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THE UNIVERSITY OF ALBERTA

A CONDUCTANCE STUDY OF METAL ION SOLVATION IN ACETONITRILE

by

HOWARD LANE YEAGER

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled A CONDUCTANCE STUDY OF METAL ION SOLVATION IN ACETONITRILE submitted by HOWARD LANE YEAGER in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

A conductance study of the alkali metal, copper(I), silver(I) and thallium(I) salts of symmetrical anions in acetontrile has been made. High precision conductance measurements were performed on sodium, potassium, rubidium, copper(I) and silver(I) tetrafluoroborate and hexafluorophosphate, copper(I), silver(I) and thallium(I) perchlorate, as well as silver(I) nitrate, thallium(I) tetrafluoroborate and potassium thiocyanate. Analysis by the Fuoss-Onsager conductance theory yielded limiting equivalent conductances, ion size parameters and, for those salts where association was detected, thermodynamic association constants. The alkali metal and thallium(I) salts were found to be associated, whereas the copper and silver salts were unassociated, with the exception of silver nitrate. Single ion conductivity values calculated were: copper(I), 64.7; silver(I), 86.0; thallium(I), 91.5; tetrafluoroborate, 108.3; hexafluorophosphate, 104.1; nitrate, 106.3; and thiocyanate, 113.4.

Mobility and association trends for the alkali metal salts have been interpreted in terms of the Lewis base properties of acetonitrile. These trends were compared to those of the salts of copper(I) and silver(I), which are specifically solvated by acetonitrile. The single ion conductivities of these ions and of thallium(I) are not readily interpretable in terms of simple solvation models.

ACKNOWLEDGEMENTS

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CHAPTER 1 INTRODUCTION

Acetonitrile has found wide use not only as a practical solvent for many synthetic and analytical applications but also as a medium for fundamental solvation studies. It is well suited as a solvent for studying oxidation-reduction reactions for it has a useful potential range which extends from +2.3 V to −2.7 V versus an aqueous saturated calomel electrode.[33] A dielectric constant of 36 allows dissolution of ionic as well as nonionic solutes. Being a polar Lewis base, this solvent stabilizes cations moderately well, although solubilities of ionic salts are not always large because it does not solvate anions to any appreciable extent. In general, only salts of large or polarizable univalent anions have reasonable solubilities.[4]

The relative ability of two solvents to solvate metal cations relative to each other may be estimated by comparing polarographic half-wave potentials in the two solvents. It has been found that the alkali metal ions are harder to reduce in water than in acetonitrile, which corresponds to a greater degree of stabilization in aqueous solution.[5] Furthermore, the difference in half-wave potentials decreases smoothly with increasing cation size, with cesium ion having the smallest difference. Similar studies have shown that the d^{10} metal cations copper(I) and silver(I) behave in the opposite way, indicating greater stabilization in acetonitrile than water.[28] Copper(I) does not disproportionate in this solvent as in water, and this stability helps make copper(II) an analytical oxidant of appreciable strength.[30] The interaction of silver(I) with acetonitrile is evidenced by the solubility of silver nitrate, in this solvent, about 9.6 M at room temperature, corresponding to a mole fraction of silver nitrate of 0.43.[23] In contrast salts such as sodium and potassium nitrate are only sparingly soluble.[4] This interaction has practical application, for the Ag, 0.01 M $AgNO_3$ couple in acetonitrile is a stable, reversible reference electrode for potentiometry in this solvent.[9] In order to learn more about the role of the solvent in ionic solution behavior, it was of interest to investigate the extent and character of this specific solvation in acetonitrile, and the effect of this solvation on cation-anion interactions.

When ionic solutes dissolve in solvents of low or moderate dielectric constant, the electrical attraction between a solvated cation and anion may approach or exceed the thermal energy of the ions. When this occurs, the ions associate to form an ion pair. This process often plays a major part in the description of a nonaqueous electrolyte solution. If the associated pairs are held together only by coulombic attraction, little change is seen in the absorption spectra of the ions as a result of such association.[36] Therefore spectrophotometry is not the ideal method for studying such equilibria. However, conductance measurements are ideally suited to these systems, for an ion pair of a symmetrical electrolyte is a neutral entity which does not contribute to the electrical conductivity of the solution. Therefore the method of investigation chosen for this study was electrolytic conductance measurements.

The measurement of electrolytic conductivities has found renewed interest in recent years due to the development of theoretical equations which successfully describe the dependence of conductance on concentration in dilute solution. This treatment, the Fuoss-Onsager conductance theory, is based on a model in which the solvent is regarded as a continuum and the ions as charged spheres of average diameter $\mathring{a}$. A summary of the theory is given in reference 16, and the complete derivation is presented in reference 17. The general expression of the theory is

$$\Lambda = \Lambda_o - S(C\gamma)^{\frac{1}{2}} + EC\gamma \log C\gamma + JC\gamma - K_A C\gamma \Lambda f^2$$

The coefficient S is the coefficient of the Onsager limiting tangent expression[38]

$$\Lambda = \Lambda_o - SC^{\frac{1}{2}}$$

and is equal to $(\alpha\Lambda_o + \beta)$. The constants α and β are in turn functions of the temperature, dielectric constant and viscosity of the solvent, as well as the solute charge type. The coefficient E is a function of these same variables, whereas J is a function of the ion size parameter $\mathring{a}$. The last term accounts for ion association and contains the thermodynamic association constant K_A and the mean ionic activity coefficient f. The degree of dissociation is represented by γ. This equation is then an extension of the Onsager limiting tangent expression for the conductance of electrolytes, with higher order terms of concentration, ion size and association all taken into account. Because of the nature of the approximations used in the derivation of the theory, it is restricted to 1:1 univalent electrolytes and ions which do not contain dipoles. Also the theory is valid for concentrations up to that corresponding to $\kappa\mathring{a} = 0.2$, where κ is the Debye-Huckel parameter. In acetonitrile this corresponds to about 8×10^{-3} $\underline{M}$. The theory has found remarkable success in fitting high precision conductance data of both nonassociated and associated electrolytes in various solvents, often within the precision of the experimental data.[18] The parameters to be evaluated then are the association constant, ion size and the limiting equivalent conductance, Λ_o. With a suitable method for splitting Λ_o values into cation and anion components, single ion conductivities may also be calculated.

Application of the Fuoss-Onsager theory to high precision conductance data for several salts in acetonitrile has shown that for large univalent cations and anions association is generally low. Thus the tetraalkylammonium bromides, iodides and picrates have K_A values under 50, with the amount of association decreasing with increasing size of cation and anion.[14] These trends are expected in terms of electrostatic theory, for a low charge density ion should have a low tendency to ion-pair. A study of the tetramethylammonium and tetrabutylammonium hexafluorophosphates[13] and of tetrabutylammonium perchlorate[7] showed them all to be essentially unassociated, as expected for these large anions. Kay and coworkers measured the conductance behavior of the alkali metal perchlorates and tetraphenylborides, finding the latter to be unassociated and the perchlorates to have association constants between 10 and 20 in acetonitrile.[27]

Low precision conductance measurements have been made on copper(I) and silver(I) salts. Hathaway and coworkers have prepared several tetrakis acetonitrile-solvated salts of copper(I); preliminary conductance measurements indicated that all are essentially strong electrolytes in acetonitrile.[21] Walden and Birr made conductance measurements on a large number of salts in acetonitrile, including silver nitrate and perchlorate.[40]

The Fuoss-Onsager theory was applied to this data, and although the nitrate and to a lesser extent the perchlorate salt indicated association, their data were of insufficient precision for exact treatment. Therefore conductance measurements were made on the silver(I) salts of the symmetrical anions tetrafluoroborate, perchlorate and hexafluorophosphate, along with silver nitrate. Other silver salts of interest such as the thiocyanate, tetraphenylboride and halides, have negligible solubility and so could not be studied.[1] Copper(I) tetrafluoroborate, perchlorate and hexafluorophosphate were studied but copper(I) nitrate was not because it could not be isolated in pure form.[21] In addition sodium, potassium and rubidium tetrafluoroborate and hexafluorophosphate were studied for comparison purposes. The anions tetrafluoroborate, hexafluorophosphate and perchlorate were chosen because of their large size, high degree of symmetry and low tendencies toward covalence. Thus any specific effects due to anion interactions should be minimized.

It would also be of interest to study other univalent metal ions in addition to the alkali metals, copper(I) and silver(I). Of several considered, only thallium(I) was found to be suitable. Gold(I) perchlorate can be prepared in acetonitrile solution, but it decomposes when attempts are made to isolate the salt in pure form.[3] Mercury(I) appears to exist as the dimer $Hg(I)_2^{2+}$ from polarographic studies.[28] Indium(I) has been found to disproportionate in acetonitrile solution, as it does in water.[22] Therefore only the conductance behaviors of thallium(I) perchlorate and tetrafluoroborate were studied.

CHAPTER 2 EXPERIMENTAL PROCEDURE

Conductance Cells and Salt Cup Dispenser

In order to make precise and accurate conductance measurements in dilute nonaqueous solutions several factors must be taken into consideration. Anhydrous solutions of accurately known concentrations must be prepared. The solutions should be anhydrous because the presence of water could affect not only the viscosity and dielectric constant of the solvent but also the nature of the solvated species. Because conventional dilution techniques suffer from the disadvantage of relatively low precision, the method of preparing solutions by adding weighed amounts of salt directly to the conductance cell, a technique first described by Daggett, Bair, and Kraus[8] and refined by Kay and coworkers was used in this research.

Figure 1 is a diagram of the salt cup dispensing device used for delivering salt samples to the conductance cell.[27] This arrangement not only prevents atmospheric contamination of the solution but also protects hygroscopic salts.

The 60/50 standard taper joint and stopcock were lubricated with silicone grease. The tungsten metal pins B were sealed into glass and hold teflon discs C and D in place. Disc D contains one hole and C eight. One end of steel pin A is fitted into a short piece of tubing

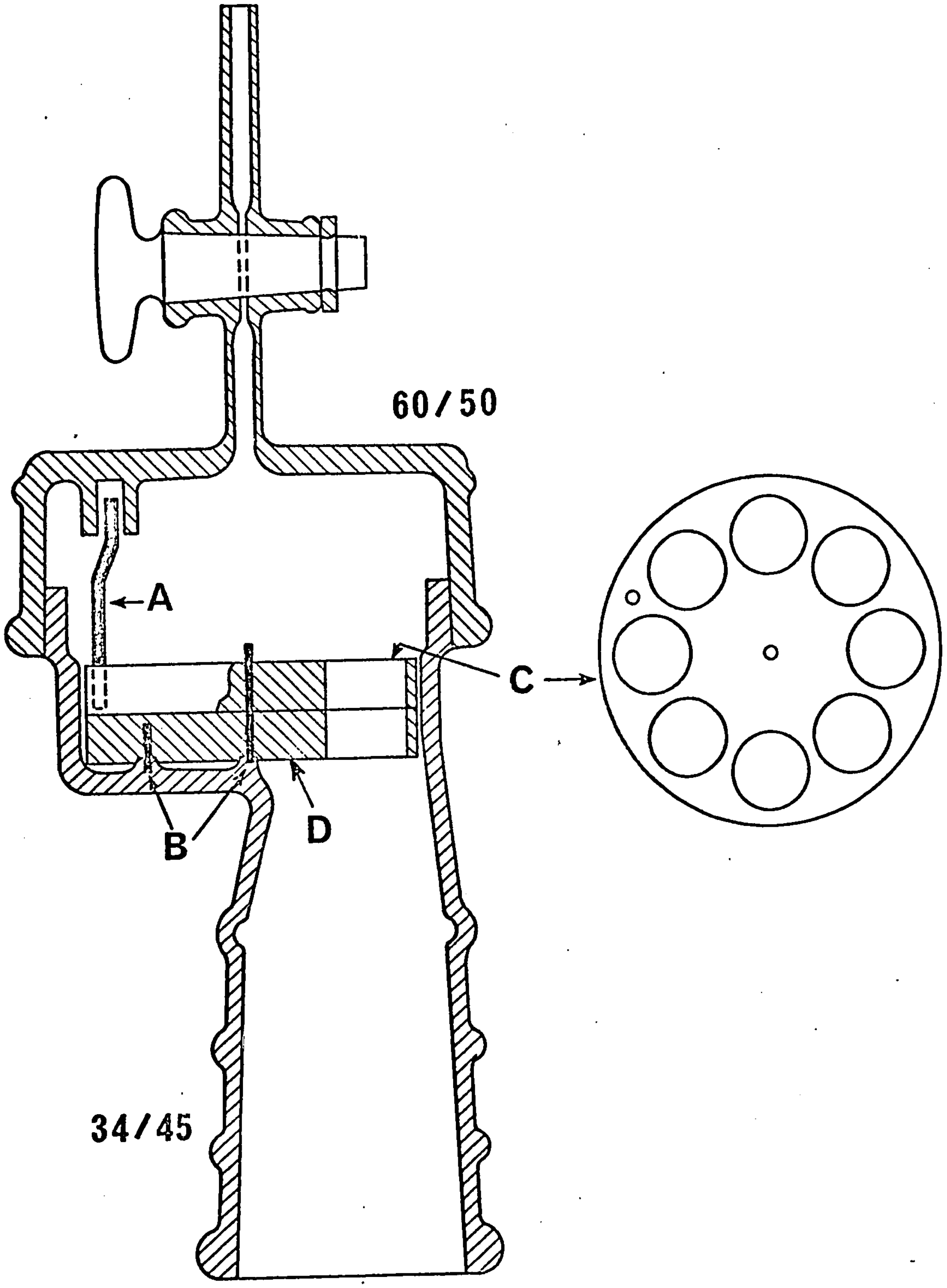

Figure 1. Salt Cup Dispensing Device

sealed into the top of the dispenser and the other end fits into disc C. When the top of the dispenser is turned the upper teflon disc rotates and successively drops eight salt sample cups into the solution. Pyrex glass cups 10 mm in height and 8 mm in diameter were used. No problems with splashing or loss of salt were encountered, as long as the dispenser was mounted properly on the conductance cell.

Three conductance cells were constructed during the course of this work. Sought-for properties were rigidity of electrodes, small frequency dependence on measured resistances and ease of use. The first cell, shown in Figure 2, was constructed from a two-liter Pyrex round--bottom flask. The center 34/45 joint held the salt cup dispenser. The other two joints were for solvent delivery. The electrodes, constructed from 0.2 mm thick platinum metal, were 14 mm in diameter. The cell constant was about 0.3 cm^{-1}. Although this cell showed good frequency dependence on measured resistances, the cell constant was found to change several per cent between determinations. The cell was also bulky and used an inordinately large amount of solvent, 1.5 liters. for each experiment. Therefore a new type of cell was used for successive measurements.

Two cells were built after the design of Figure 3. This design, patterned after that of Daggett, Bair, and Kraus,[11] is constructed from a one-liter conical flask.

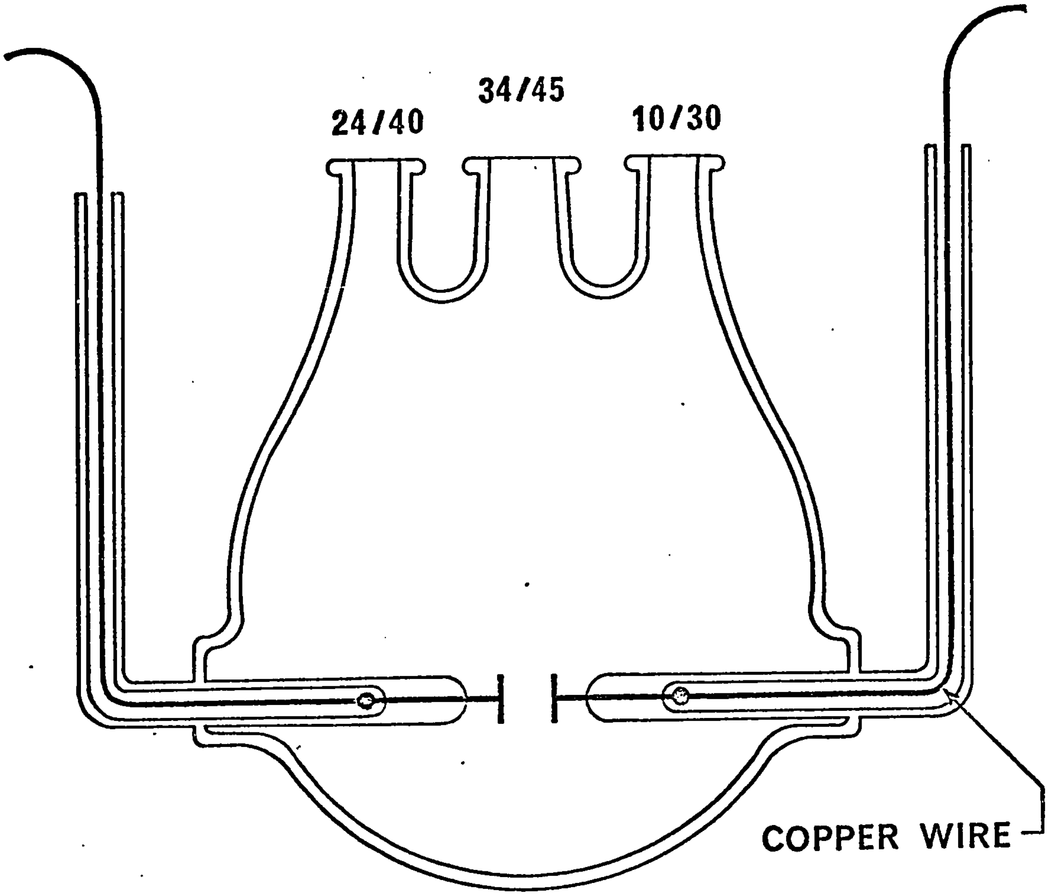

Figure 2. Two-liter Conductance Cell

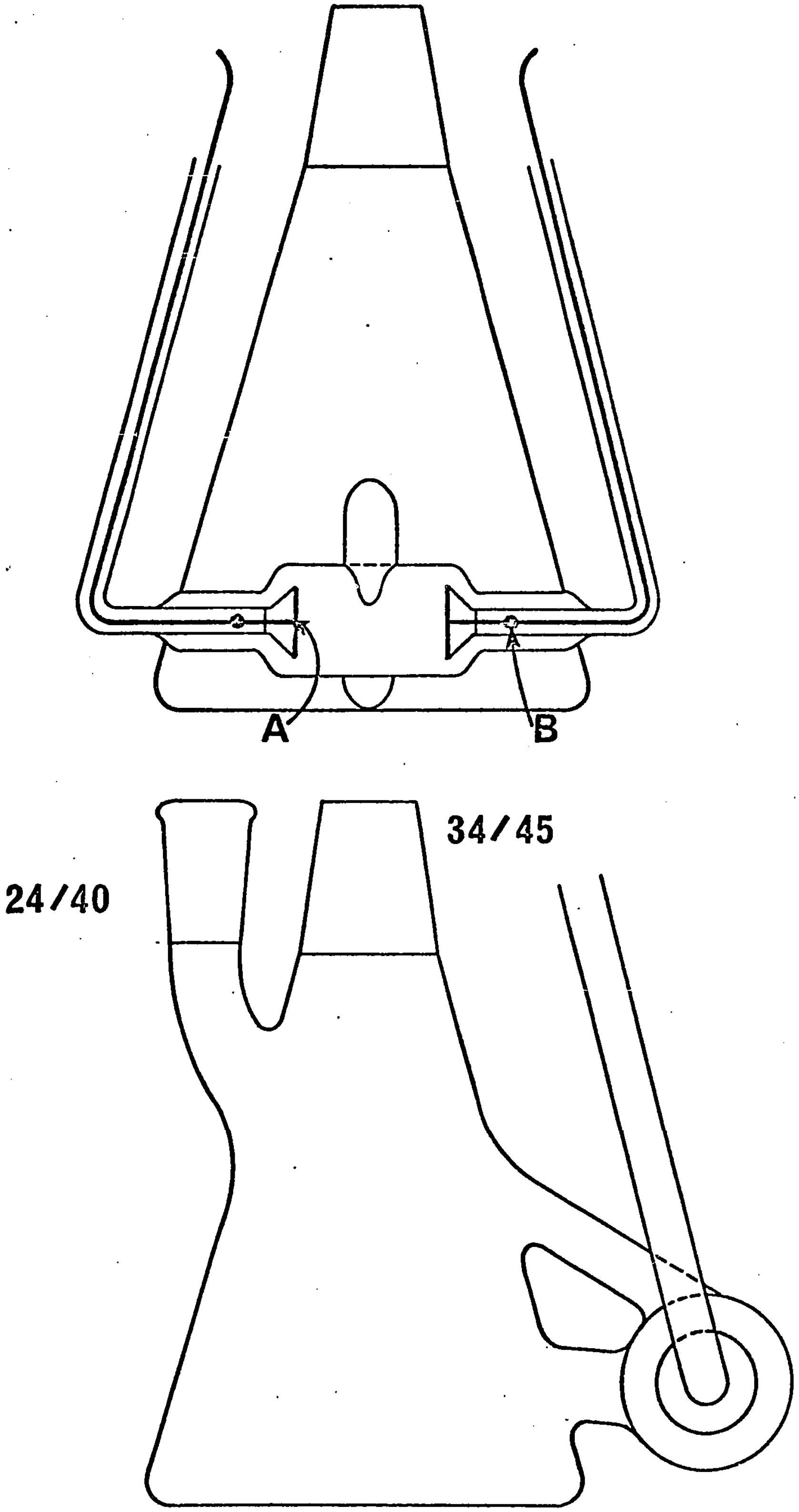

Figure 3. One-liter Conductance Cell

The top 34/45 standard taper joint is for the salt cup dispenser, while the 24/40 side-arm connnection is for solvent addition. The electrodes were of the same construction as the first cell but were completely backed with glass for extra rigidity (A). The electrode spacing was approximately 4 cm and the cell constant about 0.8 cm^{-1}. This cell used approximately 900 ml of solvent for a conductance experiment, was easy to handle and had a fairly stable cell constant. The cell constant was determined frequently; for eleven determinations the average change from the previous value was 0.07% with no systematic drift to the values. The change in measured resistance between 1 and 5 kHz was generally about 0.1%. A second conical cell was constructed as a reserve in case of breakage and because the first conical cell required the use of mercury to make electrical contact to the platinum electrode leads. The new cell had copper wires silver soldered directly to the platinum electrode leads (B). Although this cell had the same cell constant stability it showed much greater frequency dependence on measured resistances, about 0.5% between 1 and 5 kHz. This cell was almost identical in construction to the previous one, showing that only very small changes in geometry can materially affect frequency dependence.

In order to reduce this frequency dependence the electrodes were lightly platinized. Platinization must be kept to a minimum for measurements in dilute nonaqueous solutions because of the possibility of adsorption errors. The platinizing solution was that recommended by Robinson and Stokes,[38] and the electrodes were treated until a barely visible darkening of the platinum resulted. This reduced the frequency dependence by more than half.

The cells were calibrated by the procedure of Lind, Swolenik, and Fuoss.[31] Using data of several workers they calculated an averaged conductance equation for aqueous potassium chloride solutions. This equation has an estimated accuracy of 0.013% up to 0.012 M. With it the cell constant can be determined at several concentrations, instead of at only single fixed concentrations as with the Jones and Bradshaw standards.[24] With ideal cell geometry the cell constant should be independent of concentration. The change in cell constant of the first conical cell had a relative standard deviation of 0.02% for seven concentrations between 0.7 and 3 x 10^{-3} M. The second conical cell, after platinization, showed a similar small dependence of cell constant on concentration. Calculation of the average cell constant from the various concentrations was performed by computer. A sample of the calculation and the Fortran program for this computation are given in the Appendix.

Electrical Apparatus

A Leeds and Northrup Dike-Jones conductance bridge was used for all resistance measurements, in conjunction with a General Radio Model 1310-A signal generator and Model 1323-A tuned amplifier-null detector. The standard checks on the slidewires of the bridge as outlined in the instruction manual were made. A diagram of the electrical apparatus is shown in Figure 4. The components were separated several feet from each other to prevent electrical interaction. All leads were electrically shielded and the shields as well as the Wagner earthing device on the bridge were grounded. The ground consisted of a heavy gauge insulated copper cable connnected to a metal rod driven into the ground. The design and operation of the conductance bridge is described in reference 12.

Temperature Calibration and Control

Since the change in conductance of an electrolyte solution with temperature is generally a few per cent per degree, temperature control is extremely important. Therefore, special care was taken to maintain a constant temperature near 25°C during all conductance runs.

The thermostat bath consisted of a seven-gallon glass vessel insulated with 2 in. of fiberglass and filled with light paraffin oil (Fisher Scientific Co), for it has

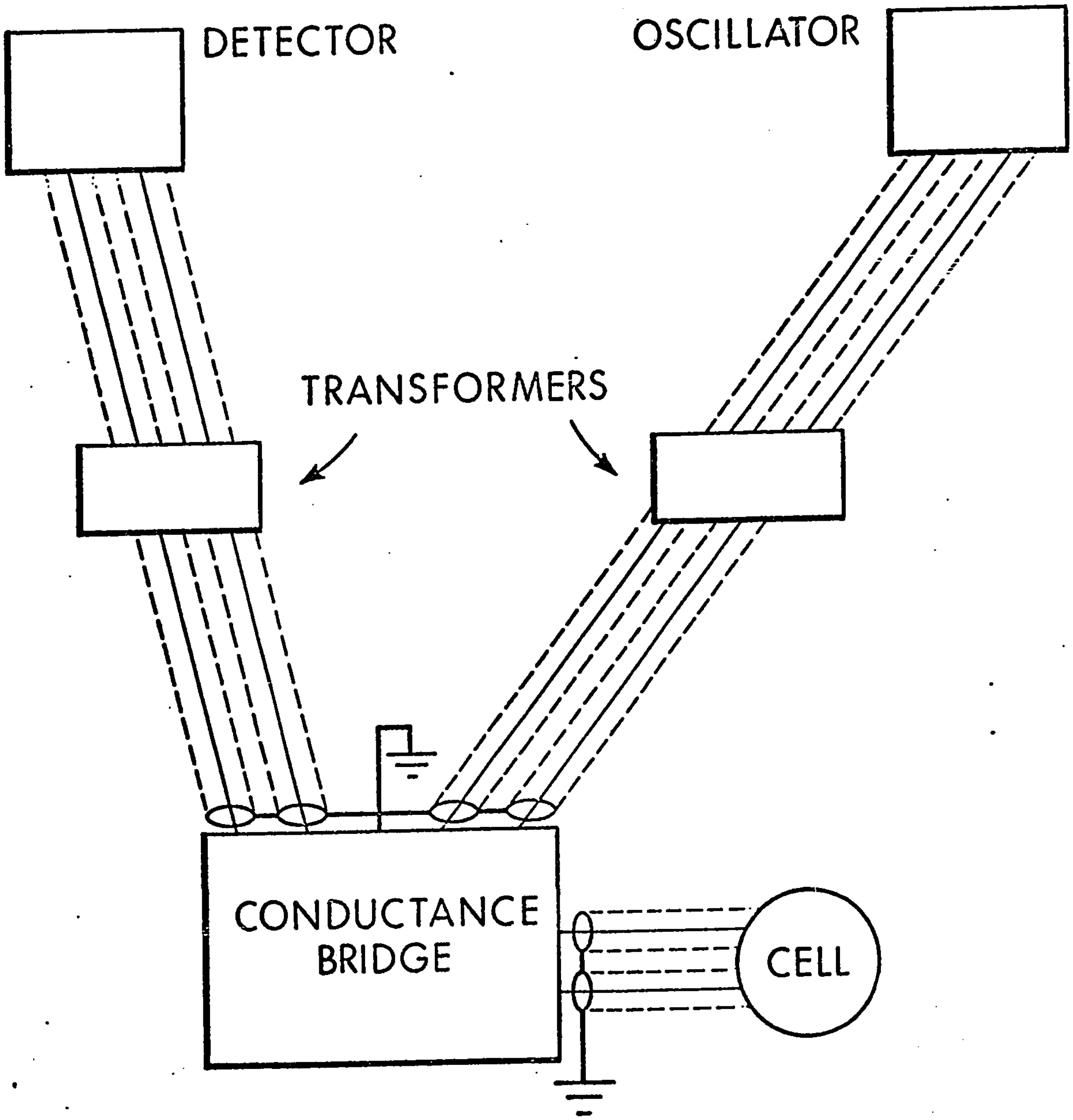

Figure 4. Electrical Components for Conductance Measurements

been shown that the use of water as a thermostatting liquid can introduce errors in precise conductance measurements.[25] The bath was stirred with a heavy duty stirring motor (Fisher Catalog No 14-501-5V1). A Fisher Proportional Temperature Control (Catalog No 15-177-50) with a thermistor probe and a 300-watt heating element provided temperature control. Tap water was circulated through the bath cooling coil during cool weather but during warm periods the tap water temperature fluctuated, and an external source of cold water was needed to circulate coolant through the bath. This unit consisted of a circulating water bath and refrigeration unit, and kept the cooling water at 18° ± 0.5°. With this arrangement the range of variation of temperature was approximately 0.006° during an experiment.

A Beckmann thermometer was used to monitor the bath temperature during conductance runs. It was calibrated using a Leeds and Northrup four leads type platinum resistance thermometer, type G-1 Mueller Bridge and optical scale galvanometer. The absolute temperature of the bath can be determined by measuring the ratio of the resistance of the platinum resistance thermometer in the bath to its resistance in an ice-water bath. After measuring the resistance of the platinum thermometer in an ice-water bath prepared with deionized water it was immersed in the thermostat bath and simultaneous readings were taken on the Beckmann and platinum thermometers. This was done at several temperatures and the resulting readings were plotted to obtain the value on the Beckmann thermometer corresponding to 25.000°C. The results are shown in Figure 5. The two plots were calibrations performed eight months apart; the Beckmann thermometer changed 0.02° in that time. This temperature difference affects the conductance results by approximately 0.05%.

Experimental Procedure

Considerable care was taken to prevent impurities from being introduced into the experimental system. The salt cups and teflon-coated stirring bars were cleaned with aqua regia, rinsed 8 to 10 times with distilled water, three times with conductance water and dried at 110° for several hours. The conductance cells, after initially being cleaned with concentrated nitric acid and steamed, were cleaned between conductance runs by rinsing several times with distilled water and conductance water and drying at 110° for several hours. Frequently the cells were treated with alcoholic potassium hydroxide, followed by 2 M hydrochloric acid solution as a precaution against organic impurities which might have come from conductance water prepared by passage through an ion-exchange column.

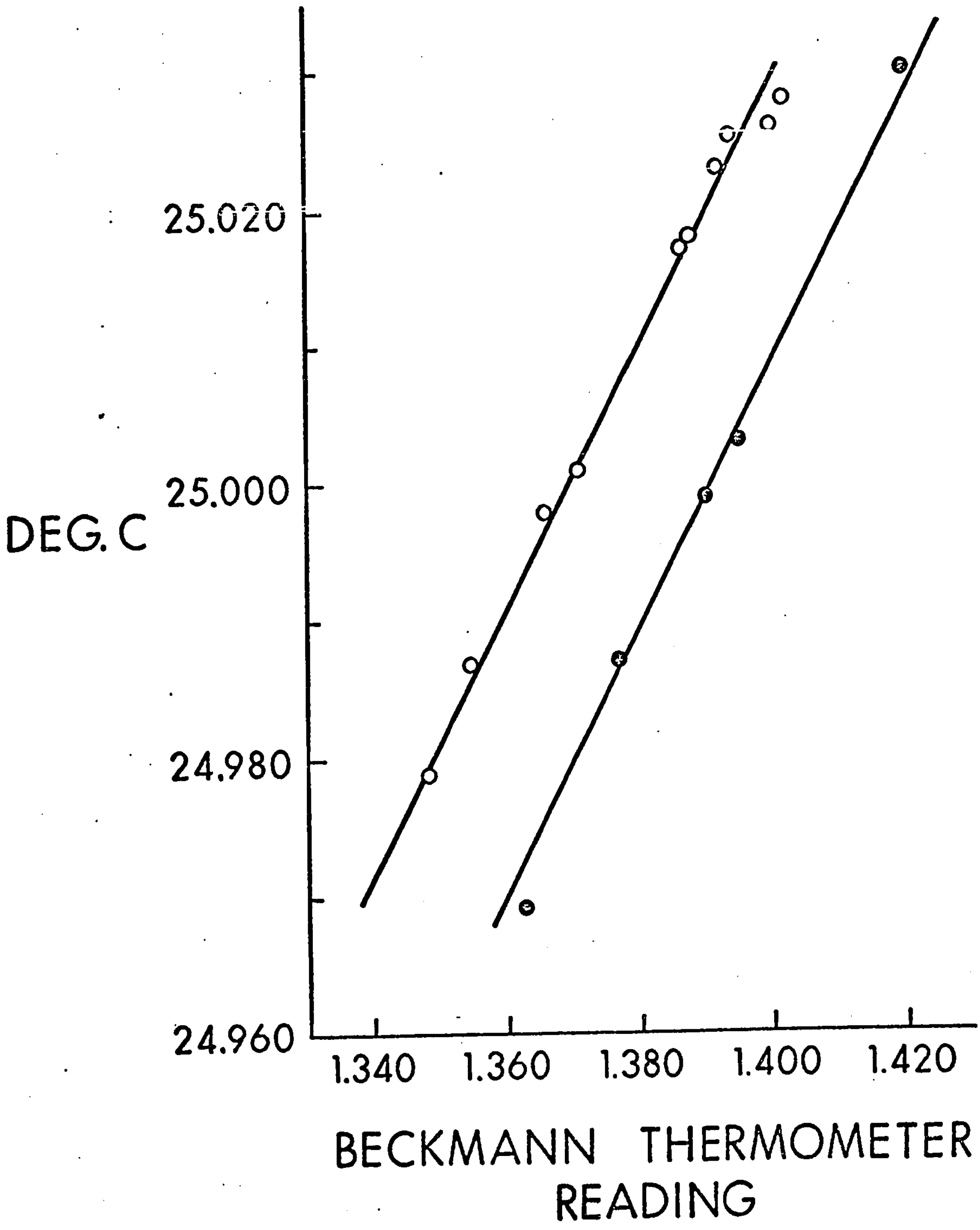

Figure 5. Beckmann Thermometer Calibration

Non-hygroscopic, stable salts were weighed in the previously described salt cups in air on a Mettler microbalance and placed in a desiccator over magnesium perchlorate desiccant until used, which was never more than a few hours. The silver and copper salts, with the exception of silver nitrate, were weighed in 8 mm diameter ground-glass capped salt cups (Kimble EXAX brand). All transfers were performed in a drybox to avoid contact with water. This procedure required weighing the empty capped cups, transferring them into the drybox and filling them with approximate amounts of salt, reweighing and finally loading them into the salt cup dispenser in the drybox. To test the accuracy of this procedure an empty cup was taken through all the steps except salt addition. Its initial and final weight differed by only 2 μg.

To perform a conductance run, the dry cell was capped and weighed on a Sartorius Model 2250 top-loading balance to ±0.02 g. Then purified acetonitrile solvent was delivered directly to the cell from the distillation reservoir under argon pressure. The delivery system was all glass with téflon stopcocks. The cell was then reweighed, a 1½-inch teflon-coated magnetic stirring bar added and the cell placed in the thermostat bath. After the salt cup dispenser was mounted and temperature equilibrium attained, the solvent conductance was measured. This was done by placing 30,000 ohms of the bridge resistors in parallel with the cell resistance and measuring the equivalent resistance. The solvent resistance was then calculated from the measured value. The salt cup dispenser was warmed slightly with a heat lamp to keep solvent from condensing in it. The cups were successively added and the solution stirred until no detectible change in the measured resistance was observed for 5 to 10 minutes. The time for attainment of this equilibrium varied from a few minutes for silver salts to several hours for alkali metal tetrafluoroborates. Once equilibrium was attained the rate of stirring did not affect the resistance readings. Before resistance measurements were made for each cup the temperature was adjusted to within 0.003° of 25°, if necessary, by adjusting the gain control on the proportional temperature control device. Resistance measurements were then made at 1, 2 and 5 kHz. For accurate resistance measurements the detector leads must be at ground potential when at balance. This requirement is met using the modified Wagner grounding device on the bridge. After the ground setting was made it was found not to change during the course of an experiment.

The lowest concentrations to be measured were set so that the solution resistances did not exceed approximately 12,000 ohms. Conical flask-type cells show capacitance effects which make extrapolation to infinite frequency impossible for high resistances. Instead of resistances becoming lower with increasing frequency a minimum is observed.[32] This problem was encountered with the conductance cells used in this research for resistances over approximately 12,000 ohms.

CHAPTER 3 SALT AND SOLVENT PREPARATION

Conductivity Water

Conductivity water was prepared by passing distilled water through a one-meter column of mixed-bed ion exchange resin into a glass reservoir. Before use the water was purged of dissolved carbon dioxide by bubbling nitrogen through the reservoir for 30 minutes.

Purification of Acetonitrile

At the outset of this work the Coetzee method of acetonitrile purification was used to produce pure solvent.[8] The specific conductance of acetonitrile prepared in this way was excellent, from 1 to 3 x 10^{-8} $ohm^{-1}cm^{-1}$, which equals the best values published.[39] (This value is essentially the lowest value measurable with the cell and bridge used in this work, for an open circuit to the conductance cell gives essentially the same value for cell resistance). However, the acetonitrile was not completely free from impurities, for several absorbance peaks were observed in the 240-275 mμ region of the spectrum and the solvent cut-off was about 220 mμ. Since silver(I) interacts strongly with aromatic hydrocarbons, the method of O'Donnell, Ayres, and Mann,[33] which produces acetonitrile of low aromatic hydrocarbon content, was used with some modification.

In this procedure about 2.5 liters of technical grade acetonitrile (Matheson, Coleman and Bell) were distilled at

10-15 ml per minute from 32 ml of benzoyl chloride (Eastman Organic Chemicals) into a receiver containing 5 ml of water, which was present to remove any distilled benzoyl chloride. The distillate was mixed with 32 g of anhydrous sodium carbonate and again distilled at the same rate while stirring. To the distillate were added 32 g of anhydrous sodium carbonate and 47 g of potassium permanganate (Fisher Chemical, U.S.P.). The mixture was stirred and distilled at the same rate. Approximately two liters of distillate were warmed and acidified with about 2 ml of concentrated sulfuric acid. Ammonium sulfate precipitated. The solution was cooled and tested for completeness of precipitation. The acetonitrile was then decanted into a distillation flask and distilled through a 1.2-meter column filled with glass helices at 10-20 ml per hour until there was no visible reaction of the distillate with calcium hydride. Then a small amount of calcium hydride was added to the distillation flask and another forecut was taken until the absorbance of the distillate was about 0.1 absorbance units at 200 mμ in a 1-cm quartz cell, using a Unicam SP800B ultraviolet spectrophotometer. The total amount of forecut was about 500 ml. The resulting acetonitrile had essentially zero absorbance down to 225 mμ and an absorbance about 0.1 at 200 mμ. Water content by Karl Fischer titration was about 5×10^{-4} $\underline{M}$. The solvent specific conductance generally varied from 3 to 10 x 10^{-8} $ohm^{-1}cm^{-1}$. It was found that conductance results were not sensitive to the solvent conductance.

Salt Preparation and Purification

For several of the salts studied in this work, conductance experiments were performed on more than one batch of material. The batches differed in the extent of purification of the salts. In this section Roman numerals refer to conductance experiments on the various batches, and these numerals correspond to those in the tables of conductance results.

The silver and copper salts prepared were also analyzed. The silver salts were titrated with 0.1 *M* potassium thiocyanate solution using a Volhard endpoint. The thiocyanate solution was standardized with primary standard silver nitrate which had been analyzed gravimetrically by silver chloride precipitation. The copper salts were analyzed by titration with 0.01 *M* EDTA using murexide indicator, the EDTA being standardized against pure copper metal. All reported purities are averages of two or more titrations, with a range of values in the titrations for each salt of about 0.1%.

Silver Nitrate

Analar analytical reagent silver nitrate was dried for 12 hours at 110°. Analysis by gravimetric chloride: 99.8% (I). Fisher Certified Reagent silver nitrate was powdered and dried in vacuum at 75° for 5 hours. Analysis: 99.9% (II).

Silver Perchlorate

Silver perchlorate was prepared by slowly adding 72% perchloric acid (G.F. Smith Chemical Co.) to an aqueous suspension of silver carbonate (Fisher Certified Reagent). The resulting solution was evaporated carefully to dryness and dried several hours in vacuum at 60° (I). The same material was re-dried in vacuum at 110° for 2 hours. Analysis: 99.8% (II). More silver perchlorate was prepared in an identical manner and recrystallized once from water distilled from alkaline potassium permanganate. The salt was dried in vacuum at room temperature for 70 hours, and analyzed to be 99.7% pure. It was again dried in vacuum at 60° for 16 hours. Analysis: 99.9% (III). The salt was weighed in air for I and II, but capped salt cups were used for III.

Silver Tetrafluoroborate

Silver tetrafluoroborate (K and K Laboratories, Inc.) was recrystallized from anhydrous acetonitrile in a drybox and dried in vacuum at room temperature for 20 hours. Analysis as $AgBF_4 \cdot 2CH_3CN$: 99.9%. A thermogram run on the salt showed a weight decrease at 150° corresponding to the loss of two moles of acetonitrile per mole of salt.

Silver Hexafluorophosphate

Silver hexafluorophosphate (K and K Laboratories, Inc.) was recrystallized twice from anhydrous acetonitrile in a drybox and dried at room temperature in vacuum for 5 hours. Analysis as $AgPF_6 \cdot 2CH_3CN$: 100.0%.

Copper(I) Perchlorate

The proceduresof Hathaway, Holah, and Postlethwaite were followed in the preparation of this salt.[21] Copper(II) perchlorate in acetonitrile was stirred with copper powder until the solution became colorless. The volume of the solution was reduced until white copper(I) perchlorate precipitated. The material was recrystallized twice from technical grade acetonitrile and once from anhydrous acetonitrile in a drybox. The salt was dried in vacuum at room temperature for 5 hours. Analysis as $CuClO_4 \cdot 4CH_3CN$: 100.1%. Tests were made of all the copper(I) salts for the presence of copper(II) by measuring their magnetic susceptibilities with a Gouy balance. The materials were diamagnetic.

Copper(I) Tetrafluoroborate

Copper tetrafluoroborate was also made following the procedure of reference 21 by refluxing nitrosyl tetrafluoroborate with excess copper powder in acetonitrile. The salt was recrystallized from dry acetonitrile in a drybox and dried in vacuum at room temperature for 5 hours. Analysis as $CuBF_4 \cdot 4CH_3CN$: 99.9%.

Copper(I) Hexafluorophosphate

Copper hexafluorophosphate was prepared by stirring a solution of silver hexafluorophosphate in acetonitrile with copper powder for 12 hours. After filtration, the volume of solution was reduced by evacuation at room temperature and the resulting precipitate was recrystallized from anhydrous acetonitrile in a drybox. $CuPF_6 \cdot 4CH_3CN$ is a white crystalline solid which rapidly turns a lavender color when subjected to vacuum at room temperature. This color change is accompanied by a weight loss corresponding to a few per cent acetonitrile. When the lavender material is equilibrated once more with acetontrile it regains its original composition and color. The salt used for conductance runs was placed, after preliminary drying for 20 minutes in a vacuum, in an acetonitrile atmosphere of about 12 hours. Analysis as $CuPF_6 \cdot 4CH_3CN$: 100.0%.

Thallium(I) Perchlorate

The procedure of Coetzee and Campion was followed in which thallium nitrate (Fisher Purified Reagent) was dissolved in water and mixed with 72% perchloric acid (G.F. Smith Co.).[5] The solution was evaporated to dryness and the resulting solid recrystallized three times from water and dried at 120° for 12 hours.

Thallium(I) Tetrafluoroborate

This salt was prepared by slowly adding 40% fluoroboric acid (Baker and Adamson) to solid thallium carbonate (Alfa Inorganics, Inc.), collecting the resulting solid and washing several times with absolute ethanol to remove excess acid. The wet salt was found to be sensitive to decomposition with evolution of acid when heated. It was dried in vacuum at room temperature for 1 hour (I). The salt was re-dried in vacuum at 50° for 3 hours and at 105° for 7 hours (II).

Thallium(I) Hexafluorophosphate

Several attempts were made to synthesize thallium hexafluorophosphate by various methods. However, the salt appeared to be quite unstable. Recrystallization from various solvent mixtures produced increasing excess percentages of Tl(I) in the product, suggesting thallium(I) fluoride formation. This also occurred when recrystallizing thallium tetrafluoroborate. Thallium analysis was performed by titration with 0.1 M standard cerate solution at 50°, using iodine monochloride as a catalyst and platinum-saturated calomel electrodes as the indicating system. A preparation analogous to the thallium tetrafluoroborate synthesis was tried, using 65% hexafluorophosphoric acid (Alfa Inorganics, Inc.). The acid contained a significant amount of hydrofluoric acid, however, and the product was impure. The conductance behavior of this salt therefore could not be studied.

Sodium Tetrafluoroborate

Sodium tetrafluoroborate (Alfa Inorganics, Inc.) was recrystallized from an 80:20 ethanol-water mixture and dried in vacuum at 120° for 5 hours (I). A portion of the material was re-dried in vacuum at 120° for 10 hours (II).

Sodium Hexafluorophosphate

Sodium hexafluorophosphate (Alfa Inorganics, Inc.) was recrystallized from absolute ethanol and dried in a vacuum at room temperature for 8 hours. Drying the salt at 50° produced decomposition.

Potassium Tetrafluoroborate

Potassium tetrafluoroborate (Alfa Inorganics, Inc.) was recrystallized from a 50:50 water-ethanol mixture and dried in a vacuum at room temperature for 8 hours, then at 120° for 8 hours.

Potassium Hexafluorophosphate

Potassium hexafluorophosphate (Matheson, Coleman and Bell) was recrystallized three times from water and dried in vacuum at room temperature for 12 hours (I). The salt was recrystallized again from water and dried under the same conditions for 10 hours (II). The material was recrystallized a fifth time and dried under the same conditions for 10 hours (III).

Potassium Chloride

Potassium chloride for cell calibrations was purified by recrystallizing the reagent grade salt twice from HCl-saturated conductivity water and once by adding 95% ethanol to a saturated aqueous solution of the salt. It was dried in vacuum at 220° for 15 hours.

Potassium Thiocyanate

Fisher Certified Reagent potassium thiocyanate was dried in a vacuum at 50° for 2 hours.

Rubidium Tetrafluoroborate

Rubidium bromide was prepared by slowly adding a slight excess of 48.5% hydrobromic acid (Baker Analyzed Reagent) to rubidium carbonate (A.D. Mackay Inc). This product was dissolved in water and slowly mixed with an aqueous solution of sodium tetrafluoroborate (Alfa

Inorganics, Inc). The precipitate was recrystallized twice from a 50:50 water-methanol mixture and dried, first in vacuum at room temperature for 4 hours, then at 105° for 6 hours. This drying procedure was used because the wet salt decomposed if heated.

Rubidium Hexafluorophosphate

This salt was prepared using the same procedure and materials as for rubidium tetrafluoroborate, with the exception that sodium hexafluorophosphate (Alfa Inorganics, Inc) was used in the second step. The material was recrystallized twice from water and dried in vacuum at 50° for 12 hours (I). The salt was recrystallized again from water and dried in vacuum at 55° for 11 hours (II).

CHAPTER 5 TREATMENT OF DATA

Calculation of Molar Concentrations

In order to calculate solution molarities the weights of solute and solvent were first vacuum corrected using the equation

$$Wt = Wt_{air} + Wt_{air}(0.0011)\left(\frac{1}{D_1} - \frac{1}{D_2}\right)$$

where Wt is the vacuum-corrected weight, Wt_{air} is the weight in air, 0.0011 is the density of air, D_1 is the density of the material being weighed and D_2 is the density of the balance weights. D_2 equals 8.4 g/cm^3 for the Mettler microbalance and 7.8 g/cm^3 for the Sartorius top loading balance, upon which the solvent was weighed. The densities of several of the salts studied were determined by measuring the volume of toluene displaced by a weighed amount of salt in a 25-ml Weld-type capillary pycnometer. These salt densities are given in Table 1.

Molar concentrations were calculated from the weight concentrations using solution densities determined from the equation

$$d = d_o + A\bar{m}$$

where d is the solution density, d_o the density of acetonitrile and $\bar{m}$ is the concentration in moles of solute per kilogram of solution. The A values were determined for

Table 1. Salt Densities and A Values

Salt	Density	A
$CuBF_4 \cdot 4CH_3CN$	1.5	0.12
$CuClO_4 \cdot 4CH_3CN$	1.5	0.14
$CuPF_6 \cdot 4CH_3CN$	1.5	0.15
$AgBF_4 \cdot 2CH_3CN$	2.0	0.15
$AgClO_4$	2.8[a]	0.16
$AgPF_6 \cdot 2CH_3CN$	1.8	0.17
$AgNO_3$	4.35[a]	0.15
$TlBF_4$	4.9	0.22
$TlClO_4$	4.9[a]	0.22
$NaBF_4$	2.5[a]	0.08[b]
$NaClO_4$		0.09[c]
$NaPF_6$	2.4[a]	0.10[b]
KBF_4	2.5[a]	0.09[b]
KPF_6	2.6	0.11
KSCN	1.9[a]	0.06
$RbBF_4$	3.1	0.13[b]
$RbPF_6$	3.0	0.15

[a] reference 20

[b] estimated

[c] reference 27, used in estimating the other sodium salt values

most of the salts by measuring the densities of 0.01 M acetonitrile solutions in a capillary pycnometer. These values are also listed in Table 1. The calculated molar concentrations are not sensitive to A; changing its value by 10% produced negligible changes in the conductance parameters. The density of pure acetonitrile was determined to be 0.7766_5 g/ml, which agrees well with literature values.[27]

Resistance Extrapolations

Normally, alternating current resistance measurements of electrolyte solutions show a small dependence on frequency. In an ideal conductance cell the electrodes have a very large double layer capacitance and the resistance is essentially independent of frequency in the region of 1 to 10 kHz. Usually however, various forms of frequency dependences are found, depending upon the geometry and condition of the electrodes and the nature of the electrolyte solution. With platinized electrodes in aqueous solutions this resistance dependence is often linear with the reciprocal of frequency, and the standard procedure for determining the true resistance is to plot R versus f^{-1} and extrapolate to infinite frequency. In other cases linear relationships between R and f^{-n} have been found, as well as intermediate cases,[38] which could be approximated by an intermediate power of f. The first conical flask cell constructed in this research gave essentially linear R versus f^{-1} plots, although not exactly so. The second cell showed different behavior. Plots of resistance against f^{-1} were concave down, but against $f^{-\frac{1}{2}}$ concave upward, as shown in Figure 6. This represents an intermediate case. In order to make consistent extrapolations a computer program was written to extrapolate resistance against f^{-n} where n ranged from 0.5 to 1.0. Using an initial value of n = 1.0, the slope of a straight line falling on the resistances measured at 1 and 2 kHz was calculated. A calculated resistance at 5 kHz for this line was determined and this value compared to the actual resistance. The value of n was then varied until the calculated and actual resistance values at 5 kHz agreed to within 0.02 ohm. Data from the first conical flask cell yielded values of n around 0.9, while that from the second cell gave values around 0.5 to 0.7. The n values varied slightly for the several concentrations of a single conductance run in an unsystematic manner. Also, the average value of n was different for different salts. However, the standard deviations of the calculated conductance parameters were generally improved somewhat over those obtained from graphically estimating the extrapolated frequencies. It was concluded that this method did improve the consistency of resistance extrapolation.

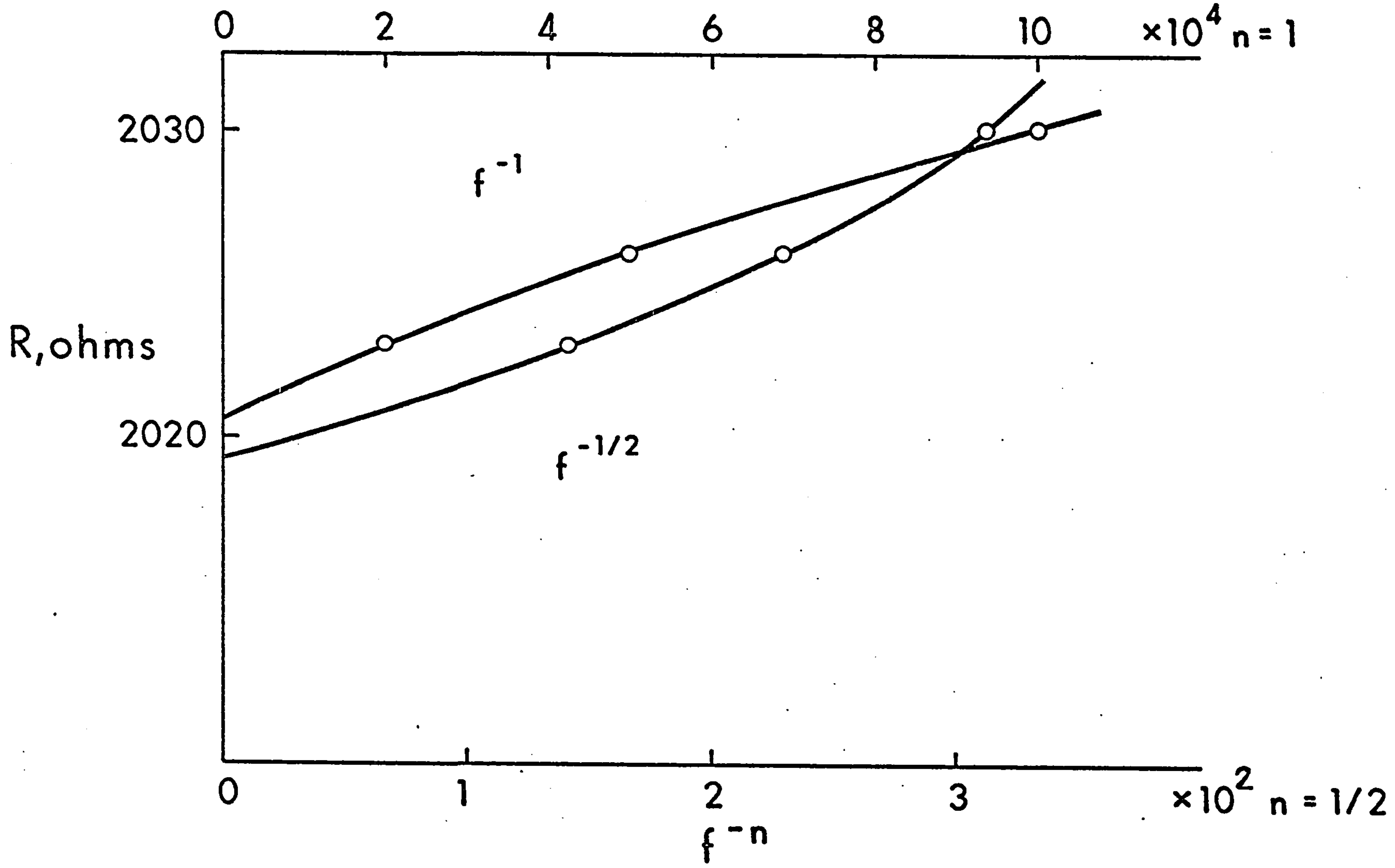

Figure 6. Frequency Dependence of Measured Resistances

The program for extrapolation and a sample of typical data are given in the Appendix.

Analysis of Data

The data were analyzed by the Fuoss-Onsager theory in the form

$$\Lambda = \Lambda_o - SC^{\frac{1}{2}} + EC \log C + JC \tag{1}$$

for nonassociated salts and, for those where association was detected, by

$$\Lambda = \Lambda_o - S(C\gamma)^{\frac{1}{2}} + EC\gamma \log C\gamma + JC\gamma - K_A C\gamma \Lambda f^2 \tag{2}$$

The calculations were performed using a least-squares computer program provided by R.L. Kay and adapted to an IBM 360/67 computer. The details of the program are described in reference 26. The analysis is performed as follows. Equation 2 is essentially linear in three unknowns, Λ_o, K_A, and J. However, the ion size parameter $\overset{\circ}{a}$, and not J, is the third parameter to be determined. Because $\overset{\circ}{a}$ is a complicated function of J, the equation was linearized with respect to three new variables and this new equation was then treated by the least-squares technique. Analysis using Equation 1 was accomplished by performing a least-squares analysis on the original equation, followed by an iteration procedure on J to determine the best value of $\overset{\circ}{a}$. Starting values for Λ_o, $\overset{\circ}{a}$ and K_A are needed for these treatments, but it was found that the analysis was insensitive to the initial estimates and the program converged within four iterations to the same set of final values. The standard deviations of the parameters and of the individual points were calculated. For acetonitrile at 25° the constants α, β, E_1 and E_2 were calculated to be 0.7393, 233.6, 5.500 and 254.5 respectively, where $S = \alpha\Lambda_o + \beta$ and $E = E_1\Lambda_o - E_2$. The dielectric constant of acetonitrile at 25° was taken as 35.95,[27] and its viscosity was measured to be 0.003412 poise, using a calibrated Cannon-Fenske type viscometer.

If the solute affects the solution viscosity, the conductance equation may be corrected by changing the JC term to $(J - B\Lambda_o)C$, where B is the viscosity coefficient. No viscosity correction was deemed necessary for any of these salts because ions of this size should not affect the viscosity of acetonitrile to any significant extent at these low concentrations.[27] The B coefficient was therefore set at zero for all runs.

The Debye-Huckel second approximation was used to calculate f^2 in equation 2. Provision is made in the program to use either the iterated value of the ion size parameter in this calculation or the initial value. The iterated value was used in these calculations.

Provision is also made in the program for weighting the experimental points, either by 1 or by C, the concentration.

It was found that the results were not measurably affected by the weighting of the data. Therefore the weighting factor of 1 was used.

CHAPTER 5 RESULTS

The molar concentrations and measured equivalent conductances are given in Table 2, along with the solvent specific conductances for each experiment. The conductance parameters, their standard deviations and salt batch numbers are given in Tables 3, 4, and 5. The $\sigma\Lambda$ values are the standard deviations of the data points. The data were analyzed using either Equation 1 or 2, depending upon the association character of the salt. Data for one silver perchlorate run as well as copper tetrafluoroborate and hexafluorophosphate, thallium tetrafluoroborate and potassium and rubidium hexafluorophosphate were analyzed by both equations and both sets of parameters are presented in Tables 3-5. The $\Delta\Lambda$ values in Table 2 are the differences beteeen the measured equivalent conductances and the values calculated by the appropriate conductance equation. For silver perchlorate and copper tetrafluoroborate and hexafluorophosphate the $\Delta\Lambda$ values corresponding to analysis by the unassociated calculation are given, while for thallium tetrafluoroborate and potassium and rubidium hexafluorophosphate the values corresponding to the associated calculation are listed.

Averaged limiting equivalent conductances and single ion conductivities from these values are listed in Table 6.

Table 2. Measured Equivalent Conductances

10^4 C	Λ	ΔΛ	10^4C	Λ	ΔΛ
$AgBF_4$ $10^8\kappa = 7.5$			$AgClO_4$ $10^8\kappa = 2.4$		
7.541	184.01	-0.02	2.018	184.39	0.01
10.836	182.05	0.00	3.352	182.84	0.02
14.091	180.42	0.01	5.122	181.15	-0.04
17.003	179.14	0.00	6.975	179.76	-0.02
19.488	178.16	0.01	8.926	178.51	0.00
22.575	177.06	0.02	10.974	177.35	0.02
25.827	175.96	-0.02	12.532	176.53	0.00
$AgBF_4$ $10^8\kappa = 7.9$			$AgClO_4$ $10^8\kappa = 7.8$		
8.178	183.43	-0.02	6.218	180.15	-0.01
11.182	181.71	0.00	8.395	178.65	-0.02
14.318	180.19	0.02	11.006	177.17	0.02
17.144	178.97	0.02	13.188	176.04	0.00
20.056	177.84	0.01	15.821	174.85	0.02
22.625	176.92	0.00	18.226	173.88	0.04
25.502	175.97	-0.02	20.811	172.85	-0.01
$AgClO_4$ $10^8\kappa = 0.8$			23.550	171.18	-0.03
0.7074	186.36	-0.06	$AgClO_4$ $10^8\kappa = 9.7$		
1.449	184.98	-0.03	4.006	182.07	0.00
2.134	184.16	0.13	7.517	179.32	-0.01
2.795	183.22	0.00	9.074	178.34	-0.02
3.533	182.42	-0.01	10.904	177.33	0.01
4.279	181.72	0.01	13.315	176.14	0.03
4.971	181.07	-0.04	16.134	174.86	0.02
			18.066	174.06	0.00
$AgClO_4$ $10^8\kappa = 5.2$			20.971	172.95	-0.03
1.654	184.38	-0.08			
3.170	182.67	0.05			
4.827	181.18	0.06			
6.166	180.16	0.05			
7.754	178.99	-0.08			

Table 2 (continued)

10^4 C	Λ	ΔΛ
$AgPF_6$ $10^8\kappa = 2.6$		
4.202	182.29	-0.01
6.604	180.39	-0.02
8.834	178.99	0.01
10.582	178.00	0.00
12.633	176.98	0.01
14.968	175.94	0.02
17.221	175.00	0.00
19.662	174.06	-0.03
$AgPF_6$ $10^8\kappa = 3.4$		
4.089	182.29	0.00
6.328	180.50	0.01
8.270	179.21	0.00
10.200	178.08	-0.01
12.219	177.04	0.00
13.981	176.23	0.01
16.620	175.11	0.00
19.083	174.16	-0.01
$AgNO_3$ $10^8\kappa = 1.9$		
1.499	185.79	0.02
2.901	182.37	-0.05
4.552	179.21	0.02
6.594	175.81	0.01
8.046	173.65	0.00
9.319	171.92	0.00
11.212	169.54	0.00
$AgNO_3$ $10^8\kappa = 25.0$		
4.986	178.52	0.00
7.478	174.59	0.00
9.249	172.13	-0.01
11.346	169.49	0.00
13.804	166.68	0.01
16.087	164.29	0.00
18.541	161.92	0.00
$AgNO_3$ $10^8\kappa = 14.7$		
5.885	176.98	0.00
8.002	173.78	0.00
10.581	170.35	0.00
13.308	167.16	0.00
15.164	165.17	0.01
18.297	162.07	-0.01
21.777	159.00	0.00
$AgNO_3$ $10^8\kappa = 9.5$		
10.565	170.57	0.00
16.373	164.10	-0.01
21.449	159.43	0.00
25.330	156.28	0.01
30.153	152.74	-0.01
35.168	149.46	0.00
40.951	146.05	0.00
$CuBF_4$ $10^8\kappa = 9.4$		
6.632	163.51	0.04
9.025	161.96	-0.01
11.693	160.53	-0.02
13.929	159.47	-0.02
16.107	158.54	-0.02
18.042	157.79	0.00
20.015	157.08	0.02
22.439	156.24	0.01
$CuBF_4$ $10^8\kappa = 5.9$		
6.195	163.80	0.04
8.248	162.40	0.00
10.412	161.15	-0.02
12.503	160.06	-0.04
15.110	158.91	-0.01
17.584	157.92	0.01
19.777	157.11	0.02

Table 2 (continued)

10^4C	Λ	$\Delta\Lambda$
$CuClO_4$	$10^8\kappa = 7.5$	
5.961	159.60	-0.03
8.180	158.18	0.01
9.624	157.37	0.03
11.633	156.32	0.02
13.134	155.58	-0.01
14.893	154.80	-0.01
16.077	154.30	-0.01
$CuClO_4$	$10^8\kappa = 4.6$	
4.990	160.28	-0.02
7.432	158.58	0.02
9.207	157.50	0.01
11.259	156.39	-0.01
13.093	155.50	-0.01
15.177	154.59	0.00
17.170	153.78	0.00
$CuPF_6$	$10^8\kappa = 12.5$	
4.718	160.83	0.06
6.473	159.44	0.02
8.506	158.04	-0.05
10.333	156.98	-0.05
12.328	155.96	-0.04
14.355	155.04	0.00
16.171	154.26	0.01
18.384	153.40	0.05
$CuPF_6$	$10^8\kappa = 5.3$	
5.592	160.38	0.06
8.121	158.56	-0.02
10.188	157.35	-0.04
12.585	156.12	-0.03
15.117	154.97	-0.02
17.796	153.89	0.01
20.017	153.06	0.03
$TlBF_4$	$10^8\kappa = 2.2$	
5.187	189.02	0.03
8.500	185.75	-0.06
12.366	182.76	0.00
16.482	180.02	0.02
19.659	178.12	0.02
23.865	175.78	-0.05
27.626	174.02	0.04
31.595	172.16	-0.02
$TlBF_4$	$10^8\kappa = 8.3$	
5.249	188.64	-0.01
8.122	185.88	0.00
11.364	183.30	0.02
14.088	181.38	0.02
18.701	178.51	-0.01
22.625	176.36	-0.01
25.977	174.67	-0.03
30.282	172.74	0.02
$TlBF_4$	$10^8\kappa = 5.6$	
3.995	190.14	0.00
6.647	187.29	0.01
9.354	184.88	0.00
12.118	182.74	-0.01
15.529	180.44	0.01
19.197	178.22	0.00
23.732	175.79	0.00

Table 2 (continued)

10^4C	Λ	$\Delta\Lambda$	10^4 C	Λ	$\Delta\Lambda$
$TlClO_4$ $10^8\kappa = 9.8$			$NaBF_4$ $10^8\kappa = 5.0$		
5.626	183.02	0.00	4.392	173.90	-0.02
9.134	179.10	0.00	7.528	170.22	0.02
12.082	176.31	0.00	10.655	167.16	0.02
15.034	173.85	0.01	14.501	163.90	0.00
18.472	171.24	0.00	18.614	160.89	-0.01
22.121	168.72	-0.02	22.994	158.04	-0.01
25.461	166.66	0.01	27.416	155.47	0.00
29.416	164.38	0.00	32.099	153.00	0.01
$TlClO_4$ $10^8\kappa = 4.6$			$NaPF_6$ $10^8\kappa = 7.1$		
6.318	182.23	0.00	3.538	171.61	-0.11
8.484	179.82	0.00	7.385	168.65	0.00
12.014	176.40	0.00	12.314	165.89	0.05
15.243	173.70	0.01	15.926	164.25	0.06
17.647	171.84	-0.01	20.636	162.41	0.07
20.898	169.55	-0.01	25.466	160.76	0.04
25.088	166.89	0.01	29.572	159.44	-0.04
30.032	164.02	0.00	33.843	158.26	-0.07
$NaBF_4$ $10^8\kappa = 3.3$			KBF_4 $10^8\kappa = 2.2$		
5.066	173.28	0.04	3.103	183.23	0.01
9.324	168.39	-0.03	6.349	178.32	-0.02
12.302	165.61	-0.05	8.332	175.89	0.00
16.645	162.18	0.00	10.670	173.32	0.00
21.074	159.15	0.04	13.140	170.94	0.05
25.068	156.69	0.03	15.615	168.66	-0.04
28.695	154.64	0.00	18.082	166.69	0.01
33.851	152.01	-0.03			

Table 2 (continued)

10^4 C	Λ	ΔΛ	10^4 C	Λ	ΔΛ
KPF_6 $10^8\kappa = 2.4$			KSCN $10^8\kappa = 18.1$		
6.705	176.81	-0.02	6.920	183.78	-0.01
11.144	173.67	0.02	9.442	181.25	0.00
14.128	171.88	0.00	12.172	178.85	0.02
17.681	170.05	0.00	15.751	176.04	0.00
21.464	168.39	0.08	18.658	173.98	-0.02
25.176	166.75	-0.06	22.621	171.46	-0.01
29.010	165.28	-0.11	25.594	169.74	0.01
32.281	164.36	0.09	$RbBF_4$ $10^8\kappa = 4.5$		
KPF_6 $10^8\kappa = 7.6$			3.673	183.80	-0.04
5.797	177.76	0.01	5.495	181.34	0.06
8.374	175.69	-0.01	7.330	179.05	0.04
12.179	173.18	-0.03	9.670	176.42	-0.03
16.452	170.87	0.03	11.724	174.34	-0.04
20.675	168.83	0.01	14.044	172.25	0.03
24.713	167.08	-0.01	15.913	170.62	0.02
28.849	165.48	0.00			
35.268	163.23	0.00	$RbPF_6$ $10^8\kappa = 17.3$		
KPF_6 $10^8\kappa = 8.4$			3.309	181.32	-0.02
			6.518	178.21	0.01
5.932	177.50	0.00	8.952	176.32	0.02
8.698	175.33	0.00	11.518	174.56	0.01
12.489	172.88	0.00	14.492	172.74	-0.03
16.697	170.57	0.00	17.903	170.93	0.00
22.140	168.02	0.00	21.186	169.33	0.00
27.809	165.70	-0.01	26.152	167.14	0.01
33.520	163.67	0.02			
41.663	161.05	-0.01	$RbPF_6$ $10^8\kappa = 7.1$		
KSCN $10^8\kappa = 6.0$			2.961	181.83	0.02
			5.514	179.08	-0.01
8.053	182.66	0.00	8.048	176.92	-0.03
12.288	178.79	0.00	11.040	174.82	0.00
16.504	175.54	0.00	13.777	173.15	0.03
19.943	173.20	0.01	17.254	171.18	-0.01
22.559	171.55	0.00	20.387	169.64	0.02
25.868	169.60	-0.01	24.137	167.91	-0.01
30.232	167.27	0.00			

Table 3. Conductance Parameters for Silver Salts

Salt	Batch	Λ_0	a	K_A	$\sigma\Lambda$
$AgBF_4$		194.54 ± 0.02	4.20 ± 0.02		0.01
$AgBF_4$		194.34 ± 0.02	4.29 ± 0.03		0.02
$AgClO_4$	I	189.63 ± 0.06	4.0 ± 0.4		0.07
$AgClO_4$	II	189.31 ± 0.09	5.1 ± 0.4		0.08
$AgClO_4$	II	189.89 ± 0.05	6 ± 1	6 ± 4	0.02
		189.83 ± 0.02	4.07 ± 0.05		0.02
$AgClO_4$	III	189.66 ± 0.02	4.06 ± 0.04		0.03
$AgClO_4$	III	189.71 ± 0.02	4.20 ± 0.03		0.02
$AgPF_6$		190.06 ± 0.02	4.56 ± 0.03		0.02
$AgPF_6$		189.96 ± 0.01	4.50 ± 0.01		0.008
$AgNO_3$	I	192.34 ± 0.06	6 ± 2	79 ± 6	0.03
$AgNO_3$	II	192.25 ± 0.03	3.1 ± 0.2	69 ± 1	0.006
$AgNO_3$	II	192.32 ± 0.03	3.9 ± 0.2	73 ± 1	0.007
$AgNO_3$	II	192.43 ± 0.04	3.14 ± 0.09	69.1 ± 0.6	0.009

Table 4. Conductance Parameters for Copper and Thallium Salts

Salt	Batch	Λ_0	a	K_A	$\sigma\Lambda$
$CuBF_4$		173.09 ± 0.06	5.9 ± 0.7	7 ± 2	0.01
		172.90 ± 0.02	4.02 ± 0.04		0.02
$CuBF_4$		173.22 ± 0.06	8.1 ± 0.9	15 ± 3	0.01
		172.89 ± 0.03	3.96 ± 0.06		0.03
$CuClO_4$		168.47 ± 0.03	4.04 ± 0.06		0.02
$CuClO_4$		168.41 ± 0.01	3.97 ± 0.03		0.01
$CuPF_6$		169.16 ± 0.05	11 ± 1	24 ± 3	0.01
		168.74 ± 0.05	3.59 ± 0.09		0.05
$CuPF_6$		169.32 ± 0.06	8 ± 1	16 ± 3	0.01
		168.98 ± 0.04	3.69 ± 0.07		0.04
$TlBF_4$	I	199.3 ± 0.1	3.0 ± 0.5	14 ± 2	0.04
		198.7 ± 0.1	0.91 ± 0.05		0.12
$TlBF_4$	I	198.95 ± 0.05	3.1 ± 0.3	14 ± 1	0.02
		198.4 ± 0.1	0.98 ± 0.06		0.13
$TlBF_4$	II	199.08 ± 0.01	3.3 ± 0.1	15.4 ± 0.5	0.006
		198.63 ± 0.08	0.83 ± 0.05		0.09
$TlClO_4$		195.12 ± 0.04	3.1 ± 0.2	32.1 ± 0.9	0.01
$TlClO_4$		195.21 ± 0.03	3.1 ± 0.1	32.4 ± 0.7	0.01

Table 5. Conductance Parameters for Alkali Metal Salts

Salt	Batch	Λ_0	a	K_A	$\sigma\Lambda$
$NaBF_4$	I	184.66 ± 0.09	5.1 ± 0.6	44 ± 2	0.04
$NaBF_4$	II	184.08 ± 0.03	2.9 ± 0.2	32.1 ± 0.9	0.02
$NaPF_6$		178.76 ± 0.05	3.90 ± 0.06		0.07
KBF_4		192.40 ± 0.08	5 ± 1	52 ± 4	0.03
KPF_6	I	187.6 ± 0.2	5 ± 1	12 ± 6	0.08
		187.07 ± 0.09	2.33 ± 0.08		0.10
KPF_6	II	187.51 ± 0.04	2.8 ± 0.2	4 ± 1	0.02
		187.35 ± 0.03	2.19 ± 0.02		0.04
KPF_6	III	187.39 ± 0.02	2.85 ± 0.09	3.9 ± 0.4	0.01
		187.20 ± 0.03	2.20 ± 0.02		0.04
KSCN		197.00 ± 0.03	3.1 ± 0.1	26.3 ± 0.6	0.007
KSCN		196.93 ± 0.06	3.1 ± 0.4	26 ± 2	0.02
$RbBF_4$		193.3 ± 0.2	0.5 ± 0.6	22 ± 8	0.05
$RbPF_6$	I	188.71 ± 0.03	2.2 ± 0.2	3 ± 1	0.02
		188.63 ± 0.02	1.79 ± 0.02		0.02
$RbPF_6$	II	188.85 ± 0.04	2.9 ± 0.4	7 ± 2	0.03
		188.69 ± 0.04	1.68 ± 0.04		0.05

The single ion conductivity of the perchlorate ion, determined from transference number measurements on tetramethylammonium perchlorate by Springer, Coetzee and Kay,[39] was used as reference in these calculations. The best values for single ion conductivities are listed in Table 7. The tetrafluoroborate and hexafluorophosphate values are averages of the copper and silver salts only.

Of the other ions studied in this work only the single ion conductivity of hexafluorophosphate has been previously estimated; a value of 103.1 (corrected to the above reference) was calculated by Coetzee[7] from one conductance run on tetrabutylammonium hexafluorophosphate.[13] Our value of 104.1 is considerably higher. Since the perchlorate single ion conductivity value is well established, it was decided to rely on its value for calculation of the other single ion conductivities.

The limiting equivalent conductances for silver perchlorate and silver nitrate reported by Walden and Birr, 189.2 and 188.0 respectively, are lower than our values.[40] Reanalysis of their data by the Fuoss-Onsager theory yielded Λ_o's slightly lower than they reported, with large standard deviations on all parameters. Their method of purification of acetontrile, repeated distillations from phosphorus pentoxide, leads to a product of poor optical quality. In addition, their use of volumetric techniques

Table 6

Limiting Salt and Single Ion Conductances

Salt	Λ_0	λ_0^+	λ_0^-
$AgBF_4$	194.4		108.4
$AgClO_4$	189.7	86.0	103.7[a]
$AgPF_6$	190.0		104.0
$AgNO_3$	192.3		106.3
$CuBF_4$	172.9[b]		108.2
$CuClO_4$	168.4	64.7	103.7[a]
$CuPF_6$	168.9[b]		104.2
$TlBF_4$	199.1		107.6
$TlClO_4$	195.2	91.5	103.7[a]
$NaBF_4$	184.7	76.9[a]	107.8
$NaPF_6$	178.8		101.9
KBF_4	192.4	83.6[a]	108.8
KPF_6	187.5		103.9
KSCN	197.0		113.4
$RbBF_4$	193.3	85.6[a]	107.7
$RbPF_6$	188.8		103.2

[a] reference 39.
[b] average value from the unassociated calculations

Table 7. Single Ion Conductances in Acetonitrile

Cu^+	64.7	BF_4^-	108.3
Ag^+	86.0	PF_6^-	104.1
Tl^+	91.5	NO_3^-	106.3
		SCN^-	113.4

to prepare solutions for conductance is inherently less accurate than the direct weight technique used here. Because of the internal consistency of the values obtained for the silver and copper salts, we believe our results to be the more accurate.

For silver perchlorate the conductance results in Table 3 show that the three batches of salt gave substantially the same results, although the precision is best for batch III, which has the highest reported purity. Although one conductance run indicated a slight amount of association, the salt appears to be essentially unassociated. Batch II of silver nitrate gave very reproducible parameters and an average association constant of 70. Thus silver nitrate appears to be the only associated silver salt studied.

Copper tetrafluoroborate and hexafluorophosphate showed evidence of association when analyzed by equation 2. The reproducibility of the association constants is not as good as would be expected, however. The nonassociated calculation shows good data fit, with reasonable ion size parameters. Since the $K_A C\gamma\Lambda f^2$ term is subtractive and the $JC\gamma$ term additive in the associated equation, small values of J and hence $\mathring{a}$ result when real association is neglected by using the unassociated equation. This can be seen in the parameters for thallium tetrafluoroborate, which was analyzed by both equations and appears to be definitely associated. Therefore the validity of the association constants for the copper salts may be open to question. This point will be discussed further in the next chapter. The Λ_o for thallium tetrafluoroborate is lower than the expected value. The salt was probably slightly impure, since it was not recrystallized before running because of decomposition problems. The association constant is quite reproducible, although it is possible that the suspected impurity, water, may affect the extent of association slightly.

The conductance behavior of potassium thiocyanate was measured to determine the extent of association of this remarkably soluble potassium salt (1.17 $\overline{m}$).[4] It was found to be slightly associated (Table 5).

The extent of association of the alkali metal tetrafluoroborates and hexafluorophosphates was also studied. The conductance behavior of the alkali metal perchlorates was measured by Kay and coworkers,[27] and were found to have association constants between 10 and 20, as shown in Table 8. It was expected that the tetrafluoroborates and hexafluorophosphates would show similar trends. These salts were very difficult to prepare to the high degree of purity required for accurate conductance work. The salts were generally sensitive to heat, and often could not be dried at elevated temperatures. Sodium hexafluorophosphate was found to decompose during storage in a desiccator over magnesium perchlorate. Also, recrystallization was difficult because of low temperature coefficients of solubility in several solvents. Potassium hexafluorophosphate was recrystallized five times though, but the difference between the conductance parameters from the third (Batch I) to the fifth (Batch III) recrystallization were negligible. The lack of purity is evidenced in the low values of limiting equivalent conductances and λ_o^- values. Judging from the measured limiting equivalent conductances, all of these salts have purities above 99.5%, with the exception of sodium hexafluorophosphate. The association constants should therefore be at least approximately correct.

In the case of the alkali metal tetrafluoroborates, an additional problem was encountered in that they were relatively insoluble and very slow to dissolve in acetonitrile. The maximum concentrations measured for these salts correspond approximately to their molar solubilities, about 1 to 3 x 10^{-3} $\underline{M}$. Several hours were needed before each added portion of salt dissolved and a stable resistance reading was obtained. Consequently a single conductance run required several days for each of these salts. The precision of fit for these runs was not as good as for most other salts, particularly for rubidium tetrafluoroborate. To check on the validity of the least-squares determined parameters, it was decided to analyze the data using a simplified version of the conductance theory which is a function of just two parameters, Λ_o and K_A.

Fuoss has described a graphical technique for evaluating conductance data of moderately associated salts using the simplified version of the conductance function

$$\Lambda = \gamma(\Lambda_o - SC^{\frac{1}{2}}\gamma^{\frac{1}{2}})$$

where all the symbols have been previously defined.[17] The degree of dissociation can be expressed as

$$\gamma = \frac{\Lambda}{\Lambda_o} F(z) \qquad \text{where } z = \frac{S}{\Lambda_o{}^{3/2}} (C\Lambda)^{\frac{1}{2}}$$

and F(z) can be expressed as a trigonometric function of z. Substituting

$$K_A = \frac{(1 - \gamma)}{C\gamma^2 f^2}$$

yields the equation

$$\frac{F(z)}{\Lambda} = \frac{1}{\Lambda_o} + \frac{C\Lambda f^2 K_A}{\Lambda_o^2 F(z)}$$

A plot of $F(z)/\Lambda$ versus $C\Lambda K_A f^2/F(z)$ will give K_A/Λ_o^2 and $1/\Lambda_o$ as slope and intercept respectively. Using an initial estimate of Λ_o, the data were graphed according to this procedure. Using the Λ_o obtained from the graphical

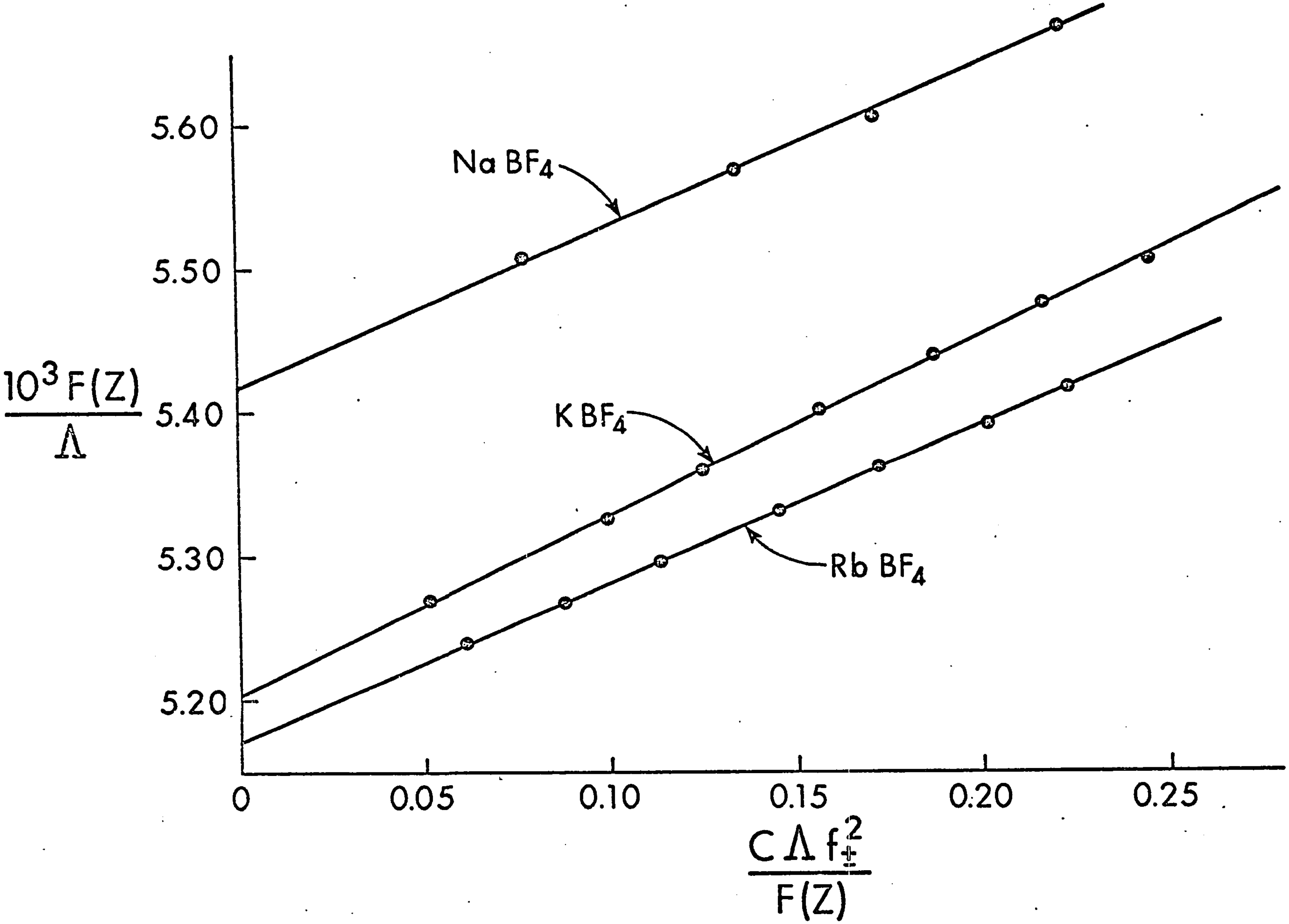

Figure 7. Conductance Plots for Alkali Metal Tetrafluoroborates

Table 7. Association Constants for Alkali Metal Tetrafluoroborates.

Salt	Least-squares		Graphical	
	Λ_0	K_A	Λ_0	K_A
$NaBF_4$	184.7	44	184.6	39
KBF_4	192.4	52	192.2	46
$RbBF_4$	193.3	22	193.3	41

Table 9. Association Constants in Acetonitrile

	BF_4^-	ClO_4^-	PF_6^-
Na^+	39[a]	10[b]	0
K^+	46[a]	14[b]	4
Rb^+	41[a]	19[b]	5
Cu^+	11	0	20
Ag^+	0	0	0
Tl^+	14	32	--

[a] value from graphical analysis

[b] reference 27

treatment the data were graphed a second time, yielding little change in Λ_o and K_A. These plots are shown in Figure 7, and the results as compared to least-squares calculated parameters are given in Table 8. The graphical analysis confirms the general magnitude of the association constants and shows a slightly more reasonable value for rubidium tetrafluoroborate, although one would expect its value to be yet a little higher. Table 9 lists these association constants as the best values for the alkali metal tetrafluoroborates.

CHAPTER 6 INTERPRETATION

Mobility and Association Trends

The trends observed for the alkali metal salts will first be considered and salts of the other metal cations compared to these trends. Single ion conductivities in acetonitrile are plotted versus the reciprocal of estimated crystallographic radii in Figure 8. Included are several other ions in addition to those studied here.[4,39] It is seen that for large ions conductance is, as expected, primarily a function of size. As the size of these ions decreases they become more mobile, with cations and anions falling approximately on the same line. However, as ion size decreases further, solvation becomes an important factor, and a reverse size-mobility dependence results. Smaller ions would be expected to be more highly solvated and this would be reflected in lower mobilities. With onset of solvation, cations and anions begin showing different size dependencies on mobility. This can be explained in terms of the ability of acetonitrile to solvate cations to a greater extent than anions, for acetonitrile, though a moderately weak Lewis base, is an even weaker Lewis acid.[4] The positive end of the dipole in the acetonitrile molecule is considerably delocalized, and so ion-dipole interactions with anions would be weaker than with cations of equal

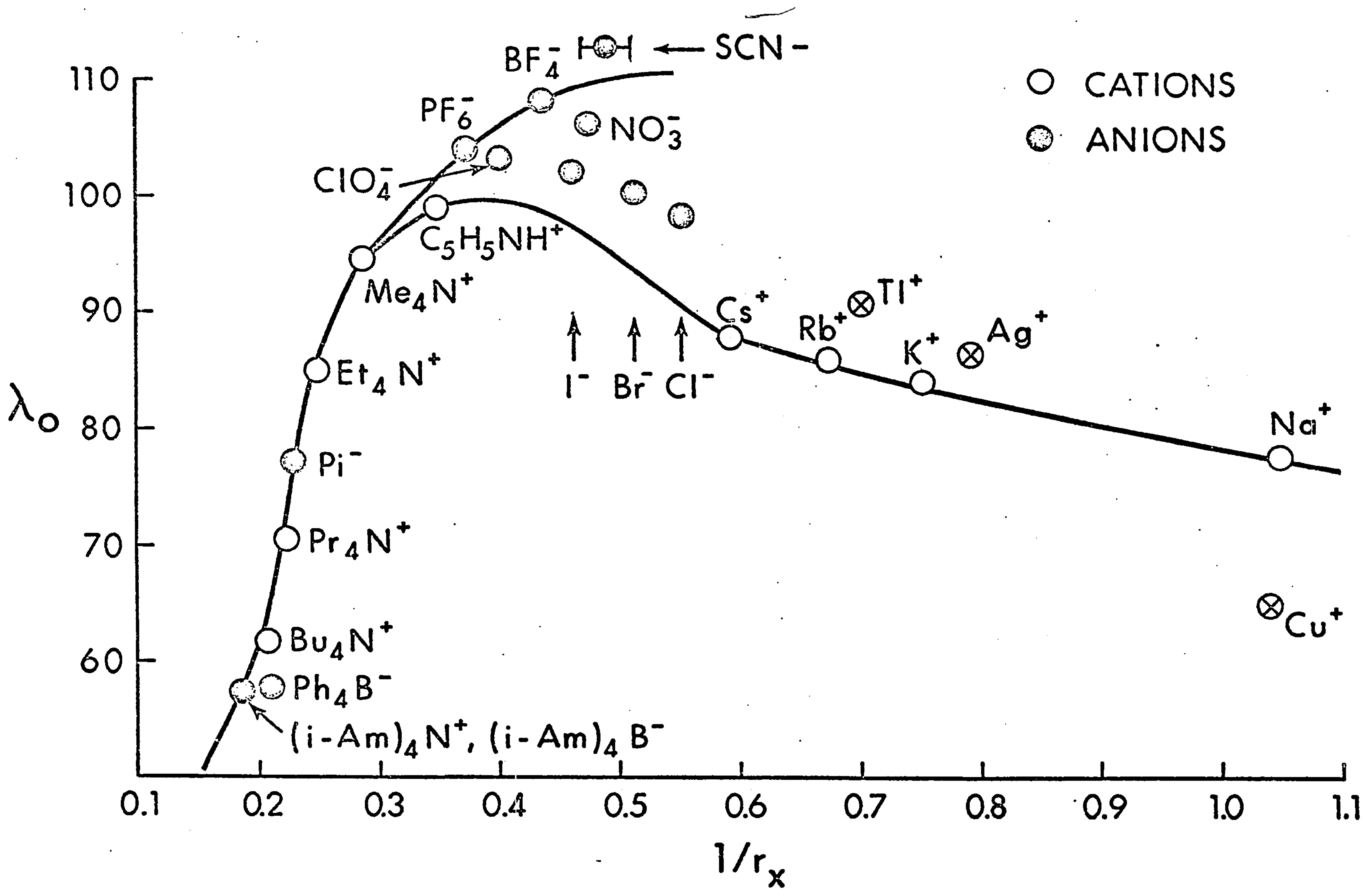

Figure 8. Single Ion Conductivities in Acetonitrile vs. Reciprocal of Crystallographic Radii

charge density.[35,39] Therefore on a size basis anions are relatively more mobile than cations. The curves in Figure 8 have been drawn through the points representing ions which would be expected to have least specific interactions with acetonitrile, the fluoro anions and the alkali metal cations.

In order to show that these trends are general, similar data are plotted in Figures 9 and 10 for two solvents with similar dielectric constants to acetonitrile, nitrobenzene[7] (D = 35) and dimethylformamide[37] (D = 37). Here the single ion conductivity-viscosity (Walden) product is plotted as the ordinate. This allows a comparison to be made between the mobilities in these solvents and in acetonitrile, which is represented by the dashed lines. Stokes'Law states that

$$\lambda_o \cdot \eta = \frac{|z|F^2}{6\pi R}$$

where z and r are the charge and radius of the ion, F the Faraday and η the viscosity of the solvent.[38] Although this model is generally accepted as being oversimplified, comparison of $\lambda_o \cdot \eta$ products is useful. Thus, both cations and anions appear to be less well solvated in nitrobenzene than acetonitrile. Nitrobenzene has been classed as a polar non-donor solvent,[29] with low Lewis acid and base properties. Figure 9 is in agreement with this

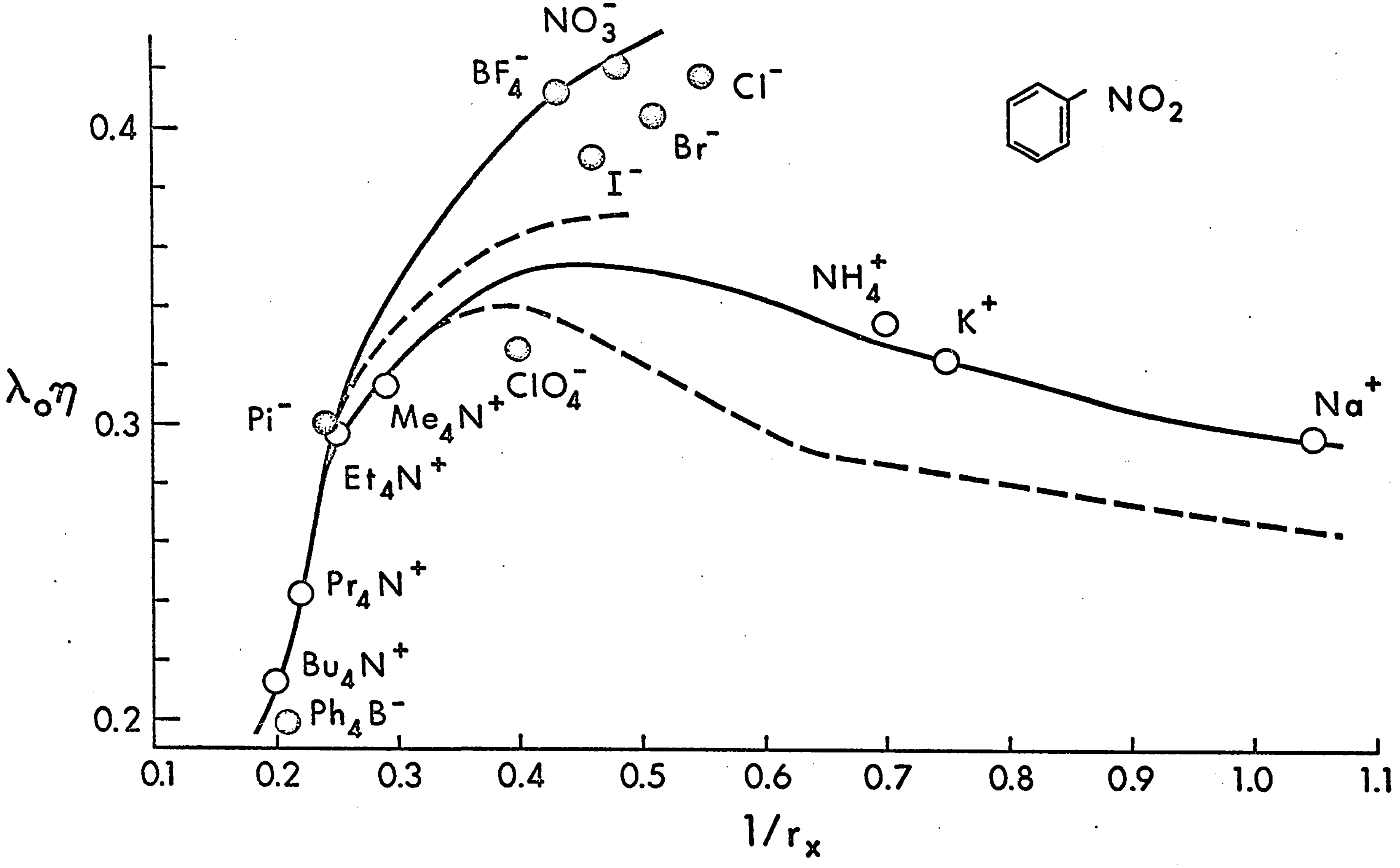

Figure 9. Single Ion Conductivity-viscosity Products in Nitrobenzene

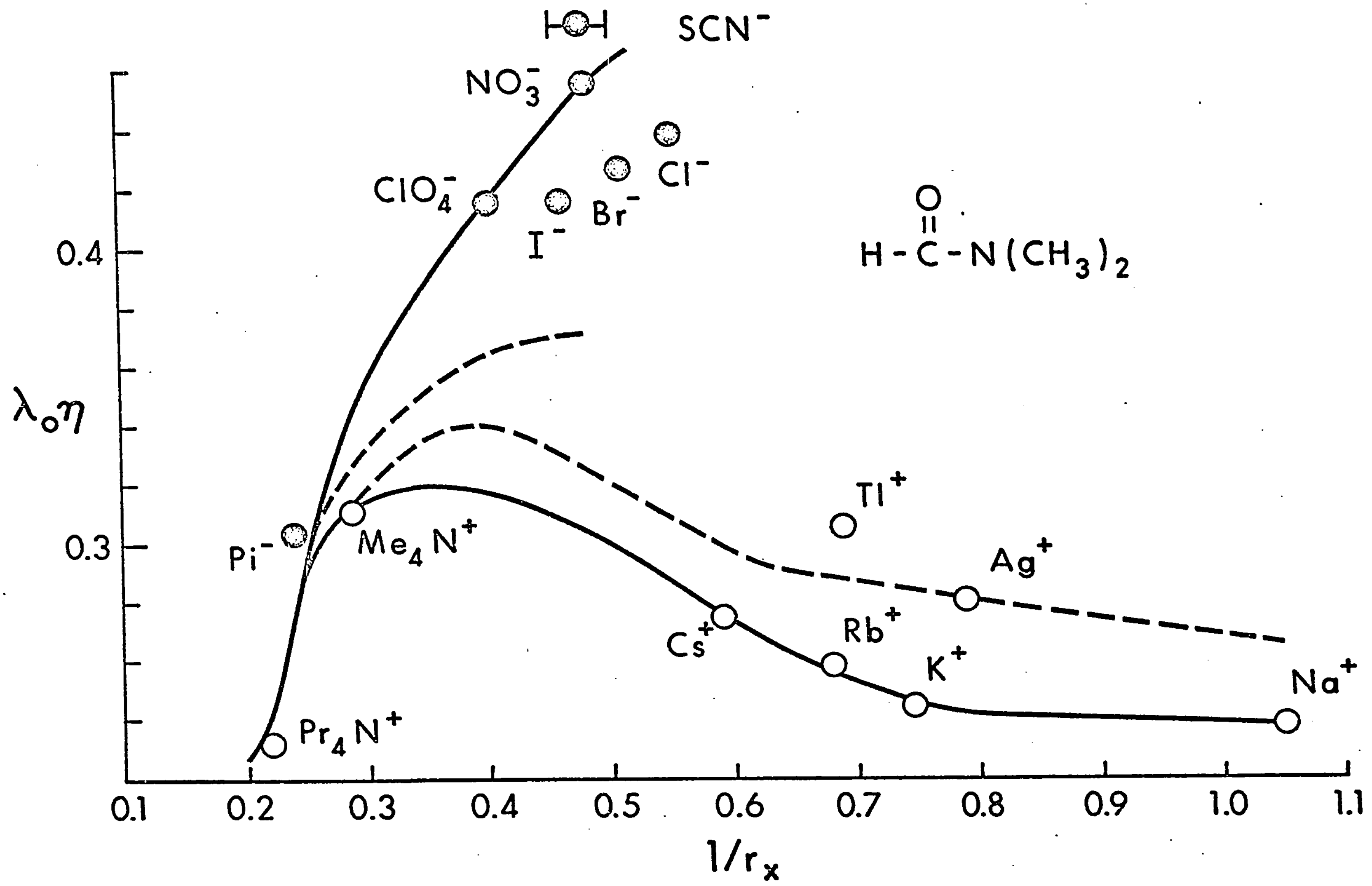

Figure 10. Single Ion Conductivity-viscosity Products in Dimethylformamide

classification. Dimethylformamide is considered to be a polar Lewis base like acetonitrile.[29] Figure 10 indicates that cations appear to be more solvated and anions less solvated in dimethylformamide than acetonitrile. Gutmann has devised a system of relating the donor properties of various solvents to one another by using a reference acceptor molecule, antimony pentachloride. He gives "donor numbers" for several solvents, the larger the number the higher the donor ability of the solvent.[19] These numbers are 4.4, 14.1 and 26.6 for nitrobenzene, acetonitrile and dimethylformamide respectively. This order is in agreement with the cation Walden products plotted here.

It is interesting to note that in nitrobenzene and dimethylformamide the mobilities of the halide ions increase with decreasing size, as would be expected for unsolvated ions. The opposite behavior is observed in acetonitrile, suggesting that the halide ions are solvated. The values for perchlorate and nitrate in acetonitrile fall below the line drawn through the fluoro anions in Figure 8. These anions may be interacting with acetonitrile to a greater extent than the tetrafluoroborate and hexafluorophosphate ions, although the small λ_o differences involved do not permit further interpretation.

Association trends also support the premise of increasing solvation with decreasing size of the alkali metal ion. Table 9 shows that association increases from sodium to rubidium for the tetrafluoroborates, perchlorates and hexafluorophosphates. Furthermore, the magnitude of the association constant decreases with increasing crystallographic radius of the anion, tetrafluoroborate being the smallest and hexafluorophosphate the largest in this series. In contrast to the alkali metals the tetraalkylammonium halide association constants decrease from the tetramethylammonium to the tetrabutylammonium salts,[14] as would be expected for relatively unsolvated cations.

Association constants in nitrobenzene and dimethylformamide appear to confirm the inferences drawn from the ionic mobility data relative to acetonitrile. The tetraalkylammonium halides and picrates are generally more associated in nitrobenzene than in acetonitrile, and the alkali metal picrates have association constants which are well over 10^3.[14] However these decrease with increasing crystallographic size of the alkali metal ion, indicating that the alkali metal ions are relatively unsolvated in nitrobenzene. In contrast the alkali metal perchlorates are all unassociated in dimethylformamide,[37] reflecting the higher degree of solvation of the alkali metal ions in that solvent.

Therefore mobility and association data are generally in agreement in reflecting extents of solvation. There are discrepancies however. The thiocyanate ion is more mobile than tetrafluoroborate in acetonitrile, but the association constant of 26 for potassium thiocyanate is almost half that of potassium tetrafluoroborate.

Copper Salts - Mobility and Association

The single ion conductivity of copper(I) deviates markedly from the curve drawn through the alkali metal ions in Figure 8. Hathaway suggests that copper(I) coordinates to four acetonitrile molecules in solution as well as is its salts, and that the complex has tetrahedral geometry.[21] The low conductance of copper(I) supports the premise of a high degree of solvation. The crystallographic radii of sodium and copper(I) ions are virtually identical but the limiting conductance of sodium ion in acetonitrile is over 12 conductance units higher than copper(I). This difference can be attributed to enhanced interaction of copper(I) with acetonitrile. If the copper(I) mobility were placed on the left branch of the curve in Figure 8 it would fall somewhere between the tetrapropylammonium and tetrabutylammonium mobilities, which would be approximately correct if the copper(I) mobility actually represented the mobility of $Cu(CH_3CN)_4^+$. This is completely speculative, however, and may be an overdrawn interpretation.

The question of the association of the copper(I) salts was briefly raised in the last chapter. Copper(I) perchlorate seems to be definitely unassociated; and the tetrafluoroborate and hexafluoroborate salts, while giving reasonable results using the unassociated equation, yield positive values of K_A using the three parameter equation. One test which can be used to check the validity of these K_A values is to see whether the three parameter equation fits the data better than the two parameter equation. The $\sigma\Lambda$ values in Table 4 show that the three parameter associated calculation does provide a better fit, although this may be partly due to the ability of three parameters to fit data better than two. Another test for association is to plot Λ' versus concentration, where

$$\Lambda' \equiv \Lambda - \Lambda_o + SC^{\frac{1}{2}} - EC \log C = JC$$

As was mentioned before if association occurs the values of Λ' will be low by the amount of the $K_A C\gamma\Lambda f^2$ term and therefore J and $\overset{\circ}{a}$ will have unreasonably low values as well. Plots of the copper tetrafluoroborate and copper hexafluorophosphate runs which analyzed for the highest K_A values are given in Figure 11, along with data from one of the copper perchlorate runs. It is seen that the plots are essentially identical with reasonable slopes. If association is real, the slopes would be smaller or

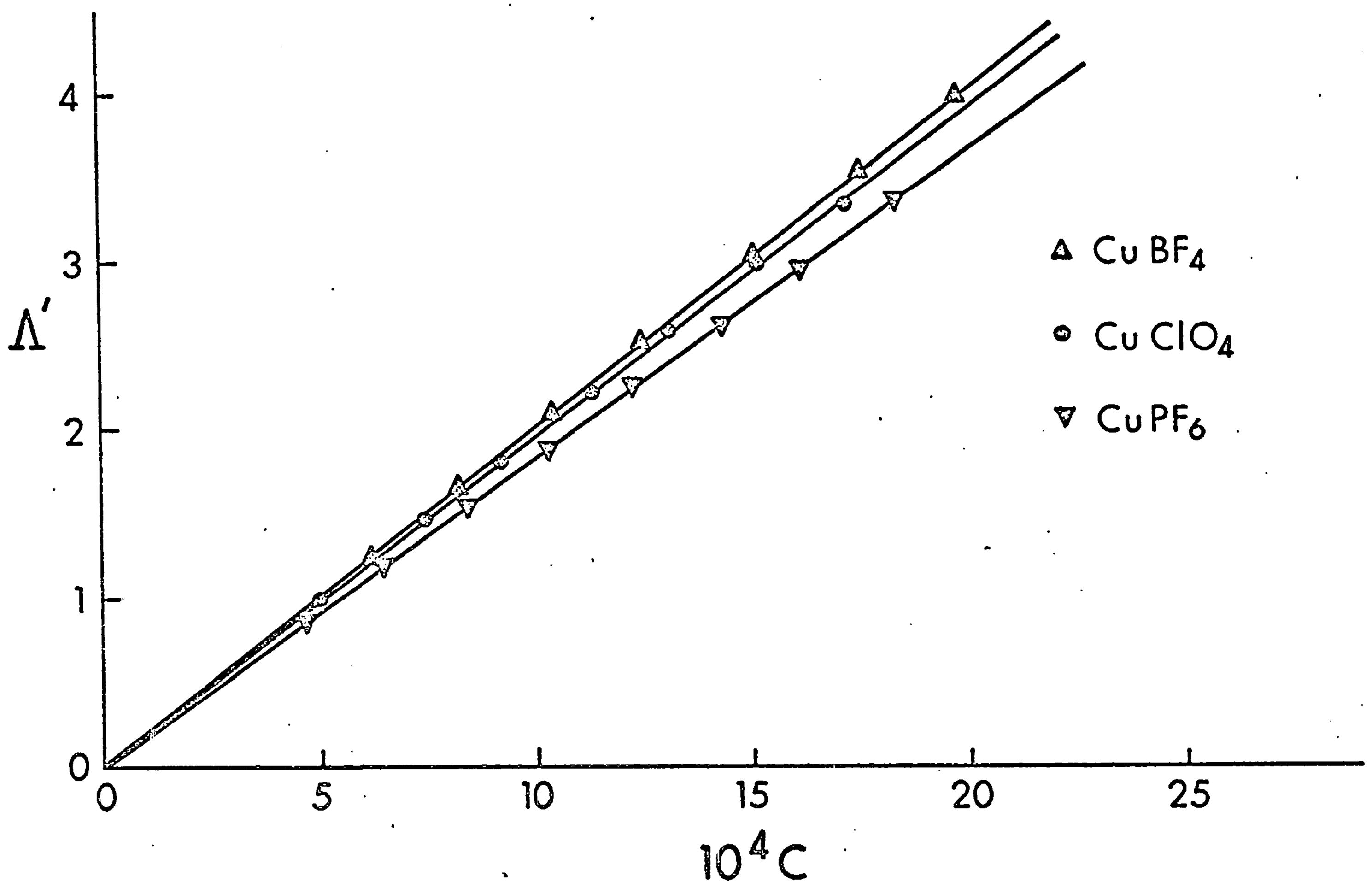

Figure 11. Λ' vs. Concentration Plots for Copper(I) Salts

even negative, as is seen in Figure 12, where thallium tetrafluoroborate ($K_A = 14$) and potassium thiocyanate ($K_A = 26$) data are given. These association constants are approximately as large as copper tetrafluoroborate and hexafluorophosphate respectively, although the $\Lambda' - c$ plots show definite signs of association. It is concluded that the amount of association of copper(I) with these anions is at most slight. This conclusion is in agreement with the interpretation of the low mobility of copper(I).

Silver and Thallium Salts - Mobility and Association

The single ion conductivities for silver(I) and thallium(I) in acetonitrile are noticeably above the line drawn through the alkali metal ion mobilities, as shown in Figure 8 . This behavior is more difficult to explain than the low mobility of copper(I). It was noted earlier that silver(I) interacts strongly with acetonitrile, and that in fact it is more strongly stabilized in acetonitrile solution than in water. The opposite behavior is found for thallium(I). Coetzee and Campion have estimated the standard reduction potential of the thallium(I-O) couple in acetonitrile referenced to the normal hydrogen electrode in water, and found the value to be 0.191 V more positive in acetonitrile than in water.[5] This was a larger positive shift than either the potassium

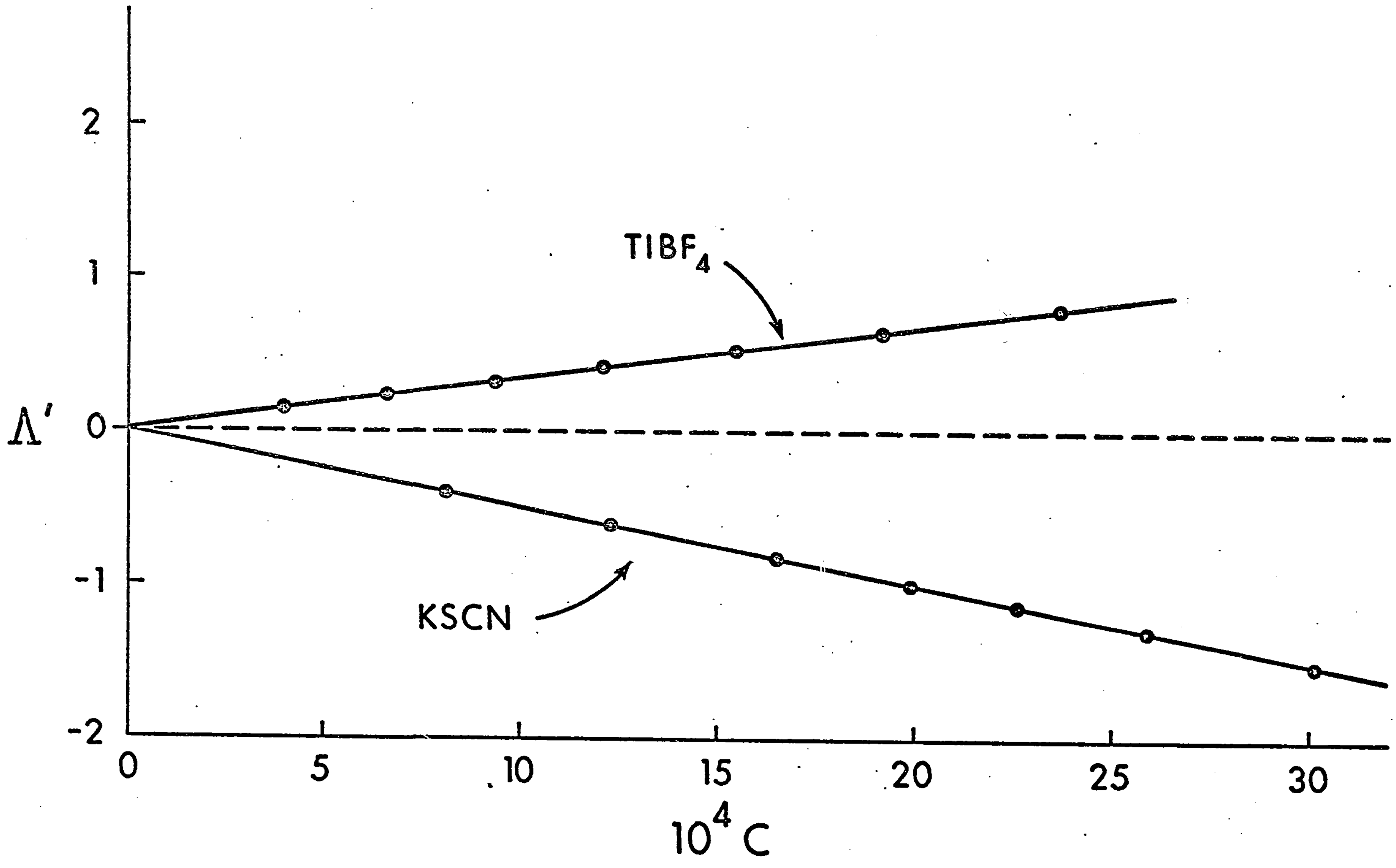

Figure 12. Λ' vs. Concentration Plots for $TlBF_4$ and KSCN

or rubidium couples, and was attributed to strong hydration of thallium(I), possibly due to its empty 5f orbital. The solubilities of thallium(I) salts in acetonitrile also reflect a lack of solvation. For example the solubility of thallium nitrate is about 3.9×10^{-4} M,[6] which is considerably smaller than the value of 9.6 M for silver nitrate.[23] In Figure 10 it is seen that the mobilities of thallium(I) and silver(I) in dimethylformamide are similar in their relation to the alkali metal ion mobilities in that solvent. It therefore appears that the high mobilities of thallium(I) and silver(I) in acetonitrile are not due to some unique property of the solvent. Furthermore these mobilities are not related in a simple way to the extent of ionic solvation, for thallium(I) and silver(I) interact with acetonitrile to distinctly different degrees.

The association of the silver and thallium salts does appear to reflect their relative stabilization in acetonitrile. Silver tetrafluoroborate, perchlorate and hexafluorophosphate have no detectable association while the tetrafluoroborate and perchlorate salts of thallium are associated. However, with symmetrical, non-complexing anions such as those used here, one would expect ion pairing to occur on the basis of electrostatic attraction, which in turn depends on the size of the ions.

In addition, relative sizes of ions in solution might be expected to be estimated by relative mobilities. Evidently the actual picture is not so simple, for silver has a higher mobility than either potassium or rubidium ions in acetonitrile, and yet is unassociated with anions which do have distinct association with these alkali metal ions. Janz and coworkers have shown by a variety of techniques that silver ion in concentrated acetonitrile solutions exists as the linear $Ag(CH_3CN)_2^+$ ion.[2,23] This silver coordination is explained in terms of hybridization of the filled $4d_z^2$ and empty 5s and $4p_z$ orbitals to form two bonding hybrid orbitals at 180° angles and a third hybrid orbital containing an electron pair at right angles to the other two.[10] Janz has also demonstrated that in concentrated silver nitrate solutions the silver ion retains its coordination to acetonitrile even when ion paired.[23] A possible explanation for the lack of association of the silver salts is that with only regions of increased electron density on the solvated silver ion available to the anion, ion pairing is discouraged. The planar nitrate ion with its nonsymmetrical charge distribution deviates from the behavior of symmetrical anions to form an ion pair of some stability. This behavior is repeated in dimethylformamide. Conductance studies showed silver(I) and thallium(I) perchlorate to be completely dissociated, but silver nitrate has a K_A of 40.[37] The low ion size parameter obtained here for silver nitrate in acetonitrile cannot be interpreted as additional evidence for this difference in behavior of the nitrate ion, for it has been shown that ion size parameters obtained from the Fuoss-Onsager theory have little physical significance in acetonitrile solution.[14]

The association behavior of the thallium salts studied in acetonitrile is quite different from that of the silver salts. Judging from the alkali metal salts, one might expect the association constant for thallium tetrafluoroborate to be about 50 and for thallium perchlorate to be about 20. The determined association constants were 14 and 32 for the tetrafluoroborate and perchlorate respectively. The low association constant of thallium tetrafluoroborate could be explained by invoking a model of the solvated thallium(I) ion similar to that of the solvated silver(I) ion in acetonitrile, although with an extra pair of s electrons the thallium(I) ion would probably only coordinate strongly to one acetonitrile molecule. This would mean that the expected K_A for thallium(I) perchlorate would be even smaller than 14, since perchlorate is a larger anion than tetrafluoroborate. In fact, the association constant is more than twice that of thallium(I) tetrafluoroborate.

The only readily apparent explanation for this increased association is that there is some specific interaction between thallium(I) and the perchlorate anion.

CONCLUSIONS

Conductance measurements on univalent metal salts in acetonitrile have produced several interesting results. For the alkali metal salts, mobilities and association constants can both be explained in terms of increasing amounts of solvation with decreasing crystallographic size of the cation. In addition, these association constants depend upon the size of the anion involved, becoming larger for smaller anions, as predicted of the basis of electrostatic attractions. By comparing conductance data with two other aprotic solvents with dielectric constants similar to acetonitrile, it is seen that similar trends result. In addition the differences among the three solvents show that the dielectric constant is only one of several factors to be considered when estimating degrees of solvation of metal ions. The dipole moment of the solvent molecule is also not of prime importance. Nitrobenzene, acetonitrile and dimethylformamide have dipole moments of 3.99 D, 3.37 D and 3.82 D respectively,[34] but nitrobenzene is the poorest and dimethylformamide the best alkali metal ion solvator of the three. As has been suggested,[27] It appears that the Lewis base properties of the solvent are most important in determining the degree of solvation of small ions.

Consideration of the copper(I), silver(I) and thallium(I) salts makes the picture become somewhat more complicated. Association constants do seem to reflect the general extent of solvation reasonably well. In addition the copper(I) single ion conductivity can be explained in terms of extensive solvation by acetonitrile, but the mobilities of silver(I) and thallium(I) are not so readily interpretable. It would appear that a more detailed look at the solvation process is needed to clarify these mobilities, and as Frank has stated "... it seems likely that when a clear picture of ionic motions in solution finally does emerge it will involve more factors than have traditionally been considered."[15]

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APPENDIX

The Fortran computer program for least-squares analysis of conductance data is given on the following pages, including subprograms for cell constant calculation and resistance extrapolations. Samples of typical computer results are also given for these programs.

Least-squares Computer Program

```
      DIMENSION C(30),Q(30),G(30),GZ(30),U(30),DFLQ(30),W(30),Z(30),
     1CG(30),SRCG(30),WZ(30),WY(30),Y(30),QI(30),R(30),WT(30),BARM(30),
     2DFN(30),FLCG(30),SQRCG(30),HR(30),AKQU(30),QP(30),ELC(30),
     3SQRC(30),SRC(30),TITLE(20)
    1 WRITE (6,2)
    2 FORMAT (1H1)
C     IF ILAB=0 LIT DATA  ILAB=1 LAB DATA  ILAB=2 LAB DATA +CELLC CALC
C     IF IWAIT=0 WEIGHTED ANDUNWEIGHTED IWAIT=1 UNWEIGHTED IWAIT=2 WEIGHTED
C     IF IACT=0 ITERATED A IN ACT COEF CALC IACT=1 INITIAL A IN ACT COEF CALC
C     IF IASS=0 ASS AND NONASS IASS=1 ASS ONLY IASS=2 NONASS ONLY
      READ (5,5) ILAB,IWAIT,IACT,IASS
    5 FORMAT (4I1)
      IF (ILAB-1) 10,20,30
   10 READ (5,11) TITLE
   11 FORMAT (20A4)
      READ (5,12) N,D,ETA,T,QZ,A,AK,X
   12 FORMAT (I10,F10.4,F10.8,5F10.4)
      READ (5,13) (C(I),Q(I),I=1,N)
   13 FORMAT (2F10.4)
      WRITE (6,14) TITLE
   14 FORMAT (1H1,20A4)
      GO TO 100
   20 READ (5,21) AVCLC
   21 FORMAT (F10.6)
   22 CALL FXTRAP (R)
      READ (5,11) TITLE
      READ (5,12) N,D,ETA,T,QZ,A,AK,X
      READ (5,23) GMWT,DENSL,DENCN,WTSOL,RSOL,DNSLT,DNAIR,PURITY
   23 FORMAT (3F10.5,F10.4,F10.1,3F10.5)
      READ (5,740) (WT(I),I=1,N)
  740 FORMAT (8F10.7)
      WRITE (6,14) TITLE
      CALL QCALC (N,R,C,Q,AVCLC,GMWT,DENSL,DENCN,WTSOL,RSOL,DNSLT,DNAIR,
```

```
     1PURITY,WT,DEN,CSOLV)
      GO TO 100
   30 CALL CELLCN (AVCLC)
      GO TO 22
  100 FLON=N
      DT=D*T
      SQRDT=SQRT(DT)
      ALPHA=820400./(SQRDT**3)
      BETA=82.501/(ETA*SQRDT)
      AB=.0016708/(DT)
      AB2=AB*2.
      ABSQ=AB*AB
      ABSQ2=ABSQ*2.
      AB4=AB*4.
      CKAP=50.29E8/(SQRDT)
      CKAP2=CKAP*CKAP
      S=(ALPHA*QZ)+BETA
      DO 171 I=1,N
      C(I)=C(I)*(1.0E-4)
      G(I)=Q(I)/(QZ-(S*SQRT((C(I)*Q(I))/QZ)))
      C(I)=C(I)/(1.0E-4)
  171 CONTINUE
      WRITE (6,181) N,D,A,X,ETA,AK,T,QZ
  181 FORMAT (1H0,7H      N=,I5,28H                DIELECT.CONST=,F8.4,14H
     1 ION SIZE    =,F11.4,/18H  VISCOSITY CONST=,F7.3,12H  VISCOSITY=,F1
     22.8,14H  ASSOC.CONST=,F11.4,/27X,12HTEMPERATURE=,F10.4,14H  LAMBDA
     3 ZERO=,F11.4)
      IF (ILAB) 183,183,187
  183 WRITE (6,184)
  184 FORMAT (1H0,50H     10000 CONC = C    LAMBDA = Q    GAMMA ZERO = GZ)
  185 WRITE (6,186) (C(I),Q(I),G(I),I=1,N)
  186 FORMAT (1H ,F17.5,F14.5,F14.6)
  187 E1=CKAP2*ABSQ/24.
      AZ=A*1.0E-8
      A=AZ
      AINT=A
```

```
      DO192 I=1,N
      C(I)=C(I)*(1.0E-4)
  192 CONTINUE
      E2=CKAP*(AB*BETA)/16.
      PSI1=CKAP2/(AB*12.)
      PSI2=E1*2.
      PSI3=E2*2.
      PSI4=(ALPHA*BETA)-(1.017*PSI3)
      PSI5=PSI2*0.9074
      FI3=11.*CKAP*BETA/(12.)
      B=8.356E6/(SQRDT**3)
  200 IF (IASS-1) 205,205,827
  205 WRITE (6,210)
  210 FORMAT (1H0,22HASSOCIATED ELECTROLYTE)
      IWATE=IWAIT
  231 IF (IWATE-1) 232,235,232
  232 WRITE (6,233)
  233 FORMAT (1H ,22H WEIGHTING FACTOR = CG)
      GO TO 237
  235 WRITE (6,236)
  236 FORMAT (1H ,21H WEIGHTING FACTOR = 1)
      A=AINT
  237 IF(IACT) 243,238,241
  238 WRITE (6,239)
  239 FORMAT (1H ,47H ITERATED )A* USED TO CALCULATE ACTIVITY COEFF.)
      GO TO 243
  241 WRITE (6,242)
  242 FORMAT (1H ,46H INITIAL )A* USED TO CALCULATE ACTIVITY COEFF.)
  243 DO 570 K=1,5
      DO542L=1,4
      S=(ALPHA*QZ)+BETA
      E=(E1*QZ)-E2
      H=(QZ*PSI1*(ABSQ2+(AB2-A)*A)+FI3)*A+
     1(((QZ*PSI2)-PSI3)*ALOG(CKAP*A))+(QZ*PSI5)+PSI4
      DHDA=QZ*PSI1*(ABSQ2+(AB4*A)-(3.0*A*A))+(((QZ*PSI2)-PSI3)/A)+FI3
      DO 325 I=1,N
```

```
      CG(I)=C(I)*G(I)
      IF (CG(I)) 290,290,295
  290 WRITE (6,292)
  292 FORMAT (1H ,30H                   CG NEGATIVE)
      GO TO 816
  295 QI(I)=QZ-(S*SQRT(CG(I)))+(F*CG(I)*(ALOG(CG(I))))
     1+(H*CG(I))-(X*(QZ*C(I)))
      G(I)=Q(I)/(QI(I))
      CG(I)=C(I)*G(I)
      IF (CG(I)) 290,290,300
  300 SQRCG(I)=SQRT(CG(I))
      FLCG(I)=F*CG(I)*(ALOG(CG(I)))
      SRCG(I)=S*SQRCG(I)
      IF (IACT) 1,305,310
  305 AZ=A
  310 U(I)=EXP((-B*SQRCG(I))/((CKAP*(AZ*SQRCG(I)))+1.0))
      Z(I)=CG(I)*DHDA
      Y(I)=(-CG(I))*U(I)*Q(I)
      DELQ(I)=Q(I)-QZ+(SRCG(I))-FLCG(I)-(H*CG(I))
     1+(X*(QZ*C(I)))+(AK*(CG(I)*(Q(I)*(U(I)))))
  325 CONTINUE
      A11=0.
      A12=0.
      A13=0.
      A22=0.
      A23=0.
      A33=0.
      A14=0.
      A24=0.
      A34=0.
      SUMQ2=0.
      DO 465 I=1,N
      IF (IWATE) 405,395,405
  395 W(I)=CG(I)
      GO TO 410
  405 W(I)=1.0
```

```
  410 WZ(I)=W(I)*Z(I)
      WY(I)=W(I)*Y(I)
      A11=W(I)+A11
      A12=WZ(I)+A12
      A13=WY(I)+A13
      A22=WZ(I)*Z(I)+A22
      A23=WZ(I)*Y(I)+A23
      A33=WY(I)*Y(I)+A33
      A14=W(I)*DELQ(I)+A14
      A24=WZ(I)*DELQ(I)+A24
      A34=WY(I)*DELQ(I)+A34
      SUMQ2=W(I)*(DELQ(I)*DELQ(I))+SUMQ2
  465 CONTINUE
      DETQZ=(A13*(A24*A23))+(A14*(A22*A33))+(A12*(A23*A34))
     1-(A12*(A24*A33))-(A13*(A22*A34))-(A14*A23*A23)
      DETA=(A13*(A12*A34))+(A11*(A24*A33))+(A14*(A23*A13))
     1-(A14*(A12*A33))-(A13*(A24*A13))-(A11*(A23*A34))
      DETAK=(A14*(A12*A23))+(A11*(A22*A34))+(A12*(A24*A13))
     1-(A12*(A12*A34))-(A14*(A22*A13))-(A11*(A24*A23))
      DETD=(A13*(A12*A23))+(A11*(A22*A33))+(A12*(A23*A13))
     1-(A12*(A12*A33))-(A13*(A22*A13))-(A11*(A23*A23))
      DELQZ=DETQZ/DETD
      DELA=DETA/DETD
      DELAK=DETAK/DETD
      IF (A+DELA) 535,535,550
  535 A=A/2.
      WRITE (6,539)
  539 FORMAT (1H ,20H           A NEGATIVE)
      WRITE (6,541) DELA
  541 FORMAT (1H ,9HDELTA A =,F13.6)
  542 CONTINUE
      GO TO 816
  550 QZ=QZ+DELQZ
      A=A+DELA
      AK=AK+DELAK
  570 CONTINUE
```

```
      E=E*2.3026
      E2=E2*2.3026
      WRITE (6,262) ALPHA,BETA,S,E,B,H,DHDA,E2
  262 FORMAT (1HO,7H ALPHA=,E12.5,7H  BETA=,E12.5,6H    S=,E12.5,6H    E
     1=,E12.5,/8H       B=,E12.5,7H     J=,E12.5,6H DJDA=,E12.5,6H   E2=,
     2E12.5)
      E=E/2.3026
      E2=E2/2.3026
      WRITE(6,332)
  332 FORMAT (1HO,62H   DEGREE DISSOC = G      ACT. COEFF = U    DELTA LA
     1MBDA = DELQ)
      WRITE (6,335) (G(I),U(I),DELQ(I),I=1,N)
  335 FORMAT (1H ,E16.5,F21.5,F22.3)
      A=A*1.0E8
      WRITE (6,564) DELAK,DELA,DELQZ,AK,A,QZ
  564 FORMAT (1HO,4X,9HDELTA AK=,E13.6,9H DELTA A=,E13.6,14H      DELTA Q
     1Z=,E13.6,/14H  ASSOC CONST=,F10.4,12H   ION SIZE=,F13.4,14H  LAMBD
     2A ZERO=,F10.4)
      A=A/1.0E8
      DEV=A14/A11
      VAR=SUMQ2/(FLON-3.)
      IF (A11-FLON) 605,602,605
  602 SIGQ=SQRT(VAR)
      GO TO 610
  605 SIGQ=SQRT(VAR/A11)
  610 PROD=VAR/DETD
      SIGQZ=SQRT(((A22*A33)-(A23**2))*PROD)
      SIGA=SQRT(((A11*A33)-(A13**2))*PROD)
      SIGAK=SQRT(((A11*A22)-(A12**2))*PROD)
      SIGA=SIGA*1.0E8
      WRITE (6,631) SIGAK,SIGA,SIGQZ,DEV,SIGQ
  631 FORMAT (1H ,4X,9HSIGMA AK=,F10.4,4X,8HSIGMA A=,F10.4,8X,9HSIGMA QZ
     1=,F10.4,/18H       AVERAGE DEV=,F8.5,34X,8HSIGMA Q=,F8.5)
      SIGA=SIGA/1.0E8
      IF (IWATE-1) 650,800,800
  650 IWATE=1
```

```
      DO 654 I=1,N
      C(I)=C(I)*1.0F4
      CG(I)=CG(J)*1.0E4
  654 CONTINUF
      WRITF(6,815)
      WRITE (6,825) (CG(I),SQRCG(I),SRCG(I),FLCG(I),HR(I),AKQU(I),QP(I),
     1I=1,N)
      WRITE (6,14) TITLF
      IF (ILAB) 651,651,652
  651 WRITE (6,184)
      WRITF (6,186) (C(I),Q(I),G(I),I=1,N)
      GO TO 653
  652 WRITE (6,24) GMWT,DFNSL,CSOLV,DENCN,AVCLC,WTSOL,RSOL,DNSLT,DNAIR,
     1PURITY
   24 FORMAT (1H0,7H MOLWT=,F10.5,10H     DENSL=,F10.5,8H  CSOLV=,F14.4,/
     18H  DENCN=,F10.5,10H     CELLC=,F10.6,8H  WTSOL=,F10.4,8H   RSOL=,F
     210.1,/8H  DNSLT=,F10.5,10H     DNAIR=,F10.6,8H PURITY=,F10.5,1H()
      WRITE (6,790)
  790 FORMAT(1H ,9X,6HWEIGHT,8X,6HRESIST,5X,7HDENSITY,8X,7H10000 C,7X,6H
     1LAMBDA)
      WRITE (6,792) (WT(I),R(I),DEN(I),C(I),Q(I),I=1,N)
  792 FORMAT (1H ,F15.6,F14.2,F12.5,F15.4,F13.3)
  653 A=A*1.0E8
      WRITE (6,181) N,D,A,X,FTA,AK,T,QZ
      A=A*1.0E-8
      WRITE (6,210)
      DO 655 I=1,N
      C(I)=C(I)*1.0F-4
      CG(I)=CG(I)*1.0E-4
  655 CONTINUE
      GO TO 235
  800 DO 805 I=1,N
      HR(I)=(H-(X*QZ))*CG(I)
      AKQU(I)=AK*(CG(I)*Q(I)*U(I))
      QP(I)=Q(I)+SRCG(I)-FLCG(I)+AKQU(I)
  805 CONTINUE
```

```
      DO 810 I=1,N
      CG(I)=CG(I)*1.0E4
      C(I)=C(I)*1.0E4
  810 CONTINUE
      WRITE(6,815)
  815 FORMAT (1H0,7X,2HCG,5X,5HCG1/2,4X,6HSCG1/2,5X,7HECGLNCG,2X,9H)J-BQ
     1Z*CG,3X,6HKAQFCG,2X,7HQ PRIME)
      WRITE (6,825) (CG(I),SQRCG(I),SRCG(I),ELCG(I),HR(I),AKQU(I),QP(I),
     1I=1,N)
  825 FORMAT (1H ,1F10.2,1F10.4,5F10.3)
      IF (IASS-1) 826,1,826
  816 DO 817 I=1,N
      C(I)=C(I)*1.0E4
  817 CONTINUE
C     BEGINNING OF NONASSOCIATED COMPUTATION
  826 WRITE (6,14) TITLE
      IF (ILAB) 827,827,829
  829 WRITE (6,24) GMWT,DENSL,CSOLV,DENCN,AVCLC,WTSOL,RSOL,DNSLT,DNAIR,
     1PURITY
      WRITE (6,790)
      WRITE (6,792) (WT(I),R(I),DEN(I),C(I),Q(I),I=1,N)
      A=A*1.0E8
      WRITE (6,181) N,D,A,X,ETA,AK,T,QZ
      A=A*1.0E-8
  827 WRITE (6,828)
  828 FORMAT (1H0,25HNONASSOCIATED ELECTROLYTE)
      DO 844 I=1,N
      C(I)=C(I)*1.0E-4
  844 CONTINUE
  831 IF (IWAIT-1) 832,835,832
  832 WRITE(6,833)
  833 FORMAT (1H ,21H WEIGHTING FACTOR = C)
      GO TO 843
  835 WRITE (6,837)
  837 FORMAT (1H ,21H WEIGHTING FACTOR = 1)
      A=AINT
```

```
843 DO 905 K=1,5
    DO 895 L=1,4
    S=(ALPHA*QZ)+BETA
    F=(F1*QZ)-F2
    H=(QZ*PSI1*(ABSQ2+(AB2-A)*A)+FI3)*A+
   1(((QZ*PSI2)-PSI3)*ALOG(CKAP*A))+(QZ*PSI5)+PSI4
    DHDA=QZ*PSI1*(ABSQ2+(AB4*A)-(3.0*A*A))+(((QZ*PSI2)-PSI3)/A)+FI3
    DO 850 I=1,N
    SRC(I)=SQRT(C(I))*S
    SQRC(I)=SQRT(C(I))
    SRC(I)=S*SQRC(I)
    FLC(I)=F*C(I)*ALOG(C(I))
    QI(I)=QZ+FLC(I)-SRC(I)
   1+(H*C(I))-(X*(QZ*C(I)))
    Z(I)=C(I)*DHDA
    DELQ(I)=Q(I)-QI(I)
850 CONTINUE
    A11=0.
    A12=0.
    A22=0.
    A14=0.
    A24=0.
    SUMQ2=0.
    DO 875 I=1,N
    IF (IWAIT) 855,855,860
855 W(I)=C(I)
    GO TO 865
860 W(I)=1
865 WZ(I)=W(I)*Z(I)
    A11=W(I)+A11
    A12=WZ(I)+A12
    A22=WZ(I)*Z(I)+A22
    A14=W(I)*DELQ(I)+A14
    A24=WZ(I)*DELQ(I)+A24
    SUMQ2=W(I)*(DELQ(I)**2)+SUMQ2
875 CONTINUE
```

```
      DETQZ=(A14*A22)-(A24*A12)
      DETA=(A11*A24)-(A12*A14)
      DETD=(A11*A22)-(A12*A12)
      DELQZ=DETQZ/DETD
      DELA=DETA/DETD
      IF (A+DELA) 880,880,900
  880 A=A/2.
      WRITE (6,885)
  885 FORMAT (1H ,20H           A NEGATIVE)
      WRITE (6,890) DELA
  890 FORMAT (1H ,9HDELTA A =,F13.6)
  895 CONTINUE
      GO TO 906
  900 QZ=QZ+DELQZ
      A=A+DELA
  905 CONTINUE
  906 E=E*2.3026
      E2=E2*2.3026
      WRITE (6,910) ALPHA,BETA,S,E,B,H,DHDA,E2
  910 FORMAT (1H0,7H ALPHA=,E12.5,7H  BETA=,E12.5,6H    S=,E12.5,6H     E
     1=,E12.5,/8H      B=,E12.5,7H     J=,E12.5,6H DJDA=,E12.5,6H   E2=,
     2E12.5)
      E=E/2.3026
      E2=E2/2.3026
      IF (A+DELA) 1800,1800,914
  914 DEV=A14/A11
      VAR=SUMQ2/(FLON-2.)
      IF (A11-FLON) 920,915,920
  915 SIGQ=SQRT(VAR)
      GO TO 925
  920 SIGQ=SQRT(VAR/A11)
  925 PROD=VAR/DETD
      SIGQZ=SQRT(A22*PROD)
      SIGA=SQRT(A11*PROD)
      WRITE (6,930)
  930 FORMAT (1H0,56X,4HDELQ)
```

```
      A=A*1.0E8
      SIGA=SIGA*1.0E8
      WRITE (6,935) DELA,DELQZ,DELQ(1),A,QZ,DELQ(2),SIGA,SIGQZ,DELQ(3),D
     1EV,SIGQ,DELQ(4)
  935 FORMAT(1H ,9H DELTA A=,E13.3,13H     DELTA QZ=,E13.3,F12.3,/10H
     1     A=,F10.4,16H     LAMBDA ZERO=,F10.4,F15.3,/10H  SIGMA A=,F10.4,
     216H       SIGMA QZ=,F10.4,F15.3,/10H  AVE DEV=,F10.4,16H          SI
     3GMA Q=,F10.4,F15.3)
      A=A/1.0E8
      SIGA=SIGA/1.0E8
      WRITE (6,940) (DELQ(I),I=5,N)
  940 FORMAT (1H ,F60.3)
      IF (IWAIT-1) 945,1800,1800
  945 IWAIT=1
      WRITE (6,1815)
      WRITE (6,1825) (SQRC(I),SRC(I),ELC(I),HR(I),QP(I),I=1,N)
      GO TO 835
 1800 DO 1805 I=1,N
      HR(I)=(H-(X*QZ))*C(I)
      QP(I)=Q(I)+SRC(I)-ELC(I)
 1805 CONTINUE
      WRITE (6,1815)
 1815 FORMAT (1H ,7X,4HC1/2,4X,5HSC1/2,5X,5HECLNC,2X,8H)J-RQZ*C,4X,7HQ P
     1RIME)
      WRITE (6,1825) (SQRC(I),SRC(I),ELC(I),HR(I),QP(I),I=1,N)
 1825 FORMAT (1H ,F10.4,3F10.3,F12.3)
      GO TO 1
      END
      SUBROUTINE QCALC (N,R,C,Q,AVCLC,GMWT,DENSL,DENCN,WTSOL,RSOL,DNSLT,
     1DNAIR,PURITY,WT,DEN,CSOLV)
      DIMENSION R(30),C(30),Q(30),WT(30),BARM(30),DEN(30)
      SUMWT=0.0
      CSOLV=AVCLC/RSOL
      WTSOL=WTSOL+WTSOL*((1.0/DENSL)-(1.0/7.8))*DNAIR
      WRITE (6,24) GMWT,DENSL,CSOLV,DENCN,AVCLC,WTSOL,RSOL,DNSLT,DNAIR,
     1PURITY
```

```
24 FORMAT (1H0,7H MOLWT=,F10.5,10H     DENSL=,F10.5,8H  CSOLV=,E14.4,/
  18H  DENCN=,F10.5,10H     CELLC=,F10.6,8H  WTSOL=,F10.4,8H   RSOL=,F
  210.1,/8H  DNSLT=,F10.5,10H     DNAIR=,F10.6,8H PURITY=,F10.5,1H()
   DO 780 I=1,N
   WT(I)=WT(I)+WT(I)*((1.0/DNSLT)-(1.0/8.4))*DNAIR
   WT(I)=WT(I)*(PURITY/100)
   SUMWT=SUMWT+WT(I)
   PARM(I)=(SUMWT*1000)/(GMWT*(WTSOL+SUMWT))
   DEN(I)=DENSL+(DENCN*PARM(I))
   C(I)=DEN(I)*PARM(I)
   Q(I)=((AVCLC/R(I))-CSOLV)/(C(I)*1.0E-3)
   C(I)=C(I)*1.0E4
780 CONTINUE
   WRITE (6,790)
790 FORMAT(1H ,9X,6HWEIGHT,8X,6HRESIST,5X,7HDENSITY,8X,7H10000 C,7X,6H
  1LAMBDA)
   WRITE (6,792) (WT(I),R(I),DEN(I),C(I),Q(I),I=1,N)
792 FORMAT (1H ,F15.6,F14.2,F12.5,F15.4,F13.3)
   RETURN
   END
```

Resistance Extrapolation Subprogram

```
      SUBROUTINE EXTRAP(R)
      DIMENSION R(30),RS(5),FQ(5),TITLE(20),RECFQ(5)
      IDATA=0
      READ (5,100) TITLE
  100 FORMAT (20A4)
      WRITE (6,103) TITLE
  103 FORMAT (1H1,20A4)
      WRITE (6,104)
  104 FORMAT (1H0,9HFREQUENCY,15X,10HRESISTANCE)
      READ (5,107) XMAX,XMIN,N
  107 FORMAT (2F5.2,I5)
      X=XMAX
      Y=XMIN
    5 READ (5,101) (RS(I),I=1,3)
  101 FORMAT (3F10.2)
      READ (5,102) (FQ(I),I=1,3)
  102 FORMAT (3F10.0)
      ICOUNT=1
      X1=X
      X2=Y
      XMAX=X1
      XMIN=X2
      IDATA=IDATA+1
    6 DO 10 I=1,3
   10 RECFQ(I)=(1.0/FQ(I)**X1)
      SLOPE=(RS(1)-RS(2))/(RECFQ(1)-RECFQ(2))
      RINF=RS(2)-(SLOPE*RECFQ(2))
      R3CALC=SLOPE*RECFQ(3)+RINF
      DELR3=R3CALC-RS(3)
      IF (DELR3) 11,12,12
   11 TEST=(-DELR3)
```

```
      GO TO 13
   12 TEST=DELR3
   13 IF (TEST.LT.0.02) GO TO 18
      ICOUNT=ICOUNT+1
      IF (ICOUNT-10) 14,14,15
   15 GO TO 18
   14 IF (DELR3) 16,16,17
   16 XMIN=X2
      X1=(XMAX+XMIN)/2.0
      X2=X1
      GO TO 6
   17 XMAX=X1
      X1=(XMAX+XMIN)/2.0
      X2=X1
      GO TO 6
   18 R(IDATA)=RINF
      WRITE (6,108)
  108 FORMAT (1H0)
      WRITE (6,105) (FQ(I),RS(I),I=1,3)
  105 FORMAT (1H ,F8.0,19X,F8.2)
      WRITE (6,106) RINF,DELR3,ICOUNT,X1
  106 FORMAT (1H ,27H EXTRAPOLATED RESISTANCE = ,F8.2,/11H DELTA R = ,F4
     1.2,13HITERATIONS = ,I2,11HEXPONENT = ,F5.3)
      IF (IDATA-N) 5,19,19
   19 RETURN
      END
```

Cell Constant Calculation Subprogram

```
      SUBROUTINE CELLCN (AVCLC)
      DIMENSION TITLE(20),WGT(10),CONC(10),WTC(10),ALMDA(10),RECR(10),
     1RES(10),CELLC(10),DEV1(10),DEV2(10)
      READ (5,11) TITLE
   11 FORMAT (20A4)
      WRITE (6,14) TITLE
   14 FORMAT (1H1,20A4)
      READ (5,31) M,WTSOLV,RSOLV,DNAIR
   31 FORMAT (I10,F10.3,F10.2,F10.6)
      READ (5,32) (WGT(I),RES(I),I=1,M)
   32 FORMAT (F10.7,F10.2)
      SUMWGT=0.0
      SUMCLC=0.0
      SUMDEV=0.0
      WTSOLV=WTSOLV+WTSOLV*(1.0-(1.0/7.8))*DNAIR
      DO 33 I=1,M
      WGT(I)=WGT(I)+WGT(I)*((1.0/2.0)-(1.0/8.4))*DNAIR
      SUMWGT=SUMWGT+WGT(I)
      WTC(I)=(SUMWGT*1000)/(74.557*(WTSOLV+SUMWGT))
      CONC(I)=0.99707*(WTC(I))-0.0272*(WTC(I)**2)
      ALMDA(I)=149.93-94.65*SQRT(CONC(I))+58.74*CONC(I)*ALOG10(CONC(I))+
     1198.4*CONC(I)
      RECR(I)=(1.0/RES(I))-(1.0/RSOLV)
      CELLC(I)=(ALMDA(I)*CONC(I))/(RECR(I)*1000)
      SUMCLC=SUMCLC+CELLC(I)
   33 CONTINUE
      AVCLC=SUMCLC/M
      DO 34 I=1,M
      VALUE=CELLC(I)
      IF (VALUE-AVCLC) 36,36,35
   35 DEV1(I)=CELLC(I)-AVCLC
```

```
      GO TO 37
   36 DEV1(I)=AVCLC-CELLC(I)
   37 SUMDEV=SUMDEV+DEV1(I)
   34 CONTINUE
      AVDEV=SUMDEV/M
      RELAD=(AVDEV*1000)/AVCLC
      SMDEV2=0.0
      DO 38 I=1,M
      DEV2(I)=DEV1(I)**2
      SMDEV2=SMDEV2+DEV2(I)
   38 CONTINUE
      STDSQ=SMDEV2/(M-1)
      STDEV=SQRT(STDSQ)
      WRITE (6,39) WTSOLV
   39 FORMAT (1H0,1X,25HVACUUM CORRECTED WT H2O =,F9.3)
      WRITE (6,40)
   40 FORMAT (1H0,2X,9HVACWEIGHT,2X,10HRESISTANCE,4X,7HMOLAR C,6X,6HLAMB
     1DA,5X,5HCELLC,2X,12HDEV FROM AVE)
      WRITE (6,41) (WGT(I),RES(I),CONC(I),ALMDA(I),CELLC(I),DEV1(I),I=1,
     1M)
   41 FORMAT (1H ,F11.6,F10.2,F15.6,F10.3,F10.6,F10.6)
      WRITE (6,42) AVCLC
   42 FORMAT (1H0,22HAVERAGE CELL CONSTANT=,F10.6)
      WRITE (6,43) AVDEV,RELAD,STDEV
   43 FORMAT (1H0,14HAVE DEVIATION=,F10.6,13H REL AVE DEV=,F7.4,3HPPT,3X
     1,9HSTD DEV =,F8.6)
      RETURN
      END
```

```
      GO TO 37
   36 DEV1(I)=AVCLC-CELLC(I)
   37 SUMDEV=SUMDEV+DEV1(I)
   34 CONTINUE
      AVDEV=SUMDEV/M
      RELAD=(AVDEV*1000)/AVCLC
      SMDEV2=0.0
      DO 38 I=1,M
      DEV2(I)=DEV1(I)**2
      SMDEV2=SMDEV2+DEV2(I)
   38 CONTINUE
      STDSQ=SMDEV2/(M-1)
      STDEV=SQRT(STDSQ)
      WRITE (6,39) WTSOLV
   39 FORMAT (1H0,1X,25HVACUUM CORRECTED WT H2O =,F9.3)
      WRITE (6,40)
   40 FORMAT (1H0,2X,9HVACWEIGHT,2X,10HRESISTANCE,4X,7HMOLAR C,6X,6HLAMB
     1DA,5X,5HCELLC,2X,12HDEV FROM AVE)
      WRITE (6,41) (WGT(I),RES(I),CONC(I),ALMDA(I),CELLC(I),DEV1(I),I=1,
     1M)
   41 FORMAT (1H ,F11.6,F10.2,F15.6,F10.3,F10.6,F10.6)
      WRITE (6,42) AVCLC
   42 FORMAT (1H0,22HAVERAGE CELL CONSTANT=,F10.6)
      WRITE (6,43) AVDEV,RELAD,STDEV
   43 FORMAT (1H0,14HAVE DEVIATION=,F10.6,13H REL AVE DEV=,F7.4,3HPPT,3X
     1,9HSTD DEV =,F8.6)
      RETURN
      END
```

```
  COPPER (I) TETRAFLUOROBORATE IN ACETONITRILE  NO, 1  AUG, 7,1968

MOLWT= 314,55492     DENSL=   0,77670  CSOLV=     0,9368E-07
DENCN=    0,77000    CELLC=  0,975450  WTSOL=  715,831E   RSOL= 9345000,0
DNSLT=    1,49000    DNAIR=  0,001100 PURITY= 100,00000%
          WEIGHT          RESIST       DENSITY        10000 C         LAMBDA
        0,100005         9045,79      0,77680          6,6321        163,514
        0,069407         5995,99      0,77684          9,0253        161,962
        0,077372         4667,69      0,77688         11,6930        160,526
        0,064856         3939,79      0,77692         13,9290        159,469
        0,063171         3427,10      0,77695         16,1067        158,540
        0,056151         3074,16      0,77698         18,0422        157,792
        0,057243         2782,75      0,77701         20,0152        157,076
        0,070326         2494,50      0,77705         22,4399        156,236

     N=      8                DIELECT,CONST= 35,9500  ION SIZE    =       5,9132
 VISCOSITY CONST=  0,0        VISCOSITY=  0,00341200  ASSOC,CONST=        7,3470
                              TEMPERATURE=  298,1500  LAMBDA ZERO=      173,0921

NONASSOCIATED ELECTROLYTE
 WEIGHTING FACTOR = 1

 ALPHA= 0,73927E 00  BETA= 0,23355E 03     S= 0,36137E 03     F= 0,69649E 03
     B= 0,75297E 01       J= 0,20436E 04 DJDA= 0,40444E 11    F2= 0,25448E 03

                                                      DELQ
 DELTA A=    -0,134E-12     DELTA QZ=      0,156E-04   0,035
       A=     4,0239    LAMBDA ZERO=  172,8988        -0,011
 SIGMA A=     0,0355        SIGMA QZ=      0,0224     -0,018
 AVE DEV=     0,0000         SIGMA Q=      0,0207     -0,019
                                                      -0,015
                                                       0,003
                                                       0,016
                                                       0,009
```

```
     C1/2       SC1/2       SCLNC   (J-B07)C     Q PRIME
   0.0258       9.306      -1.468      1.355     174.280
   0.0300      10.856      -1.914      1.844     174.732
   0.0342      12.257      -2.388      2.390     175.270
   0.0373      13.487      -2.771      2.847     175.726
   0.0401      14.503      -3.133      3.292     176.175
   0.0425      15.340      -3.448      3.687     176.589
   0.0447      16.167      -3.762      4.090     177.005
   0.0474      17.118      -4.140      4.586     177.494
```

```
  THALLIUM(I) PERCHLORATE IN ACETONITRILE  NOV. 17. 1968

 MOLWT= 303.81992     DENSL=    0.77670  CSOLV=      0.97635-07
 DENCN=    0.22000    CELLC=  0.975720  WTSOL=  729.5198   PSOL= 8970000.0
 DNSLT=    4.89000    DNAIR=  0.001100 PURITY=.100.00000%
         WEIGHT          RESIST      DENSITY          10000 C         LAMBDA
       0.140552         9436.70     0.77686           5.6261        183.018
       0.100097         5350.00     0.77696           9.1237        179.101
       0.084125         4109.27     0.77704          12.9215        176.312
       0.084266         3349.22     0.77713          15.9342        173.846
       0.098392         2767.70     0.77722          18.4716        171.241
       0.104149         2345.71     0.77733          22.1209        168.724
       0.095324         2062.27     0.77742          25.4600        166.661
       0.112892         1810.66     0.77753          29.4164        164.380

       N=      8                DIELECT.CONST= 35.9500  ION SIZE   =      3.5000
 VISCOSITY CONST=  0.0          VISCOSITY=  0.00341000  ASSOC.CONST=     30.0000
                                TEMPERATURE=  298.1500  LAMBDA ZERO=   195.2000

ASSOCIATED ELECTROLYTE
 WEIGHTING FACTOR = 1
 ITERATED (A) USED TO CALCULATE ACTIVITY COEFF.

 ALPHA= 0.73227E 00  BETA= 0.23355E 03     S= 0.27780E 03    F= 0.91872E 02
     B= 0.75297E 01       J= 0.18282E 04 DJDA= 0.49555E 11   E2= 0.25448E 02

  DEGREE DISSOC = G       ACT. COEFF = U    DELTA LAMBDA = DELO
     0.98522E 00               0.84260             -0.002
     0.97742E 00               0.80623              0.001
     0.97136E 00               0.78239             -0.003
     0.96577E 00               0.76223              0.014
     0.95953E 00               0.74209              0.005
     0.95318E 00               0.72353             -0.025
     0.94309E 00               0.70844              0.006
     0.94201E 00               0.69244              0.005
```

```
   DELTA AK=-0,509992E-03 DELTA A=-0,144378E-11      DELTA QZ=-0,998263E-05
ASSOC CONST=    32,0277    ION SIZE=         2,9673  LAMBDA ZERO=  195,1230
   SIGMA AK=     0,0152     SIGMA A=     0,1909       SIGMA QZ=     0,0361
    AVERAGE DEV=-0,00000                                    SIGMA Q= 0,01244

     CC        CG1/2      SCG1/2      FCGLNCG   (J-POZ)CG    KAOFCG   Q PRIME
    5,54      0,0235      9,395      -1,478      1,013      2,744    196,134
    8,43      0,0290     11,098      -2,229      1,622      4,139    196,756
   11,74      0,0343     12,242      -2,816      2,146      5,136    197,265
   14,52      0,0381     14,326      -3,374      2,655      6,176    197,791
   17,72      0,0421     15,915      -3,992      3,240      7,229    198,268
   21,09      0,0459     17,348      -4,620      3,855      8,262    198,953
   24,14      0,0491     18,561      -5,172      4,413      9,147    199,542
   27,71      0,0526     19,997      -5,802      5,046     10,124    200,194
```

```
      RESISTANCE EXTRAPOLATIONS   TLBF4   JULY 14. 1969
FREQUENCY                    RESISTANCE


   1000.                          8641.60
   2000.                          8631.10
   5000.                          8622.70
 EXTRAPOLATED RESISTANCE =       8612.05
DELTA R = 0.01ITERATIONS =       9EXPONENT = 0.634


   1000.                          5292.60
   2000.                          5285.30
   5000.                          5279.20
 EXTRAPOLATED RESISTANCE =       5270.34
DELTA R = -.02ITERATIONS =       7EXPONENT = 0.573


   1000.                          3845.92
   2000.                          3839.98
   5000.                          3834.88
 EXTRAPOLATED RESISTANCE =       3826.91
DELTA R = -.00ITERATIONS =       6EXPONENT = 0.541


   1000.                          2929.17
   2000.                          2924.05
   5000.                          2919.76
 EXTRAPOLATED RESISTANCE =       2913.56
DELTA R = 0.00ITERATIONS =       7EXPONENT = 0.573


   1000.                          2385.20
   2000.                          2380.74
   5000.                          2376.80
 EXTRAPOLATED RESISTANCE =       2370.93
DELTA R = 0.02ITERATIONS =       6EXPONENT = 0.541


   1000.                          2009.81
   2000.                          2005.72
   5000.                          2002.31
 EXTRAPOLATED RESISTANCE =       1997.53
DELTA R = 0.01ITERATIONS =       6EXPONENT = 0.594


   1000.                          1681.74
   2000.                          1678.00
   5000.                          1674.93
 EXTRAPOLATED RESISTANCE =       1670.84
DELTA R = 0.02ITERATIONS =       5EXPONENT = 0.606
```

```
 CELL CONSTANT DETERMINATION  JUNE 13,1968

VACUUM CORRECTED WT H2O =  952.355

 VACWEIGHT  RESISTANCE    MOLAR C        LAMBDA      CELLC   DEV FROM AVE
  0.052547    7987.10   0.737831E-03    147.370  0.876310  0.000279
  0.038655    4643.30   0.128053E-02    146.579  0.876389  0.000141
  0.025833    3634.10   0.164317E-02    146.151  0.876522  0.000008
  0.031783    2869.91   0.208931E-02    145.689  0.876567  0.000037
  0.023445    2485.70   0.241838E-02    145.383  0.876550  0.000020
  0.028339    2140.28   0.281611E-02    145.044  0.876453  0.000077
  0.030845    1860.04   0.324897E-02    144.705  0.876424  0.000107

AVERAGE CELL CONSTANT=  0.876530

AVE DEVIATION=  0.000096 REL AVE DEV= 0.1091PPT   STD DEV =0.000140
```