441 (1871)

(8) Gladstone H. Phil. Mag. (IV) 36 311 (1868)

(9) Wiedemann G Pogg. Ann. 126 1 (1865) 135 177 (1863)

(10) Rontgen W. G. and Schneider J., Wied. Ann. 29 165 (1886)

(11) Kohlrausch Wied. Ann. 6 146 (1879) Ann. Physils. 6 1 (1879)

(12) Rauolt F. M. Ann. Chim. Phys. (VI) 4 401 (1885)

(13) Arrhenius, S. Ztsche. Phys. Chem. 1 631 (1887)

(14) Ostwald ibid. 2 36 (1888)

(15) Ostwald ibid. 3 170 241 (1889)

(16) Bredig, G. Ztsche. Phy. Chem. 13 289 (1894)

(17) Partington, J. R. J. Chem. Soc. 97 1160 (1910)

(18) Kendall, J., JACS. 36 1069 (1914)

(19) Van Saar, J. J., Ztsche. Phys. Chem. 18 274 (1895) ibid. 19 318 (1896)

(20) Sutherland W. Phil. Mag. (VI) 3 161 (1902) Phil. Mag. (6) 14 1 (1907)

(21) Noyes, A. A. Science 20 584 (1904)

(22) Milner, S. R. Phil. Mag. 23 551 (1912) 35 214 (1918)

(23) Milner, S. R. ibid. 25 742 (1913)

(24) George and Chapman Phil.Mag. (VI) 41 799 (1921)

(25) La Mer, V. K. Trans. Am. Electrochem. Soc 51 507 (1927)

(26) La Mer, V. K. ibid. 523

(27) Ghosh J Chem Soc 113 449 627 707 790 (1918)

(28) Kraus, C. A. JACS 43 2514 (1921)
Arrhenius S. Z. Phys.Chem. 100 9 (1922)

(29) George and Chapman Phil.Mag. (VI) 41 (1921)

Sand, H. S. ibid. 45 129, 281 (1923)

Kallman, H. Z. Phys.Chem. 98 433 (1921)

(30) Bates and Kushmann JACS. 41 1991 (1919)

(31) Hill, A. E. ibid. 43 254 (1921)

(32) Bragg, W. H. & Bragg W. L. (see book) for x-rays & x 1 Structure p 165 London 1924

(33) Debye, P. and Huckel, E. Phys. Zeit 24 185 305 (1923)

(34) Joos, G. Blumentritt, M Physik Z, 28 836 (1927)

(35) Onsager, L Phys.Zeit. 27 388 (1926) 28 277 (1927)
Trans. Farad. Soc. 23 337 (1927)

(36) Hittorf, W. Pogg.Ann. 89 177 (1853) 106 337, 513 (1855)
98 1 (1856) 103 1 (1858)

(37) International Critical Tables III page 24

(38) Kohlrausch & Holborn Leitvermoger der electrolyte Tensner Leipsig

(39) Streiff, Anton J. & Rossini Fredrick D. Research Natl. Bur. of Standards 35 355-373 (1945) Research Paper 1676

(40) Jones, W. M. and Giague, W. F. JACS. 69 983-7 (1947)

(41) Gunning, H. E. & Gordon A. R. J. Chem.Phys. 10 126 (1942)

(42) LeRoy, D. J. and Gordon A. R. J. Chem.Phys. 6 398-402 (1938)

(43) Jones, G. & Bradshow, B. C. JACS. 65 1780 (1933)

(44) Kraus, Charles A. & Fuoss, Raymond M. JACS. 55 21 (1933)

(45) Unmack, Augusta Murray - Rust D. M. & Hartley, Harold Proc Roy. Soc. (London) A132 427 (1931)

(46) McIntosh, Robt. E. Mead, Darwin J. Fuoss, Raymond M. JACS. 62 506 (1940)

(47) Fowler, D. Leigh & Kraus, Charles A. JACS. 62 2237 (1940)

(48) Daggett, Harry M., Jr. Blair, Edward J. Kraus, Charles A. JACS. 73 799 (1951)

(49) Pickering, Harold L. and Kraus, Charles H. JACS 71 3288 (1949)

(50) Evers, E. Charles & Knox, Andrew G. JACS. 73 1739-44 (1951)

(51) Taylor, Edward G. & Kraus, Charles A. JACS. 69 1731 (1947)

(52) Wischonke, Charles R. and Kraus, Charles A. XXIX JACS. 69 2472 (1947)

(53) Mead, D. J. Ramsey, J. B. Rothrock, D. A., Jr. and Kraus, C. A. JACS. 69 528 (1947)

(54) Kline, Ernest R. and Kraus, Charles A. JACS 69 814 (1947)

(55) Gleysteen, Leland F. and Kraus, Charles A. JACS. 69 451 (1947)

(56) Tucker, Lawrence M. and Kraus, Charles A. JACS. 69 454 (1947)

(57) Wischonke, Charles R. and Kraus, Charles A. JACS. 69 2472 (1947)

(58) Williams, John Warren JACS. 47 2644 (1925)

(59) Kraus, Charles A. and Bray, W. C. JACS. 35 1315 (1913)

(60) Gronwall, L. H. La Mer, V. K. and Sandved, K. Physik-Z. 29 358 (1928)

(61) Shedlovsky, T. JACS 54 1405 (1932)

(62) Walden, P. and Birr, E. J. F physik. Chem. A163 263-80 (1933)

(63) Walden, P. and Birr, E. J. F physik.Chem. A163 321-80 (1933)

(64) Wright, C. P. Murray-Rust, D. M. and Hartley, Harold J.Chem.Soc. 1931 199-214

(65) Sadek, Hussein, and Fuoss JACS. 72 301 (1950)

(66) Thompson, Walter E. & Kraus, Charles A. JACS. 69 1056-20 (1947)

(67) Tucker, Lawrence M. & Kraus, Charles A. JACS. 69 454-6 (1947)

(68) Reynolds, Myron B. & Kraus, Charles A. JACS. 70 1709-13(1948)

(69) Fowler, D. Leigh & Kraus, Charles A XXV JACS. 62 2237-40 (1940)

(70) Bjerrum, N. Kgl. Damke. Vidensk. Selskab. 7 #9 (1926)

(71) Fuoss, R. M. & Kraus, C. A. JACS. 55 476, 1019 (1933)

(72) Kirkwood, J. G. J. Chem. Phys. 2 767 (1934)

(73) Fuoss, R. M. & Kraus, C. A. JACS. 55 2387 (1933)

(74) Fuoss, R. J. JACS. 56 2017 ((1934)

(75) Fuoss, R. M. & Kraus C. A. ibid. 57 1 (1935)

(76) Wien, Max and Melsch, J. Ann. Physik. (4) 83 305 (1927)

(77) Wien, M. and Schiele, J. Ann. Physik Z. 32 545 (1931)

(78) Debye, P. & Falkenhagen, H. Physik Z. 29 121, 401 (1928)

(79) Sack, H. Physik. Z. 29 627 (1928)

(80) Shedlovsky, T. JACS. 52 1793 (1930)

(81) Walden, P. Z. Physik. Chem. 58 129 (1907)

(82) Fonssereau, G. J. de Physique. 2 (4) 189 (1885)

(83) Newbury, E. J. Chem. Soc. 113 701 (1918)

(84) Eastman, E. D. JACS. 42 1648 (1920)

(85) Bronsted, J. N. and Nielsen, R. F. Trans. Faraday Soc. 31 1478 (1935)

(86) Gunning, H. E. and Gordon, A. R., J. Chem. Phys. 10 126-131 (1942)

(87) Gunning, H. E. and Gordon, A. R. ibid. 11 18 (1943)

Schiff, H. I, and Gordon, A. R. ibid. 16 336-9 (1948)

(88) MacInnes, Duncan A. J Franklin Inst. 225 661-687 (1938)

(89) Walden, P. Z physik. Chem. 58 490 (1907) 59 394 (1907) 65 139 (1909)

(90) Walden, P. ibid. 58 129 (1907)

(91) Williams, John Warren JACS. 47 2644 (1925)

(92) Lattey, R. T. and Gatty, O. Phil. Mag. 7 985 (1929)

(93) Hantzsch and Berger Ber. 61 1338

(94) Taylor, H. Austin and Vesselovsky, Vladimir V. J. Phys.Chem. 39 1095-1101 (1935)

(95) Cottrell, T. L. and Reid, T. J. J. Chem.Phys. 18 1306 (1950)

(96) Onsager, L. & Fuoss, R. M. J.Phys.Chem. 36 2689 (1932)

(97) Oberbeck, A. Crelles Jour 81 62 (1876)

(98) Squires, Lombard & Squires, Jr. Walter Trans. Am. Inst. Chem. Engrs. 33 1-12 (1937)

(99) Boido, Denise Peintures Pigments vernis 23 51-5 78-85 103-110 146-153 (1947)

Persog, Bernard, and Boido, Denise.Compt.rend. 223 669-70 (1946)

(100) Kuhn, Hans J Colloid Sci. 5 331-348 (1950)

(101) Pauling, Lewis and Huggins M L Z Krist 87 205 (1934)

(102) Brown, A. S. and MacInnes, D. J. JACS. 57 1356 (1935)

(103) Jones, Grinnell, and Bradshaw, B.B. JACS. 55 1780 (1933)

(104) Shedlovsky, Theodore; and Brown, Alfred Seely JACS. 56 1066 (1934)

(105) McKinney Jr., C. Dana; and Hall, R. T. Ind.Eng.Chem. Anal. Ed. 15 460 (1943)

(106) Almy, E. G.; Griffin, W. C.; and Wilcox, C. S. Ind.Eng.Chem.-Anal. Ed. 12 392 (1940)

(107) Brady, L. S. Anal.Chem. 20 1033 (1948)

(108) Warren, G. G. Can Chem.Proc.Ind. 29 370 (1945)

(109) Kohlrausch and Maltby Wiss. Abh. Phys. Tech. Reich. 3 157 (1900)

(110) Fuoss, R. M. and Kraus, C. A. JACS. 55 476 (1933)

(111) Fuoss, R. M. ibid. 57 488 (1935)

(112) Mead, D. S., Fuoss, R. M. and Kraus, C. A. Trans. Faraday Soc. 32 594 (1936)

(113) Kraus, Charles A. J Franklin Inst. 225 687-707 (1938)

(114) Williams, J. W. Chem.Reviews 8 303-19 (1931)

(115) Walden, P. Z physik.chem. 61 633-9

(116) Walden, P. ibid. 65 228 (1906)

(117) Wagner, J. ibid. 46 872

(118) Philip, James C. and Oakley, Henry B. J.Chem.Soc.(London) 125 1189 (1924)

(119) Creighton J Franklin Institute 189 641

(120) Henry Bulletin de la classe des Sciences Academie Royale de Belgigue 1906 732

(121) Owen, B. B. JACS. 61 1393 (1939)

(122) Methods of Analysis of the Association of Official Agricultural Chemists Washington, D.C. 6th Ed. (1945) 27.20

(123) Luder, William F.; Kraus, Philip B. with Kraus, Charles A.; and Fuoss, Raymond M. JACS. 58 225 (1936)

(124) Onsager, L. Physik. Z 28 277 (1927)

(125) Lewis, G. N. Proc. Am. Acad. 13 359 (1907)

(126) Walden, P. physick.Chem. 55 207, 249 (1906)

(127) Dick, H. and Birr, E. R. Z. Angew. Chem. 41 443 (1928)

(128) Murray-Rust, D.M.; Gatty, O.; and MacFarland, W.A.; Chem.Soc. Annual Reports 27 326 (1930)

(129) Pritzl, Peter, P.; and Adkins, Homer JACS. 53 234 (1931)
Dunstam, Wyndam R.; and Goulding, Ernest; J.Chem.Soc. 77 1262 (1900)

(130) Manov Bates Homer and Aeree JACS. 65 1765 (1943)

(131) Murray-Rust, D.M.; Hadow, H. S.; Hartley, Sir Harold J. Chem. Soc. 1931 215

(132) Schiff, H. J. and Gordon A. R. J. Chem.Phys. 16 336 (1948)