PRECISION CONDUCTANCE MEASUREMENTS OF SOME QUATERNARY AMMONIUM HALIDES IN NITROMETHANE

A Thesis

by

A.K. Ramachandran Unni

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

Department of Chemistry,
McGill University,
Montreal, Canada

April 1958

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude and thanks to:

Dr. H.I. Schiff, under whose direction and guidance this work was carried out;

Dr. L. Elias for his useful suggestions, and generous help in glassblowing;

The Technical Co-operation Service of the Government of Canada for providing a scholarship, travel grants and other expenses under the Colombo Plan;

and the Government of Kerala State, India, for the sanction of deputation from service during the course of this work.

TABLE OF CONTENTS

I - INTRODUCTION

One of the earliest contributions to the theory of electrolytic conductance was made by Kohlrausch (1), who observed that the equivalent conductance of an electrolyte at infinite dilution is the sum of two independent factors characteristic of the anion and cation respectively. This is known as Kohlrausch's "Law of Independent Migration of Ions".

The classical theory of Arrhenius (2) published in 1885 was the next significant advance. He postulated that when an electrolyte is dissolved in a solvent, it partially dissociates into charged particles (now called ions). Another postulate of his theory was that the degree of dissociation of the electrolyte depends on the concentration of the solution, increases with dilution, and becomes complete in an infinitely dilute solution. He considered the ions to be quite independent entities, and apart from the fact that the ions present in the solution are in equilibrium with some undissociated molecules, they were regarded as being quite free from the influence of one another. The observed decrease in equivalent conductance with increasing concentration was attributed to a diminution in the degree of dissociation of the electrolyte.

The main support for this theory came from the work of Ostwald (3). The combination of the Law of Mass Action, applied to the dissociation process of electrolytes, with the degree of dissociation derived from the conductance ratio led to Ostwald's Dilution Law. For a uni-univalent electrolyte, this takes the form

$$K = \frac{\alpha^2 c}{(1 - \alpha)} ,$$

where K is the dissociation constant, α the degree of dissociation and c the concentration of the electrolyte at any given temperature. Aqueous solutions of weak electrolytes, such as acetic acid, were found to obey this law, but it failed completely at high concentrations and with strong electrolytes. Various modifications were proposed in an attempt to fit the experimental data to the theory. A better fit was obtained for weak electrolytes, but the "anomaly of strong electrolytes" remained unexplained.

The assumption by Arrhenius that highly charged ions could exist as independent entities without mutual interaction proved to be a serious weakness in his theory. This assumption required that ions should have the same mobilities in concentrated as in dilute solutions, and subsequent measurement of transference numbers (4) showed this to be untrue.

In an attempt to account for the conductance behaviour of strong electrolytes, Debye and Huckel postulated the Interionic Attraction Theory (5). In this theory, the solute is considered to be entirely dissociated into ions. The electrical forces between the ions are responsible for the observed variations in the properties of the solution upon dilution. The ions attract or repel one another by Coulomb forces, which tend to produce a definite arrangement of the ions, while thermal forces, on the other hand, tend to bring about a purely random distribution. The properties of an ionic solution can thus be accounted for by the interplay of these two effects. Since electrostatic forces increase as ions approach one another, ions cannot have the same mobilities and thermodynamic properties in concentrated as in dilute solutions, as postulated by Arrhenius.

The Debye-Huckel theory furnished a theoretical basis for the concept of "activity" introduced empirically by G.N. Lewis (6) in 1908 to account for the observed deviation of the thermodynamic behaviour of solutions from the ideal state. Furthermore, the mathematical treatment of the theory made available a successful method of evaluating activity coefficients from the physical properties of the solution. The theory can also be applied to non-thermodynamic phenomena such as electrolytic conductance and transference. The mathematical treatment of this problem by Debye and Huckel, extended by Onsager (7), led to an equation of the form

$$\Lambda = \Lambda_o - (A + B\Lambda_o)\sqrt{c},$$

where Λ is the equivalent conductance of the electrolyte at a concentration c, Λ_o the equivalent conductance at infinite dilution, and A and B are constants which can be computed from a knowledge of the dielectric constant of the solvent, the temperature and universal constants. This equation will be further considered in the discussion of results. It is essentially of the same form as that obtained experimentally by Kohlrausch earlier (8), and predicts a decrease in Λ with increasing concentration of the electrolyte. For the majority of aqueous solutions for which data are available, the limiting expression is very closely obeyed for concentrations up to 0.002 equivalent per litre. The observed deviations from theory at higher concentrations are partly due to simplifications introduced in the mathematical treatment of the theory. The conductance data for strong electrolytes in water at higher concentrations can be fitted to semi-empirical equations, which, however, are of the form to be expected from the approximations made in deriving Onsager's theoretical equation.

The same treatment is useful in dealing with the ionic portion of weak electrolytes. Several examples of an intermediate type of electrolyte, which is neither strong nor weak, are known, notably the solutions of most salts in non-aqueous media. In such media, the assumptions in the Debye-Huckel theory, particularly that of complete dissociation, become less valid as the dielectric constant, a very important property in electrolyte theory, decreases. Recent research in non-aqueous media has shown that ionogens which are strong electrolytes in water often behave as weak electrolytes in solvents of lower dielectric constant. In media with low dielectric constants, and in concentrated solutions, the short range interactions between ions, and between ion-dipoles become significant and must be taken into account (9). Specific solute-solvent interactions must also be considered.

Onsager's equation is strictly applicable only in the limiting case of very dilute solutions. This implies that the theory can be properly tested only if high precision experimental data are available for solutions of very low concentration. Conductance data, with an accuracy of 1 to 2 parts in 10,000 are available, mostly for aqueous solutions. For non-aqueous solvents, however, few data of such high precision are available.

Considerable attention has been paid to solvents of very low dielectric constant, in which there is a great deal of ion interaction, but few reliable measurements have been made with solvents of intermediate dielectric constant. The dielectric constant of nitromethane lies between that of solvents having high dielectric constants, such as water, where the behaviour of strong electrolytes conforms closely to the limiting Onsager equation, and solvents of very low dielectric constant where the theory becomes almost invalid. For this reason nitromethane was chosen as the solvent for the present study. Hartley (10) has studied the conductance behaviour of some quaternary ammonium salts in nitromethane. A comparison of the conductance data in nitromethane with similar data in solvents such as methanol (11) and nitrobenzene (12) should be instructive. Nitromethane and methanol are structurally dissimilar, but have about the same dielectric constant. The alcohol molecule possesses both electron-donor and acceptor properties, thus enabling it to form coordinate links with both cation and anion. Nitromethane, being an electron-donor, can only form such bonds with the cation. Any solvation of the anion probably depends on weak electrostatic interaction with solvent dipoles.

The choice of the quaternary ammonium halides was based on reasons of solubility. The conductance behaviour of tetramethyl and tetraethyl ammonium chlorides and bromides has been investigated by Elias (13) in this laboratory. In the present research the conductances of the next higher members of the homologous series, tetrapropyl and tetrabutyl ammonium chlorides and bromides, were studied for purposes of comparison. For the sake of simplicity in subsequent discussion, these salts will be represented by the formulae Pr_4NCl, Pr_4NBr, Bu_4NCl, and Bu_4NBr where Pr and Bu stand for the n-propyl and n-butyl radicals respectively. Conductance data were obtained for these salts in nitromethane at 25°C for concentrations from 0.01 to 0.0001 N.

The apparatus required for high precision conductance measurement by the alternating current technique is very elaborate. The conventional method, using a high frequency alternating current and platinum black electrodes, is fairly satisfactory for moderately dilute aqueous solutions. However, in dilute non-aqueous solutions, the use of platinised electrodes vitiates conductance data because of adsorption effects. Resistances of over 10,000 ohms must frequently be measured, and bright platinum electrodes must be employed to minimise adsorption of solute. Elimination of polarization errors calls for the use of very high frequencies, and the design of the conductance cell and bridge is critical. The capacitance current leakages in the cell and circuit, and other inductive effects inherent in the use of high frequencies, must be overcome.

It is possible to obtain conductance data of comparable accuracy by the direct-current method, and the apparatus required is very much simpler. Newberry (14) and Eastman (15) investigated the possibilities of the direct-current method, but only for relatively concentrated solutions. The problem of polarization was eliminated by the use of reversible electrodes. They used a simple modification of the common method for measuring the resistance of a metallic conductor by determining the fall of potential along it during the passage of a known current. Later Bronsted and Nielsen (16) used the same method for measuring the conductance of solutions as dilute as 0.002 N, and obtained agreement with the alternating current data within 0.02%.

The direct-current method, as developed by Gunning and Gordon

(17), has yielded data with an accuracy comparable to that obtained by the best existing a.c. techniques. In principle, the method consists of passing a known current through the electrolyte solution, and measuring the fall of potential across two probe electrodes located between the main, current-carrying electrodes. The use of reversible probe electrodes eliminates polarization. Only very small currents are passed through the solution in the cell so that the chemical changes occurring are very small and do not affect the accuracy of the measurements. The main electrodes may become polarized during the passage of current; but if they are sufficiently well isolated from the main body of the cell to prevent the products of electrolysis from contaminating the solution between the probes, reproducible potential readings are obtained. The only current passed through the probes is the very small momentary one required to obtain potentiometer balance, while measuring the potential drop between them.

Recently, Ives and Swaroopa (18) have described a method of conductance measurement by the direct-current technique. They located the potential-measuring electrodes in side-tubes connected by narrow tubing to points in the solution where the potential gradient was zero. By this arrangement they obviated the need to locate the probes accurately and reproducibly, an essential requirement with Gordon's method because of the potential gradient near the probe electrodes. A quinhydrone electrode, stabilized by potassium hydrogen phthalate, was used by Ives and Swaroopa. Their results, using various solutions and electrodes, showed a variation of about 0.1%. More recently, the direct-current method has been used by

Lim (19) to measure the conductance of concentrated solutions of sodium and potassium chlorides in water, using a modification of the Ives-Swaroopa cell.

High precision conductance data have been obtained for sodium and potassium halides in anhydrous methanol and water by the d.c. method (20, 21). At the outset of the work with nitromethane in this laboratory, it was observed by Bulani (22), that the silver halides on the electrodes were soluble in nitromethane solutions of the quaternary ammonium halides. This difficulty was overcome by Elias and Schiff (23), who developed a modification of the Gordon cell. This has removed the limitation inherent in the original Gordon method that it could be used only with solutions for which suitable reversible electrodes are available.

II. EXPERIMENTAL

Preparation and Purification of Materials

(A) Solvents

(i) Conductivity Water:- Conductivity water was prepared by batch distillation of distilled water. About one gram of potassium permanganate and five grams of potassium hydroxide were added to seven litres of distilled water. The distillation apparatus consisted of an all copper still fitted at the top with several baffle plates. The condenser was made of quartz and a thoroughly washed pyrex flask served as the receiver. A first fraction of about 1½ litres was discarded and the middle cut of 2-2½ litres collected. This sample of water had a specific conductance of about 1 x 10^{-6} mhos. at 25°C.

All glassware was scrupulously cleaned. The sequence of washing was as follows: hot chromic acid, tap water, warm potassium hydroxide solution, and tap water. The vessels were kept in hot hydrochloric acid for several hours to remove surface alkalinity and then flushed continuously with warm tap water, rinsed several times with distilled water and finally with conductivity water.

(ii) Nitromethane:- The preparation of nitromethane in a sufficient state of purity for use in the conductance measurements was done in much the same way devised by Tink (24) and Bulani (22) in this laboratory. The method involved distillation at reduced pressure and subsequent fractional crystallization.

The nitromethane was obtained from Distillation Products Limited as an almost colourless liquid. It was washed twice with aqueous 5% sodium carbonate, once with aqueous 5% sulphuric acid, and three times with conductance water. The distillation was carried out in an all pyrex glass apparatus of the usual vacuum type design shown in Fig. 1. The pot had a capacity of 5 litres and was heated by a "Glass-Col" heating mantle. The fractionating column, 3.6 cms. in diameter and about 300 cms. long, was packed with glass helices. Distillation was carried out at 4-6 cms. pressure which was regulated by a Cartesian manostat. The reflux ratio was adjusted to 10:1, using a conventional magnetic take-off at the head of the distillation apparatus. Dry ice-acetone cold traps and a vacuum oil pump were used. A middle cut of about 2 litres was collected after discarding the first 1½ litres. This middle fraction of nitromethane was fractionally crystallized by fitting the receiver flask containing it with a side flask of 500 ml. capacity and placing the system in a wooden box packed with dry ice. The box was then agitated by a mechanical shaker. When the nitromethane had frozen (usually about ½ hr.), the flask was removed and the contents allowed to melt. When all of it had melted except for a few crystals, the assembly was placed in the box again and allowed to freeze with continuous agitation. The nitromethane froze slowly and when all but about 250-300 mls. of it had solidified, the remaining liquid was poured over into the side-flask. Since this liquid has a lower freezing point it would presumably contain a high proportion of the impurities which may be present in the distilled

DISTILLATION APPARATUS

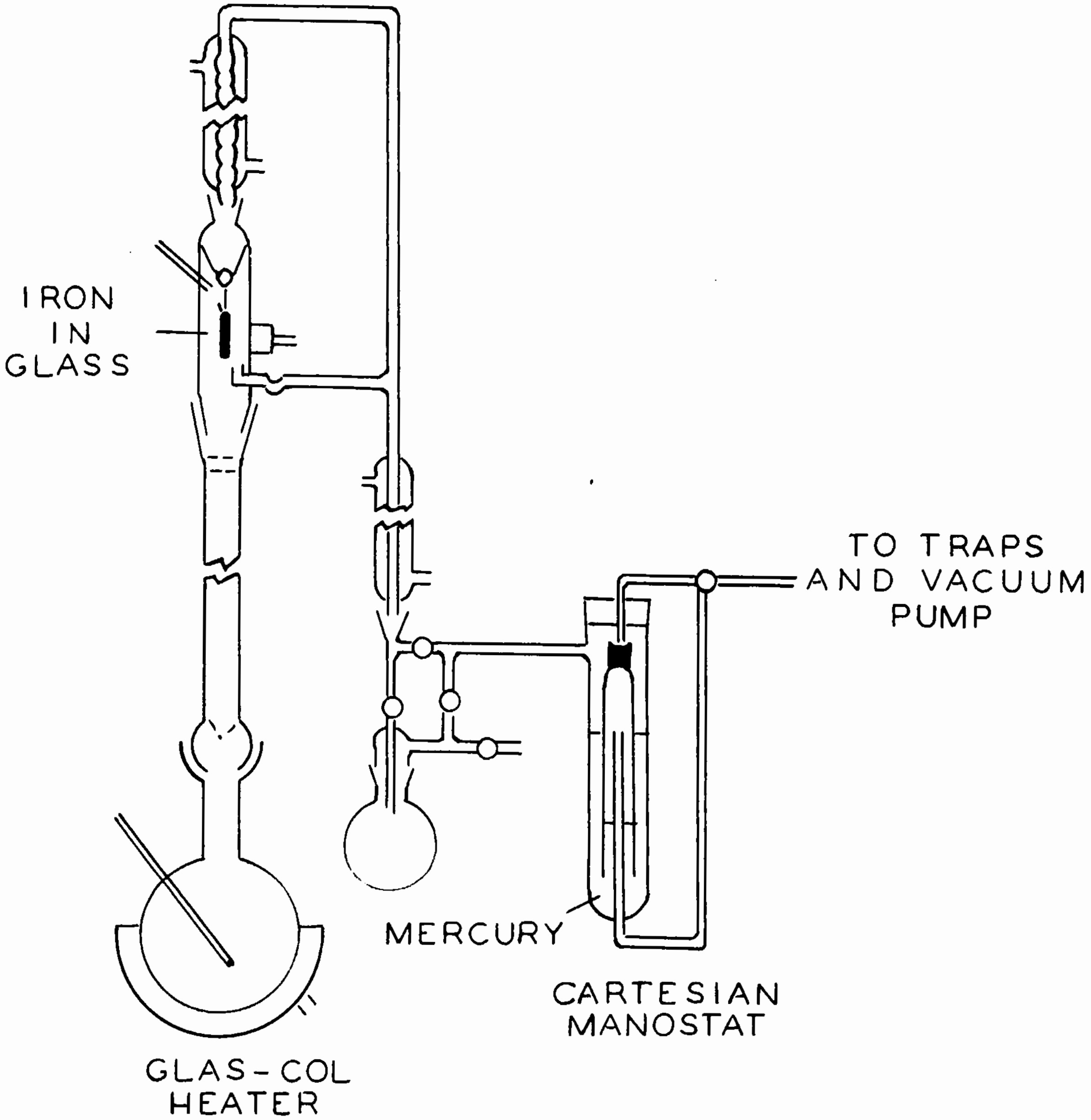


FIGURE I.

nitromethane. The colourless crystals were then allowed to melt at room temperature. The fractional crystallization usually took about 5 hours. The purified nitromethane was then transferred under pressure of pure dry nitrogen through a delivery tube attached to the flask by means of a standard taper joint. The density and specific conductance of the solvent were 1.13122 ± 0.00002 gm./cm.^{3}, and (0.5 - 1.0) x 10^{-8} ohm^{-1} cm.$^{-1}$ respectively at 25°C. The water content was determined by Karl Fischer titration (25) and found to be 0.001 weight per cent. It was found that nitromethane purified as described and used in conductance runs could be recovered in a pure state by distillation alone. The conductance alone was found not to be a sufficient criterion of purity of the solvent. The purity of the nitromethane thus obtained has been determined absolutely by Elias (13) following the freezing curve method of Rossini (26). The samples with a density of 1.13124 ± 0.00004 gm./cm.^{3} at 25°C were found to be 99.96 mole per cent pure.

(B) Salts

(i) Potassium Chloride:- The potassium chloride used for determining the cell constant was the "Analar" grade supplied by the Mallinkrodt Company. A hot saturated solution of the salt in conductivity water was filtered through a sintered glass funnel to remove any insoluble impurities. The salt was then recrystallized twice from conductivity water, and dried in vacuum at 110°C. Immediately before use, the salt was fused in a platinum boat placed in an electric furnace. A slow stream of pure nitrogen was passed over the salt during fusion. The fused salt in the boat was allowed to cool in a dessicator and then weighed.

(ii) Quaternary Ammonium Halides

(a) Determination of Salt Purity:- The purity of all the quaternary ammonium halides was determined by gravimetric analysis for the corresponding halide. A quantity of the salt large enough to give at least a gram of the silver halide precipitate was weighed to an accuracy of 50 micrograms, and then dissolved in about 500 ml. of conductivity water. The solution was acidified with 3 ml. 1:1 nitric acid and a slight excess of the calculated quantity of 0.1 N silver nitrate solution was added slowly with stirring. The solution was heated slowly just to boiling and the precipitated silver halide coagulated by stirring for a few minutes. The beaker was covered with a watch-glass and the contents allowed to stand in the dark for 3-4 hours. After making sure that the precipitation was complete, the solution was filtered through a sintered glass crucible. The precipitate was washed several times with 0.01 N nitric acid until free of silver nitrate and then transferred to the crucible. The precipitate was washed thrice on the filter with conductance water to remove the last traces of nitric acid. The crucible and contents were dried in an air oven at 110°C overnight, allowed to cool in a dessicator and weighed. The precision of the analysis was found to be better than 0.03% from the result of analysis of fused potassium chloride purified as described earlier.

(b) Preparation and Purification:- Tetrapropyl ammonium bromide was prepared by reacting equimolecular quantities of distilled n-propyl bromide and tri-n-propylamine in methanolic solution for about 24 hours at the reflux temperature of the mixture. Most of the unreacted reagents were then removed by extracting the mixture (after cooling) with distilled heptane. The methanol layer containing the salt was then evaporated to dryness under reduced pressure. The crude product thus obtained was purified by recrystallization from distilled acetone followed by reprecipitation from acetone solution by addition of heptane. The salt was then dried in vacuum at 132°C for 24 hours. The purity of the salt determined by gravimetric analysis was 99.97%. Density = 1.19 gm./cm.^{3}

<u>Tetrapropylammonium Chloride</u>:- This salt was prepared by the metathesis of a methanol solution of tetrapropylammonium iodide with freshly prepared and thoroughly washed silver chloride. The iodide itself was prepared by refluxing equimolecular quantities of n-propyl iodide and tri-n-propylamine in methanol medium for about 24 hours. The salt was recovered and purified by recrystallization as described earlier. The treatment of the purified Pr_4NI with silver chloride in methanol medium was continued slowly until all the iodide was converted into chloride. The presence of even traces of the iodide could be detected by the starch test following oxidation with nitric acid. The solution was then gently warmed and filtered through a sintered glass funnel and evaporated to dryness in vacuum. The salt was purified by three reprecipitations from acetone solution with reagent grade ether. After drying at 132°C for 24 hours in vacuum, the purity of the salt was determined. Analysis 99.96%. Density = Pr_4NCl 1.10 gm./cm.^{3}

<u>Tetrabutylammonium Bromide</u>:- The procedure suggested by

Fuoss (27) was followed for the preparation of this salt. Tri-n-butylamine and n-butylbromide were distilled at 132°C. Equimolecular quantities of the two reactants were refluxed in methanol solution for about 30 hours. Water was then added and the unreacted reagents extracted with heptane. The aqueous layer containing the salt was cooled to -15°C, and filtered. The wet mass was immediately transferred into a dessicator over P_2O_5 and the dessicator evacuated. After this preliminary vacuum drying, the salt was purified by repeated reprecipitation from acetone solution with ether. The pure salt was dried in vacuum at 80°C for 24 hours. Melting point 118°C. Purity = 99.98%. Density = 1.13 gm/cm.^{3}

Tetrabutylammonium Chloride:- This salt was prepared in a manner analogous to that used in the preparation of the corresponding tetrapropyl salt. The procedure employed was the metathesis of a methanol solution of purified tetrabutyl ammonium iodide with freshly prepared and thoroughly washed silver chloride. After making sure that the conversion of iodide to chloride was complete by the starch test as before, the solution was gently warmed, filtered through sintered glass and evaporated to dryness in vacuum. The salt which was found to be extremely hygroscopic, was given a preliminary drying in vacuum at room temperature. It was then dissolved in acetone and reprecipitated thrice with reagent grade anhydrous ether. After drying in vacuum for 24 hours at 56°C, the salt was analyzed. Purity = 99.98%. Melting point = 75°C. This salt was handled inside a dry box because of its extremely hygroscopic nature.

(c) Effect of Drying Temperature on Salt Purity:- The salts were dried in vacuum in an Abderhalden type of "drying pistol" with a trap immersed in dry ice-acetone mixture serving as the dessicant. The part of the drying tube holding the salt was heated by the vapours of a suitable boiling liquid. The drying temperature best suited for each salt was determined by trial. Each salt was purified as described earlier and then dried in vacuum for about 24 hours at several different temperatures. The purity of the samples dried for approximately the same length of time at different temperatures was determined by gravimetric analysis. The drying time had only a slight effect in improving the purity of the salt. The effect of drying temperature on salt purity for Pr_4NCl is represented in Table I.

TABLE I

Effect of drying temperature on salt purity - Pr_4NCl

Drying Temperature	Per Cent Purity
80°C	99.51
100°	99.83
110°	99.95
132°	99.96
160°	99.61

Pr_4NCl was therefore subsequently dried at 132°C. Different batches of the salt purified and dried at 132°C gave reproducible conductance data. Salt samples purified by reprecipitation from acetone solution with ether or heptane and dried at 132°C yielded reproducible analysis and conductance data. Furthermore, the Bu_4NBr was prepared by an alternative method (neutralization of Bu_4N OH in methanol medium with anhydrous HBr); when dried at 80°C in vacuum for 24 hours, the salt was found to be 99.98% pure and had a melting point of 118.5°C. The conductance data obtained with this sample of Bu_4NBr agreed with the data using the batch of salt prepared earlier.

(d) Salt Purity and Conductance:- To find out the effect of purity of the salt on conductance, the equivalent conductance of a 0.01 N solution of Pr_4NCl in nitromethane was determined. This was repeated using the samples of salt dried at various temperatures. The results are given in Table II.

TABLE II

Drying Temperature	Per Cent Purity	Equivalent Conductance (Λ)
80°C	99.51	82.82
100°	99.83	82.95
110°	99.95	83.00
132°	99.96	83.01
160°	99.61	82.75

It is evident from the above results that Pr_4NCl could be dried at 110°-132°C. Temperatures up to 100°C are not high enough as shown by the purity of the salt and conductance. At 160°C some decomposition occurs.

This is revealed by the low conductance and purity of the salt and from the odour of amine in the salt. It was also found that the longer the drying time at this temperature the less pure the salt became. This could presumably be due to the gradually increasing decomposition with time. To eliminate the error due to any possible "aging effect" of the salts, freshly purified and dried samples were used in the conductance runs. It was observed that temperatures up to 100°C are not high enough for drying the tetrapropyl ammonium halides; Bu_4NBr had to be dried at 80° or even 100°C. However, Kraus and coworkers (28) have used temperatures as low as 40°C.

Description of the Apparatus

(i) The Gordon Conductivity Cell (17)

Fig. 2 shows the front and side views of the conductance cell used. The original Gordon cell had a capacity of about 400 ml. However, a smaller cell holding about 150 ml. was used to reduce the amount of solvent required per experiment. Etched lines on the ground glass joints helped to ensure that the electrodes were reproducibly located in the cell.

The probe electrodes were made of thin platinum strips 1 mm. wide and 6 mm. long, sealed into Nonax glass in such a way that no edges were exposed. They were silver-plated in a solution containing 10 gms. per litre of twice recrystallized potassium silver cyanide. A current density of 1 milliampere per sq.cm. was used and the electrodes were plated for about 6 hours after the manner of Brown (29). The silver-plated electrodes were washed thoroughly with conductance water, and placed in concentrated ammonia for a few hours to remove any adsorbed cyanide ions. After washing with conductance water, the electrodes were anodized for $\frac{1}{2}$ hour in a 0.1 N aqueous potassium chloride or bromide solution using the same current density. The main, current-carrying electrodes were made of platinum foil approximately 1 x 2 $cm.^2$ in area and joined to copper leads by platinum wire sealed through glass. They were heavily plated with silver. The main and probe electrodes were rinsed well and placed in test tubes containing conductance water, when not in use. Before replating, the electrodes were placed in strong ammonia to dissolve the silver halide layer and then anodized in concentrated nitric acid to remove the silver.

After being treated as described earlier, the cell was kept filled with conductance water, when not in use. Thereafter it was periodically cleaned with chromic acid solution to remove any slight traces of grease. Following this treatment the cell was thoroughly flushed with large quantities of tap water, and finally with conductance water.

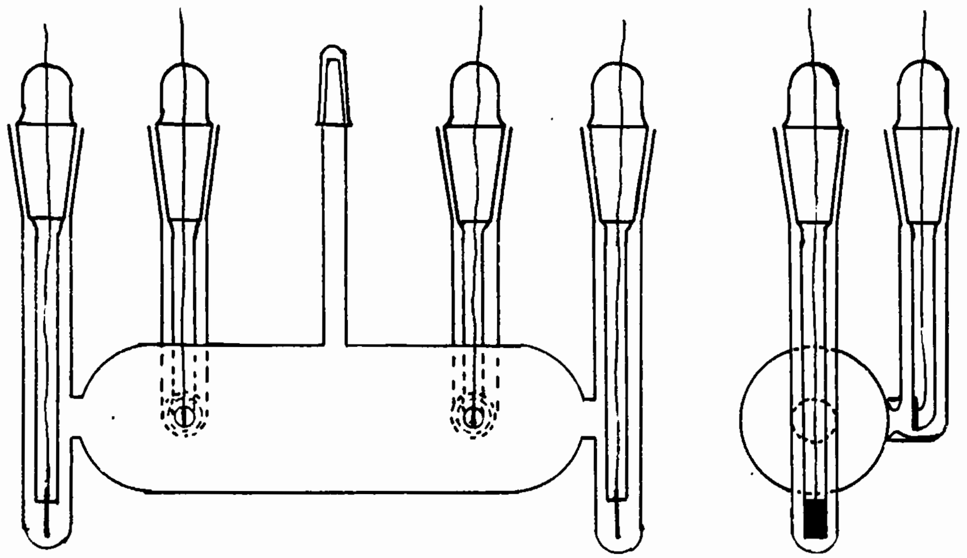
Before a conductance determination, the cell was rinsed continuously with tap water, and then ten times with conductance water. It was next dried in an inverted position by flushing with pure dry nitrogen for more than an hour. The cell was kept clamped in the normal position, three of the electrode compartments were covered with glass hoods, and the solution was transferred into the cell through the fourth electrode compartment. For about five minutes prior to this, the electrodes were allowed to sit in a sample of the cell solution. The cell was filled to a level just below the ground glass joints; the electrodes were inserted and carefully aligned. The cell was then placed in the oil bath for one hour to allow it to come to temperature equilibrium.

Modification of the Gordon Cell

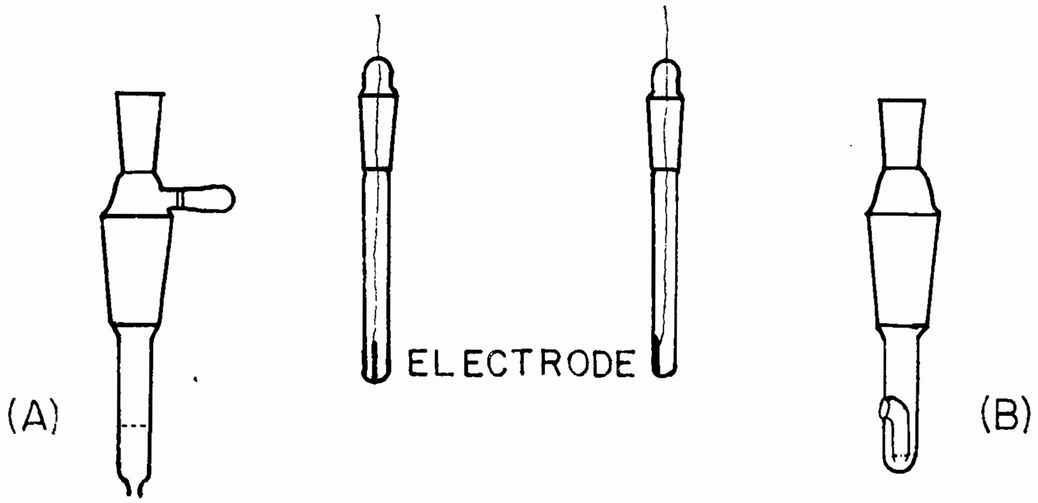
The original Gordon method suffered from the limitation that it could be used only with solutions for which suitable reversible electrodes are available. A modification of this method was devised by Elias and Schiff (23) in this laboratory. This modification has rendered the direct-current conductance method applicable to any electrolyte.

Each silver-silver halide probe was immersed in an appropriate halide solution and contact with the solution under investigation was made through liquid junctions. With such an arrangement, the probes functioned reversibly with respect to the solution in direct contact with them, though they were not reversible with respect to the solution measured. Probe chambers of the type shown in Fig. 2 (23) were employed to effect the liquid junctions. Type (A) chambers were used in the present research since nitromethane solutions are denser than the aqueous potassium halide solutions used to fill the probe chambers. The probe chamber was closed with a finger "cot" at the lower end and filled with the appropriate halide solution to a level just below the rubber bulb. The probe electrode was inserted in the chamber and the 12/30 ground glass joint wetted with the solution to ensure an air-tight seal. With the lower end of the chamber open, the rubber bulb was pressed to expel about 2 ml. of solution. An equal volume of cell solution was drawn up by carefully releasing the

FIG.2



(a) GORDON CELL



(b) LIQUID JUNCTION PROBE CHAMBERS

bulb with the tip of the chamber immersed in a sample of the cell solution. The position of the boundary is shown in the diagram by a dotted line.

The probe chambers were placed in the probe side arms of the cell, after being wiped clean on the outside with filter paper. The cell was then filled with solution and placed in the constant temperature bath. The method described by Gunning and Gordon (17) was employed for the electrical measurements.

The accuracy and reproducibility of conductance data obtained by the liquid junction method were thoroughly investigated by Elias and Schiff (23). They studied 1) the effect of concentration of probe solutions relative to that of the cell solution, 2) the influence of the liquid junction potentials, 3) the dependence of the measured resistance on the current through the cell circuit, and 4) the effect of diffusion. Their results showed conclusively that the accuracy and reproducibility of conductance data obtained by this method are quite comparable to those obtained by the original Gordon method for concentrations down to about 2×10^{-4} N.

The liquid junction method described above was applied to nitromethane solutions of Pr_4NCl, Pr_4NBr, Bu_4NCl and Bu_4NBr. The probe solution was an aqueous potassium chloride or bromide solution depending on the salt under study. The conductances of the very dilute solutions in the concentration range $1 - 5 \times 10^{-4}$ N were measured in the unmodified Gordon cell since the silver halide probes were not impaired in such dilute solutions.

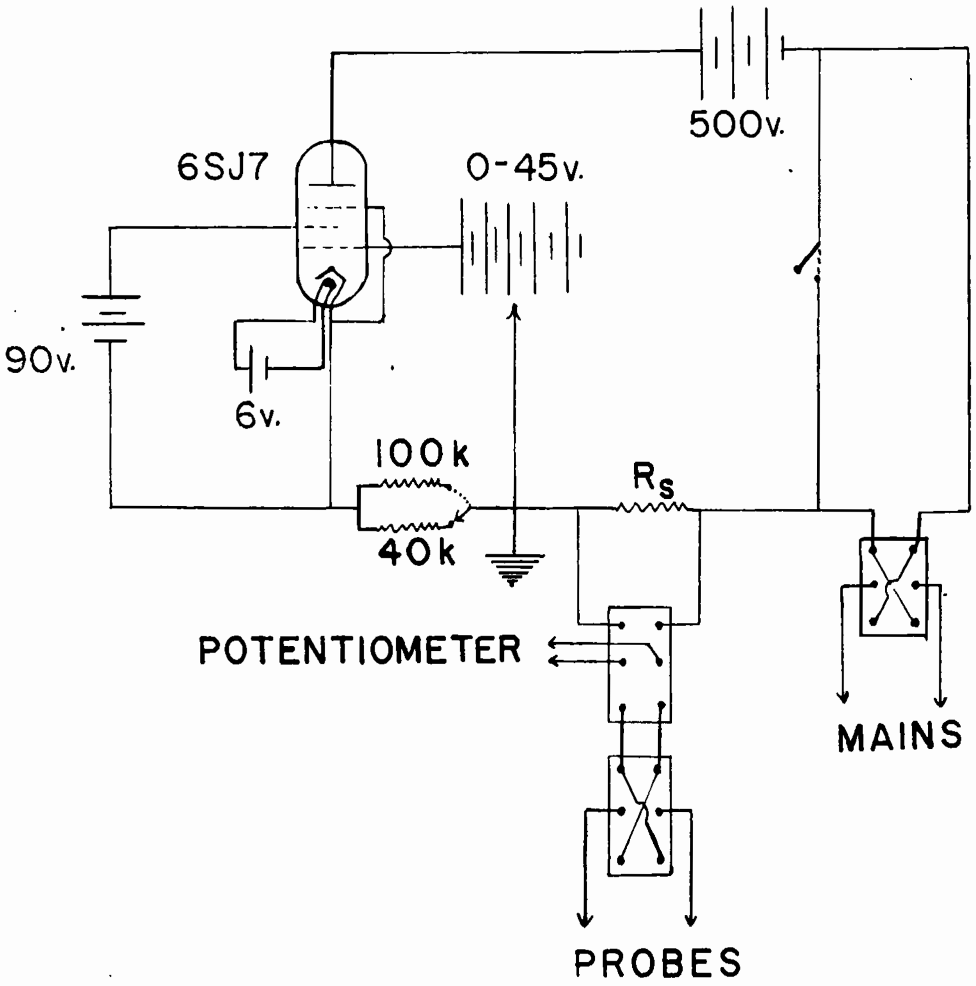
(iii) The Electrical Circuit (Fig. 3)

A small steady plate current from a 6SJ7 pentode, operated on a negative feed-back principle, was passed through the cell and a standard 1000 ohm resistor in series. This "constant-current" device was similar to that of Le Roy and Gordon (30). The circuit had the characteristic that the plate current was almost independent of the load resistance. The current through the cell remained constant within 0.01 to 0.02 per cent during an experiment. The normal working range of current was 1 to 0.1 milliampere, obtained by varying the grid voltage. The potential drop E_s across the standard resistor was first measured, then the voltage drop E_c+ across the probes. The direction of current through the cell was then reversed, the voltage drop, E_c-, across the probes measured and finally the voltage E_s was again measured. The small static bias potential between the electrodes was eliminated along with any difference in liquid junction potentials by taking the mean of the two values of E_c, viz., E_c+ and E_c-, for any particular value of E_s. The measured resistance $R = 1000 \frac{E_c}{E_s}$. Electromotive force measurements were made with a Leeds and Northrup type K_2 potentiometer and a ballistic galvanometer of sensitivity 2×10^{-10} ampere per millimeter scale deflection at one metre distance.

Despite the fact that the reversing switches and all wiring were well insulated, interference from stray current leaks was noticed particularly during the hot and humid summer months. The magnitude of this effect was such that it was almost impossible to obtain any accurate conductance

FIG. 3

ELECTRICAL CIRCUIT



data in such weather. The following tables give some of the conductance data obtained for nitromethane solutions in humid weather using the modified and unmodified Gordon cell. The data obtained with an approximately 0.01 N Bu_4NBr solution in nitromethane are shown in Table III. The probe solution was aqueous 0.01 N potassium bromide.

TABLE III

Dependence of Measured Resistance on Current

E_s	E_c	E_c/E_s
1.11210V	+0.22520V	0.20405
	-0.22865	
1.11190		
	+0.22521	
	-0.22855	0.20405
1.11185		
0.53394	+0.10760	0.20490
	-0.11120	
0.53392		
	+0.10762	0.20495
	-0.11122	
0.53386		

TABLE IV

5×10^{-4} N Bu_4NBr solution in nitromethane (Gordon cell)

E_s	E_c	$\frac{E_c}{E_s}$
0.21585V	+0.82109V - 0.81916	3.7997
0.21583		
	+0.82085 -0.81930	3.7994
0.21581		
0.18125	+0.69070 -0.68865	3.8050
0.18126		
	+0.69082	3.8051
0.18126	-0.68862	

The change in the ratio $\frac{E_c}{E_s}$, the "apparent" resistance with current was found to be much higher than 0.01%, the required limit of accuracy of the measurements. This deviation could be attributed to the occurrence of stray current leaks.

Further evidence for the apparent erratic behaviour of the silver-silver halide probes was obtained from the following experiment. With a 0.002 N aqueous solution of KBr in the Gordon cell, the current through the circuit was set and a series of readings were taken of the potential drop, E_c+, across the probes for a few minutes. The direction of current was then reversed and another series of e.m.f. readings, E_c-, was taken. The results are shown in Table V.

TABLE V

E_s	E_c+	E_s	E_c-
1.11745V	0.57255V	1.11745V	0.56911V
	0.57271		0.56941
	0.57305		0.56970
	0.57311		0.57000
	0.57327		0.57020
	0.57340		

The apparent values of both E_c+ and E_c- increased steadily, even though the current remained constant. This indicated that the probes were apparently not acting reversibly. Even after replating the electrodes very carefully, this kind of apparent erratic behaviour persisted. Furthermore, the apparent static bias potential between the probes showed a continuous increase with time.

However, the measured resistance of any electronic resistor was found to remain independent of the current passed through the circuit. The cell was duplicated by means of wire-wound resistors of comparable magnitude and resistors in the range 200-15,000 ohms (the range measured with the nitromethane solutions investigated), were measured in the usual way. The accuracy and reproducibility of the results were quite good which seemed to indicate that the stray current leak was possibly associated with the cell, rather than with other parts of the circuit.

In an attempt to overcome this problem of stray current leaks, the leads from the probes to the circuit were first shielded and the shielding earthed. This step did not bring about any improvement. Next the space surrounding the leads from the probes inside the glass tubes was dried by packing it with silica gel. The top of the glass tubes leading from the probes was sealed with wax to ensure air-tightness. In this way the space around the leads from the probes was kept dry and the resistances of several nitromethane solutions of different concentrations were then measured. The data obtained are presented in Tables VI and VII.

The data in Table VI refer to an approximately 0.0075 N nitromethane solution of Bu_4NBr using the liquid junction method.

TABLE VI

Dependence of Measured Resistance on Current

E_s	E_c	E_c/E_s
1.22135V	+0.33090V	0.27041
	-0.32960	
1.22128		
	+0.33089	0.27041
	-0.32958	
1.22128		
0.53357V	+0.14493V	0.27041
	-0.14365	
0.53360		
	+0.14493	0.27042
0.53360	-0.14366	

The data in Table VII were obtained for an approximately 0.0005 N nitromethane solution of Bu_4NBr by the Gordon method.

TABLE VII

Dependence of Measured Resistance on Current

E_s	E_c	E_c/E_s
0.11375V	+0.40395V -0.40450	3.5536
0.11375	+0.40400 -0.40450	3.5537
0.32025V	+1.13765V -1.13820	3.5533
0.32025		
	+1.13762 -1.13820	3.5532
0.32025		

The apparent variation of the measured resistance with current was found to be within 0.01%, the limit of accuracy of the measurement. With moist air in the space surrounding the leads from the probes, the leads are presumably not efficiently insulated. Under such conditions, stray current leaks could occur which could explain the apparent erratic results obtained during humid weather. The leakage problem which used to make accurate conductance measurements almost impossible during humid weather was thus pretty well overcome.

Temperature Control:- One of the essential requirements for conductance work of high precision is accurate temperature control. To ensure an accuracy of 1 part in 10,000, the temperature must be regulated to 0.005°C or better. A temperature regulation of this order was obtained in the bath used which contained about 12 gallons of light transformer oil, efficiently agitated by a large ten-bladed stirrer. The container was well insulated with 2" of cork and the bath was heated by two knife-type immersion heaters, and cooled by water passing through a copper coil, all placed close to the stirrer. Thermoregulation was effected by a five-finger, mercury-toluene regulator used along with an electronic relay. The temperature was regulated to better than ±0.005°C by adjusting the current to the heaters and the flow of water through the cooling coil. Temperature was measured with a mercury-in-glass thermometer graduated in hundredths of a degree and having a working range of 24-26°C. It was calibrated against a standard platinum resistance thermometer at the National Research Council, Ottawa.

Preparation and Handling of Solutions

Solutions were prepared in a 500 ml. pyrex flask fitted with a 29/42 standard taper inner joint. A delivery tube was fitted to the flask for transferring solutions. Before preparing nitromethane solutions of the salts, the flask was cleaned, dried in an air oven overnight and swept out with pure dry nitrogen for 15 minutes to remove any moisture condensed inside the flask.

Solvents and solutions were transferred by pressure of purified dry nitrogen. Nitrogen gas from the cylinder was allowed to bubble successively through a series of wash bottles containing Fieser solution to remove oxygen, lead acetate solution to absorb any H_2S, concentrated potassium hydroxide to remove any CO_2 and concentrated sulphuric acid to remove ammonia. The purified gas was then passed through a tower packed with anhydrous magnesium perchlorate to dry it, and finally filtered through glass wool.

All solutions were prepared gravimetrically. A semi-micro balance was used to weigh samples of salts and the accuracy of the weighing was better than 50 micrograms. Solvents and solutions were weighed on a general laboratory balance to within 10 milligrams. Sufficient quantities of solutions and salts were weighed to ensure an accuracy of at least 0.01%. All weights were corrected to vacuum.

Salt samples were dried in vacuum overnight in a small clean weighing bottle at a suitable temperature. The salts are very hygroscopic, particularly the chlorides which were handled in a dry box in an atmosphere of pure dry nitrogen. However, no increase in weight was observed in the course of the weighings. After drying, the salt was weighed in a weighing bottle and carefully transferred into the solution flask. By transferring approximately the required amount of solvent into the solution flask, a stock solution of a particular desired concentration was made. The flask with the solution was closed and weighed. Whenever the stopper had to be removed from the flask, exposure of the salt or solution to air was kept to a minimum. The stock solution thus prepared was in turn diluted gravimetrically to provide solutions of lower concentrations. By repeating the dilution process, a part or the whole range of concentration was investigated. Solutions made up by dilution from different stock solutions yielded conductance data which agreed within the accuracy of measurement. This established the accuracy and reproducibility of the dilution technique. Some of the more dilute solutions were prepared from stock solutions whose concentrations were evaluated conductimetrically.

Density of Solvent and Solutions

To compute volume concentrations from the measured weight concentrations, densities were determined for the concentration range used. A Shedlovsky type pycnometer (31) of about 20 ml. capacity with the stem capillary graduated in thousandths of a millilitre was used. The stem was a section of a serological pipette. The pycnometer was cleaned, dried and weighed empty. It was then filled by means of a medical syringe and a long stainless steel hypodermic needle. The liquid was brought somewhere within the graduated capillary region, the pycnometer was closed with a ground glass cap and placed in a thermostat regulated to 25 ± 0.005°C and allowed to attain temperature equilibrium. After about 15 minutes, the steady level of the liquid meniscus was read with the aid of a lens. The pycnometer was removed from the bath, wiped clean on the outside and weighed and the usual vacuum correction was applied to the weight. The pycnometer was calibrated for volume at 25°C with conductance water, using the density data from the International Critical Tables (32); the precision of the calibration was better than 1 part in 50,000.

The densities of the nitromethane solutions for the concentration range used may be represented by the relation

$$d = 1.13122 + bM,$$

where b = +0.00048, -0.01744, -0.00353 and -0.00527 for Pr_4NBr, Pr_4NCl, Bu_4NBr and Bu_4NCl respectively. M is the concentration in moles of salt per 1000 grams of solution.

Aqueous Solutions

To make up the solution for calibrating the conductance cell, dry recrystallized potassium chloride was placed in a platinum boat and inserted into an electrically heated silica tube. A stream of pure dry nitrogen was passed through the tube. After fusion,the salt was allowed to cool in a dessicator. The platinum boat and fused KCl were then weighed, and transferred to the solution flask. The density data for the aqueous KCl solutions were taken from the literature (33). The conductance of any of the aqueous solutions was observed to decrease slightly with time as successive portions were removed from the solution flask. This was presumably due to the gradual removal of CO_2 from the solution by the nitrogen used for transferring. To eliminate the error thus involved, potassium chloride solution was prepared in conductance water degassed for a few minutes with a water aspirator vacuum. The weighings were made after degassing the water.

The Cell Constant

The value of the cell constant was determined from the observed conductance of the hundredth demal aqueous KCl solution defined by Jones and

Bradshaw (34); viz. 0.745263 gm.KCl per 1000 grams of solution has a specific conductance of 0.0014087_7 mhos at 25°C when corrected for the conductance of the solvent. The mean of four determinations yielded a cell constant of $0.16462 \pm 0.00000_4$. The cell constant was redetermined on completion of the experimental work and found to agree with the initial value.

The Solvent Conductance

In making allowance for the solvent conductance, the "normal" type of solvent correction was applied to the aqueous potassium chloride solutions and the nitromethane solutions. This type of correction discussed by Davies (35) is based on the assumption that any ions present in the solvent contribute to the conductance of the solution to the same extent as they would do in the absence of the salt. In other words $L_{(solution)} = L_{solute} + L_{solvent}$ where L represents the respective specific conductances. Hence the solvent conductance was merely subtracted from the total measured conductance of the solution to obtain the conductance due to the solute.

The solvent conductance usually ranges from 0.001% of the total conductance for the highest concentration studied (0.01 N) and to 0.1% for the lowest concentration (1×10^{-4} N); hence, to ensure an accuracy of 0.01% in the data, the solvent conductance must be known to within 10% of itself for nitromethane solutions, and to better than 1% for aqueous solutions. The conductance of nitromethane was obtained using a small a.-c. cell with shiny platinum electrodes and a commercial conductivity bridge. The specific conductance of a dilute aqueous KCl solution was measured in the a.-c. cell as well as in the d.-c. cell. From these results the cell constant of the a.-c. cell was determined as 0.0182 and the precision of the a.-c. measurements was about 3%.

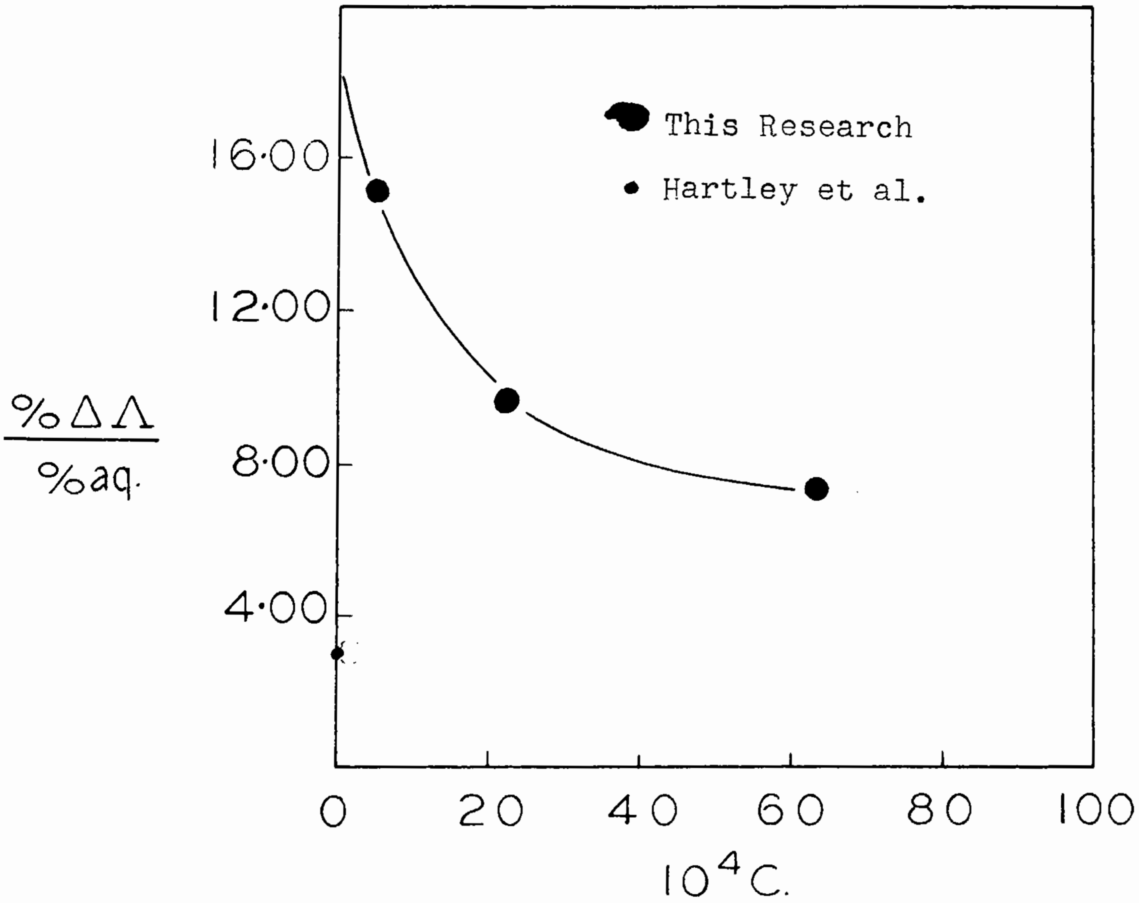
The water conductance was measured with the Gordon cell using silver-silver bromide probes which were placed in the cell just before taking the measurements.

The Water Correction

The basic assumption involved in the "normal" type of solvent correction described earlier is that there is no interaction between solute and solvent. However, Hughes and Hartley (36) noticed that addition of traces of water produced considerable changes in the conductance of methanol solutions. Schiff (37) has determined quantitatively the effect of water on the conductance of methanol solutions of NaCl and KCl. Hartley (10) has investigated the influence of small amounts of added water on the viscosity of nitromethane. He noticed a rather peculiar effect that the viscosity of nitromethane is lowered by the addition of water, a more viscous liquid. 0.1% by weight of water was found to lower the viscosity of nitromethane by about 0.3%. The influence of traces of water on the conductance of nitromethane solutions was determined quantitatively as described below.

The equivalent conductance of a 0.007 N solution of Pr_4NBr in nitromethane was measured using the liquid junction method. The water content of the solution was determined by titration with Karl Fischer reagent (25) of samples taken from the cell both before and after the run. The mean of the two values was taken. The reagent was standardized before each analysis against sodium acetate trihydrate. This salt is quite stable and is readily soluble in the nitromethane and in anhydrous methanol used in standardization. To the same sample of 0.007 N nitromethane solution of Pr_4NBr mentioned above, a drop of water was added from a burette. The conductance of the solution was measured and allowance was made for the slight change in concentration. The water content was determined again by titration. This process was repeated for various additions of water up to 0.03% by weight and starting with stock solutions of different known concentration. The resultant percentage increase in equivalent conductance was plotted against the percentage of water added; the increase was found to be linear in the water content for the range used. The curve was extrapolated to calculate the conductance of a water-free solution of the same concentration. This was necessary since the original nitromethane solutions contained a very small amount of water. Thus, it was found that the presence of one per cent by weight of water caused an increase of 7.3 per cent in the conductance of a 0.007 N Pr_4NBr solution. The same process was carried out for 0.002 N and 0.0005 N Pr_4NBr solutions, and the corresponding increases were 9.6% and 15.0% respectively. These results are plotted as a function of salt concentration in Fig. 4. Accordingly, the Λ values for solutions in the concentration range 0.0001 to 0.003 N were corrected to allow for the small amount of water present.

If the radii of the ions remain constant and the very small change in dielectric constant due to the addition of traces of water is neglected, one would expect that for a completely dissociated salt, the increase



● This Research
• Hartley et al.
16·00
12·00
8·00
4·00
%ΔΛ / %aq.
0
20
40
60
80
100
10⁴C.

FIGURE 4

in conductance would be proportional to the decrease in viscosity. From Hartley's results the decrease in viscosity of nitromethane caused by 0.1% by weight of water is about 0.3%. It is obvious from the results here that the mobility change is quite imperfectly compensated by the viscosity change in the mixtures. Fuoss (38) has found that Bu_4NBr acts as a much stronger electrolyte in mixtures of nitrobenzene and methanol than it does in either solvent alone. He suggested that this is due to specific interactions between the two solvents and the two ions involved. The dissociation constants also indicated interaction between solvent and solute "of a nature which requires more than the continuum theory" for its interpretation. The ion sizes (39) 'a', as computed from the dissociation constants, assuming "spherical ions and a coulomb continuum", were found to be different for the salt in the two solvents. Since the a-parameter measures the probability of approach of two ions of opposite charge, this seems reasonable. The a-values for Bu_4NBr were calculated and found to be different in methanol, nitromethane and mixtures of the two solvents (40). The hydrodynamic properties likewise were found to vary with solvent composition. The Walden product $\Lambda_0 \eta$ (discussed later) for Bu_4NBr in methanol-nitromethane was found to vary indicating that "the sphere-continuum model" was not applicable.

III. RESULTS

Results are given for the conductance at 25°C of the four salts studied (Tables VIII - XI inclusive). The concentration c is in equivalents per litre and the equivalent conductance Λ in ohm^{-1} cm.^{2} Values of the Shedlovsky function Λ_0' are also listed in the third column of the tables. The significance of Λ_0' will be discussed later.

TABLE VIII

$\mathrm{Pr_4NBr}$

10^4c	Λ	Λ_0'
100.347	83.91_0	103.80
99.639	83.95_8	103.80
98.884	84.03_4	103.78
77.335	85.73_7	103.16
69.192	86.51_0	102.98
50.707	88.39_6	102.48
50.697	88.42_7	102.50
29.665	91.32_0	102.07
28.786	91.46_9	102.06
20.584	92.97_5	101.94
20.425	93.02_6	101.92
14.912	94.20_0	101.84
9.8980	95.70_4	101.87
5.2272	97.42_7	101.93
5.0768	97.48_2	101.94
4.7582	97.61_5	101.92
2.0800	99.15_7	102.00
1.8437	99.31_3	101.99
0.98640	100.04	102.00
0.95790	100.11	102.02

TABLE IX

Pr_4NCl

10^4c	Λ	Λ'_o
99.886	83.78_2	103.60
99.733	83.77_0	103.59
98.188	83.88_0	103.54
70.316	86.15_1	102.74
69.271	86.24_7	102.71
67.113	86.43_5	102.64
49.628	88.26_5	102.17
49.035	88.34_9	102.17
48.418	88.41_4	102.15
33.699	90.34_2	101.79
30.136	90.92_3	101.75
28.209	91.20_2	101.67
19.386	92.83_8	101.50
18.588	92.98_4	101.48
17.681	93.22_1	101.49
9.5529	95.29_5	101.38
8.6436	95.58_5	101.38
8.3397	95.71_5	101.41
8.1971	95.78_5	101.41
4.5806	97.24_5	101.45
4.1685	97.43_6	101.46
3.9929	97.53_5	101.43
1.9661	98.75_0	101.51
1.7003	98.97_0	101.54
1.3393	99.34_2	101.62
1.2643	99.39	101.60

TABLE X

Bu_4NBr

10^4c	Λ	Λ_0'
99.704	79.96_5	99.50
99.449	80.00_6	99.49
96.889	80.15_1	99.40
94.693	80.33_8	99.36
74.392	81.84_3	98.66
74.044	81.89_1	98.67
62.189	82.94_6	98.30
50.546	84.08_8	97.91
48.601	84.36_1	97.88
44.353	84.77_8	97.72
34.613	86.02_5	97.43
30.477	86.64_2	97.35
24.517	87.56_5	97.16
19.826	88.44_2	97.07
17.892	88.83_0	97.02
16.184	89.16_9	96.96
10.118	90.69_5	96.86
10.044	90.72_5	96.87
9.7629	90.85_1	96.86
7.3623	91.56_5	96.83
6.9192	91.73_5	96.82
5.0077	92.47_5	96.80
5.0081	92.49_2	96.81
3.2636	93.33_8	96.84
2.3776	93.91_0	96.88
2.3814	94.01_0	96.87
1.1736	94.80_1	96.90
1.0574	94.93_2	96.89

TABLE XI

Bu_4NCl

10^4c	Λ	Λ_0'
99.000	79.95_9	99.47
95.941	80.24_0	99.38
94.661	80.36_1	99.37
84.605	81.04_2	99.00
74.565	81.82_1	98.64
55.162	83.53_8	97.98
52.207	83.81_5	97.86
47.794	84.28_1	97.71
44.688	84.61_2	97.59
34.171	85.87_8	97.21
29.231	86.60_0	97.07
23.460	87.51_1	96.89
21.372	87.81_8	96.77
19.411	88.23_0	96.76
17.281	88.64_8	96.69
14.758	89.19_8	96.63
8.9964	90.71_5	96.52
7.9710	91.04_5	96.50
7.8333	91.03_5	96.48
5.7760	91.80_5	96.45
4.6410	92.30_0	96.47
4.6255	92.34_1	96.47
4.1850	92.53_1	96.49
1.7888	93.91_0	96.64
1.6876	94.10_0	96.61
0.82750	94.91_0	96.67

IV. A DISCUSSION OF THE RESULTS

1. Definitions

The specific conductance of a solution, L, is defined as the reciprocal of the resistance offered by a unit centimetre cube of the solution. If the measured resistance of a solution using a cell and electrodes of any given dimensions is R, then $L = \frac{k}{R}$, where k is the cell factor determined by calibrating the cell with a solution of known conductance.

From a theoretical point of view, a far more important basis for comparison for electrolytes is the conductance of one equivalent weight in solution when placed between two parallel conducting plates 1 cm. apart. This quantity is known as the equivalent conductance and is represented by Λ with a subscript showing the concentration, to which it refers. The equivalent conductance is $\Lambda_c = \frac{1000L}{c}$ where L is the specific conductance of a solution containing c gm-equivalents of the electrolyte per litre.

The equivalent conductance depends on the degree of dissociation of the solute in solution and on the mobility of the ions which is defined as the velocity under a potential gradient of 1 volt/cm.

2. The Interionic Attraction Theory

As was indicated in the introduction, the electrolytic conductance of a solution depends on the number of ions carrying the current and on the velocities with which these ions travel. The Arrhenius treatment of the first of these variables, which implicitly assumes constant ionic mobilities, has been invalidated by experiment. The interionic attraction theory considers the second of these variables.

For many years the "anomaly of strong electrolytes" was the most important problem in theoretical electrochemistry, but it has finally been explained for dilute solutions on the basis of Coulomb electrical forces between the ions. The effect of the electric charges of the ions on the properties of strong electrolytes has been treated by Van Laar (41), Sutherland (42) and Milner (43). But owing to the approximations which these workers made in their complex mathematical analysis of the effects of interionic forces, their theories attracted little attention. J.C. Ghosh (44) calculated the changes upon dilution of the osmotic pressure and of the conductance. His treatment was based on the assumption that the ions have crystal lattice distributions, but neglected thermal vibration. Consequently, his results did not agree with the facts. Ghosh's theory, however, considered that there was a certain order in the ion distribution which led Debye and Huckel to work out a simpler and more satisfactory mathematical solution to the problem.

Owing to Coulomb forces, any selected ion, a positively charged one for instance, will, on the average, have more negative ions near it than if the distribution were purely random. Thus, on a time average, every ion may be regarded as being surrounded by an 'ionic atmosphere' of opposite sign. The net charge of the atmosphere is, of course, equal in magnitude but opposite in sign to that of the central ion. The charge density of the ionic atmosphere decreases with the distance from the central ion.

Debye and Huckel assumed that the Boltzmann statistics could be applied to a system of ions acted upon by opposing thermal and electrostatic forces. The other assumptions made by them may be summarized as follows:

(1) All strong electrolytes are completely dissociated so that the number of ions is known accurately for any given salt concentration.

(2) The solvent is considered to be a continuous medium - i.e., the macroscopic values of the viscosity and the dielectric constant of the solvent are effective for the solution.

(3) The Coulomb law of forces is applicable to ions and forces other than electrostatic are ignored.

(4) Solutions are considered to be so dilute that ions are at very large distances from one another and corrections for the overlapping of ionic atmospheres can be neglected.

(5) The resistance to motion of an ion through a solution is given by Stokes' law.

(6) Ions are regarded as point charges.

For an undisturbed electrolyte, the ionic atmosphere can be regarded as spherically symmetrical around the central ion. The ion atmosphere treated as a reality in mathematical discussions is actually the result of a time average of the distribution of the ions. Each ion serves as a centre of an ion atmosphere and the relative position of each ion with respect to the other charged bodies in the solution influences the atmospheres of all the other ions. Debye and Huckel (5) and Onsager (7) have shown that interionic attractions and repulsions produce two effects both of which result in the lowering of ionic mobilities with increasing ion concentrations. These are the "Electrophoretic Effect" and the "Relaxation" or "Asymmetry Effect".

When an external potential gradient is applied to a solution, the ions will move in the direction of the field and the symmetry of the ionic atmosphere is disturbed. Each ion will constantly have to build up a fresh atmosphere in front of it, while the charge density behind decays gradually. The rate at which these processes occur, with respect to the velocity of the central ion, determines the extent of asymmetry of the atmosphere about the central ion. Since the atmosphere bears a charge opposite to that on the central ion, the resulting asymmetry will cause a retardation of velocity. This influence on the speed of an ion is called the "Relaxation or Asymmetry Effect". The mathematical treatment of this effect is highly involved, but it has been solved for ionic solutions of high dilution. The effect depends on the limiting mobility of the ions. Being a purely electrostatic effect,it is independent of the viscosity of the medium.

<u>Electrophoretic Effect</u>. The atmosphere is comprised of ions which are considered to carry a certain number of solvent molecules with them. An applied potential gradient will tend to move the ion atmosphere, with its associated solvent molecules, in a direction opposite to that in which the central ion, with its solvent molecules, is moving. Consequently, the

central ion will be retarded in its motion by the electro-viscous drag of its atmosphere.

3. The Onsager Equation

In deriving the effect of the relaxation force, Debye and Huckel did not take into account the natural Brownian movement of the ions. Onsager (7) made allowance for this later. He recalculated the time of relaxation term and modified the theory to account for the interaction of the ionic atmospheres. He also modified the electrophoretic term and showed that it is not necessary for Stokes' law to be strictly applicable in the immediate vicinity of the ions.

Based on these considerations, Onsager obtained an equation of the form $\Lambda = \Lambda_o - (A + B\Lambda_o)\sqrt{c}$, for uni-univalent electrolytes, assuming complete dissociation. The significance of the various symbols in this equation has been given in the introduction. The first term in the brackets takes account of the electrophoretic and the second term the relaxation effect. According to Onsager, these constants are comprised of the following terms:

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

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

where ϵ, the electrostatic charge = $4.802_5 \times 10^{-10}$ e.s.v.

k, the Boltzmann constant = $1.380_4 \times 10^{-16}$ ergs/degree

N, the Avogadro number = 6.0230×10^{23} per mole v, the velocity of light = 2.99776×10^{10} cms./sec.

T, the absolute temperature = 273.16 + °C.

The values of the universal constants were taken from Manov, et al. (45). Substituting these values,

$$A = \frac{82.5}{\eta\,(DT)^{1/2}} \qquad \text{and} \qquad B = \frac{8.20 \times 10^{5}}{(DT)^{3/2}}$$

D is the dielectric constant of the medium and η its viscosity.

The Onsager equation is of the same form as the Kohlrausch empirical relation $\Lambda = \Lambda_o - k\sqrt{c}$. However, the Onsager equation provides a theoretical method of calculating the parameter k. The limiting Onsager expression for conductance has been found to work very well for dilute aqueous solutions of strong electrolytes, such as the alkali halides (46).

It is of interest to apply the Onsager equation to the data of this research. For nitromethane at 25°C, D = 37.0 (47) and η = 0.627 (11). With these values the conductance equation becomes

$$\Lambda = \Lambda_o - (125.1 + 0.708\,\Lambda_o)\sqrt{c}$$

Fig. 5 shows the plot of the equivalent conductances against $\sqrt{c}$ for the four quaternary ammonium halides studies. The dotted lines in the figure represent the theoretical slopes, $(125.1 + 0.708\,\Lambda_o)$. The curves were in all cases linear in the concentration range 1 - 5×10^{-4} N within experimental precision. At higher concentrations, however, there are small, but real, deviations from the limiting Onsager expression. The plots become convex to the concentration axis. The experimental curves lie above the theoretical slopes at high concentrations; as the concentration decreases,

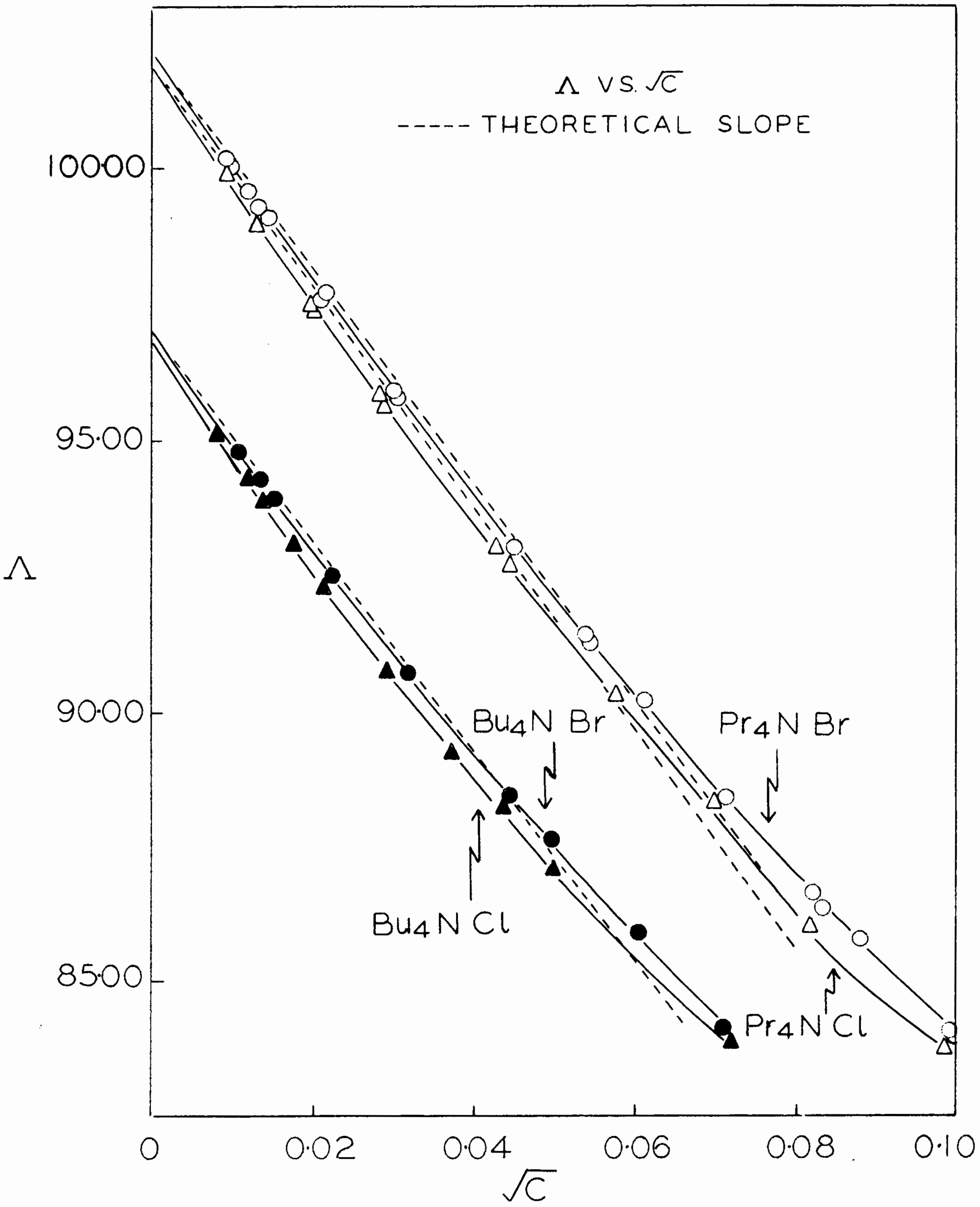

Λ VS. $\sqrt{C}$
----- THEORETICAL SLOPE
100·00
95·00
90·00
85·00
Λ
0
0·02
0·04
0·06
0·08
0·10
$\sqrt{C}$
Bu4N Br
Bu4N Cl
Pr4N Br
Pr4N Cl

FIGURE 5

they cut across the theoretical slope and approach it again from below. Such deviations are taken as evidence for association due to the formation of ion pairs (48). Values of Λ_o were obtained by extrapolation of large-scale plots of Λ against $\sqrt{c}$ and by a least-mean-squares analysis, of the most dilute points. Both methods gave identical results. The values of Λ_o and the limiting experimental slopes are given, along with the theoretical Onsager slopes and the per cent deviation, in Table XII.

TABLE XII

Salt	Λ_o	Limiting Experimental slope (S_E)	Theoretical slope (S_T)	% deviation $\frac{(S_T-S_E)\,100}{S_T}$
Pr_4NBr	102.10	-207	-197.4	-5
Pr_4NCl	101.88	-218	-197.2	-10.5
Bu_4NBr	97.04	-201	-193.8	-3.7
Bu_4NCl	96.83	-209	-193.7	-8.0

On the basis of the per cent deviation, the tetrabutyl salts are slightly stronger electrolytes in nitromethane than the tetrapropyl salts. Also, the chlorides appear to be less dissociated than the corresponding bromides.

4. The Shedlovsky Function

A very sensitive test for conductance data was proposed by Shedlovsky (49). The Shedlovsky function designated by Λ_o' is defined by rearranging the Onsager equation into the form

$$\Lambda_o' = \frac{\Lambda + A\sqrt{c}}{1 - B\sqrt{c}}$$

If the Onsager equation were valid for finite concentrations, this quantity would be a constant equal to Λ_o. However, in practice this condition is not fulfilled as the value of Λ_o' varies with concentration. Hence, a plot of Λ_o' against some function of the concentration is essentially a deviation plot. Shedlovsky suggested that Λ_o' is a linear function in c and that $\Lambda_o' = \Lambda_o + hc$. The empirical constant 'h' in this equation acquires a theoretical significance when the higher terms of the Debye-Huckel-Onsager expansion are considered. At zero concentration Λ_o' is equal to Λ_o. If the curve approaches Λ_o from above, the electrolyte is considered to be completely dissociated and a minimum in the plot is assumed to be due to ion-pair formation (39). Shedlovsky plots for the nitromethane solutions of the salts studied are given in Figs. 6-9 inclusive. The precision of Λ_o' in the concentration range 0.001 to 0.01 N was about 0.01 to 0.02%, and for the more dilute points the precision was 0.02 to 0.03%. The value of Λ_o' was found to be much more insensitive to concentration changes than Λ. The Shedlovsky plots were therefore used to compute values of Λ at round concentrations. Large-scale plots of Λ_o' against c were drawn; tangents were drawn at even concentrations and values of $d\Lambda_o'/dc$ calculated. Experimental concentrations differing by only small amounts from even concentrations were chosen. The tangents were constant

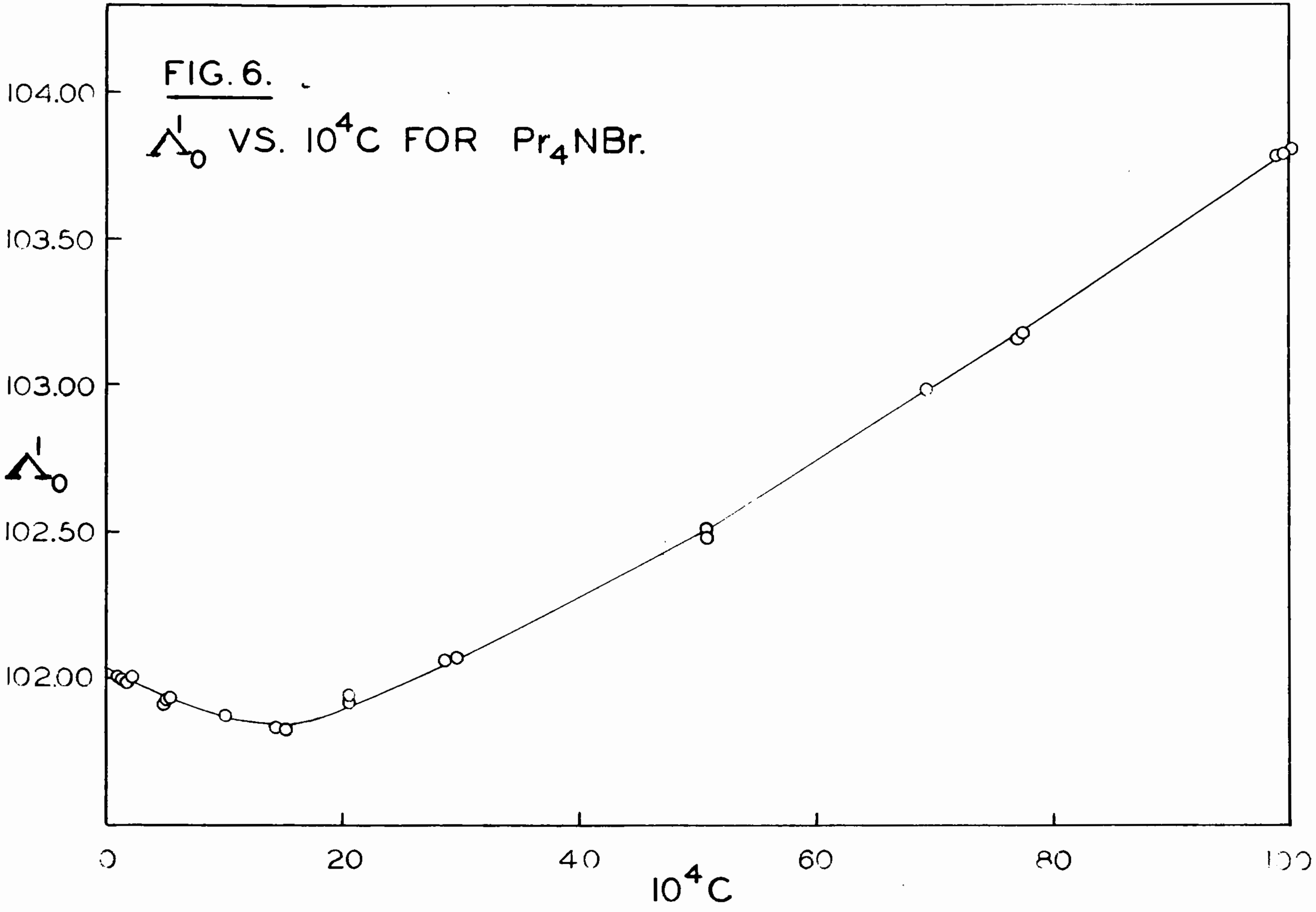


FIG. 6.

Λ'_0 VS. 10^4C FOR Pr_4NBr.

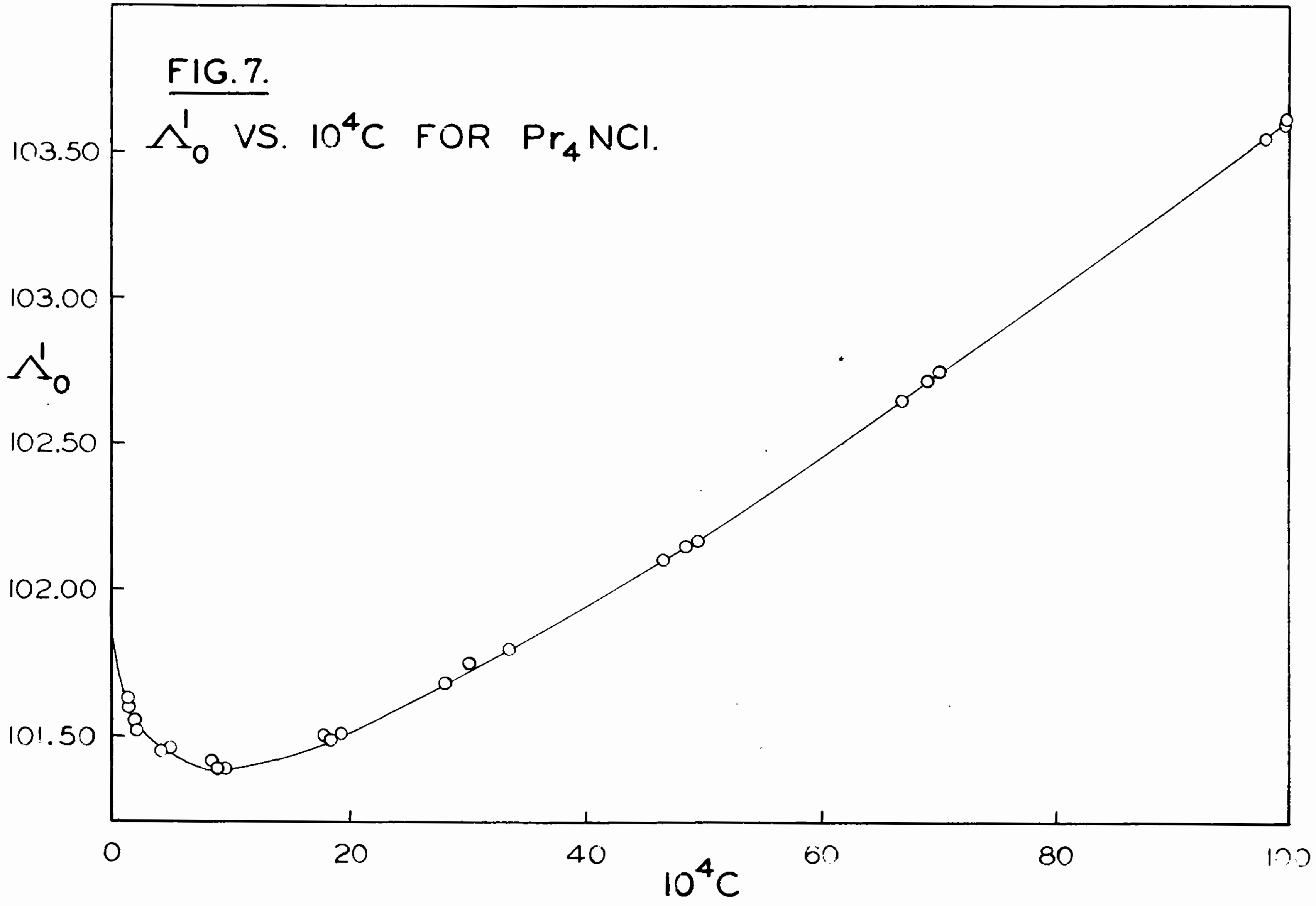


FIG. 7.

Λ_0' VS. 10^4C FOR Pr_4NCl.

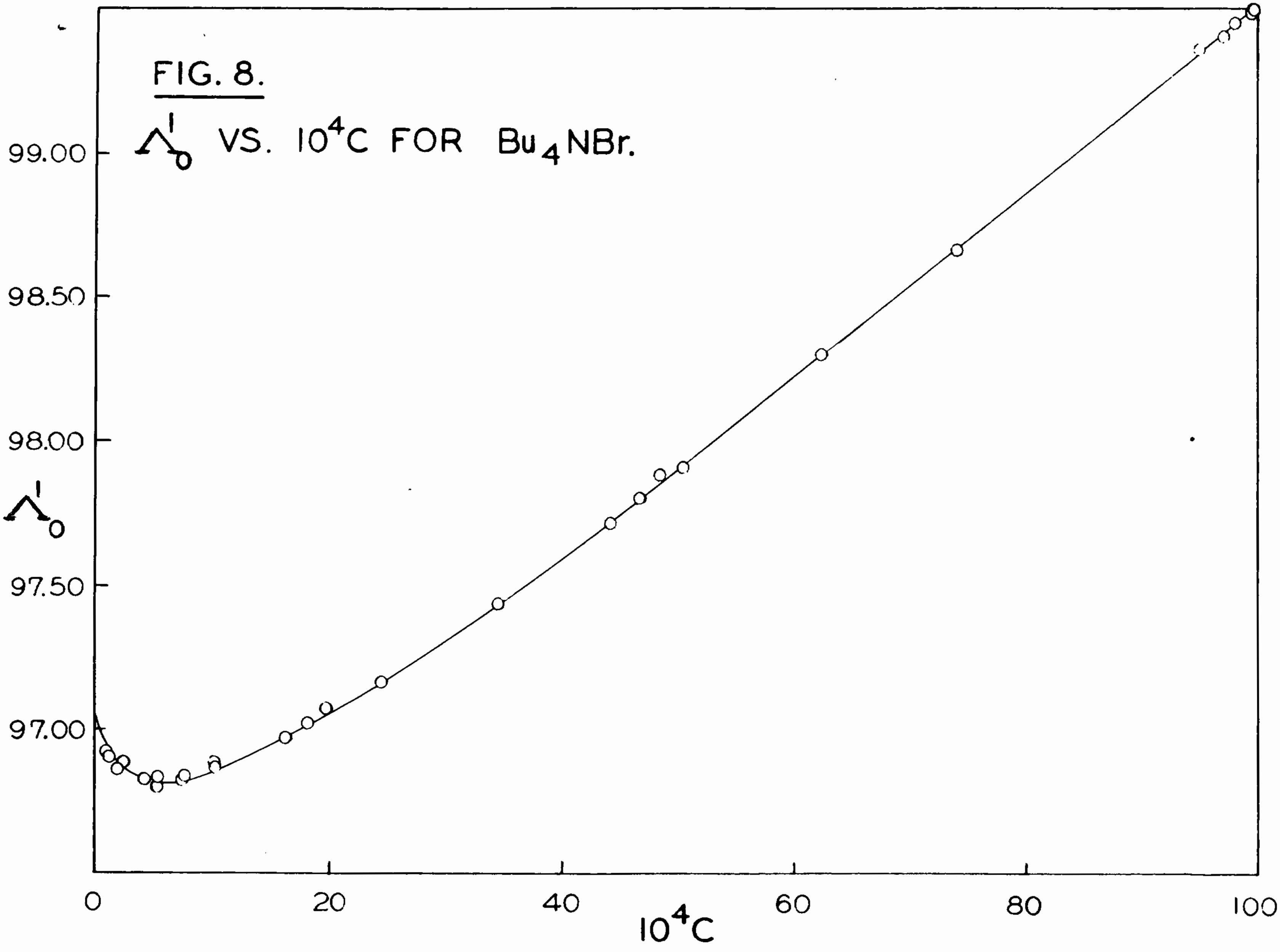


FIG. 8.

Λ_0^1 VS. 10^4C FOR Bu_4NBr.

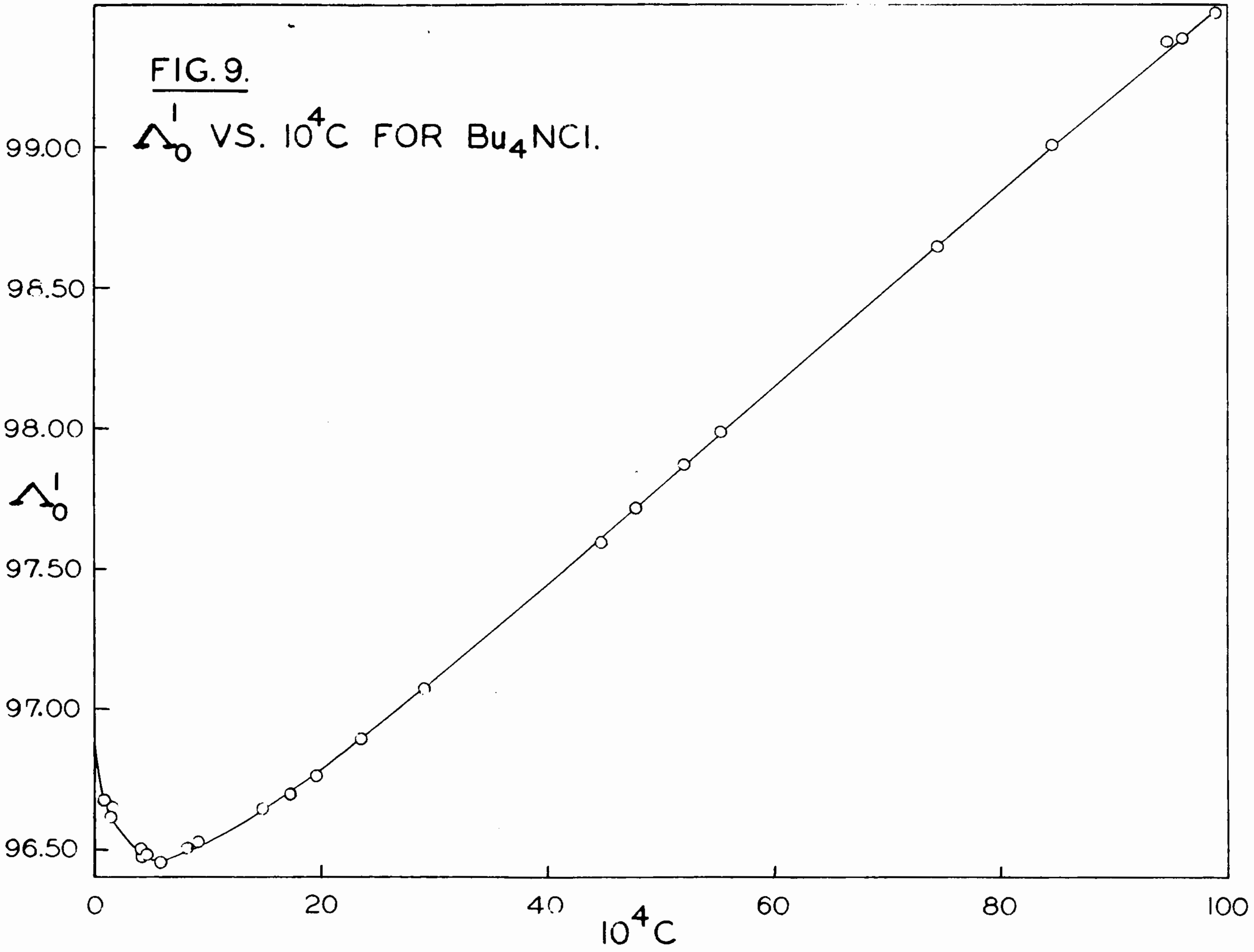


FIG. 9.

Λ_0^1 VS. 10^4C FOR Bu_4NCl.

over the small range of concentrations involved. It was thus possible to correct each of the experimental measurements to the nearest round concentration and these corrections were at the most a few hundredths of a conductance unit in Λ_o'. The corresponding values of equivalent conductance Λ were computed using the relationship

$$\Lambda_o' = \frac{\Lambda + A\sqrt{c}}{1 - B\sqrt{c}}$$

and the results are given in Table XIII.

TABLE XIII

Equivalent Conductance at Round Concentrations

10^4c	Pr_4NCl	Pr_4NBr	Bu_4NCl	Bu_4NBr
100	83.76_0	83.95_0	79.96_0	79.97_0
75	85.72_0	85.97_3	83.75_0	83.80_2
50	88.21_4	88.49_4	84.04_0	84.14_2
20	92.72_1	93.10_0	88.14_0	88.39_2
10	95.17_4	95.66_2	90.42_2	90.74_5
5	97.26_0	97.53_0	92.18_0	92.48_0
2	98.76_4	99.21_0	93.86_1	94.14_0

The limiting equivalent conductances (Λ_o) for the salts could also be determined by extrapolation of the Shedlovsky plots. However, because of the relatively large curvatures in the plots of the chlorides, the values of Λ_o obtained in this way involve an uncertainty of about 0.1 unit. For the bromides, on the other hand, the values of Λ_o thus obtained agree reasonably well with the corresponding values obtained by extrapolation of the Λ vs $\sqrt{c}$ plots discussed earlier.

Shedlovsky and Brown (31) proposed an empirical extension of Onsager's equation of the form

$\Lambda_o = \Lambda_o' - Bc - Eclogc$, where B and E are empirical parameters. Onsager has shown that a c log c term would also be required if higher order terms were included in the derivation of his equation. The Shedlovsky and Brown equation has been found to provide a good analytical fit for conductance data of aqueous solutions of strong electrolytes up to moderate concentrations (31). An attempt was made to fit the equation to the data of this research. However, no suitable values could be found for the empirical parameters except for Pr_4NBr. Table XIV shows the average observed values of Λ_o' for Pr_4NBr at round concentrations and also the corresponding values of Λ_o' calculated from the analytical expression $\Lambda_o' = 102.10 + 1007c + 402\ c \log c$, where c is the concentration in equivalents per litre.

TABLE XIV

Shedlovsky-Brown Equation

$$\Lambda_o' = \Lambda_o + Bc + Ec \log c$$

$B = 1007$; $E = 402$

10^4c	Λ_o' (observed)	Λ_o' (calculated)
2	101.99	102.00
5	101.92	101.94
10	101.87	103.11
20	101.91	101.94
30	102.07	102.08
40	102.28	102.27
50	102.50	102.51
70	103.00	103.09

It is evident that there is a reasonably good agreement except for the concentration 0.001 N.

Treatment of Nitromethane Solutions as Weak Electrolytes

Since the observed slope of the plot of Λ versus $\sqrt{c}$ is more negative than that predicted by the Onsager equation and the Shedlovsky expression fails to represent the experimental data, the nitromethane solutions cannot be classified as typically "strong" electrolytes. An attempt will now be made to treat them as 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 (50) and considerably simplified by Shedlovsky (51).

Considering the equilibrium between the ions and undissociated molecules of a uni-univalent electrolyte AB in solution, $AB \rightleftharpoons A^+ + B^-$, Ostwald's expression modified to include the activity coefficients of the constituents yields the following equation

$$K = \frac{c\alpha^2 f_A f_B}{(1-\alpha) f_{AB}} = \frac{c\alpha^2 f^2}{(1-\alpha)} \qquad (4\text{-}1)$$

where f is the mean activity coefficient of the electrolyte and the undissociated electrolyte is assumed to have unit activity coefficient. K is the dissociation constant, and α the degree of dissociation of the electrolyte. α must be computed from the relationship $\alpha = \frac{\Lambda}{\Lambda_e}$ where Λ is the observed equivalent conductance and Λ_e that of the completely dissociated salt but calculated at the concentration αc.

$$\alpha = \frac{\Lambda}{\Lambda_o - (A\Lambda_o + B)\sqrt{c\alpha}} \qquad (4\text{-}2)$$

The Onsager equation is modified by Shedlovsky to the form

$$\Lambda = \Lambda_o - \frac{\Lambda}{\Lambda_o}(A\Lambda_o + B)\sqrt{c\alpha} \qquad (4\text{-}3)$$

This may be written in the form

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_o} + \frac{(A\Lambda_o + B)\sqrt{c\alpha}}{\Lambda_o^2} \qquad (4\text{-}4)$$

Combining equation (4) with the equation (2) for α, one is able to get the following quadratic equation

$$\alpha = \frac{\Lambda}{\Lambda_o} + \frac{(A\Lambda_o + B)\sqrt{c\alpha}}{\Lambda_o^{2}} \qquad (4\text{-}5)$$

A function z is defined by the expression

$$\frac{(A\Lambda_o + B)}{\Lambda_o^{3/2}}\sqrt{c\Lambda} \qquad (4\text{-}6)$$

Then the solution of (5) gives

$$\alpha = \frac{\Lambda}{\Lambda_o}\left(\frac{z}{2} + \sqrt{1 + \left(\frac{z}{2}\right)^2}\right)^2 \qquad (4\text{-}7)$$

which yields on expansion,

$$\alpha = \frac{\Lambda}{\Lambda_o}\left(1 + z + \frac{z^2}{2} + \; . \; . \; . \; .\right) = \frac{\Lambda}{\Lambda_o} F \qquad (4\text{-}8)$$

Combining this with equation (1), there results

$$\Lambda F = \Lambda_o - \frac{F^2 f^2 \Lambda^2 c}{K\Lambda_o} \qquad (4\text{-}9)$$

According to equation (9) a plot of ΛF against $\frac{F^2 f^2 \Lambda^2 c}{\Lambda_o}$ should give a straight line with a slope equal to $\frac{1}{K}$. The conductance for the salts studied were analyzed by this method using the Λ_o values obtained by extrapolation of the Kohlrausch plots. The value of z was computed from the observed conductance Λ, and the Onsager constants A and B. F was calculated taking the first three terms in equation (8), $F = 1 + z + z^2$, and consequently α was then calculated; the value of f was obtained using the limiting Debye-Huckel equation (52) which is given by $-\log f = 1.575\sqrt{\alpha c}$ for the nitromethane solutions at 25°C. The results of these computations are shown in Tables XV-XVIII, inclusive.

TABLE XV

Pr_4NCl

10^4c	Λ	z	F	α	f^2	ΛF	$\frac{F^2f^2\Lambda^2c}{\Lambda_o}$
99.88	83.78	0.1755	1.1909	0.9793	0.4880	99.77	4.762
75.00	85.72	0.1538	1.1656	0.9807	0.5371	99.92	3.948
50.00	88.21	0.1274	1.1355	0.9831	0.6014	100.16	2.961
28.21	91.20	0.0973	1.1020	0.9866	0.6823	100.51	1.908
20.00	92.71	0.0826	1.0860	0.9884	0.7245	100.69	1.442
10.00	95.17	0.0592	1.0610	0.9911	0.7957	100.98	0.7964
4.581	97.24	0.0415	1.0424	0.9951	0.8567	101.38	0.3959
1.966	98.75	0.0268	1.0272	0.9956	0.9044	101.44	0.1796
1.339	99.34	0.0221	1.0223	0.9968	0.9197	101.56	0.1247

TABLE XVI

Pr_4NBr

10^4c	Λ	z	F	α	f^2	ΛF	$\frac{F^2f^2\Lambda^2c}{\Lambda_o}$
100.34	83.91	0.1755	1.1909	0.9789	0.4873	99.93	4.787
69.19	86.51	0.1480	1.1589	0.9821	0.5501	100.26	3.748
50.71	88.40	0.1280	1.1362	0.9839	0.5992	100.44	3.003
28.79	91.47	0.0981	1.1029	0.9883	0.6791	100.88	1.949
20.42	93.03	0.0834	1.0869	0.9905	0.7217	101.11	1.476
9.898	95.70	0.0589	1.0606	0.9943	0.7966	101.50	0.7958
5.227	97.43	0.0432	1.0441	0.9965	0.8475	101.73	0.4491
2.080	99.16	0.0275	1.0279	0.9985	0.9006	101.93	0.1907

TABLE XVII

Bu_4NCl

10^4c	Λ	z	F	α	f^2	ΛF	$\frac{F^2f^2\Lambda^2c}{\Lambda_o}$
74.56	81.82	0.1588	1.1714	0.9897	0.5366	95.84	3.795
52.21	83.81	0.1345	1.1435	0.9898	0.5940	95.86	2.942
29.23	86.60	0.1023	1.1075	0.9905	0.6772	95.91	1.881
19.41	88.23	0.0841	1.0876	0.9910	0.7278	95.96	1.343
8.996	90.72	0.0581	1.0598	0.9929	0.8053	96.14	0.6915
4.641	92.30	0.0421	1.0430	0.9942	0.8560	96.27	0.3802
1.789	93.91	0.0263	1.0266	0.9956	0.9078	96.41	0.1559
0.8280	94.91	0.0180	1.0182	0.9980	0.9374	96.64	0.0749

TABLE XVIII

Bu_4NBr

10^4c	Λ	z	F	α	f^2	ΛF	$\frac{F^2f^2\Lambda^2c}{\Lambda_o}$
74.04	81.89	0.1578	1.1703	0.9876	0.5380	95.84	3.770
50.55	84.09	0.1322	1.1409	0.9886	0.5991	95.94	2.873
24.52	87.56	0.0939	1.0983	0.9910	0.6994	96.17	1.634
19.83	88.44	0.0849	1.0885	0.9920	0.7252	96.27	1.373
10.12	90.70	0.0614	1.0633	0.9938	0.7946	96.44	0.7706
5.010	92.48	0.0436	1.0446	0.9955	0.8508	96.60	0.4099
2.380	93.91	0.0303	1.0308	0.9976	0.8942	96.80	0.2055
1.174	94.80	0.0214	1.0216	0.9980	0.9247	96.85	0.1049

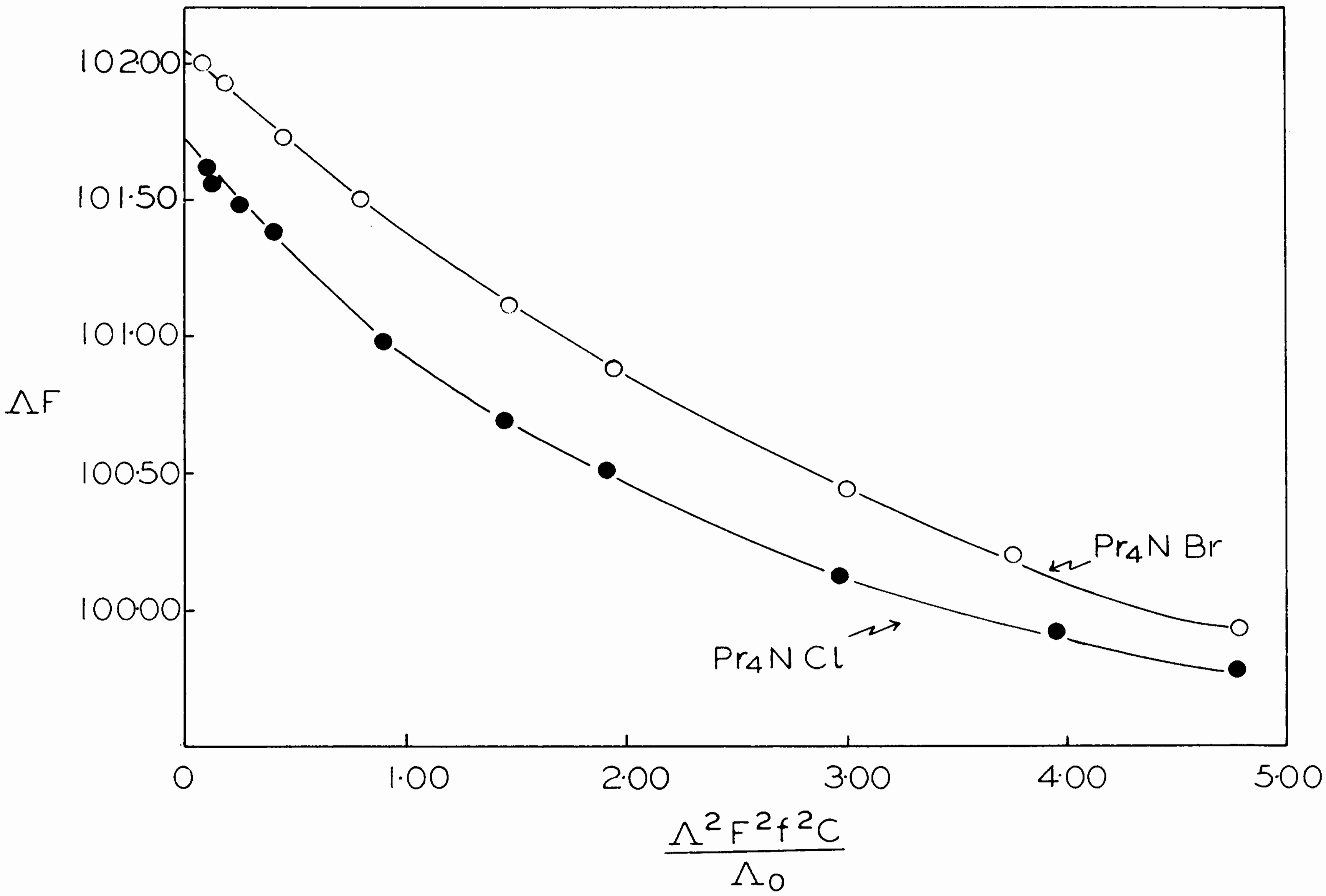

102·00
101·50
101·00
100·50
100·00
ΔF
0
1·00
2·00
3·00
4·00
5·00
$\frac{\Lambda^2 F^2 f^2 C}{\Lambda_0}$
$Pr_4N\,Br$
$Pr_4N\,Cl$

FIGURE 10

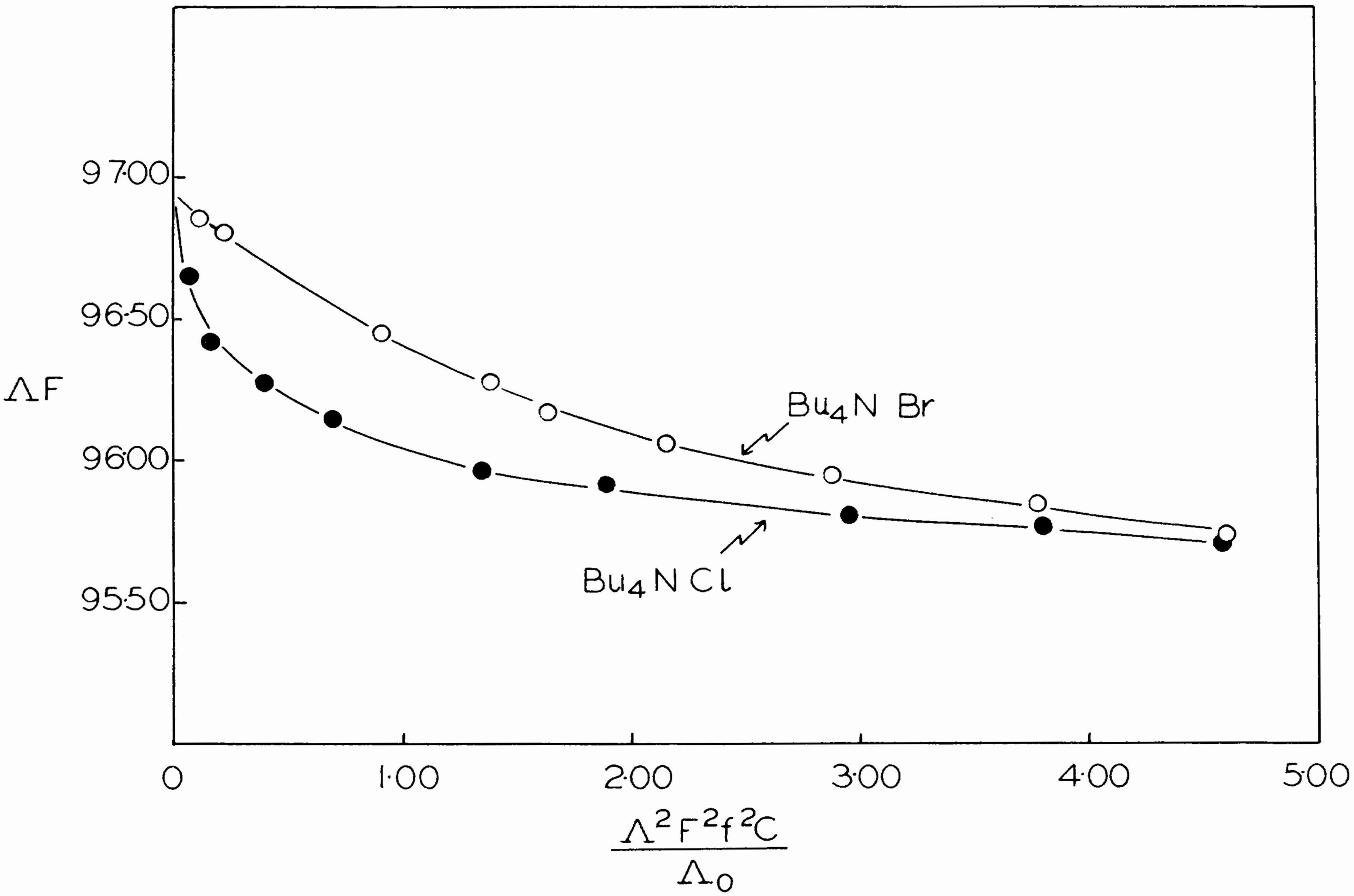

ΛF
97·00
96·50
96·00
95·50
0
1·00
2·00
3·00
4·00
5·00
$\frac{\Lambda^2F^2f^2C}{\Lambda_0}$
$Bu_4N\ Br$
$Bu_4N\ Cl$

FIGURE 11

The degree of dissociation of the salt calculated in this way ranges from 0.98 to 0.998 for the concentrations involved. The data in the last two columns of the tables are plotted in Figs. 10 and 11 from which it is evident that the straight line relationship expected for weak electrolytes does not apply. Therefore, on the basis of the Fuoss-Shedlovsky treatment just discussed, these salts in nitromethane cannot be considered to be truly "weak" and this is in agreement with the high values of the degree of dissociation listed in the tables.

6. Ion Pair Formation

Bjerrum (53) in 1926 suggested that due to the strong electrostatic attractions between oppositely charged ions, ion pairs might be formed. When the energy of mutual electrical interaction between two oppositely charged ions exceeds their thermal energy, the ions form an ion pair. These ion pairs differ from the undissociated salt in so far as the charges are still separated. However they will not contribute to the conductance since their net charge is zero in the case of symmetrical electrolytes. Ion pair formation will be facilitated 1) if the ions are small, 2) if the ions possess high valency and 3) if the solvent has a low dielectric constant. Bjerrum's concept of ion pair formation was further elaborated by Fuoss and Kraus (39) and by Kirkwood (54). According to the Boltzmann distribution, the time average number of ions, dn, in a small element of volume, dV, at a distance r from a given ion will be

$$dn = ne^{-z_+z_-\epsilon^2/DrkT}.dV \qquad (4\text{-}6\text{-}1)$$

where z_+ and z_- are the valencies of the cation and anion.

If the volume element is a spherical shell of thickness dr, then

$$dV = 4\pi r^2 . dr, \text{ so that}$$

$$\frac{dn}{dr} = 4\pi n\, r^2 e^{-z_+ z_- \epsilon^2 / DrkT} \qquad (4\text{-}6\text{-}2)$$

For two spherical ions of opposite charge, the curve of $\underline{dn}$ against r has a minimum. The interionic distance, r, at which this minimum occurs can be obtained by differentiating equation 2 with respect to r and equating to zero; thus

$$r_{min.} = q = \frac{|z_+ z_-|\,\epsilon^2}{2DkT} \qquad (4\text{-}6\text{-}3)$$

Bjerrum then makes an arbitrary assumption that ions inside the sphere with radius q are associated, and that those outside this sphere are free. The value of q, frequently referred to as the "Bjerrum critical distance" evidently depends on the ratio of the electrostatic potential energy of an ion pair, $\underline{z_+ z_- \epsilon}^2/Dr$, to the thermal kinetic energy of an ion, which is $\frac{3}{2}$ kT, i.e., to the ratio of the energies tending to hold an ion pair together and tending to knock it apart. Two further assumptions are involved in this treatment: a) that the effect of all ions other than the pair under consideration is negligible and b) the effective dielectric constant for the small portion of solvent lying between two ions close enough to form an ion pair is the macroscopic value D. These assumptions can be no more than approximations. However, Gurney (55) has presented arguments which seem to justify the use of the macroscopic dielectric constant in the cases of ion-ion, and ion-dipole contacts:

Bjerrum's critical distance "q" can be related to the parameter "a", the so-called ionic diameter, which can be interpreted as the distance between centres of charge of the ions when they are in contact. If $a > q$, no ion pair formation is possible. Combining this concept with the law of mass action, Bjerrum obtained the following equation for the dissociation constant of uni-univalent electrolytes.

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{\epsilon^2}{DkT}\right)^3 \int_2^b e^y y^{-4}\,dy \qquad (4\text{-}6\text{-}4)$$

$$\text{where } b = \frac{\epsilon^2}{aDkT} \qquad (4\text{-}6\text{-}5)$$

For a uni-univalent electrolyte in nitromethane at 25°C, the "Bjerrum critical distance" $q = 7.58\text{Å}$.

Although no literature values exist for "a" (of the quaternary ammonium halides in nitromethane) they would, by analogy with other electrolytes, be expected to be less than this value. This would indicate that these salts in nitromethane solution might exist, to some extent, in the form of ion pairs.

The relation proposed by Bjerrum (4-6-4) has been found to describe ion association satisfactorily in solvents of low dielectric constant (39), but the integral in the equation contains an arbitrary cut-off limit at $r = \frac{\epsilon^2}{2DkT} = ab$. The Bjerrum cut-off has been criticized by Fuoss (56) as leading to an unrealistic situation: "beyond a precisely and sharply definable critical limit of dielectric constant, ion association should cease abruptly". Fuoss (56) has developed recently a new mathematical analysis of conductance data by means of a general conductance equation proposed by Onsager and Fuoss. The ion size parameter, "a", can be estimated by this method of analysis. This has been done below and the "a" values thus estimated will be used later to test the validity of Bjerrum's theory of ion association.

7. The Fuoss-Onsager Conductance Equation

Experimental results for a wide variety of electrolytic systems show that the Λ versus $\sqrt{c}$ plots approach the Onsager tangent (7) $\Lambda = \Lambda_o - (\alpha \Lambda_o + \beta)\sqrt{c}$ in the limit of zero concentration. In the case of aqueous solutions of the alkali halides the Λ vs $\sqrt{c}$ plots diverge upwards from the limiting tangent as concentration increases from zero. In most non-aqueous systems, the plots approach the limit from below the limiting tangent and this is explained by ion-association or incomplete dissociation. Attempts have been made in recent years to explain the theoretical origin of these deviations and to predict the shape of the curves on the basis of the finite size of the ions.

The limiting Onsager equation has for its basis a model in which ions are considered as point charges. A calculation of the electrophoresis term by Onsager (57), based on charged spheres of average diameter a, has shown that the $\beta c^{1/2}$ term in the equation should be replaced by $\frac{\beta c^{1/2}}{(1 + \kappa a)}$ for symmetrical electrolytes. The effect of the divisor is to diminish the magnitude of the term as concentration increases, and produce a curve which is concave-upwards. The relaxation term $\alpha \Lambda_o c^{1/2}$ was also reinvestigated, using the spherical model. Falkenhagen (58) in 1952 showed that terms of first and higher orders in concentration appear in the limiting equation when account is taken of the finite size of the ions. Fuoss and Onsager (59, 60) have derived a general conductance equation with inclusion of higher order terms and the ion size parameter. This equation accurately reproduced experimental data for aqueous solutions of the alkali halides up to moderate concentrations (less than 0.1 N), and has the limiting form

$$\Lambda = \Lambda_o - (\alpha \Lambda_o + \beta)c^{1/2} + D\, c \log c + (J_1 c - J_2 c^{3/2})(1 - \alpha c^{1/2}) \quad (4\text{-}7\text{-}1)$$

in which the constants J_1 and J_2 are explicit functions of ion size, Λ_o and properties of the solvent. Fuoss and Onsager have described a method of obtaining the parameters Λ_o and "a" from Λ, c-data for unassociated uni-univalent electrolytes, for which the Λ vs $\sqrt{c}$ plots are concave-down at low concentrations.

By combining the above equation with the law of mass action, Fuoss (61) has derived a generalized conductance equation which includes the case of association of free ions into ion pairs. He has shown that limiting equivalent conductance, "ion size" and dissociation constant may be obtained by graphical treatment of conductance data at low concentrations. A viscosity correction is also applied when one ionic species is bulky compared to the solvent molecules. Large ions, such as the quaternary ammonium ions interfere with the motion of the oppositely charged ions by causing them to move in a medium of viscosity η somewhat greater than that, η_o, of the pure solvent. The equivalent conductance is proportional to the mobility of the ions which in turn is inversely proportional to the viscosity of the solvent medium to a first approximation. To estimate this correction, Fuoss assumes that the viscosity η at non-zero concentrations is given by the Einstein equation (62), $\eta = \eta_o(1 + \frac{5}{2}\phi)$ where ϕ is the volume fraction of the solute. This is connected with the concentration, c, by the relation $\phi = \frac{4\pi R^3}{3} \frac{Nc}{1000} = \delta c$ where R is the hydrodynamic radius of the bulky ion. The effect of the increase in viscosity is represented to a first approximation by a small linear term in c in the conductance equation.

At low concentrations the Fuoss-Onsager conductance equation for unassociated electrolytes can be modified to include the viscosity term to give

$$\Lambda = \Lambda_o - S\sqrt{c} + E\,c \log c - \frac{5}{2}\Lambda_o \delta c + J_1 c(1 - \alpha\sqrt{c})(1 - \frac{J_2}{J_1}\sqrt{c}) \qquad (4\text{-}7\text{-}2)$$

The significance of these terms and the method of calculation might best be illustrated by a sample calculation. Let us consider a nitromethane solution of Pr_4NBr having a concentration $c = 5.0707 \times 10^{-3}$ N and an equivalent conductance of $\Lambda = 88.40$. $\Lambda_o = 102.08$ (from Λ vs $\sqrt{c}$ plot).

For this solvent at 25°C, (T = 298.16°K)

$D = 37.00$; $\eta_o = 0.00627$ poise; $DT = 1.1032 \times 10^4$

$\sqrt{DT} = 105.03$; $(DT)^{3/2} = 1.158 \times 10^6$

$\underline{S = (\alpha \Lambda_o + \beta)}$ (4-7-3)

$$\alpha = \frac{8.204 \times 10^5}{(DT)^{3/2}} = 0.708$$

$$\beta = \frac{82.40}{\eta_o \sqrt{DT}} = 125.1$$

$\therefore$ $\underline{S} = (0.708 \times 102.08) + 125.1 = \underline{197.38}$

$$\underline{E = E_1 \Lambda_o - E_2} \qquad (4\text{-}7\text{-}4)$$

$$E_1 = 2.3026 \frac{\kappa^2 a^2 b^2}{24c}$$

$$b = \frac{\epsilon^2}{aDkT}$$

$$2 = \frac{8\pi N c \epsilon^2}{1000\ DkT}$$

$$= 2.3026 \times \frac{8\pi N c \epsilon^2 . \epsilon^4}{1000\ DkT\ (D^2k^2T^2)\ 24c}$$

$$= \underline{5.0484}; \qquad E_1 \Lambda_o = 515.44$$

$$\underline{E_2} = 2.3026 \frac{\kappa ab\beta}{16\sqrt{c}}$$

$$= 2.3026 \quad \frac{8\pi N c \epsilon^2}{1000DkT} \quad \frac{\epsilon^2}{DkT} \quad \frac{\beta}{16\sqrt{c}}$$

$$= \underline{130.59}$$

$$\therefore \; E = (515.44 - 130.59) = \underline{384.85}$$

Although E_1 and E_2 contain both a and c, these quantities only occur in such combinations as ab or $\frac{\kappa^2}{c}$ which are independent of c or a.

J_1 and J_2

If the ions are partially associated, c in equation (4-7-2) must be replaced by γc where γ is the degree of dissociation. The value of γ is defined by the equation $\gamma = \frac{\Lambda}{\Lambda_i}$ (4-7-5). Combining this with the law of mass action, the association constant $A = \frac{[A^+ . B^-]}{[A^+][B^-]} = \frac{(1-\gamma)}{cf^2\gamma^2}$ (4-7-6)

(where f is the mean activity coefficient of the ions), we get

$$\frac{\Lambda}{\Lambda_i} = 1 - A\,cf^2\gamma^2 \tag{4-7-7}$$

or

$$\Lambda_i = \Lambda + A\,cf^2\gamma\Lambda \tag{4-7-8}$$

Equating this to equation (4-7-2) for Λ_i with c replaced by γc gives

$$\Lambda + A\,cf^2\gamma\Lambda = \Lambda_o - S\sqrt{c\gamma} + E\,c\gamma\log c\gamma - \frac{5}{2}\Lambda_o\delta c\gamma$$
$$+ J_1\gamma c(1 - \alpha\sqrt{\gamma c})\ (1 - \frac{J_2}{J_1}\sqrt{\gamma c} \tag{4-7-9}$$

Rearranging,

$$\frac{\Lambda + S\sqrt{c\gamma} - E\,c\gamma\log c\gamma - \Lambda_o}{c\gamma(1 - \alpha\sqrt{c\gamma})} = J_1 - J_2\sqrt{c\gamma} - \frac{A\Lambda f^2}{(1-\alpha\sqrt{c\gamma})} - \frac{5}{2}\Lambda_o\delta \tag{4-7-10}$$

Let the deviation from the Onsager equation,

$$\Lambda - (\Lambda_o - S\sqrt{c\gamma} + E\,c\gamma\log c\gamma) = \Delta\Lambda \tag{4-7-11}$$

and let

$$\frac{\Lambda f^2}{(1 - \alpha\sqrt{c\gamma})} = x \tag{4-7-12}$$

$$\frac{\Delta\Lambda}{c\gamma(1 - \alpha\sqrt{c\gamma})} = y \tag{4-7-13}$$

Then $y = J_1 - J_2\sqrt{c\gamma} - Ax - 5/2\,\Lambda_o\delta$ (4-7-14)

To evaluate y, we require a value for γ

$\underline{\gamma}$ was calculated to a first approximation by the equation

$$\gamma_o = \frac{\Lambda}{\Lambda_o - S\sqrt{\frac{c\Lambda}{\Lambda_o}}} \tag{4-7-15}$$

derived from equations (4-7-5) and (4-7-9), neglecting the E and J_1 terms in the latter. These terms have opposite signs and to a large extent the errors made in neglecting them compensate each other. In our example

$$\gamma_o = \frac{88.40}{102.08 - 197.38\sqrt{\frac{0.0050707 \times 88.40}{102.10}}}$$

$$= \underline{0.9932}$$

$\underline{\Delta\Lambda}$

γ_o	$\sqrt{c\,\gamma_o}$	$\log c\gamma_o$	$E\,c\,\gamma_o \log c\gamma_o$	$S\sqrt{c\,\gamma_o}$	$(1 - \alpha\sqrt{c\,\gamma_o})$
0.9930	0.070960	- 2.2980	- 4.4531	14.0054	0.94976

From these data, $\Delta\Lambda$ was calculated using equation (4-7-11).

$$= (88.40 + 14.0054 + 4.4531 - 102.08)$$

$$= \underline{4.7780}$$

$$y = \frac{\Delta\Lambda}{c\ _o(1 - \alpha\ c\ _o)} \qquad (4\text{-}7\text{-}13)$$

$$= \frac{4.7780}{0.0050707 \times 0.9932 \times 0.94976} = 999.1$$

<u>To get x</u>

Knowing γ_o, f can be calculated using the Debye-Huckel relation:

$$-\log f = \frac{1.5755\sqrt{c\,\gamma_o}}{1 + 0.479a^o\sqrt{\gamma_o c}} \qquad (4\text{-}7\text{-}16)$$

However, to use this equation it is necessary to know the ion size parameter "a". Fuoss estimated this from a series of conductance measurements in mixed solvents in the following way. If ion association depends on the parameter, $b = \frac{\epsilon^2}{aDkT}$, in the Bjerrum treatment discussed earlier, the extent of association of a given electrolyte can be varied by using solvent mixtures to change the dielectric constant D. Fuoss (56) found that the logarithm of the association constant is a simple linear function of $\frac{1}{D}$

for some quaternary ammonium salts in water-dioxane mixtures. From the slope of the log A versus $\frac{1}{D}$ plot, he obtained a value of 5.55 Å for "a" for Bu_4NI. Since this method of getting "a" could not be used in the present work, it was necessary to guess a starting value for the Pr_4NBr in nitromethane. From Fuoss' value for Bu_4NI a value of 4.5 Å for "a" in the case of Pr_4NBr seemed reasonable. Substituting this value for "a" into equation (4-7-16) along with the value of γ_o = 0.9932 obtained above gives f = 0.8000.

Hence

$$\underline{x} = \frac{\Lambda f^2}{(1 - \alpha\sqrt{c\gamma_o})} = \frac{88.40 \times 0.6400}{0.94976} = \underline{59.57}$$

The values of y and x were computed for other concentrations in a similar manner and the results are presented in Table XIX.

TABLE XIX

Pr_4NBr

10^4c	Λ	γ_o	f^2	y	x
50.7070	88.40	0.9932	0.6400	999.1	59.57
28.7860	91.47	0.9936	0.7061	996.8	67.12
20.4245	93.03	0.9943	0.7422	990.6	71.32
9.8980	95.70	0.9960	0.8078	993.1	79.06
5.2272	97.43	0.9974	0.8538	1004.5	84.55
2.0800	99.16	0.9989	0.9036	1066.7	90.52

At low concentrations, the J_2 term in equation (4-7-14) is small and may be neglected in the first approximation so that

$$y \simeq J_1 - Ax - 5/2\,\Lambda_0\delta \qquad (4\text{-}7\text{-}14)$$

Therefore a plot of y against x should be linear; the slope gives the association constant A; the ordinate at c = 0 ($x = \Lambda_0$) is now y(0) =

$$J_1 - A\,\Lambda_0 - 5/2\,\Lambda_0\delta \qquad (4\text{-}7\text{-}17)$$

Fig. 12 shows the plot of y versus x. The plot being nearly horizontal, no reliable value of the slope (and hence of A) could be obtained. A is approximately 0.27 and the ordinate y(0) at c = 0 is 996.

$$\therefore \quad J_1 - 5/2\,\Lambda_0\delta = y(0) + A\,\Lambda_0$$

$$= 996 + (0.27 \times 102.08) = 996 + 27.6$$

$$= 1023.6$$

However, it is not possible to evaluate J_1 and δ separately by this treatment. The expression for J_1 is

$$J_1 = \theta_1\,\Lambda_0 + \theta_4 \qquad (4\text{-}7\text{-}18)$$

$$\text{where } \theta_1 = \frac{\kappa^2 a^2 b^2}{12c}\left[\frac{1 + 2b}{b^2} + 0.9074 + \ln\frac{\kappa a}{\sqrt{c}}\right. \qquad (4\text{-}7\text{-}19)$$

$$\theta_4 = \alpha\beta + \frac{8\beta\kappa a}{9\sqrt{c}} - \theta_2 \qquad (4\text{-}7\text{-}20)$$

$$\theta_2 = \frac{\beta\kappa ab}{8\sqrt{c}}\left[0.8504 + \ln\frac{\kappa a}{\sqrt{c}}\right] \qquad (4\text{-}7\text{-}21)$$

J_1 was calculated using these equations assuming for "a" the same value, namely 4.5Å, as that employed in computing the activity coefficient f

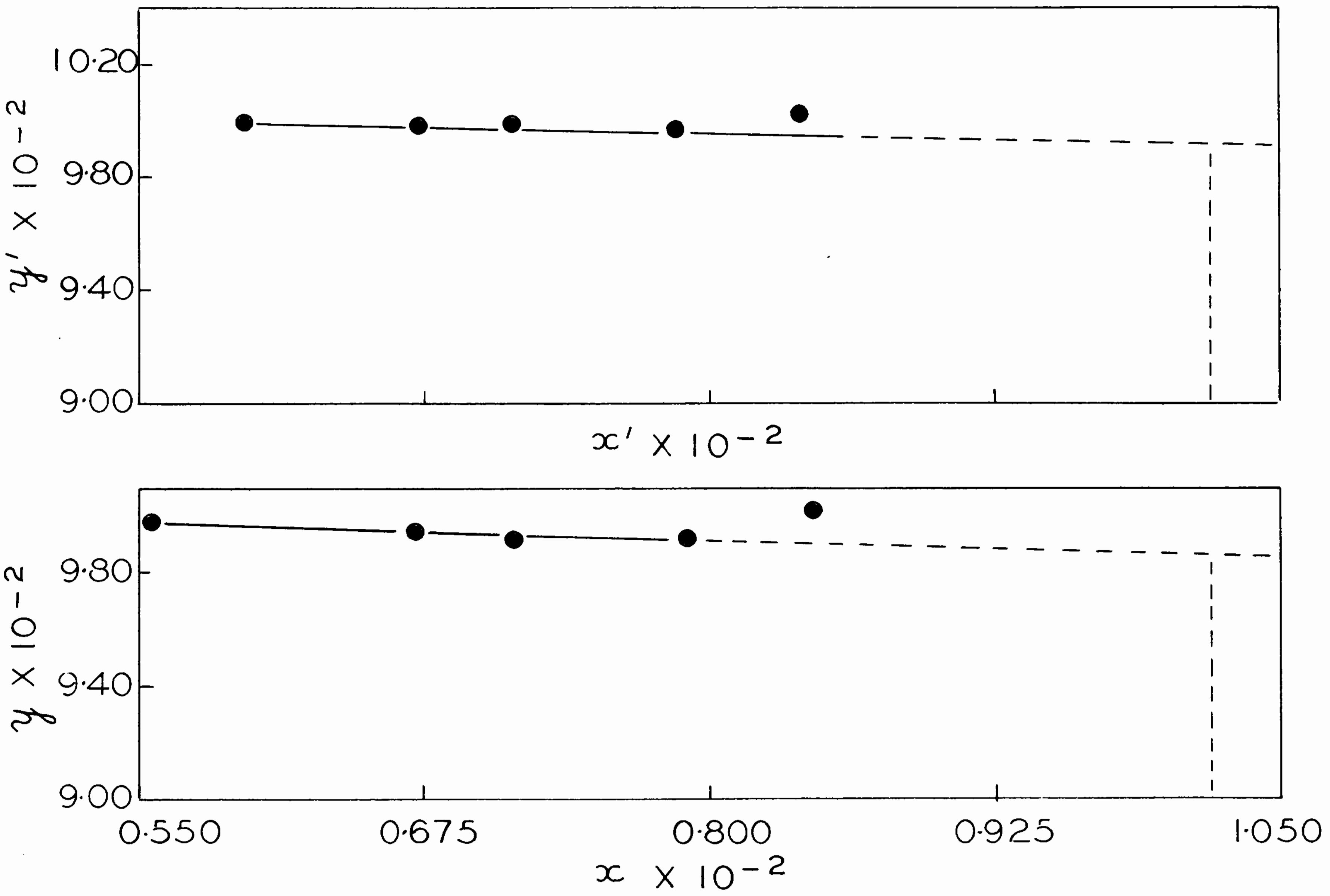

10·20
9·80
9·40
9·00
$y' \times 10^{-2}$
$x' \times 10^{-2}$
9·80
9·40
9·00
$y \times 10^{-2}$
0·550
0·675
0·800
0·925
1·050
$x \times 10^{-2}$

FIGURE 12.

Thus

$$\theta_1 = 10.337$$

$$\theta_2 = 183.52$$

$$\theta_4 = 144.63$$

$$\therefore \quad J_1 = (10.337 \times 102.08) + 144.63$$

$$= \underline{1200}$$

$$y(0) = J_1 - A \Lambda_o - 5/2 \Lambda_o \delta \qquad (4\text{-}7\text{-}17)$$

$$J_1 - y(0) - A \Lambda_o = 5/2 \Lambda_o \delta$$

$$1200 - 996 - 27.6 = 5/2 \times 102.08 \delta$$

$$\delta = \frac{176.4}{255.2} = \underline{0.6912}$$

Recalling that the hydrodynamic radius R of the large ion is related to δ by the expression

$$R = 7.32 \, \delta^{1/3} \, \text{Å},$$

$$\underline{R = 6.47 \, \text{Å}}.$$

Second approximation

J_2 in equation (4-7-14) can also be evaluated from the expression

$$J_2 = \theta_3 \Lambda_o + \frac{8\beta \kappa^2 a^2}{9c} \qquad (4\text{-}7\text{-}22)$$

where
$$\theta_3 = \frac{(ab\kappa)^3 \sqrt{2}}{24c^{3/2} b} \left(\frac{1 + 2b}{b^2} - 1.0774 \right) \qquad (4\text{-}7\text{-}23)$$

Note:

The θ terms involved in J_1 and J_2 are functions of a, both explicitly and also implicitly through b, but are, however, independent of c, which only appears in the ratio $\frac{\kappa^2}{c} = \frac{\pi \epsilon^2 N}{125DkT}$.

For a = 4.5 Å,

$$\theta_3 = 2.6383 \quad ; \quad \frac{8\beta\kappa^2 a^2}{9c} = 464.3$$

$$\text{Hence } \underline{J_2} = (-2.6383 \times 102.08) + 464.3$$

$$= \underline{195}$$

γ was then calculated to a second approximation with E, J_1, J_2 and δ terms retained,

$$\gamma = \frac{\Lambda}{\left\{\Lambda_o - S\sqrt{c\gamma_o} + E\, c\gamma_o \log c\gamma_o + J_1 c\gamma_o(1 - \alpha\sqrt{c\gamma_o})(1 - \frac{J_2}{J_1}\sqrt{c\gamma_o}) - 5/2\, \Lambda_o \delta c \gamma_o\right\}} \qquad (4\text{-}7\text{-}24)$$

Thus in the present example,

$$\gamma = 0.9867$$

This gives a new value of y (called y'), where

$$y' = y + J_2\sqrt{c\gamma} \qquad (2\text{-}7\text{-}26)$$

$$\underline{y'} = 999.1 + 13.8 = \underline{1012.9}$$

Similarly a new value of x (called x'), can be calculated using equation (4-7-24) in (4-7-15) and (4-7-12). The results are presented in Table XX.

From the plot of y' versus x' (Fig. 12), y'(0) was found to be 986 and the slope A = 0.21. J_1 was re-evaluated to a second approximation using the relation

$$J_1' = y'(0) + A\Lambda_o + 5/2\, \Lambda_o \delta$$

TABLE XX

Pr_4NBr

$J_1 = 1200$; $J_2 = 195$

10^4c	Λ	γ_o	γ	f^2	y	y'	x	x'
50.7070	88.40	0.9932	0.9867	0.6400	999.1	1013.0	59.57	60.88
28.7860	91.47	0.9936	0.9926	0.7061	996.8	1007.0	67.12	68.23
20.4250	93.03	0.9943	0.9946	0.7422	990.6	999.4	71.32	72.31
9.8980	95.70	0.9960	0.9974	0.8078	993.1	999.2	79.06	79.81
5.2272	97.43	0.9974	0.9987	0.8538	1004.5	1009.0	84.55	85.13
2.0800	99.16	0.9989	0.9995	0.9036	1066.7	1069.5	90.52	90.81

using the same value for the δ term as obtained earlier.

$$\text{Thus } \underline{J_1'} = 986 + (0.21 \text{ x } 102.08) + 176.4$$
$$= 1183.4$$

When J_1' is calculated from equation (4-7-18) for different values of "a", it is found to be nearly linear in "a" as is evident from Fig. 13.

From the plot of J_1 versus "å", this value of 1183.4 was seen to correspond to an "a" = 4.42Å. This is reasonably close to the value of 4.5Å assumed in the calculation. The use of 4.42Å rather than 4.5Å would not have affected the values obtained for the terms in the general conductance equation. When the extent of association is small, the term $A\Lambda_o$ would be negligible relative to J_1 (a), and would produce an almost identical

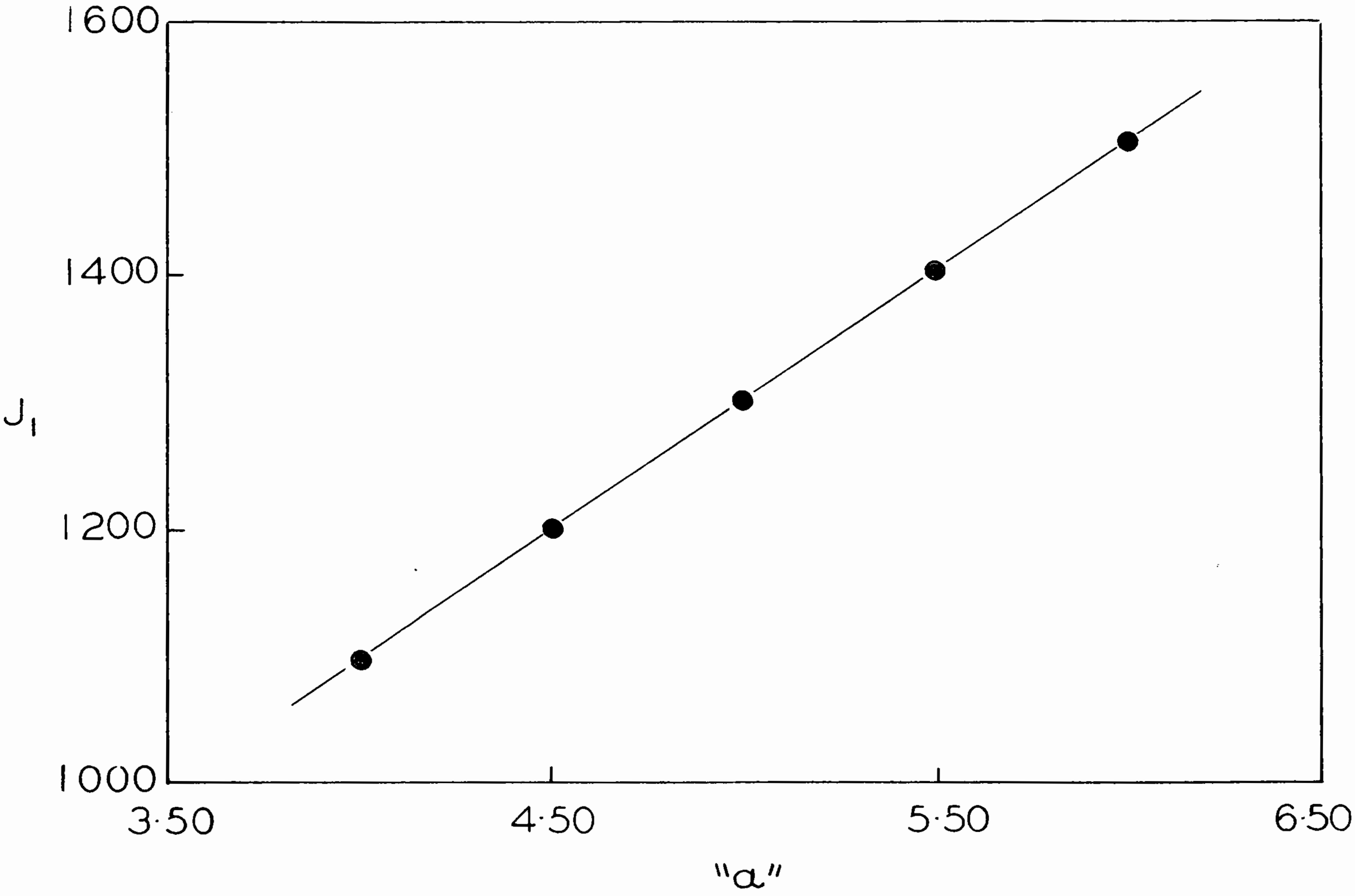


FIGURE 13

value of ion size.

Alternate Calculation

When the association constant, A, approaches unity, Fuoss suggests an alternate method of calculation in which γ is approximated by unity in calculating x' and y'. If we represent Λ''' by the equation:

$$\Lambda''' = \frac{\Lambda + \beta\sqrt{c} - E\ c \log c}{(1 - \alpha\sqrt{c})} - J_1 c + J_2 c^{3/2} + 5/2\ \Lambda_o \delta\ c \qquad (4\text{-}7\text{-}26)$$

then Λ''' is also given by

$$\Lambda''' = \Lambda_o - A\left[\frac{c\Lambda f^2}{(1 - \alpha\sqrt{c})}\right] = \Lambda_o - Az \qquad (4\text{-}7\text{-}27)$$

The results of the computations are given in Table XXI where

$$\Lambda'' = \frac{\Lambda_o + \beta\sqrt{c} - E\ c \log c}{(1 - \alpha\sqrt{c})} \qquad (4\text{-}7\text{-}28)$$

Fig. 14 shows the plot of Λ''' versus z. The slope of the latter permits evaluation of A, and the intercept at c = 0 gives the final value of Λ_o.

TABLE XXI

$10^4 c$	Λ	Λ''	Λ'''	z
50.7070	88.40	107.19_0	102.07_0	0.3127
28.786	91.47	104.98_3	102.06_7	0.1932
20.425	93.03	104.12_5	102.05_4	0.1457
9.8980	95.70	103.07_6	102.07_0	0.0783
5.2272	97.43	102.61_0	102.07_8	0.0442
2.0800	99.16	102.30_3	102.09_0	0.0188

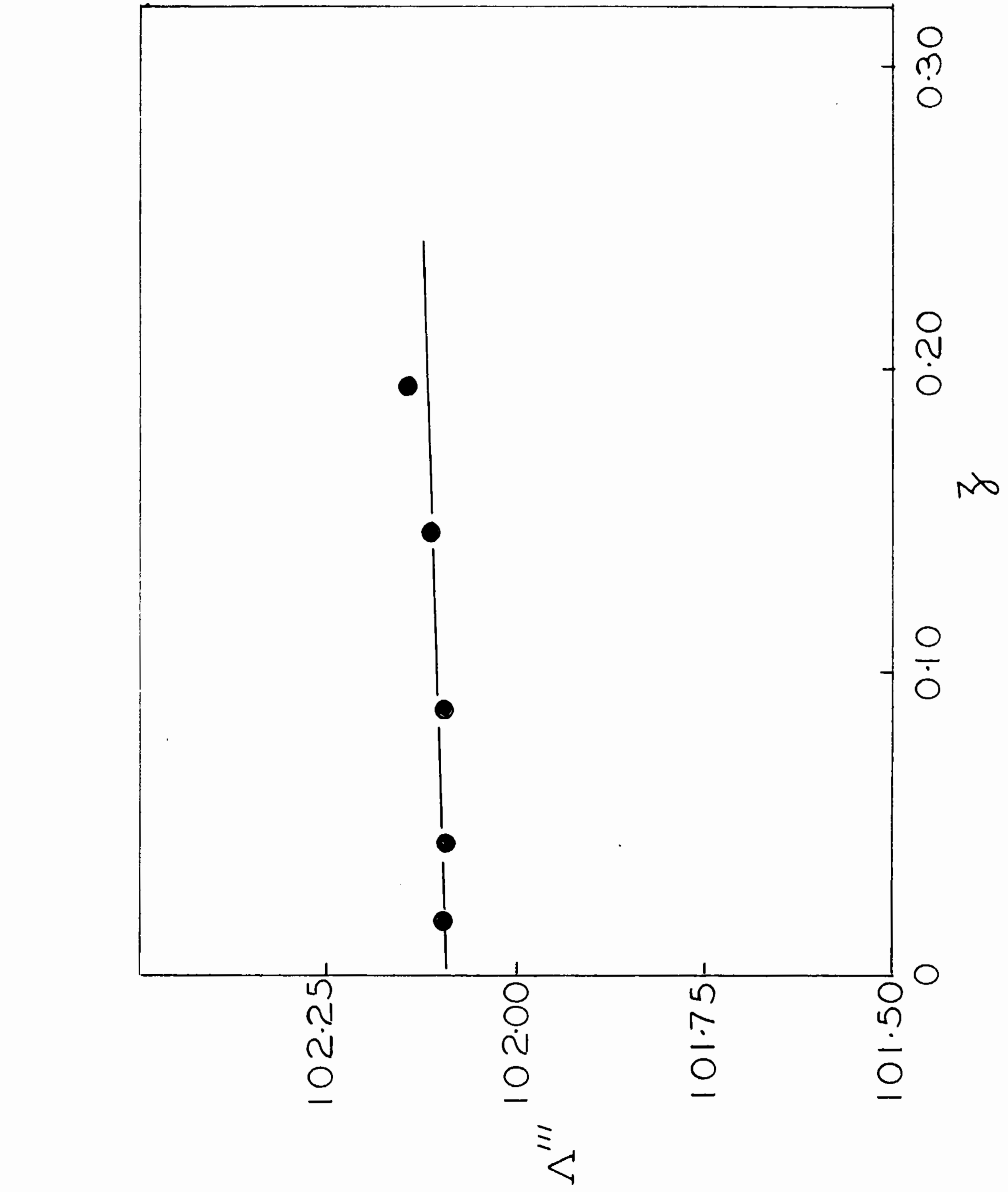


FIGURE 14

Calculation of Λ''

In our example

Λ	$\sqrt{c}$	$\alpha\sqrt{c}$	$E\ c \log c$	$\beta c^{1/2}$	Λ''
88.40	0.07121	0.050417	-4.477	8.9084	107.19

$J_1\ c = 6.085$; $J_2 c^{3/2} = 0.070$; $5/2\ \Lambda_o \delta\ c = 0.894$

$$\therefore \quad \Lambda''' = 107.19 - 6.085 + 0.070 + 0.894$$

$$= 102.07$$

The plot of Λ''' vs z being nearly horizontal within experimental error, the slope could not be evaluated accurately. However, the intercept at $c = 0$ gave the value 102.08 for Λ_o.

Tetrabutylammonium Bromide

The conductance data for Bu_4NBr was analyzed by the same procedure assuming a value of 97.04 for Λ_o (obtained from the Λ versus $\sqrt{c}$ plot). From a series of conductance data for Bu_4NI in water-dioxane mixtures, Fuoss estimated "a" for this salt as 5.55Å. This value was used in the present work in calculating the activity coefficient, f, from equation (4-7-16). y and x were computed for a series of concentrations to a first approximation using approximate values of γ, (γ_o), calculated according to equation (4-7-15). The plot of y versus x gave A = 3.12 and y(0) = 882.

$$\therefore \quad J_1 - 5/2\ \Lambda_o \delta = y(0) + A\ \Lambda_o$$

$$= 882 + 302.8$$

$$= \underline{1184.8}$$

In order to separate J_1 and δ, J_1 was calculated using equation (4-7-18), taking the value 5.55Å for "a". This yielded a value 1348 for J_1.

$$y(0) = J_1 - A\Lambda_o - 5/2\,\Lambda_o\delta \quad (4\text{-}7\text{-}17)$$

$$5/2\,\Lambda_o\delta = J_1 - A\Lambda_o - y(0)$$

$$= 1348 - 1184.8$$

$$= \underline{163.2}$$

$$\therefore\ \delta = \frac{163.2}{242.7} = 0.6724$$

Recalling that $R = 7.32\,\delta^{1/3}$Å,

$$R = 6.41\text{Å} \qquad (4\text{-}7\text{-}22)$$

J_2 was then evaluated from equation (4-7-22), and γ calculated to a second approximation using equation (4-7-24). y' and x' were computed and the results are given in Table XXII. Fig. 15 shows the plot of y' versus x'.

TABLE XXII

Bu_4NBr

10^4c	Λ	γ	f^2	y'	x'
50.546	84.09	0.9948	0.6496	1024.2	57.50
34.613	86.02	0.9959	0.6922	1016.6	62.11
24.517	87.56	0.9964	0.7288	1005.3	66.12
19.826	88.44	0.9980	0.7500	990.8	68.48
10.117	90.69_5	0.9985	0.8086	978.0	75.02
5.0078	92.47_5	0.9990	0.8582	-	-

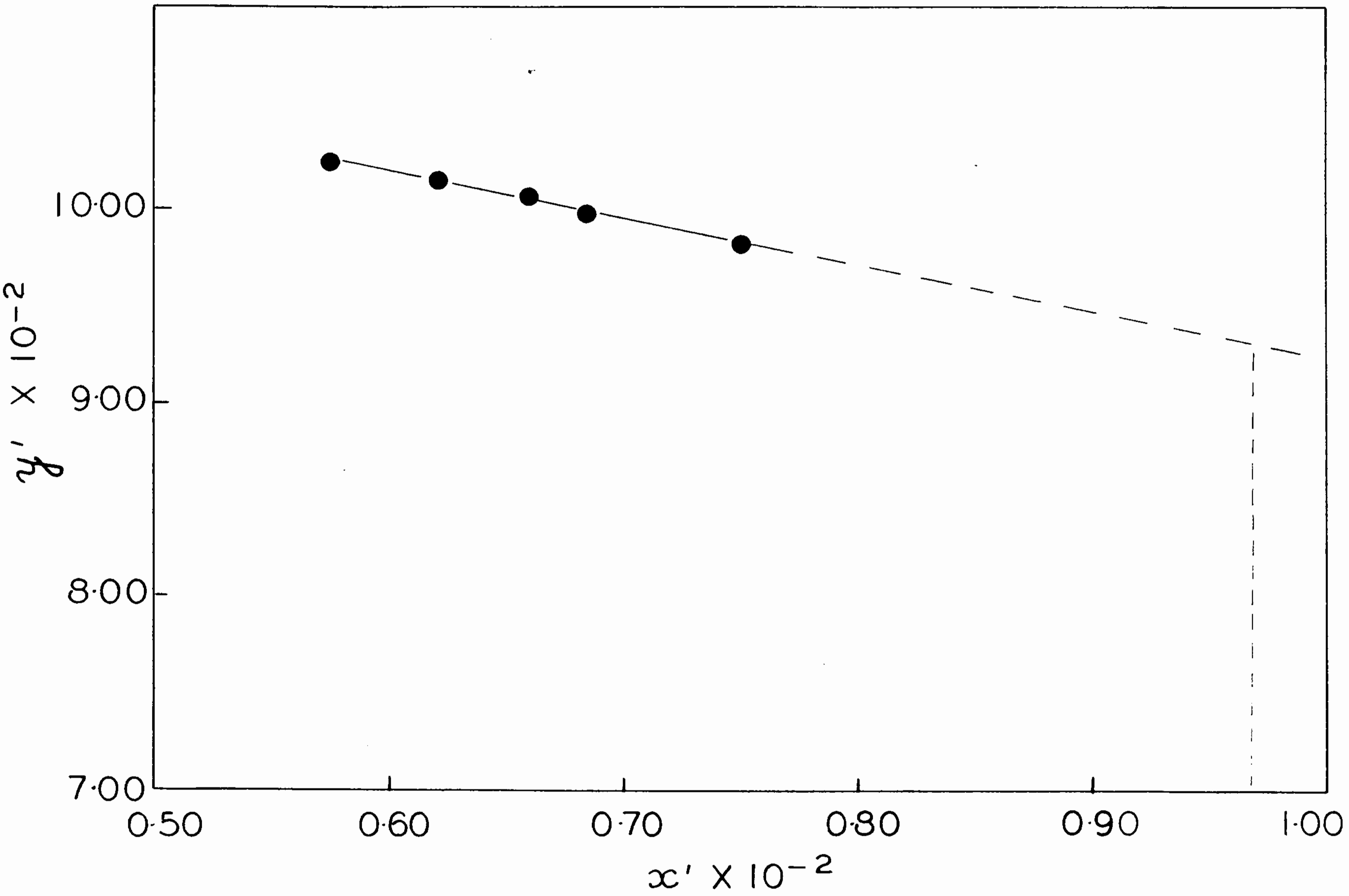


FIGURE 15.

From the y' versus x' plot, the slope A was found to be 3.00 and the intercept y(0) = 910. Re-evaluation of J_1 using the relation $J_1' = y'(0) + A\ \Lambda_o + 5/2\ \Lambda_o \delta$ gave $J_1' = 910 + 291.2 + 163.2$

$= \underline{1364.4}$

By the same procedure as that described for Pr_4NBr, this value of J_1 = 1364.4 was found to correspond to a value of 5.64Å for "a".

The association constant being small, the alternate method of calculation described for Pr_4NBr was applied to the data for Bu_4NBr as well. The results are listed in Table XXIII.

TABLE XXIII

Bu_4NBr $J_1 = 1364$; $J_2 = 520$.

10^4c	Λ	Λ''	Λ'''	z
50.546	84.09	102.30	96.20_0	0.2681
34.613	86.02	100.63	96.58_1	0.2034
24.517	87.56	99.54	96.66_2	0.1556
19.826	88.44	99.06	96.72_6	0.1313
10.117	90.69_5	97.97	96.77	0.0746
5.0078	92.47_5	97.41	96.81_5	0.0400
2.3776	93.91	97.21	96.92_6	0.0202

From the plot of Λ''' versus z, (Fig. 16) which was linear, the slope and intercept at c = 0 gave the values 2.02 for A and 96.97 for Λ_o.

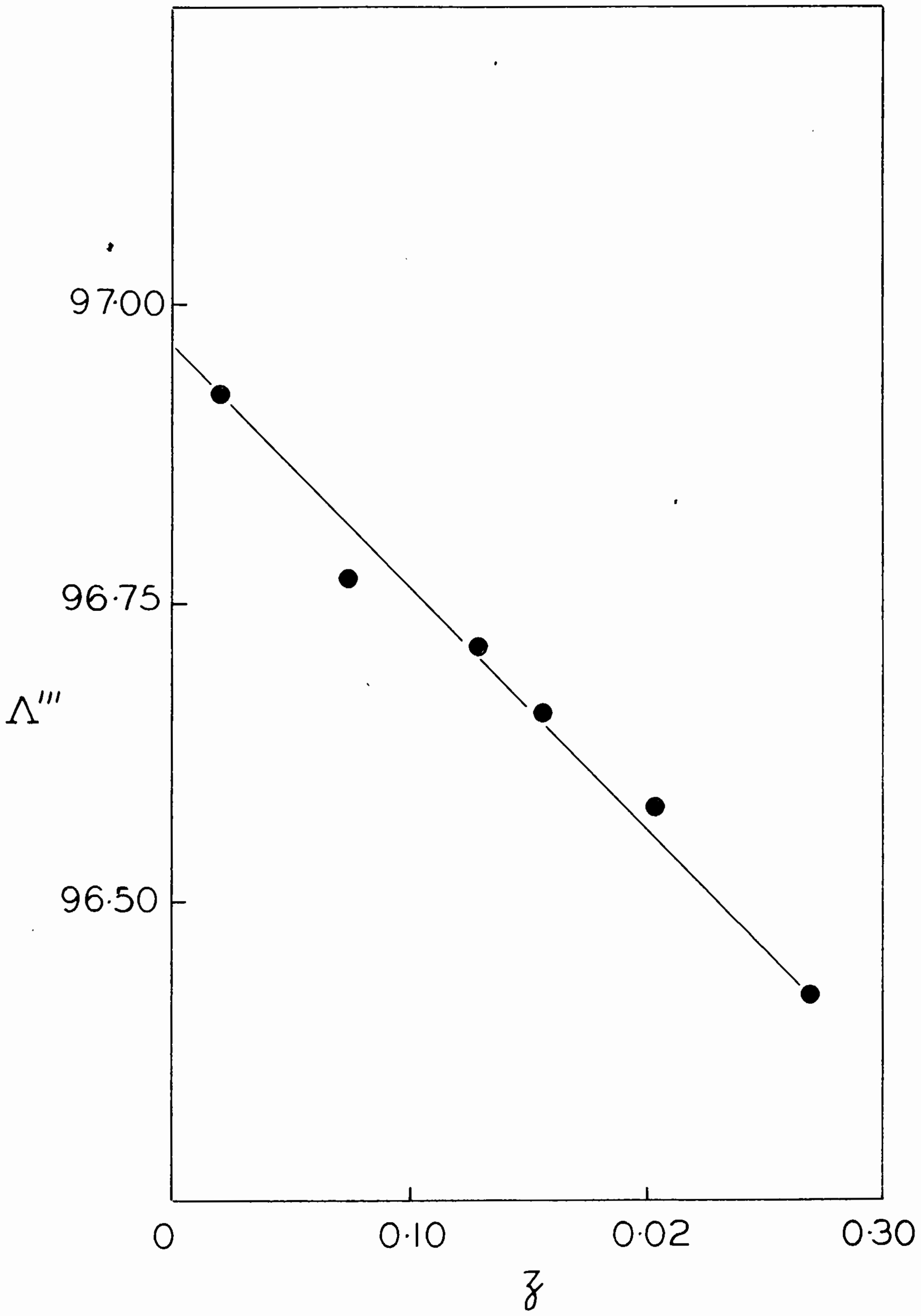


FIGURE 16

Tetrabutylammonium Chloride

The conductance data for Bu_4NCl were treated by the procedure described for Bu_4NBr. Assuming that $\Lambda_o = 96.83$ (from the Λ vs $\sqrt{c}$ plot), and "a" = $5.55\mathring{A}$, γ_o and hence f were computed for various concentrations. The corresponding values of y were calculated to a first approximation and a plot of y versus x was made from which A was found to be 6.22 and the intercept y(0) = 743.

$$J_1 - 5/2\ \Lambda_o \delta = y(0) + A\ \Lambda_o$$
$$= 743 + 603.7$$
$$= \underline{1346.7}$$

In order to separate J_1 and δ, J_1 was calculated using equation (4-7-18), taking the value $5.55\mathring{A}$ for "a". This yielded a value 1345 for J_1.

$$\therefore\ 5/2\ \Lambda_o \delta = 1345 - 1346.7$$
$$= -\ 1.7$$

This treatment leads to a negative value for R, the hydrodynamic radius of the Bu_4N^+ ion.

Alternatively, assuming that R and hence δ have the same values for Bu_4N^+ in the chloride and bromide, δ was taken as 0.672 (the value estimated in the case of Bu_4NBr). J_1 was then evaluated from the relation

$$J_1 = y(0) + A\ \Lambda_o + 5/2\ \Lambda_o\ \delta$$
$$= 1346.7 + 162.8$$
$$= \underline{1509.5}.$$

J_1 was calculated for various values of "a" and a plot of y vs "a" was made. From the plot this value of J_1 = 1509.5 was found to correspond to an "a" value of 6.44Å

J_2 was then computed using equation (4-7-22) and γ was estimated to a second approximation, the new value of 6.44Å being used for "a" in calculating the activity coefficients. y' and x' were then computed as before and the results are given in Table XXIV. Fig. 17 shows the plot of y' vs x'. This plot gave the value of A (the slope) as 6.8 and y'(0) = 795. Re-evaluation of J_1 using the relation $J_1' = y'(0) + A\,\Lambda_o + 5/2\,\Lambda_o \delta$ yielded

$$\begin{aligned} J_1' &= 795 + 658.4 + 162.8 \\ &= \underline{1616.2} \end{aligned}$$

From the nearly linear relation between J_1 and "a", this value of J_1 (1616.2) was found to correspond to a value of 7.03Å for "a".

TABLE XXIV

Bu_4NCl

10^4c	Λ	γ	f^2	y'	x'
50.2070	83.81	0.9823	0.6464	1088	57.08
29.231	86.60	0.9893	0.7106	1061	63.98
19.411	88.23	0.9918	0.7520	1005	68.47
8.9960	90.71_5	0.9947	0.8176	932	75.86
4.6410	92.30	0.9960	0.8630	-	-

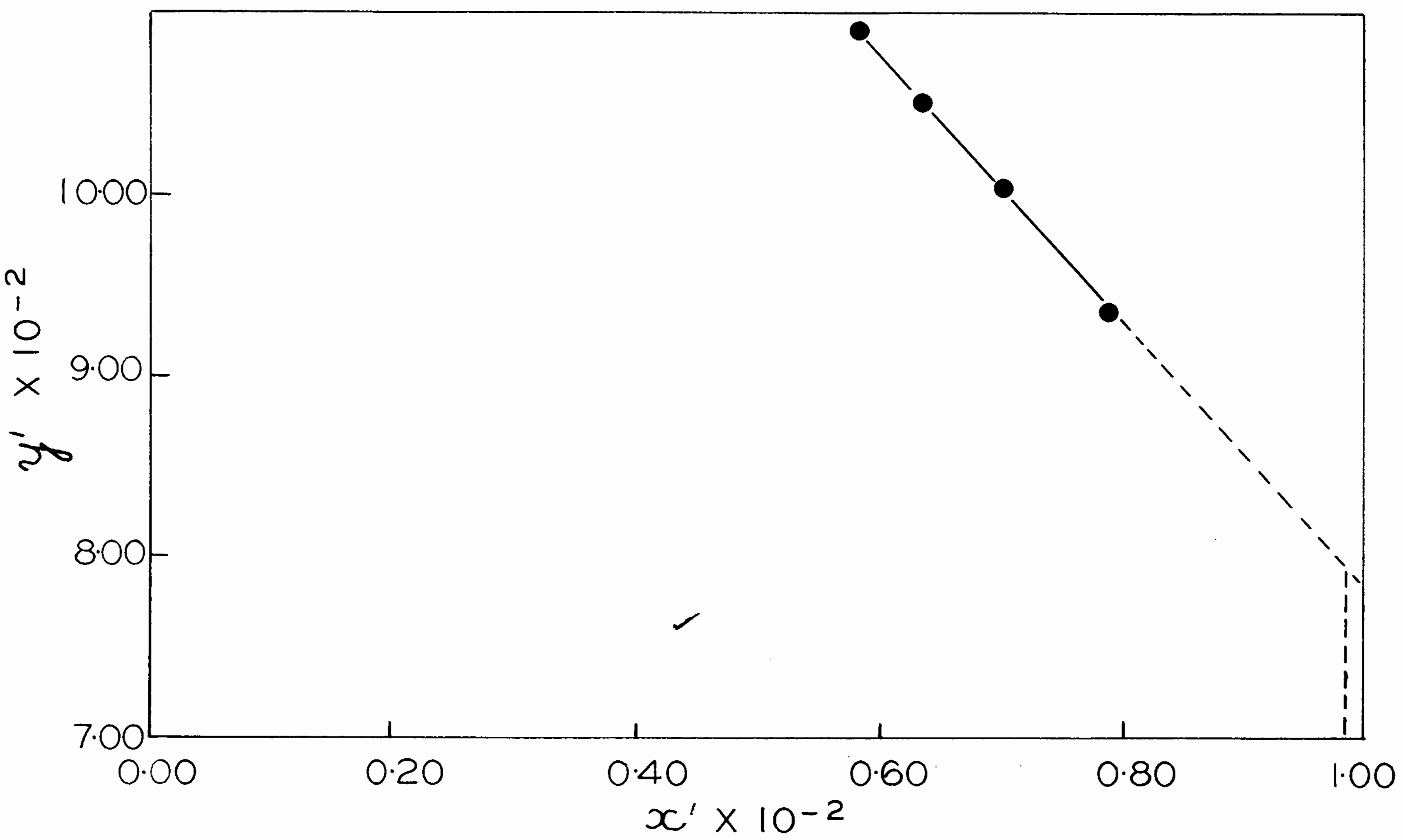


FIGURE 17

Tetrapropylammonium Chloride

Taking the value 101.88 for Λ_o from the Kohlrausch extrapolation, and assuming the same "a", namely 4.5Å, as for Pr_4NBr, γ_o was computed, and hence x and y. The plot of y vs x was linear with a slope (A) equal to 10.3 and the intercept y(0) equal to 530.

$$J_1 - 5/2 \Lambda_o \delta = y(0) + A \Lambda_o$$
$$= 530 + 1049.4$$
$$= \underline{1579.4}$$

J_1 calculated using euqation (4-7-18), with "a" = 4.5Å was found to be 1198. As in the case of Bu_4NCl, this value leads to a negative value for δ and hence R. Using the value of δ obtained for Pr_4NBr, J_1 was evaluated. Thus $\delta = 0.6912$

$$J_1 = 1579.4 + 5/2 \Lambda_o \delta$$
$$= 1579.4 + 176.1$$
$$= \underline{1755.5}$$

As before J_1 was calculated for various values of "a" and from the plot of J_1 versus "a" the value of "a" corresponding to 1755.5 was found to be 7.78Å.

J_2 was computed using equation (4-7-22), and γ was estimated to a second approximation taking this value of 7.78Å in calculating the activity coefficients. y' and x' were then calculated for various concentrations and the results are given in Table XXV. From the plot of y' versus x',

(Fig. 18), the slope gave the value of A as 11.5; the intercept y(0) = 505. The new value of J_1 is now

$$J_1' = y'(0) + A\ \Lambda_o + 5/2\ \Lambda_o \delta$$

$$= 505 + 1172 + 176$$

$$= \underline{1853}$$

From the linear relation between J_1 and "a", this value of J_1 was found to correspond to "a" = 8.79Å.

TABLE XXV

Pr_4NCl

10^4c	Λ	γ	f^2	y'	x'
50.000	88.21	0.9858	0.6418	976.9	59.58
28.209	91.20	0.9910	0.7090	926.1	67.18
20.000	92.71	0.9922	0.7448	870.4	71.30
10.000	95.17	0.9929	0.8071	668.5	78.56
4.5806	97.24_5	0.9948	0.8623	354.3	85.14

The utility of the Fuoss-Onsager equation as an analytical expression to represent conductance data will now be considered. When the ions are associated, their general conductance equation for electrolytes containing large ions takes the form:

$$\Lambda = \Lambda_o - S\sqrt{c\gamma} + E\ c\gamma \log c\gamma - 5/2\ \Lambda_o \delta\ c\gamma$$
$$+ J_1 c\gamma(1 - \alpha\sqrt{c\gamma})(1 - \frac{J_2\sqrt{c\gamma}}{J_1}) \qquad (4\text{-}7\text{-}9)$$

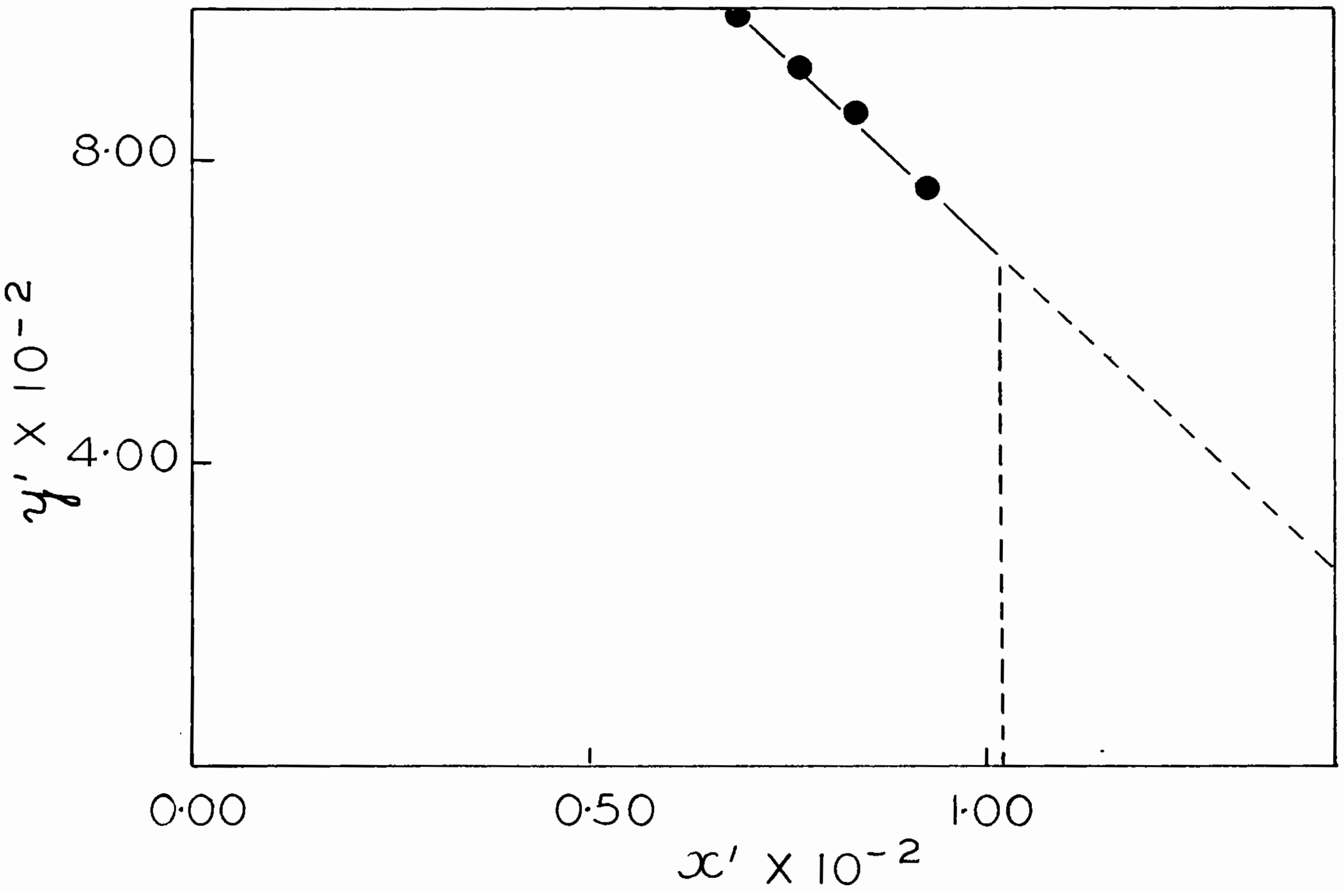


FIGURE 18

The following table shows the experimental values of the equivalent conductances (Λ observed), and the values of Λ calculated from the above equation for Pr_4NBr. The values of the parameters used in the equation were derived as indicated earlier. Thus $a = 4.5\mathring{A}$; $J_1 = 1200$; $J_2 = 195$.

TABLE XXVI

Pr_4NBr

$\Lambda_o = 102.08$

10^4c	Λ (observed)	Λ (calculated)
69.100	86.51	86.46
50.707	88.40	88.40
20.424	93.03	93.05
9.898	95.70	95.72
5.2272	97.43	97.43

It is evident that the agreement between $\Lambda_{(calculated)}$ and $\Lambda_{(observed)}$ in the above table is reasonably good. Thus the equation represents the conductance data for Pr_4NBr in nitromethane within the experimental error up to about 0.005 N. When the parameters derived earlier for Bu_4NBr were used in the equation, no fit was obtained. However, if "a" is treated as an adjustable parameter chosen to get the best fit of data, it is possible to make it represent experimental values. For example, if $a = 4.95\mathring{A}$ rather than $5.64\mathring{A}$ derived earlier, the results presented in the following table are obtained.

TABLE XXVII

Bu_4NBr

$a = 4.95\text{Å}$; $J_1 = 1240$

$J_2 = 392$; $\Lambda_o = 96.97$

10^4c	Λ(observed)	Λ(calculated)
74.040	81.89	81.85
50.546	84.09	84.10
34.613	86.02	86.02
24.517	87.56	87.58
19.826	88.44	88.46
2.3776	93.91	93.92

The observed values of Λ agree with the corresponding calculated values within the experimental error up to a concentration of about 0.005 N. For the two chlorides Fuoss' method of analysis of the conductance data yielded values of "a" equal to 7.03Å and 8.79Å. When these values of "a" are used, the agreement between the observed and calculated values of Λ for Pr_4NCl and Bu_4NCl is not satisfactory. However, if a = 4.4Å is used for Pr_4NCl and a = 4.9Å is chosen for Bu_4NCl, the equation reproduces the observed conductance data within about 0.1%, for concentrations up to about 0.005 N.

The mathematical and physical approximations made in the derivation limit the validity of the Fuoss-Onsager equation (4-7-2) to values of κ a less than about 0.2. For the nitromethane solutions this corresponds to a concentration of about 0.005 N. The following table gives the values of Λ_o of the salts studied, as obtained by extrapolations by the various methods previously discussed.

TABLE XXVIII

Salt	Fuoss-Onsager Equation	Λ vs $\sqrt{c}$ plot	Λ_o' vs c plot
Pr_4NBr	102.08	102.10	102.04
Pr_4NCl	101.86	101.88	102.00
Bu_4NBr	96.97	97.04	97.00
Bu_4NCl	96.83	96.83	96.90

Thus as an analytical expression the Fuoss-Onsager equation is found to be useful.

However, as a theoretical treatment for electrolytes the equation produces some anomalies. For example, the theory indicates that the chlorides have large values of "a". On the basis of Bjerrum's theory of ion pair formation, higher values of "a" would indicate that the chlorides should be less associated than the corresponding bromides. However, the values of association constant obtained from the Fuoss-Onsager equation indicate that the chlorides are more associated than the bromides. Thus, the association constants for Pr_4NCl and Bu_4NCl are 6.8 and 11.5 whereas those for the corresponding bromides are 0.2 and 2.0 respectively. Fuoss (56) suggests that a thermodynamic approach to the problem of ion association made by Denison and Ramsey (63) is preferable to the statistical one of

Bjerrum's as the former has the following advantages over the Bjerrum model: 1) only ions in actual contact are counted as pairs; 2) association is not automatically excluded beyond a critical value of the parameter "b".

However, to test the Fuoss-Onsager equation rigorously, it would be necessary to obtain "a" values by measuring conductance of the salts for varying values of the dielectric constants of the solvent medium. The range must be wide enough to include solvent mixtures in which the association constant has a value of at least 10. Because of the lack of such data for these salts, it was necessary to guess starting values of "a", or in the case of the chlorides, the value of δ, (the viscosity factor) which depends on the hydrodynamic radius of the large ion.

The values of "a" obtained above can be used to calculate the association constant (A) from the Bjerrum theory of ion pairs. Thus the association constant

$$A = K^{-1} = \frac{4\pi N}{1000}\left(\frac{\epsilon^2}{DkT}\right)^3 Q(b) \qquad (4\text{-}6\text{-}4)$$

where $Q(b) = \int_2^b y^{-4}\, e^y\, dy$

and $$b = \frac{\epsilon^2}{aDkT} \qquad (4\text{-}6\text{-}5)$$

For Bu_4NBr, "a" = 5.55 (as derived from the Fuoss-Onsager equation earlier)

$$\therefore\ b = \frac{\epsilon^2}{aDkT} = \frac{15.15 \times 10^{-8}}{5.55 \times 10^{-8}} = 2.730$$

The values of log Q(b) computed by Fuoss (39) for various "b" values were plotted against each other and from the plot the above value of b (2.730) was found to correspond to log Q(b) = - 0.6000. Hence

$Q(b) = 0.2512$, and from equation (4-6-4)

$$\underline{A} = K^{-1} = 0.263 \times 10^{2} \times 0.2512$$

$$= \underline{6.61}$$

For Bu_4NCl, "a" = 7.03Å

By a similar calculation

$$\underline{A = 1.57}$$

8. Robinson and Stokes' Equation

An alternative modification of Onsager's limiting law has been proposed by Robinson and Stokes (64) and this explains the conductance behaviour of some strong uni-univalent electrolytes in water. Their equation for moderate concentrations takes the form

$$\Lambda = \Lambda_o - \frac{(\alpha \Lambda_o + \beta)\sqrt{c}}{1 + B\mathring{a}\sqrt{c}}$$

where $(\alpha \Lambda_o + \beta)$ is the Onsager coefficient, $B = \dfrac{50.29}{(DT)^{1/2}}$, and $\mathring{a}$ is a disposable parameter, the mean distance of closest approach of the ions in angstroms. Using this equation to represent the conductance of the ionic portion of the salt, the degree of dissociation γ is given by

$$\gamma = \frac{\Lambda}{\Lambda_o - \dfrac{(\alpha \Lambda_o + \beta)\sqrt{\gamma c}}{(1 + B\mathring{a}\sqrt{\gamma c})}}$$

This equation can then be used with the law of mass action and the activity coefficient. By successive approximations, consistent values of γ can be obtained satisfying the three equations and hence the dissociation constant can be computed.

This method was applied to nitromethane solutions of Bu_4NCl. Using the value 96.80 for Λ_o, the dissociation constant K was computed for various values of $\mathring{a}$ and the results are shown in Table XXIX. B for nitromethane at 25°C = 0.479.

TABLE XXIX

Dissociation constant (K) of Bu_4NCl

10^4c	Λ	$\mathring{a}$ = 4.5Å	$\mathring{a}$ = 5.0Å	$\mathring{a}$ = 5.5Å	$\mathring{a}$ = 6.5Å
52.207	83.81	0.300	0.264	0.226	0.186
29.231	86.60	0.215	0.191	0.172	0.144
19.411	88.23	0.162	0.150	0.137	0.120
8.996	90.72	0.105	0.100	0.094	0.085

No reasonable value of $\mathring{a}$ could be found for which the dissociation constant was invariant. Similar results were obtained when the method was applied to the other salts, and hence the data of this research do not conform to the Robinson and Stokes' equation.

9. Walden's Rule

Several attempts have been made to estimate individual ionic conductivities from those of salts on a hydrodynamic basis. The relation proposed empirically by Walden (65) and familiarly known as Walden's Rule has been developed theoretically by combining Coulomb's law and Stokes' law.

According to Stokes' law, $v = \frac{F}{6\pi \eta r}$ (4-9-1)

where v is the steady velocity with which a particle of radius r moves through a medium of viscosity η when a force F is applied. If a potential gradient E is applied,

$$v = \frac{\lambda_o \pm E}{F} \qquad (4\text{-}9\text{-}2)$$

where $\lambda_o \pm$ is the limiting ionic conductance and F is the Faraday constant equal to $E\epsilon$ where ϵ is the electronic charge. Eliminating v from the above two relationships gives

$$\eta \lambda_o^{\pm} = \frac{\epsilon F}{6\pi r_{\pm} \eta} \qquad (4\text{-}9\text{-}3)$$

so that $$\eta \Lambda_o = \eta(\lambda_o^{+} + \lambda_o^{-}) = \frac{\epsilon F}{6\pi \eta}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \qquad (4\text{-}9\text{-}4)$$

where r represents the radius of the ionic species.

From equation (4-8-3) it follows that the product of the (limiting) ionic conductance and the viscosity of the medium will be constant irrespective of the solvent if any given ion retains the same radius and behaves as a sphere in a continuous medium. Ions are believed to be solvated in solution and the degree of solvation to be determined by the dielectric constant of the solvent, and the size of the ions. The rule should then be expected to hold best for large ions, such as the quaternary ammonium ions. Such ions conform more closely to Stokes' law and tend to be less solvated than small ions.

The limiting conductance-viscosity product of the quaternary ammonium salts studied are presented in Table XXX, along with the corresponding data for nitrobenzene (12) and dimethylformamide (63).

TABLE XXX

Conductance-Viscosity Products ($\Lambda_o\eta$) at 25°C.

		Nitromethane	Nitrobenzene	Dimethyl-formamide
Viscosity η (poise)		0.00627	0.01811	0.00796
Λ_o, Me_4NBr	a	117.83	-	92.60
$\Lambda_o\eta$, Me_4NBr		0.738	-	0.738
Λ_o, Et_4NCl	a	110.37	38.55	-
$\Lambda_o\eta$, Et_4NCl		0.694	0.700	-
Λ_o, Et_4NBr	a	110.60	-	89.30
$\Lambda_o\eta$, Et_4NBr		0.693	-	0.710
Λ_o, Pr_4NBr	b	102.08	-	82.80
$\Lambda_o\eta$, Pr_4NBr		0.640	-	0.659
Λ_o, Bu_4NBr	b	97.04	33.48	-
$\Lambda_o\eta$, Bu_4NBr		0.608	0.607	-

a Previous work (13)

b This work.

Walden's rule seems to be reasonably well obeyed for these electrolytes. For $\eta\Lambda_o$ to be constant both $r_\pm$ must not alter with change of solvent. A better test would be the constancy or otherwise of the product $\eta\lambda_o^+$ or $\eta\lambda_o^-$.

10. Ionic Conductances

No measurements of the transport number of any ion in nitromethane are available. However, a method of evaluating individual ionic conductances from those of salts has been developed by Fowler and Kraus (64). They assumed that with a salt of a large cation and anion, of comparable size the individual ionic conductances are equal to one half that of the salt. Accordingly, Kraus (12) has reported the limiting conductance of Bu_4N^+ in nitrobenzene as 11.9, deriving this result by halving the limiting conductance of tetrabutyl ammonium triphenyl borofluoride. On the basis of the Walden relation, the ionic conductance of Bu_4N^+ in nitromethane is 34.3. The limiting conductances of the other ions in nitromethane can then be found assuming the additivity rule of ionic conductances (1). The values thus obtained are listed in Table XXXI.

TABLE XXXI

Limiting Ionic Conductances in Nitromethane at 25°C.

Ion	Pr_4N^+	Bu_4N^+	Cl^-	Br^-
λ_o	39.3	34.3	62.6	62.8

11. Comparison of Nitromethane Conductance Data

Table XXXII lists the limiting equivalent conductances (Λ_0), percentage deviation from the limiting Onsager equation and the degrees of dissociation (γ) in nitromethane of the salts studied in this work and of those by Elias (13).

TABLE XXXII

Comparison of Nitromethane Conductance data at 25°C.

Salt	Λ_o ohm^{-1} cm.^{2} equiv^{-1}	$\lambda^o_{Br} - \lambda^o_{Cl}$	$\frac{(S_T - S_E)100}{S_T}$	γ at 0.002 N
		Previous Work (13)		
Me_4NBr	117.83	0.21	-55	0.9443
Me_4NCl	117.62		-72	0.9238
Et_4NBr	110.60	0.23	-10	0.9840
Et_4NCl	110.37		-13	0.9832
		This Work		
Pr_4NBr	102.10	0.22	-5.0	0.9948
Pr_4NCl	101.88		-9.5	0.9922
Bu_4NBr	97.04	0.21	-3.6	0.9980
Bu_4NCl	96.83		-7.4	0.9918

$\frac{(S_T - S_E)100}{S_T}$ in column 4 of the above table is the percentage deviation of the experimental slopes (S_E) of the Λ versus $\sqrt{c}$ plots from the theoretical (limiting) Onsager slope (S_T). The degree of dissociation, γ, in the last column was calculated for 0.002 N solutions using the Shedlovsky-Fuoss treatment discussed earlier. On the basis of the per cent deviation shown in column 4, the tetramethyl salts in nitromethane are weaker electrolytes than the corresponding tetraethyl salts. The tetrapropyl and butyl salts are relatively strong electrolytes. The bromides are dissociated in all cases to a greater extent than the corresponding chlorides. The regular gradation in properties in passing from the tetramethyl to the tetrabutyl salts is clearly brought out. The degree of dissociation of each salt in 0.002 N solution is rather high, although for a common anion, it tends gradually to increase slightly with increasing size of the quaternary ammonium cation. The data in column 3 show that the difference between the limiting equivalent conductance of bromide and chloride salts with a common cation is 0.22 ± 0.01. This result substantiates the Kohlrausch law of independent migration of ions (1). A further test of the Kohlrausch law can be made by reference to the data in the following table.

TABLE XXXIII

	$\lambda^{o}_{Me_4N^+} - \lambda^{o}_{Et_4N^+}$	$\lambda^{o}_{Et_4N^+} - \lambda^{o}_{Pr_4N^+}$	$\lambda^{o}_{Pr_4N^+} - \lambda^{o}_{Bu_4N^+}$
(From the Bromides)	7.23	8.50	5.06
(From the Chlorides)	7.25	8.49	5.05

Since literature data for the conductivities of Pr_4NBr, Pr_4NCl and Bu_4NCl in nitromethane are lacking, no true comparison of the results of this research with those of other workers can be made. However, nitromethane conductance data at 25°C for Bu_4NBr have been obtained by Elias (13) in this laboratory. Fuoss (40) has investigated the conductance of Bu_4NBr in methanol-nitromethane mixtures, and in the pure solvents at 25°C. The results of this research (a) are compared in the table below with those obtained by Elias (b) and by Fuoss (c) for Bu_4NBr in nitromethane at 25°C.

TABLE XXXIV

Limiting equivalent conductance (Λ_o) of

Bu_4NBr in Nitromethane

Λ_o(a)	Λ_o(b)	Λ_o(c)
97.04	97.10	86.80

It can be seen that there is reasonably good agreement between the values obtained for Λ_o by this research and that by Elias. There is, however, a wide discrepancy between the value determined by Fuoss for $\Lambda_o Bu_4NBr$ and those of this research and of Elias. The values were in all the three cases determined by extrapolation of the Λ versus $\sqrt{c}$ plots to zero concentration.

Fuoss purified nitromethane by two distillations from phosphorus pentoxide and the middle fraction was used. He observed that the specific conductance of the sample was of the order of 10^{-7} mhos, which increased on standing. One of the difficulties connected with using drying agents is their subsequent removal. For example, Walden (67) found that even after five distillations traces of phosphorus pentoxide after its use as a drying agent remained in the distillate. Hartley et al. (10) have reported that this drying agent was unsuitable as it formed a sol in nitromethane and a white solid was deposited in the condenser on distillation. They avoided the difficulties by refluxing the nitromethane for several hours while bubbling dry air through it followed by distillation. The conductance of the solvent was taken as a measure of purity. The method of purification of nitromethane used in this research has been described earlier. The purity of the solvent as determined absolutely by the freezing curve method of Rossini (26), showed that density values could be used as a check on purity whereas conductance alone is not a sufficient criterion. No data are given by Fuoss or Hartley for the purity of the solvent. Fuoss reports the density as 1.1251 gm./ml. while the solvent used in this research has a density of 1.13122 gm./ml. and Hartley reports an average value of 1.13120 gm./ml. The specific conductance of the solvent used in the present study was $(0.5 - 1) \times 10^{-8}$ mhos at 25°C and the purity 99.96 mole per cent.

The salt was prepared by the same method in this research as that used by Fuoss who, however, dried the salt at a lower temperature. From the effect of drying temperature on salt purity and conductance of solutions determined quantitatively for Pr_4NCl earlier, it is indicated that if the temperature is not high enough, salt dried at a lower temperature yields a lower conductance. However, the magnitude of this effect is not sufficient to explain the wide discrepancy in the Λ_o values for Bu_4NBr obtained by Fuoss and in this research. It could probably be explained on the basis of the purity of the solvent.

Hartley (10) observed that addition of small quantities of water increased the conductivity of electrolytes in nitromethane, this increase being greater for salts with large divergences from ideal behaviour. However, in the case of the tetraethyl ammonium salts which, he found, obeyed the limiting Onsager equation very closely, the increase in conductivity was very close to that expected from the decrease in viscosity of the solutions due to the addition of water. In this research, on the other hand, it was observed that the magnitude of this increase in conductivity is greater than can be explained by the diminution in viscosity. This has been discussed earlier in Part II.

12. Comparison with other solvents

A close comparison of the conductance behaviour of the quaternary ammonium salts in nitromethane and dimethylformamide (68) may be made from the following table. Both these solvents possess about the same dielectric constant, and both are electron-donors.

TABLE XXXV

$$\frac{\eta\,(\text{Nitromethane})}{\eta\,(\text{Dimethylformamide})} = 1.27$$

Salt	$\frac{\Lambda_o\,(\text{Nitromethane})}{\Lambda_o\,(\text{Dimethylformamide})}$
Me_4NBr	1.27
Et_4NBr	1.24
Pr_4NBr	1.24

The observed conductance ratio agrees with the calculated viscosity ratio of 1.27, and this close correspondence of conductance phenomena probably results from similar solvation effects occurring in these media. The conductance behaviour of these salts in dimethylformamide as well as in nitrobenzene (12) was found to conform to the Fuoss-Shedlovsky treatment of weak electrolytes by which the dissociation constants and limiting conductances were therefore determined. However, the present data did not comply with the same analysis.

The discrepancy between theory and experiment might arise from some type of ion-solvent interaction which the theory does not take into account. These effects might be masked in the equivalent conductance data since they result from the sum of the anion and cation conductances. It would therefore appear advisable to combine the present data with transference numbers to obtain ionic conductances. Such measurements are now under way in this laboratory.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

1. The electrical conductivities of nitromethane solutions of Pr_4NCl, Pr_4NBr, Bu_4NCl and Bu_4NBr have been determined at 25°C with a precision of 0.02%. The concentration range extended from 0.01 N to 0.0001 N.

2. The limiting equivalent conductances Λ_o, of these salts have been determined. The values were 101.88 ± 0.05, 102.08 ± 0.02, 96.83 ± 0.05 and 97.04 ± 0.03 ohm^{-1} $cm.^2$, for Pr_4NCl, Pr_4NBr, Bu_4NCl and Bu_4NBr respectively.

3. The effect of drying temperature on salt purity and conductance has been estimated quantitatively for nitromethane solutions of Pr_4NCl. The drying temperature suitable for each salt has been determined individually.

4. The addition of small quantities of water increases the conductivity of electrolytes in nitromethane. This effect was determined quantitatively for Pr_4NBr. The increase in conductance is greater than can be explained by the diminution in the viscosity of the solution caused by the addition of water.

5. The data have been considered from the point of view of the Debye-Huckel-Onsager theory of strong electrolytes. In each case the observed slope of the plot of equivalent conductance, Λ, **versus** square root of concentration, $\sqrt{c}$, was more negative than that predicted by the limiting Onsager equation. The curves for the bromides were linear for concentrations less than 1×10^{-3} N, while for the chlorides the linearity existed for concentrations up to about 5×10^{-4} N within experimental precision. Limiting equivalent conductances have been determined by extrapolation of the Λ versus

$\sqrt{c}$ plots and of the Shedlovsky plots, (Λ_o' versus c). The fact that the Λ versus $\sqrt{c}$ plots lie below the theoretical slopes and the failure of the Shedlovsky expression, ($\Lambda_o' = \Lambda_o + hc$), to represent the experimental data both indicate that these solutions are not strictly "strong" electrolytes. The bromides appear to be stronger than the chlorides.

6. The conductance data for the salts were analysed by the Shedlovsky-Fuoss extrapolation method for incompletely dissociated electrolytes. The results indicated that these salts in nitromethane cannot be considered to be truly "weak".

7. The data have been analysed by a modified general conductance equation recently proposed by Fuoss and Onsager. Limiting equivalent conductances, association constants and the ion size parameter, "a", were estimated. The equation fits the data well for Pr_4NBr only. The results obtained for the other salts produce some anomalies from a theoretical point of view. Thus, on the basis of Bjerrum's theory of ion pair formation the above results indicate that the chlorides should be less associated than the bromides. If "a" is treated as an adjustable parameter, suitable values can be found to make the Fuoss-Onsager equation fit the data for the salts Pr_4NCl, Bu_4NBr and Bu_4NCl.

8. Analysis of the conductance data by the equation of Robinson and Stokes, which takes into account the finite size of ions, showed that the equation does not fit the data.

9. The Walden rule appears to be reasonably well obeyed by these electrolytes.

10. Approximate ionic mobilities have been calculated on the basis of Walden's rule, assuming for the Bu_4N^+ ion $\eta\lambda_o = 0.216$.

BIBLIOGRAPHY

1. F. Kohlrausch, Ann. Physik, 6, 1, 145 (1879).
2. S. Arrhenius, Z. Physik. Chem., 1, 631 (1887).
3. W. Ostwald, Z. Physik. Chem., 2, 36 (1888).

   ibid., 3, 170, 241 (1889).
4. E.W. Washburn, J. Am. Chem. Soc., 31, 322 (1909).

   E.W. Washburn and E.B. Millard, J. Am. Chem. Soc., 37, 694 (1915).
5. P. Debye and E. Huckel, Physik. Z., 24, 185, 305 (1923).

   ibid., 25, 97 (1924).
6. G.N. Lewis, Proc. Am. Acad., 13, 359 (1907).
7. L. Onsager, Physik. Z., 27, 388 (1926); 28, 277 (1927).

   Trans. Farad. Soc., 23, 341 (1927).
8. F. Kohlrausch and L. Holborn - Leitvermogen der electrolyte Teubner, Leipzig.
9. C.A. Kraus, J. Franklin Inst., 225, 687 (1938).
10. C.P. Wright, D.M. Murray-Rust and H. Hartley, J. Chem. Soc., 199 (1931).
11. T.H. Mead, O.H. Hughes and H. Hartley, J. Chem. Soc., 1207 (1933).
12. C.R. Witschnke and C.A. Kraus, J. Am. Chem. Soc., 69, 2472 (1947).
13. L. Elias, Ph.D. Thesis, McGill University (1956).
14. E. Newberry, J. Chem. Soc., 113, 701 (1918).
15. E.D. Eastman, J. Am. Chem. Soc., 42, 1648 (1920).
16. J.N. Brønsted and R.F. Nielsen, Trans. Farad. Soc., 31, 1478 (1935).
17. H.E. Gunning and A.R. Gordon, J. Chem. Phys., 10, 126 (1942).
18. D.J.G. Ives and S. Swaroopa, Trans. Farad. Soc., 49, 788 (1953).
19. H.H. Lim, Austral. Jour. Chem., 9, 443 (1956).

20. J.P. Butler, H.I. Schiff and A.R. Gordon, J. Chem. Phys., 19, 752 (1951).

21. G.C. Benson and A.R. Gordon, J. Chem. Phys., 13, 473 (1945).

22. W. Bulani, Ph.D. Thesis, McGill University (1954).

23. L. Elias and H.I. Schiff, J. Phys. Chem., 60, 595 (1956).

24. R.R. Tink, Ph.D. Thesis, McGill University (1953).

25. K. Fisher, Z. angew. Chem., 48, 394 (1935).

26. F. Rossini, J. Natl. Bur. Std., 35, 355 (1945).

27. H. Sadek and R.M. Fuoss, J. Am. Chem. Soc., 72, 301 (1950).

28. H.M. Dagget, E.J. Bair and C.A. Kraus, J. Am. Chem. Soc., 73, 799 (1951).

29. A.S. Brown, J. Am. Chem. Soc., 56, 646 (1934).

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

31. T. Shedlovsky and A.S. Brown, J. Am. Chem. Soc., 56, 1066 (1934).

32. International Critical Tables, Vol. III, page 24.

33. H. Landolt and R. Bornstein, "Physikalisch-Chemische Tabellen" J. Springer, Berlin.

34. G. Jones, B.B. Bradshaw, J. Am. Chem. Soc., 55, 1780 (1933).

35. G.W. Davies, "The Conductivity of Solutions", John Wiley and Sons, New York (1930).

36. O.L. Hughes and H. Hartley, Phil. Mag., 15, 610 (1933).

37. H.I. Schiff, Ph.D. Thesis, Toronto University (1948).

38. H. Sadek and R.M. Fuoss, J. Am. Chem. Soc., 72, 301 (1950).

39. R.M. Fuoss and C.A. Kraus, J. Am. Chem. Soc., 55, 1019 (1933).

40. R.C. Miller and R.M. Fuoss, J. Am. Chem. Soc., 75, 3076 (1953).

41. J.J. Van Laar, Z. Physik. Chem., 19, 318 (1896).

42. W. Sutherland, Phil. Mag., 6, 14 (1907).

43. S.R. Milner, Phil. Mag., 35, 214 (1918).

44. J.C. Ghosh, J. Chem. Soc., 113, 449, 627, 790 (1918).

45. Manov, Bates, Hamer and Acree, J. Am. Chem. Soc., 65, 1765 (1943).

46. T. Shedlovsky, J. Am. Chem. Soc., 54, 1411 (1932).

T. Shedlovsky, Brown and MacInnes, Trans. Electrochem. Soc., 66, 165 (1934).

47. R.T. Lattey and O. Gately, Phil. Mag., 7, 985 (1929).

48. R.M. Fuoss, J. Chem. Ed., 32, 527 (1955).

49. T. Shedlovsky, J. Am. Chem. Soc., 54, 1405 (1932).

50. R.M. Fuoss and C.A. Kraus, J. Am. Chem. Soc., 55, 476 (1933).

51. T. Shedlovsky, J. Franklin Inst., 225, 739 (1938).

52. D.A. MacInnes, "Principles of Electrochemistry", Reinhold Publishing Corp., New York, 1939, page 144.

53. N. Bjerrum, K. Danske vidensk.Selsk., 7, No. 9 (1926).

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

55. R.W. Gurney, "Ionic Processes in Solution", McGraw-Hill Book Co., N.Y. (1953). Chap. 2.

56. R.M. Fuoss and C.A. Kraus, J. Am. Chem. Soc., 79, 3304 (1957).

57. L. Onsager, and R.M. Fuoss, J. Phy. Chem., 36, 2689 (1932).

58. H. Falkenhagen, M. Leist and G. Kelby, Ann. Physik., 6, 11, 51 (1952).

59. R.M. Fuoss and L. Onsager, J. Phys. Chem., 61, 668 (1957).

60. R.M. Ruoss and L. Onsager, Proc. Nat. Acad. Sci., 41, 274, 1010 (1955).

61. R.M. Fuoss, J. Am. Chem. Soc., 79, 3301 (1957).

62. A. Einstein, Ann. Physik., 19, 289 (1906)
ibid. 34, 591 (1911).

63. J.T. Denison and J.B. Ramsey, J. Am. Chem. Soc., 77, 2615 (1955).

64. R.A. Robinson and R.H. Stokes, J.Am. Chem. Soc., 76, 1991 (1954).

65. P. Walden, Z. Physik. Chem., 55, 207 (1906).

66. D.L. Fowler, and C.A. Kraus, J. Am. Chem. Soc., 62, 2237 (1940).

67. P. Walden and E.J. Birr, Z. Physik, Chem., A163, 263 (1933).

68. P.G. Sears, E.D. Wilhoit and L.R. Dawson, J. Phys. Chem., 59, 373 (1955).