# CONDUCTANCE AND VISCOSITY STUDIES OF POTASSIUM IODIDE AND TETRABUTYLAMMONIUM IODIDE IN FORMAMIDE

by

Sarala Kumari Prem

Submitted in Partial Fulfillment of the Requirements
for the Degree of
Master of Science
in the
Chemistry
Program

Inally Mahadeviah June 17, 1977
Adviser Date

Leon Rand June 21, 1977
Dean of the Graduate School Date

YOUNGSTOWN STATE UNIVERSITY
August, 1977

YOUNGSTOWN STATE UNIVERSITY

Graduate School

THESIS

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PRESENTED BY **Sarala Kumari Prem**

ACCEPTED BY THE DEPARTMENT OF **Chemistry**

Inally Mahadeviah June 17, 1977
Major Professor Date

Richard C. Phillips June 17, 1977
Date

James A. Reeder June 17, 1977
Date

Leon Rand June 21, 1977
Dean, Graduate School Date

# ABSTRACT

## CONDUCTANCE AND VISCOSITY STUDIES OF TETRABUTYLAMMONIUM IODIDE AND POTASSIUM IODIDE IN FORMAMIDE

Sarala Kumari Prem
Master of Science
Youngstown State University, 1977

Conductance studies of tetrabutylammonium iodide and potassium iodide solutions in formamide were made at temperatures of 10°C, 27°C, 40°C and 50°C over a series of concentrations ranging from 0.0005 to 0.15N. Formamide is an associated solvent with a high dielectric constant and extensive studies have not been made so far because of the difficulties involved in its purification and preservation. Tetrabutylammonium iodide and potassium iodide provided an interesting study with a common anion but with cations of different sizes and charge densities. Conductance studies revealed that tetrabutylammonium iodide acted as a strong electrolyte whereas potassium iodide behaved as a weak electrolyte. Limiting equivalent conductances of tetrabutylammonium iodide were evaluated using Shedlovsky's equation[a] which compared well with values obtained from using the Fuoss-Onsager equation.[b]

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[a] T. Shedlovsky, J. Amer. Chem. Soc., 54, 1405 (1932).

[b] R. M. Fuoss and Accascina "Electrolytic Conductance", Interscience Publishers, Inc., New York, 1959.

A suitable explanation could not be given for the unusual behavior of potassium iodide in formamide. Though the smaller size and the higher charge density on the potassium ion when compared with that of tetrabutylammonium ion are indications of strong solvation, it is possible that in the case of potassium ion solvation is ion-solvent interaction without the attachment of specific solvent molecules. Hence the less solvated potassium ion permits the close approach of iodide ions resulting in the formation of ion-pairs.

Viscosity studies were conducted for both potassium iodide and tetrabutylammonium iodide at 10°C, 27°C and 40°C over a series of concentration ranges. Studies revealed deviations from linearity from the Jones and Dole equation.[c] These deviations were explained as due to the depolymerization of associated solvent molecules causing a net decrease of viscosity. This decrease in viscosity in these systems was more than the increase in viscosity due to the friction of ions on the solvent molecules, thus causing negative curvatures at low concentrations.

[c] G. Jones and M. J. Dole, J. Amer. Chem. Soc., 51, 2950 (1929).

# ACKNOWLEDGEMENTS

The author wishes to express her indebtedness to Dr. Inally Mahadeviah for his invaluable guidance, encouragement and counseling throughout the period of her graduate study. She also wishes to express her gratitude to Dr. James Reeder and Dr. Richard Phillips for their numerous suggestions and guidance for this research project and for reading this manuscript. Her grateful thanks are due to Dr. Thomas Dobbelstein, the chairman,and all of the faculty members of the department for helping to make the period of her graduate study an enjoyable and positive experience. The award of a graduate teaching assistantship for the spring quarter of 1976 by Dr. Leon Rand, dean of the graduate school, and the department is also gratefully acknowledged. Her grateful thanks are due to Mr. Rodolf Bogiovanni, Mr. Richard Muntean and Mr. Piyush Gokhale who aided her in this research project and to Mr. Dale Manos for his invaluable technical assistance. Thanks are also due to all the graduate students, the office staff, and the stockroom staff for their ready assistance during the period of her graduate study.

Finally the author wishes to thank her husband and the members of her family for being a constant source of encouragement. Her special thanks are due to her sister and brother-in-law, Dr. and Mrs. Nathaniel for their financial aid in pursuing her graduate study in this country.

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# LIST OF SYMBOLS

| SYMBOL | DEFINITION |
|---|---|
| Å | Angstrom |
| A | Viscosity coefficient defined by equation (14) |
| a | Ion size parameter |
| B | Constant defined by Shedlovsky's equation (7) |
| $B'$ | Viscosity $B'$ coefficient defined by equation (14) |
| C | Concentration in gram equivalent per liter of the solution |
| cm | Centimeter |
| D | Dielectric constant |
| d | Density in gram per milliliter |
| E | Theoretical constant defined by Fuoss-Onsager equation |
| g | Gram |
| Hz | Hertz (cycles per second) |
| J | Function defined by Fuoss-Onsager equation |
| K | Dissociation constant |
| M | Molar solution |
| ml | Milliliter |
| N | Normal solution |
| T | Absolute temperature |
| $\alpha$ | Debye-Hückel constant defined by equation (2) |
| $\beta$ | Debye-Huckel constant defined by equation (2) |
| $\Lambda$ | Equivalent conductance |
| $\Lambda_o$ | Limiting equivalent conductance |
| $\Lambda_o'$ | Theoretical equivalent conductance defined by Shedlovsky's equation |

# LIST OF SYMBOLS

| SYMBOL | DEFINITION |
|---|---|
| $\Lambda'$ | Theoretical equivalent conductance defined by Fuoss-Onsager equation |
| $\eta$ | Viscosity |
| $\eta_o$ | Viscosity of the solvent |
| $\eta_r$ | Relative viscosity |

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# CHAPTER I

## INTRODUCTION

The investigation of the properties of solutions of electrolytes has received considerable attention in the recent years with a view to understand the specific factors involved in the solvent-solute interactions.

There is a substantial body of experimental data for conductance studies in nonaqueous solvents. R. M. Fuoss and C. A. Kraus[1] measured the conductance of tetraisoamylammonium nitrate at 25°C in dioxane, water and in a series of mixtures of dioxane and water covering the dielectric constant range of 21 to 80 and found that for mixtures of dielectric constant greater than 44 the salt was completely dissociated.

Brewster and co-workers[2] measured the conductances of halides, nitrates and nitrites of alkali metals in ethanolamine and evaluated the limiting equivalent conductance (equivalent conductance at infinite dilution) and the dissociation constant by Fuoss-Shedlovsky's procedure.[3] They showed that for the three alkali metals lithium, sodium and potassium the conductance was directly related to the crystallographic radius suggesting that the smallest alkali cations were highly solvated due to ion-dipole forces.

French and Glover[4] measured the conductances of seven alkali halides and two tetra alkylammonium salts in the high dielectric constant solvent N-methyl formamide over a wide range of concentrations at 15°C and 25°C. The results were compared with the conductances of the solutions of NaBr and KBr in the solvent of lower dielectric constant N:N-dimethyl formamide. In contrast to the results of N-methyl formamide, the results in N:N-dimethyl formamide showed that the equivalent conductances decreased rapidly with increasing concentration as expected for those ions in a solvent of lower dielectric-constant. They extended their work to similar systems in N-methyl acetamide[5] (dielectric constant 169.7) at more than one temperature covering a wide range of concentrations. Though N-methyl acetamide was found to be a powerful dissociating solvent, plots of equivalent conductance $\Lambda$ vs. square root of concentration $\sqrt{C}$ showed a slight deviation from linearity at higher concentrations. No suitable explanation was given though ion-pair formation was ruled out, as the Bjerrum equation[6,7] would require the sum of ionic radii to be less than that which was obtained in this system. The product of limiting equivalent conductance $\Lambda_0$ and the viscosity of the solvent $\eta_0$ known as the Walden products for the inorganic salts were found to be lower than those in other solvents of high dielectric constants with the exception of HCN. This was explained as due to the higher effective ionic radius of the inorganic cations in N-methyl acetamide solution, resulting from solvation by the large solvent molecule. The high dipole moment of N-methyl acetamide also tended to promote solvation.

Studies of conductance on alkali halides, ammonium and substituted ammonium halides in N-methyl acetamide by Dawson and co-workers[8,9] also point to the conclusion that solvents of high dielectric constants caused complete dissociation of salts. They however reported that alkali metal ions were more highly solvated, and they described solvation here as ion-solvent interaction without the attachment of specific solvent molecules.

Dawson and co-workers[10] also studied the conductance of HCl and KCl in formamide and reported that the plots of equivalent conductance ($\Lambda$) vs. square root of concentration ($\sqrt{C}$) for these solutions resembled those of the same elctrolytes in water in that they approached the limiting slopes from above, indicating complete absence of ion-association. They extended their work to other salts like KI, $Bu_4NI$, NaI, etc.[11] in the same solvent at 25°C between the concentration ranges 0.003 and 0.1N and evaluated their limiting equivalent conductances by Shedlovsky's[12] method. The measurements were, however, done only in the concentrated region because of the difficulties involved in the purification of the solvent and its preservation.

In spite of the numerous difficulties associated with the purification and preservation of formamide of desirable quality, there is need for additional information concerning the properties of solutions of electrolytes in solvents of high dielectric constant like formamide. The objective of the present study is to extend the previous studies using formamide as an electrolytic solvent for KI and $Bu_4NI$ at more than one temperature and concentrations extending to very dilute region. Formamide, an associated solvent with a high dielectric constant is also an excellent solvent for both organic and inorganic salts. Tetra-n-butylammonium iodide and potassium iodide with their common anions but with cations of different sizes and charge densities also provide an interesting study.

Viscosity studies of both potassium iodide and tetrabutylammonium iodide solutions in formamide are also undertaken at temperatures 10°C, 27°C, and 40°C over a series of concentration ranges. This is done in order to study the Walden products and also to test the applicability of the Jones and Dole equation[13] to these systems.

# CHAPTER II

# THEORY

## Theory of Conductance

Michael Faraday was the first to recognize the important part played by the ions in the behavior or an electrolytic solution. Fifty years later in the year 1883 Arrhenius proposed his classic electrolytic theory of dissociation, which appears to agree with the data for the weak electrolytes such as acetic acid in water but does not agree with the data for strong electrolytes such as most inorganic salts, strong acids and bases. The difficulty lay in the assumption that the ionic mobilities are independent of concentration.

The first successful attempt to describe the behavior of strong electrolytes was made by Debye and Hückel,[14] who formulated their inter-ionic theory. Accordingly, the properties of solutions are due to the interplay of electrostatic forces and thermal motion. Under equilibrium conditions, the time average distribution of ions in solution produces a symmetrical ionic atmosphere, but when an electric field is applied disturbances upset this. The ion moves from the center of its ionic atmosphere and as a result is subjected to a retarding force. Thermal motions tend to restore the atmosphere to its symmetrical form and position, and the time taken to achieve this is called the time of relaxation, which is extremely small. The average retarding force exerted on the central ion is called the relaxation effect. There is a second force that retards ion motion. It is termed electrophoretic effect and arises from the tendency of an ion to drag along molecules of the solvent through motion. Also since ions of opposite charges move in opposite directions while the applied field operates, an ion does not move through a stationary medium but against a stream of solvent molecules in the other way.

Although both these effects were considered in a treatment of conductance by Debye and Hückel, a more useful analysis was produced by Onsager[15] and Onsager and Fuoss[16] between the years 1927 and 1930.

Kohlrausch observed empirically that the conductances of dilute solutions of strong electrolytes follow the relation

$$\Lambda = \Lambda_o - K\sqrt{C} \tag{1}$$

in which K is a constant, C is the concentration, $\Lambda$ is equivalent conductance at a given concentration, and $\Lambda_o$ is the conductance at infinite dilution.

Based on Kohlrausch data, Onsager[17] derived the quantitative equation for the conductance of very dilute electrolytic solutions.

$$\Lambda = \Lambda_o - (\alpha\Lambda_o + \beta)\sqrt{C} \tag{2}$$

where C is the concentration, and $\alpha$ and $\beta$ are constants which depend upon the nature of the solvent and the temperature

$$\alpha = \frac{8.20 \times 10^5}{(DT)^{3/2}} \tag{3}$$

$$\beta = \frac{82.5}{(DT)^{1/2}\,\eta} \tag{4}$$

where D is the dielectric constant at the absolute temperature T and $\eta$ is the viscosity.

Onsager showed that equation (2) is the limiting relation between equivalent conductance $\Lambda$ and the concentration C for strong electrolytes. The validity of the above equation was tested by Shedlovsky[18, 19] by making careful measurements of conductance at salt concentrations as low as 0.0003 N. The values of the limiting conductance $\Lambda_o$ were computed by rearranging equation (2) as

$$\Lambda_o = \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} \qquad (5)$$

The equivalent conductances of a number of typical uni-univalent strong electrolytes were plotted against the square root of concentration as abscissae. A plot of Onsager's equation for these electrolytes showed that a straight line was obtained in each case with a slope equal to $\alpha\Lambda_o + \beta$ indicating that the equation was valid up to a concentration of about 0.001 M above which concentration there was a slight definite upward deviation. This fact is important as it lends support to the interionic attraction theory. The above theory is of greater utility in dealing with the results of measurements of salt solutions in non-aqueous solvents than it has been for corresponding aqueous solutions. Careful studies of the conductances of electrolytes in methyl alcohol and ethyl alcohol carried out by Hartley and associates[20, 21] followed equation (1) at least for dilute solutions. But in most cases the value of K was considerably greater than that predicted by Onsager's equation, equation (2).

An empirical equation applicable to solutions of strong uni-univalent electrolytes up to about 0.1 N was presented by Shedlovsky[22] in the form

$$\frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} = \Lambda_o + BC \qquad (6)$$

in which B is an empirical constant. For the conductances of solutions of a great number of uni-univalent electrolytes the equation (6) expresses the data very nearly within the experimental error up to a concentration of 0.1N.

### Evaluation of Limiting Equivalent Conductance

When accurate data on equivalent conductances are available at low concentrations, a simple graphical method to obtain $\Lambda_o$ is to follow Kohlrausch's early suggestion of plotting values of equivalent conductances $\Lambda$ vs square root of concentration $\sqrt{C}$ then evaluating $\Lambda_o$ from the $\Lambda$ intercept at C equal to zero. The resulting line for strong electrolytes at low concentrations has, in general, very nearly the slope required by Onsager's equation. The difficulty with the method is that greatest weight is given to the data obtained in very dilute solutions where the experimental errors are the greatest.

Another method also based on the assumption that Onsager's equation is the true limiting relation, depends on Shedlovsky's rearrangement of equation (6) which is given as

$$\Lambda_o' = \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} = \Lambda_o + BC \qquad (7)$$

The method of extrapolation consists in plotting values of $\Lambda_o'$

defined by equation (7) against concentration C then extrapolating that plot to C equal zero.

The value of $\Lambda_o$ obtained by the above method can be further checked by adapting the conductance equation of Fuoss and Onsager[23] for unassociated 1:1 electrolytes which is given as

$$\Lambda = \Lambda_o - SC^{\frac{1}{2}} + EC \log C + JC \qquad (8)$$

where S is related to Onsager coefficients $\alpha$ and $\beta$. E is a constant defined by the same variable as S, and J is a function of ion size. The values of S, and E are computed from the values given by the authors[23] as

$$S = \alpha\Lambda_o + \beta \qquad (9)$$

where $\alpha$ and $\beta$ are Onsager's coefficients.

$$E = E_1 \Lambda_o - E_2 \qquad (10)$$

where $$E_1 = \frac{6.7747 \times 10^{12}}{D^3 T^3} \qquad (11)$$

and $$E_2 = \frac{0.9977 \times 10^{8}}{\eta D^2 T^2} \qquad (12)$$

The procedure for evaluating the final value of $\Lambda_o$ is to get the first approximation of $\Lambda_o$ of Shedlovsky's method as already suggested and then using this value to compute the values of E and S in equations (9) and (10). The equation (8) can be reduced to the linear form

$$\Lambda' = \Lambda + SC^{\frac{1}{2}} - EC \log C = \Lambda_o + J(a)C \qquad (13)$$

where $\Lambda'$ is essentially the observed conductance and J is an explicit function of 'a', where 'a' is the ion size parameter. The values of $\Lambda'$ given by (13) are plotted against concentration.

The intercept gives the final value of $\Lambda_o$ and the slope determines J(a). The object of using the above method is only the evaluation of $\Lambda_o$. If the intercept differs too much from Shedlovsky's value the cycle of operations may be repeated.

## Theory of Viscosity

Viscosity, the force required to produce unit rate of shear between two layers separated by unit distance, is an important property of liquids. With the development of interionic theory much of the interest in this subject has been directed towards accurate determinations of the viscosities of dilute solutions of electrolytes, and the interpretation of the results. Grüneisen[24] appears to have been the first to make very accurate measurements of viscosities at high dilutions, and he showed in contradiction to the earlier views, that the viscosity is not a linear function of the concentration in dilute solutions. The departure from linearity increases rapidly as the concentration is reduced. This behavior of electrolytes has been termed as Grüneisen effect[25]. This effect is absent in solutions of non-electrolytes.

It was shown experimentally by Jones and Dole[26] that the relative viscosities of solutions of strong electrolytes vary with the square root of concentration at high dilutions. It was pointed out that the viscosities of many solutions can be represented by the equation

$$\eta_{rel} = \eta/\eta_o = 1 + A\sqrt{C} + B'C \qquad (14)$$

up to a concentration of 0.1N.

Where $\eta_{rel}$ is the relative viscosity, $\eta$ is the viscosity of the solution, $\eta_o$ is the viscosity of the pure solvent and C is the concentration in moles per liter; A and $B'$ are constants. The coefficient $B'$ is usually referred in the literature as the "Viscosity $B'$-coefficient". It is a measure of the order or disorder introduced by the ions into their cospheres, although no satisfactory theoretical treatment has yet been given[27]. A positive $B'$-coefficient indicates that the ions tend to order the solvent structure and increase the viscosity of the solution while a negative $B'$-coefficient indicates disordering and a decrease of viscosity. Negative $B'$-coefficient values have been obtained for many salts composed of large, relatively unhydrated ions at low temperatures. On the other hand the observed temperature coefficients of $B'$ are always positive so that the effect of salts at high temperature would be to increase the viscosity of the solution throughout the entire range of the concentration up to 0.1N.

The constant A varies less with the temperature. It probably represents the stiffening effect on the solution, of the electric forces between the ions which tend to maintain a space lattice structure. It is negative for all strong electrolytes and zero for non-electrolytes. The numerical values can however be obtained from

$$\eta/\eta_o - 1 / \sqrt{C} = A + B' \sqrt{C} \qquad (15)$$

which applies to solutions of a single electrolytes dissociating into only two kinds of ions.

# CHAPTER III

# EXPERIMENTAL PROCEDURE

## Measurement of Conductance

The conductance measurements were carried on a conductivity bridge of line operated model RC-1682. The bridge was built in a single unit, compact and portable. Voltage for the amplifier, oscillator and null duplicator was provided by a built in D.C. power supply. The model was provided with scales which could be used for measuring resistance as well as conductance. The calibration accuracy of the scale was within ±1% of the reading overall except at the extreme ends of the scale. A bridge frequency of 1000Hz was made use of during measurements.

## Temperature Control

Conductance determinations at 27°C, 40°C and 50°C were done in separate oil baths equipped with mercury thermo regulators and stirrers. The oil used in the bath was white mineral oil supplied by Sargent Welsh. The oil had a specific gravity of 0.85 and a viscosity of 185 saybolt. Conductance measurements at 10°C were made in a constant flow portable cooling unit provided with a microtrol controlling thermostat and a memory dial. During measurements the temperatures of the baths were maintained within the limits of ±0.02°C.

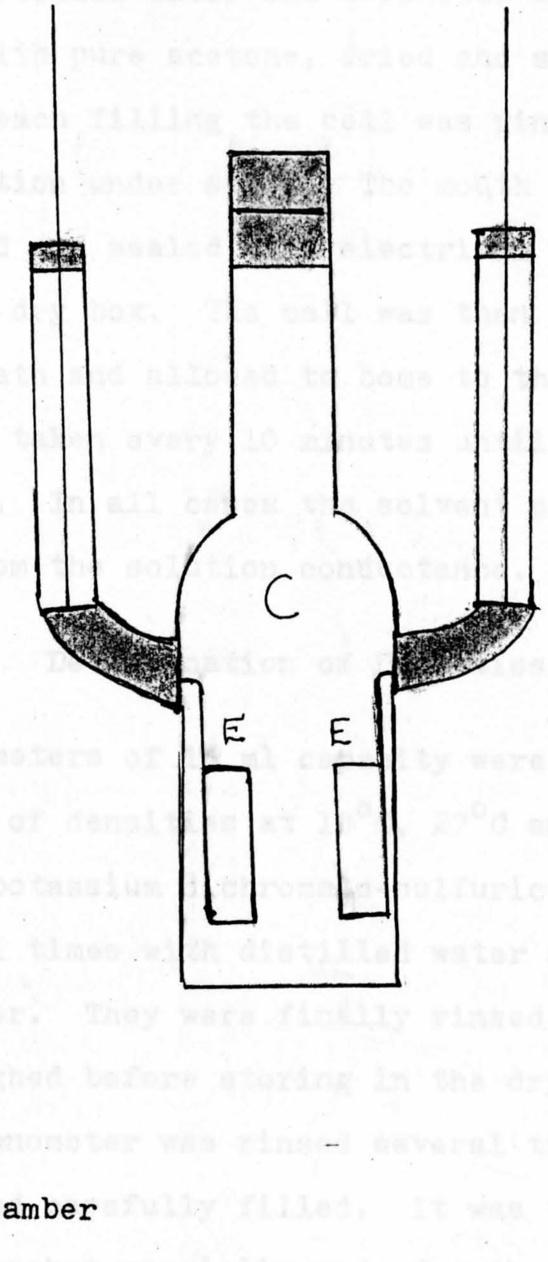
## Conductance Cell

The conductance cell used in this work was designed as shown in the Figure 1. It was made of pyrex glass with a mixing chamber of about 25 ml capacity. The electrodes were lightly platinized using the standard procedure[28]. The cell constant was determined with 0.01N potassium chloride solution using the specific conductivity values and procedure of Jones and Bradshaw[29]. The potassium chloride used in this work was "Fisher Reagent Grade" supplied by Fisher Scientific Company. The salt was dried at 150°C overnight and cooled in a vacuum desiccator. Exactly 0.7440 g of the salt was weighed out and dissolved in deionized water and made up to 1000 ml in a measuring flask. Cell constants were experimentally determined at each of the following temperatures viz; 10°C, 27°C, 40°C and 50°C, from the specific conductance values of 0.01M potassium chloride solution. The values are given in Table 1.

TABLE 1

| Temperature | Specific Conductance of KCl Solution | Cell Constant |
|---|---|---|
| 10°C | 0.00101 | 0.12322 |
| 27°C | 0.001464 | 0.125904 |
| 40°C | 0.001825 | 0.125925 |
| 50°C | 0.002102 | 0.12822 |

Figure 1



E=electrode

C=mixing chamber

## Procedure for Taking Measurements

The conductance cell was cleaned with potassium dichromate-sulfuric acid cleaning solution and washed several times with distilled water and deionized water. Then it was rinsed well with pure acetone, dried and stored in the dry box. Before each filling the cell was rinsed several times with the solution under study. The mouth of the cell was then stoppered and sealed with electrical tape before taking it out of the dry box. The cell was then placed in the appropriate bath and allowed to come to thermal equilibrium. Readings were taken every 10 minutes until constant values were obtained. In all cases the solvent conductance was subtracted from the solution conductance.

## Determination of Densities

Pycnometers of 15 ml capacity were used for the determination of densities at 10°C, 27°C and 40°C. They were cleaned with potassium dichromate-sulfuric acid solution, washed several times with distilled water and then with deionized water. They were finally rinsed, with dry acetone, dried and weighed before storing in the dry box. Before each filling, a pycnometer was rinsed several times with the solution under study and carefully filled. It was then transferred to a small wire basket specially made for the purpose and suspended in the appropriate bath for 15 minutes and allowed to come to the temperature. It was then taken out, carefully dried and placed in the desiccator for 10 minutes, before weighing. The apparatus was allowed to remain in the balance chamber for a few more minutes and the weighing was repeated until constant weight was obtained. Extreme care had to be taken and the experiment had to be repeated several times during the determination of densities as the difference in densities between two solutions was very small in the low concentration ranges.

### Viscosity Measurements

The viscosity determinations were done at 10°C, 27°C and 40°C according to the recommendations set forth by the American Society for Testing Materials.[30] The differences in the viscosities of these dilute solutions were very small and great care was taken to make accurate measurements. Only one viscometer was used for all the measurements. The viscometer used in this work was of Cannon-Fenske type, model 100 F474. The usual precautions as already mentioned were taken in the cleaning and filling operations. Ten ml of the solution was pipetted into the apparatus in each case. The apparatus was sealed with electrical tape before taking it out of the dry box and then placed in the appropriate bath for ten minutes. The tape was then removed and the measurements were done in as short time as possible in order to avoid errors due to the absorption of moisture. The viscometer constants at 100°F and 210°F were given by the manufacturers as 0.01490 and 0.01483 centistokes per second, respectively. The viscometer constants at other temperatures were computed by extrapolation or intrapolation. The computed values used in this work are as given in Table 2.

TABLE 2

| Viscometer Number | Temperature | Viscometer Constant |
|---|---|---|
| 100F 474 | 10°C | 0.014937 |
| 100F 474 | 27°C | 0.014918 |
| 100F 474 | 40°C | 0.0148934 |

The timing device used for viscosity measurements was a spring operated stopwatch supplied by Sargent Welsch Scientific Company, model S-77440, which could be read to the nearest 0.02 second. The same stopwatch was used for all measurements. Its accuracy was checked against time signals broadcast by the National Bureau of Standards station.

### Temperature Control

The viscosity measurements were made in water baths equipped with a mercury thermoregulator and relay. During measurements the temperature of the bath did not vary more than ±0.02°C.

### Purification of the Solvent

"Baker" grade formamide made by J. T. Baker Chemical Company, Phillipsburgh, New Jersey 08865 was used as the solvent. This solvent has a dielectric constant of 109.5 at 25°C as reported by Leader,[31] which is one and a half times greater than that of water. It is a colorless, odorless, hygroscopic liquid, denser and more viscous than water. Its freezing point is 2.3°C and it is a good solvent for both inorganic and organic salts. According to Verhoek[32] the pure material is not stable. The conductance increases by a factor of eight or ten in ten days or two weeks and the exposed solvent had a gain of weight of 0.2% in one hour, 1% in five and one half hours and 10% in one hundred and forty hours, indicating an extremely hygroscopic liquid. However, it was found that amounts of water up to 1% had no large effect in either conductometric or potentiometric experiments.

Various attempts to purify the solvent were unsuccessful and hence it was decided to use the "Baker" grade as such and use sufficient precautions to prevent exposure to moisture and air. The sealed bottles were opened only inside the dry box under a positive pressure of nitrogen. Only the stock solution was made in advance and dilution from the stock solution was made each day with the solvent from the freshly opened bottle. Measurements were made the same day for that particular dilution.

## Purification of the Salts

### Potassium Iodide

"Baker analyzed" reagent grade of lot no. 417869 was used. The sample was dried overnight at 140°C and cooled in a vacuum desiccator for four hours before weighing.

### Tetra-n-butylammonium Iodide

"Eastman Kodak" (4702) sample was used. The salt was dried to constant weight in vacuo at 60-65°C. The melting point of 144-145°C checked well with the literature value.[33]

## Preparation of the Solutions

All solutions were prepared in a dry box by transferring a known weight of the salt to calibrated measuring flasks and dissolving it in an exact volume of the solvent. More dilute solutions were made by further dilutions, using calibrated pipettes and burets. Sufficient amounts of solutions of both the salts were prepared and preserved in well stoppered and sealed brown bottles. Measurements of conductance, viscosity and density were made from fresh solutions made each day by dilution of the stock solutions. Transfers of solutions into the conductivity cell, viscosity and pycnometers were done inside the dry box and measurements were done as described earlier.

# CHAPTER IV

# RESULTS AND DISCUSSION

## Conductance Studies of Tetrabutylammonium Iodide

Properties of the solvent are listed in Table 3. The dielectric constant values were obtained from the work of Leader.[34] Results derived from the conductance data for tetrabutylammonium iodide in formamide are summarized in Tables 4, 5, and 6 (p. 22-24). The conductance of each solution was corrected by subtracting the conductance of the solvent and the data represent the averages of duplicate and triplicate determinations. Linear Kohlrausch plots were obtained at each temperature for the concentration ranges 0.015N to 0.15N solutions. Limiting equivalent conductance values were obtained by extrapolation of the plots as indicated in Figure 2 (p. 25). Data obtained at concentration 0.0015N had to be excluded from the plots because of the large solvent correction involved.

Limiting equivalent conductances were also examined by the use of the Shedlovsky rearrangement of the Onsager equation directly from experimental conductance values $\Lambda$, as given in equation (7). Limiting equivalent conductance values calculated in this manner are designated $\Lambda_o'$, and are found to deviate from the true limiting equivalent conductance $\Lambda_o$, by a linear function of the concentration. For tetrabutylammonium iodide this equation takes the forms,

$$\Lambda_o' = \frac{\Lambda + 8{\cdot}7972\ \sqrt{C}}{1-0{\cdot}1388\ \sqrt{C}} = \Lambda_o + BC \qquad (16)$$

$$\Lambda_o' = \frac{\Lambda + 14{\cdot}12735\ \sqrt{C}}{1-0{\cdot}1378\ \sqrt{C}} = \Lambda_o + BC \qquad (17)$$

$$\Lambda_o' = \frac{\Lambda + 19{\cdot}0509\ \sqrt{C}}{1-0{\cdot}1407\ \sqrt{C}} = \Lambda_o + BC \qquad (18)$$

at 10°C, 27°C and 40°C, respectively.

TABLE 3

PROPERTIES OF THE SOLVENT

| T | d | $\eta$ | $L \times 10^4$ | D |
|---|---|---|---|---|
| 10°C | 1.1420 | 0.05187 | 3.943 | 115.5 |
| 27°C | 1.1191 | 0.0322 | 5.917 | 109.5 |
| 40°C | 1.1187 | 0.02406 | 7.807 | 103.5 |
| 50°C | 1.1165 | 0.02025 | 8.5907 | 100.0 |

T=temperature

d=density in g/ml

$\eta$=viscosity in poises

L=specific conductance ($ohm^{-1}\ cm^{-1}$)

D=dielectric constant

## TABLE 4

## CONDUCTANCE DATA OF TETRABUTYLAMMONIUM IODIDE IN FORMAMIDE AT 10°C

| C | $\sqrt{C}$ | $L \times 10^4$ | $\Lambda$ | $\Lambda'_o$ | $\Lambda'$ |
|---|---|---|---|---|---|
| 0.0015105 | $3.887 \times 10^{-2}$ | 0.0616 | 4.0788 | -- | -- |
| 0.015105 | 0.1229 | 1.7867 | 11.83 | 13.135 | 13.06 |
| 0.045315 | 0.2129 | 4.99 | 11.01 | 13.275 | 13.16 |
| 0.075525 | 0.2748 | 8.009 | 10.6 | 13.53 | 13.37 |
| 0.105735 | 0.3252 | 10.72 | 10.14 | 13.61 | 13.42 |
| 0.15105 | 0.3887 | 14.54 | 9.63 | 13.79 | 13.56 |

$\Lambda$ =Equivalent Conductance (mhos $cm^2$ / equi)

$\Lambda'_o$ =Theoretical Conductance from Shedlovsky's equation

$\Lambda'$ =Theoretical Conductance from Fuoss-Onsager equation

L=Specific Conductance ($ohm^{-1}$ $cm^{-1}$)

C=Concentration in g. equivalents per liter

## TABLE 5

## CONDUCTANCE DATA OF TETRABUTYLAMMONIUM IODIDE IN FORMAMIDE AT 27°C

| C | $\sqrt{C}$ | L x $10^4$ | $\Lambda$ | $\Lambda'_o$ | $\Lambda'$ |
|---|---|---|---|---|---|
| 0.0015105 | 3.887 x $10^{-2}$ | 0.1259 | 8.335 | -- | -- |
| 0.015105 | 0.1229 | 3.0226 | 20.0046 | 22.13 | 22.19 |
| 0.045315 | 0.2129 | 8.56 | 18.8932 | 22.58 | 22.69 |
| 0.075525 | 0.2748 | 13.283 | 17.5874 | 22.34 | 22.51 |
| 0.105735 | 0.3252 | 17.375 | 16.4324 | 22.05 | 22.25 |
| 0.15105 | 0.3887 | 23.04 | 15.2535 | 21.96 | 22.21 |

$\Lambda$ =Equivalent Conductance (mhos.cm$^2$ / equi.)

$\Lambda'_o$ =Theoretical Conductance from Shedlovsky's equation

$\Lambda'$ =Theoretical Conductance from Fuoss-Onsager equation

L=Specific Conductance (ohm$^{-1}$ cm$^{-1}$)

C=Concentration in g. equivalents per liter

## TABLE 6

### CONDUCTANCE DATA OF TETRABUTYLAMMONIUM IODIDE IN FORMAMIDE AT 40°C

| C | $\sqrt{C}$ | $L \times 10^4$ | $\Lambda$ | $\Lambda'_o$ | $\Lambda'$ |
|---|---|---|---|---|---|
| 0.0015105 | $3.887 \times 10^{-2}$ | 0.2518 | 16.67 | -- | -- |
| 0.015105 | 0.1229 | 4.004 | 26.68 | 29.53 | 29.65 |
| 0.045315 | 0.2129 | 12.026 | 26.54 | 30.596 | 31.72 |
| 0.075525 | 0.2748 | 18.637 | 23.01 | 29.38 | 31.34 |
| 0.105735 | 0.3252 | 23.674 | 22.39 | 29.96 | 30.33 |
| 0.15105 | 0.3887 | 31.229 | 20.67 | 29.16 | 29.63 |

$\Lambda$ =Equivalent Conductance (mhos $cm^2$ / equi.)

$\Lambda'_o$ =Theoretical Conductance from Shedlovsky's equation

$\Lambda'$ =Theoretical Conductance from Fuoss-Onsager equation

L=Specific Conductance ($ohm^{-1}$ $cm^{-1}$)

C=Concentration in g. equivalents per liter

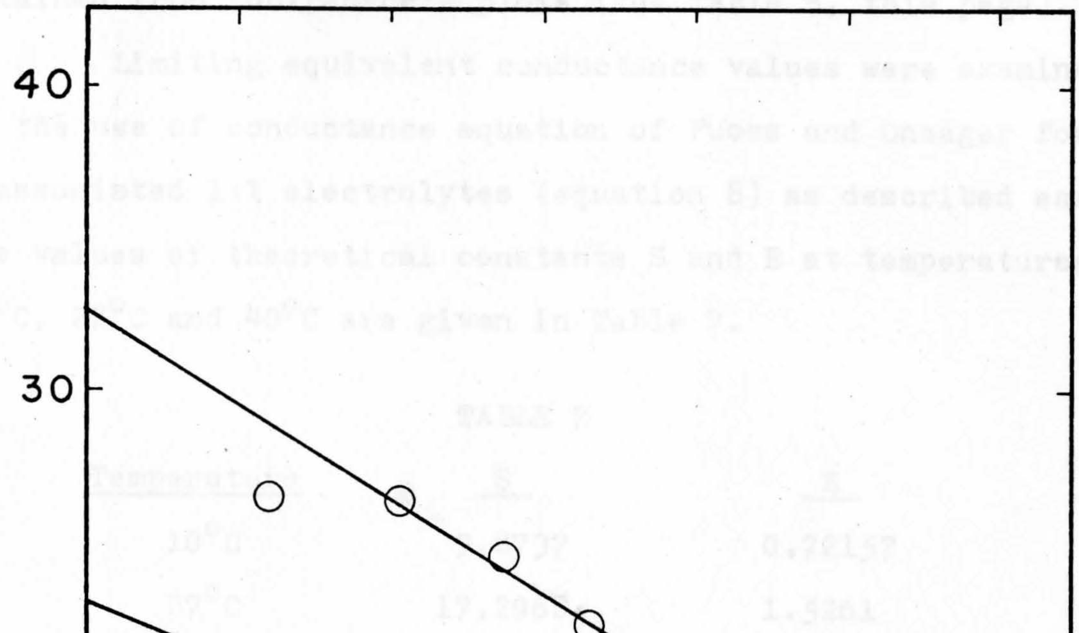


Fig. 2. Kohlrausch Plots. Equivalent conductance of Tetrabutylammonium iodide in formamide versus square root of concentration. The triangles, hexagons and the circles correspond to 10°C, 27°C and 40°C, respectively.

Linear plots were obtained at each temperature by plotting $\Lambda_0'$ vs C as indicated in Figure 3 (p. 27). Intercepts gave the values of $\Lambda_0$ which closely correspond with the values obtained from Kohlrausch's plots (see Table 8, this page).

Limiting equivalent conductance values were examined by the use of conductance equation of Fuoss and Onsager for unassociated 1:1 electrolytes (equation 8) as described earlier. The values of theoretical constants S and E at temperatures 10°C, 27°C and 40°C are given in Table 7.

TABLE 7

| Temperature | S | E |
|---|---|---|
| 10°C | 9.8737 | 0.72157 |
| 27°C | 17.2968 | 1.5261 |
| 40°C | 23.6096 | 2.506 |

Values of limiting equivalent conductances derived by this method (Figure 4, p. 28) closely agree with the values obtained from the other methods. A comparison of $\Lambda_0$ obtained from different methods are as in Table 8.

TABLE 8

COMPARISON OF $\Lambda_0$ FROM DIFFERENT METHODS

| Temperature | Kohlrausch | Shedlovsky | Fuoss-Onsager |
|---|---|---|---|
| 10°C | 12.5 | 13 | 13 |
| 27°C | 23 | 23 | 23 |
| 40°C | 32.75 | 32.5 | 32.5 |

The limiting equivalent conductance value obtained at 27°C closely corresponded with the value 23.37 obtained

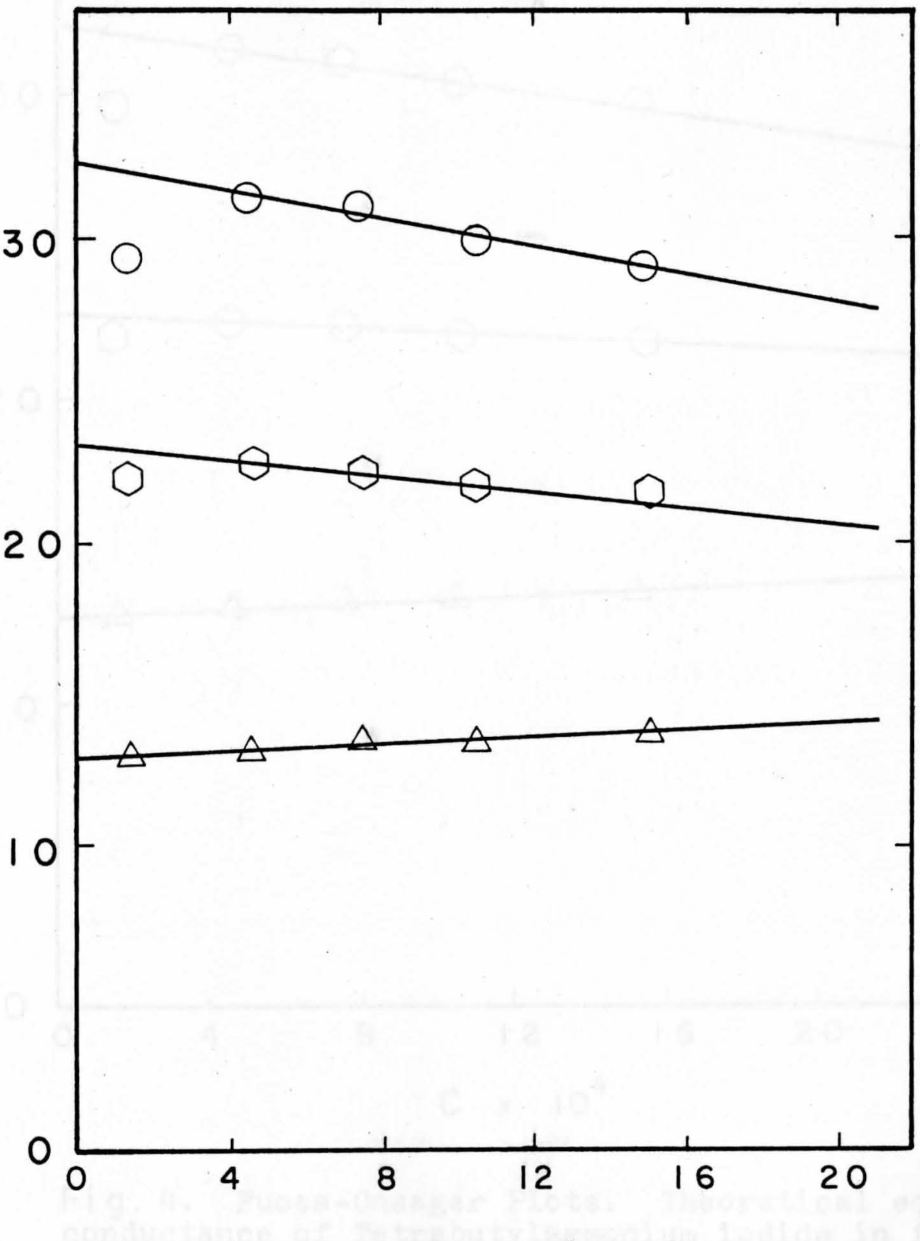


Fig. 3. Shedlovsky's Plots. Theoretical equivalent conductance of Tetrabutylammonium iodide in formamide versus concentration. The triangles, hexagons and the circles correspond to 10°C, 27°C and 40°C, respectively.

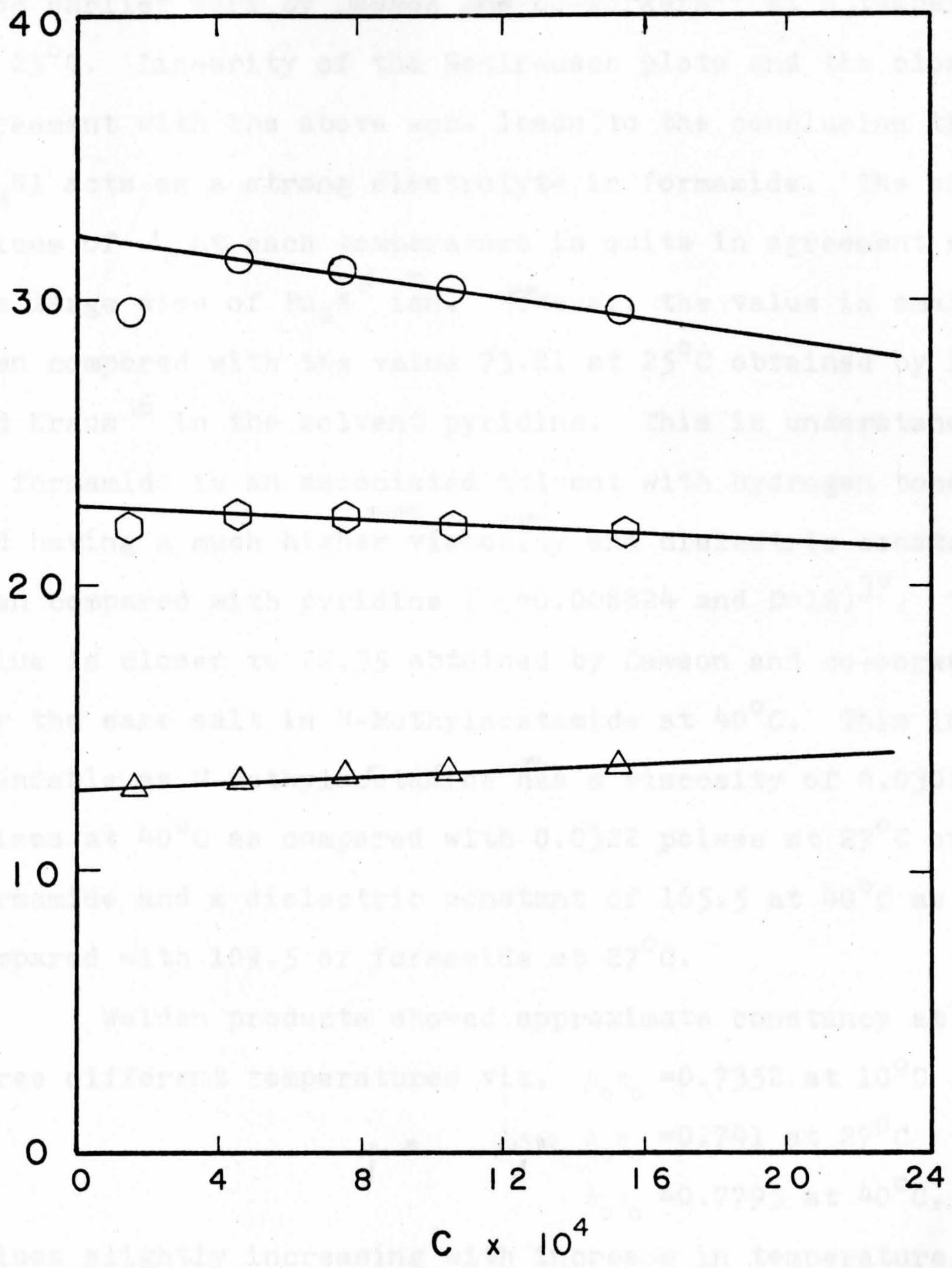


Fig. 4. Fuoss-Onsager Plots. Theoretical equivalent conductance of Tetrabutylammonium iodide in formamide versus concentration. The triangles, hexagons and circles correspond to 10°C, 27°C and 40°C, respectively.

from earlier work by Dawson and co-workers[35] at a temperature of 25°C. Linearity of the Kohlrausch plots and the close agreement with the above work leads to the conclusion that $Bu_4NI$ acts as a strong electrolyte in formamide. The small values of $\Lambda_o$ at each temperature is quite in agreement with the large size of $Bu_4N^+$ ion. However, the value is smaller when compared with the value 73.21 at 25°C obtained by Luder and Kraus[36] in the solvent pyridine. This is understandable as formamide is an associated solvent with hydrogen bonding and having a much higher viscosity and dielectric constant when compared with pyridine ( $\eta$=0.008824 and D=12)[37]. The value is closer to 22.35 obtained by Dawson and co-workers[38] for the same salt in N-Methylacetamide at 40°C. This is understandable as N-Methylacetamide has a viscosity of 0.0302 poises at 40°C as compared with 0.0322 poises at 27°C of formamide and a dielectric constant of 165.5 at 40°C as compared with 109.5 of formamide at 27°C.

Walden products showed approximate constancy at the three different temperatures viz, $\Lambda_o\eta_o$ =0.7352 at 10°C

$\Lambda_o\eta_o$ =0.741 at 27°C

$\Lambda_o\eta_o$ =0.7795 at 40°C, the

values slightly increasing with increase in temperature. Products of $\bar{\Lambda}$ and $\eta$ also showed an approximate constancy with increase in concentration, which is a further indication that tetrabutylammonium iodide acts as a strong electrolyte (see Figure 5, p. 30 and Tables 9, 10 and 11, p. 31-33).

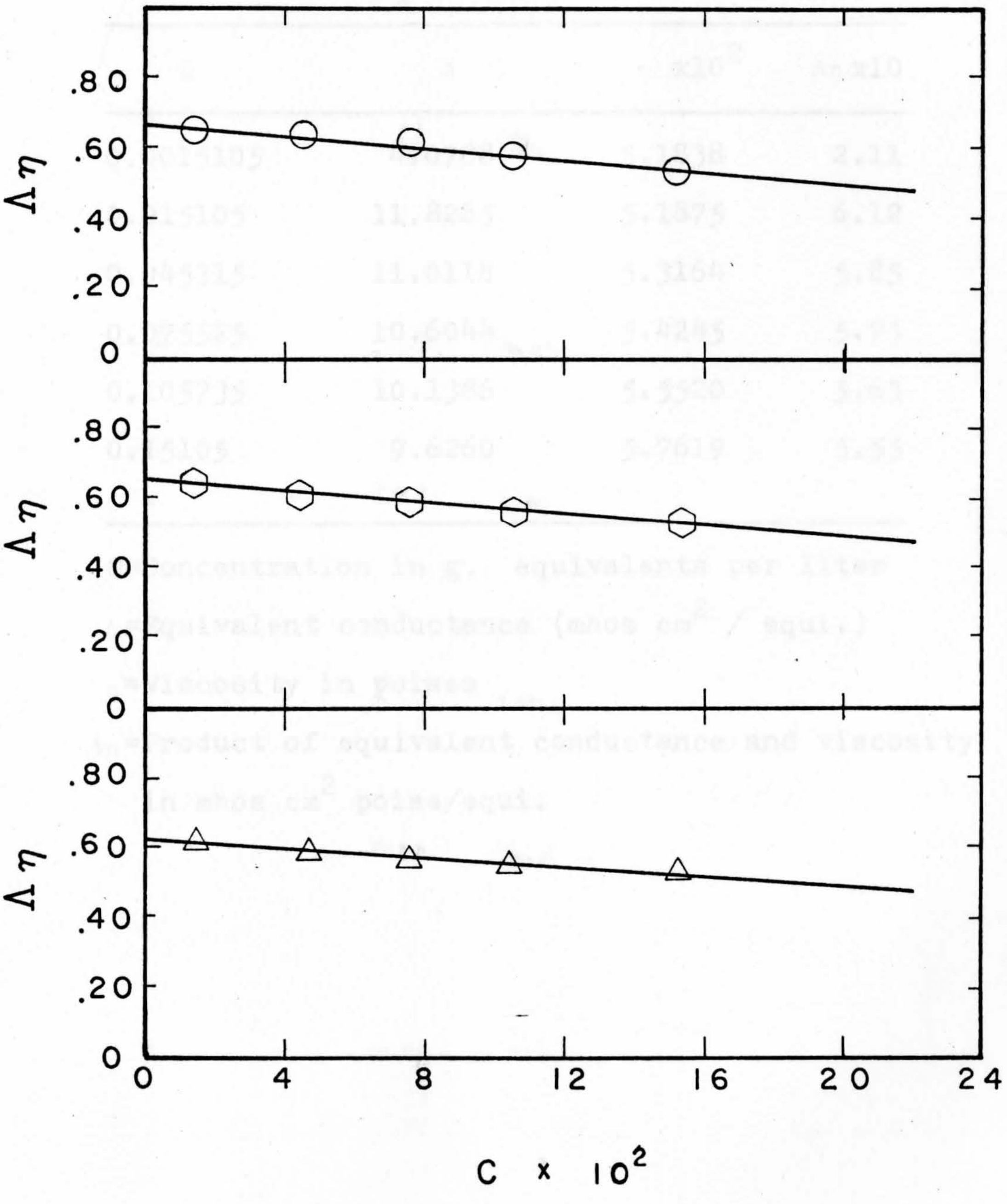


Fig. 5. Product of equivalent conductance and viscosity of Tetrabutylammonium iodide in formamide versus concentration. The triangles, hexagons and the circles correspond to 10°C, 27°C and 40°C, respectively.

## TABLE 9

## CONDUCTANCE AND VISCOSITY OF TETRABUTYLAMMONIUM IODIDE IN FORMAMIDE AT $10^{o}C$

| C | $\Lambda$ | $\eta$ x$10^2$ | $\Lambda\eta$ x10 |
|---|---|---|---|
| 0.0015105 | 4.0788 | 5.1838 | 2.11 |
| 0.015105 | 11.8285 | 5.1875 | 6.12 |
| 0.045315 | 11.0118 | 5.3164 | 5.85 |
| 0.075525 | 10.6044 | 5.4245 | 5.75 |
| 0.105735 | 10.1386 | 5.5520 | 5.63 |
| 0.15105 | 9.6260 | 5.7619 | 5.55 |

C=Concentration in g.. equivalents per liter

$\Lambda$=Equivalent conductance (mhos $cm^2$ / equi.)

$\eta$=Viscosity in poises

$\Lambda\eta$=Product of equivalent conductance and viscosity in mhos $cm^2$ poise/equi.

## TABLE 10

## CONDUCTANCE AND VISCOSITY OF TETRABUTYLAMMONIUM IODIDE IN FORMAMIDE AT 27°C

| C | $\Lambda$ | $\eta$ x10$^2$ | $\Lambda\eta$ x10 |
|---|---|---|---|
| 0.0015105 | 8.335 | 3.2369 | 2.70 |
| 0.015105 | 20.0046 | 3.2503 | 6.50 |
| 0.045315 | 18.8932 | 3.2645 | 6.05 |
| 0.075525 | 17.5874 | 3.3521 | 5.90 |
| 0.105735 | 16.4324 | 3.4182 | 5.62 |
| 0.15105 | 15.2535 | 3.550 | 5.42 |

C=Concentration in g.. equivalents per liter

$\Lambda$ =Equivalent conductance (mhos cm$^2$ / equi.)

$\eta$ =Viscosity in poises

$\Lambda\eta$ =Product of conductance and viscosity (mhos cm$^2$ poise/equi.)

## TABLE 11

## CONDUCTANCE AND VISCOSITY OF TETRABUTYLAMMONIUM IODIDE IN FORMAMIDE AT 40°C

| C | $\Lambda$ | $\eta$ x$10^2$ | $\Lambda\eta$ x10 |
|---|---|---|---|
| 0.0015105 | 16.670 | 2.4226 | 4.04 |
| 0.015105 | 26.680 | 2.4354 | 6.51 |
| 0.045315 | 26.5383 | 2.4533 | 6.50 |
| 0.075525 | 23.010 | 2.5128 | 5.92 |
| 0.105735 | 22.39 | 2.5727 | 5.76 |
| 0.15105 | 20.675 | 2.5960 | 5.38 |

C=Concentration in gm. equivalents per liter

$\Lambda$ =Equivalent conductance (mhos $cm^2$ / equi.)

$\eta$ =Viscosity in poises

$\Lambda\eta$ =Product of conductance and viscosity in mhos $cm^2$ poise/equi.

## Conductance Studies of Potassium Iodide

Tables 12, 13, 14 and 15 (p. 36-38) give the conductance data of potassium iodide in formamide at 10°C, 27°C, 40°C and 50°C in the concentration ranges 0.0005N to 0.15N solutions. Deviation from linearity of plots of $\Lambda$ vs $\sqrt{C}$ and the steep curves obtained (see Figures 6 and 7, p. 40-41) indicate that potassium iodide acts as a weak electrolyte at these temperatures. The plot of 10°C is not as steep as at other temperatures, probably due to the high viscosity of the solutions (more than 0.05 poises) at 10°C.

This behavior of potassium iodide is quite in contrast to the earlier work done in other solvents of high dielectric constants by Dawson and co-workers[39] and by French and Glover[40,41] whose data showed complete dissociation of salts even at appreciable concentrations. The results of the present work could not, however, be ignored, as the differences between the solvent and the solution conductances were too large to attribute the effect to the large solvent correction. An error analysis showed that the solvent corrections were well within the experimental error.

It was also not possible to compare the present data with the work done by Dawson and co-workers[42] in the same solvent, as their measurements were done only at higher concentrations and also the studies were conducted at only one temperature, viz 25°C. However, the linear portion of Shedlovsky's plot when extrapolated (see Figure 8, p. 42) gave a value of 28.25 at 27°C which compared well with the limiting equivalent conductance value of 29.31 obtained at 25°C for a similar plot by Dawson and co-workers. Limiting equivalent conducance values obtained at different temperatures are as in Table 16 (p. 43).

### TABLE 12

### CONDUCTANCE DATA OF POTASSIUM IODIDE IN FORMAMIDE AT 10°C

| C | $\sqrt{C} \times 10^2$ | $L \times 10^4$ | $\Lambda$ | $\Lambda_0'$ |
|---|---|---|---|---|
| 0.0005804 | 2.4089 | 0.154 | 26.54 | -- |
| 0.005804 | 7.618 | 1.066 | 18.37 | 19.19 |
| 0.0087054* | 9.330 | 1.417 | 16.28 | 17.32 |
| 0.011607* | 10.77 | 1.940 | 16.72 | 17.94 |
| 0.023214* | 15.24 | 4.313 | 16.45 | 18.18 |
| 0.043156* | 20.77 | 7.147 | 16.56 | 18.93 |
| 0.14626 | 38.24 | 22.55 | 16.63 | 20.49 |

*Concentrations used for evaluation of limiting equivalent conductance.

$\Lambda$ = Equivalent conductance

$\Lambda_0'$ = Theoretical conductance from Shedlovsky's equation

L=Specific conductance ($ohm^{-1}$ $cm^{-1}$)

C=Concentration in g. equivalents per liter

## TABLE 13

## CONDUCTANCE DATA OF POTASSIUM IODIDE IN FORMAMIDE AT 27$^{o}$C

| C | Cx$10^2$ | Lx$10^4$ | $\Lambda$ | $\Lambda_o'$ |
|---|---|---|---|---|
| 0.0005804 | 2.4089 | 2.633 | 453.73 | -- |
| 0.00174108 | 4.1725 | 2.849 | 163.642 | -- |
| 0.002902 | 5.387 | 3.19 | 109.92 | -- |
| 0.0040625 | 6.3738 | 3.485 | 85.6985 | -- |
| 0.005223 | 7.227 | 3.987 | 76.34 | -- |
| 0.005804 | 7.618 | 1.633 | 28.14 | 29.53 |
| 0.0087954* | 9.330 | 2.329 | 26.76 | 28.44 |
| 0.023214* | 15.24 | 6.1063 | 26.52 | 29.29 |
| 0.043156* | 20.77 | 11.457 | 26.55 | 30.35 |
| 0.14626 | 38.24 | 23.418 | 24.62 | 31.69 |

*Concentrations used for evaluation of limiting equivalent conductance.

$\Lambda$ =Equivalent conductance

$\Lambda_o'$=Theoretical conductance from Shedlovsky's equation

L=Specific conductance (ohm$^{-1}$ cm$^{-1}$)

C=Concentration in g. equivalents per liter

## TABLE 14

## CONDUCTANCE DATA OF POTASSIUM IODIDE IN FORMAMIDE AT 40°C

| C | $\sqrt{C}x10^2$ | $Lx10^4$ | $\Lambda$ | $\Lambda_o'$ |
|---|---|---|---|---|
| 0.0005804 | 2.4089 | 3.3382 | 575.65 | -- |
| 0.00174108 | 4.1725 | 4.0928 | 235.08 | -- |
| 0.002902 | 5.387 | 3.965 | 136.63 | -- |
| 0.0040625 | 6.3738 | 4.717 | 116.187 | -- |
| 0.005223 | 7.227 | 5.436 | 104.07 | -- |
| 0.005804 | 7.618 | 2.2289 | 39.445 | 40.896 |
| 0.0087054* | 9.330 | 3.022 | 34.72 | 36.98 |
| 0.023214* | 15.24 | 8.059 | 34.72 | 38.45 |
| 0.043156* | 20.77 | 15.30 | 35.45 | 40.59 |
| 0.14626 | 38.24 | 46.95 | 34.69 | 44.36 |

*Concentration used for evaluation of limiting equivalent conductance.

$\Lambda$ =Equivalent conductance

$\Lambda_o'$ =Theoretical conductance from Shedlovsky's equation

L=Specific conductance ($ohm^{-1}$ $cm^{-1}$)

C=Concentration in g. equivalents per liter

## TABLE 15

## CONDUCTANCE DATA OF POTASSIUM IODIDE IN FORMAMIDE AT 50°C

| C | $\sqrt{C}\times10^2$ | $L\times10^4$ | $\Lambda$ |
|---|---|---|---|
| 0.0005804 | 2.4089 | 3.891 | 671.21 |
| 0.00174108 | 4.1725 | 4.545 | 261.07 |
| 0.002902 | 5.3807 | 4.995 | 172.12 |
| 0.0040625 | 6.3738 | 5.254 | 129.34 |
| 0.005223 | 7.227 | 6.104 | 116.87 |
| 0.005804 | 7.618 | 2.462 | 42.42 |
| 0.023214 | 15.24 | 9.36 | 40.32 |

C=Concentration in gm. equivalents per liter

L=Specific conductance (1/ohm.cm)

$\Lambda$=Equivalent conductance

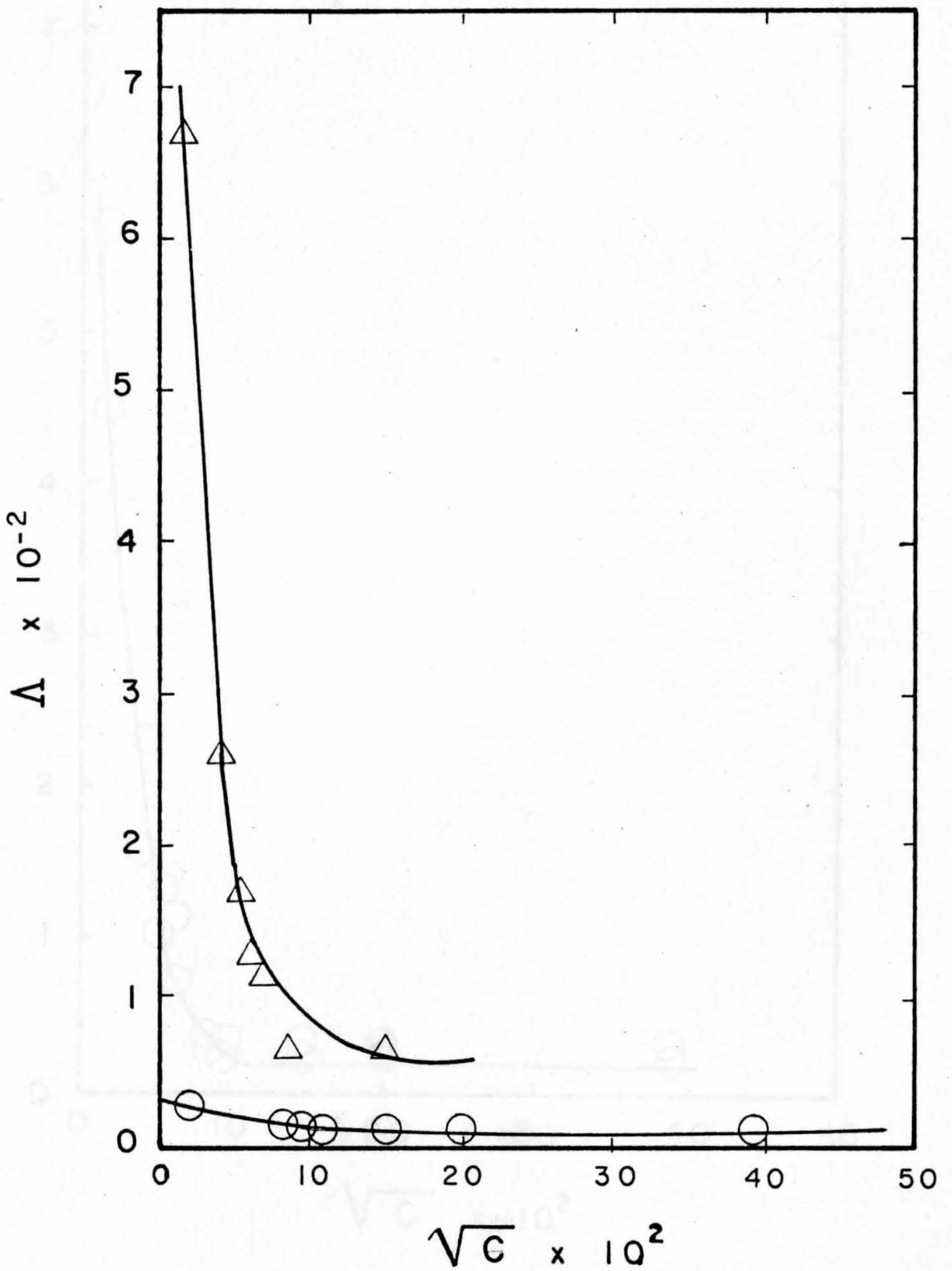


Fig. 6. Kohlrausch Plots. Equivalent conductance of Potassium iodide in formamide versus square root of concentration. The circles and triangles correspond to 10°C and 50°C, respectively.

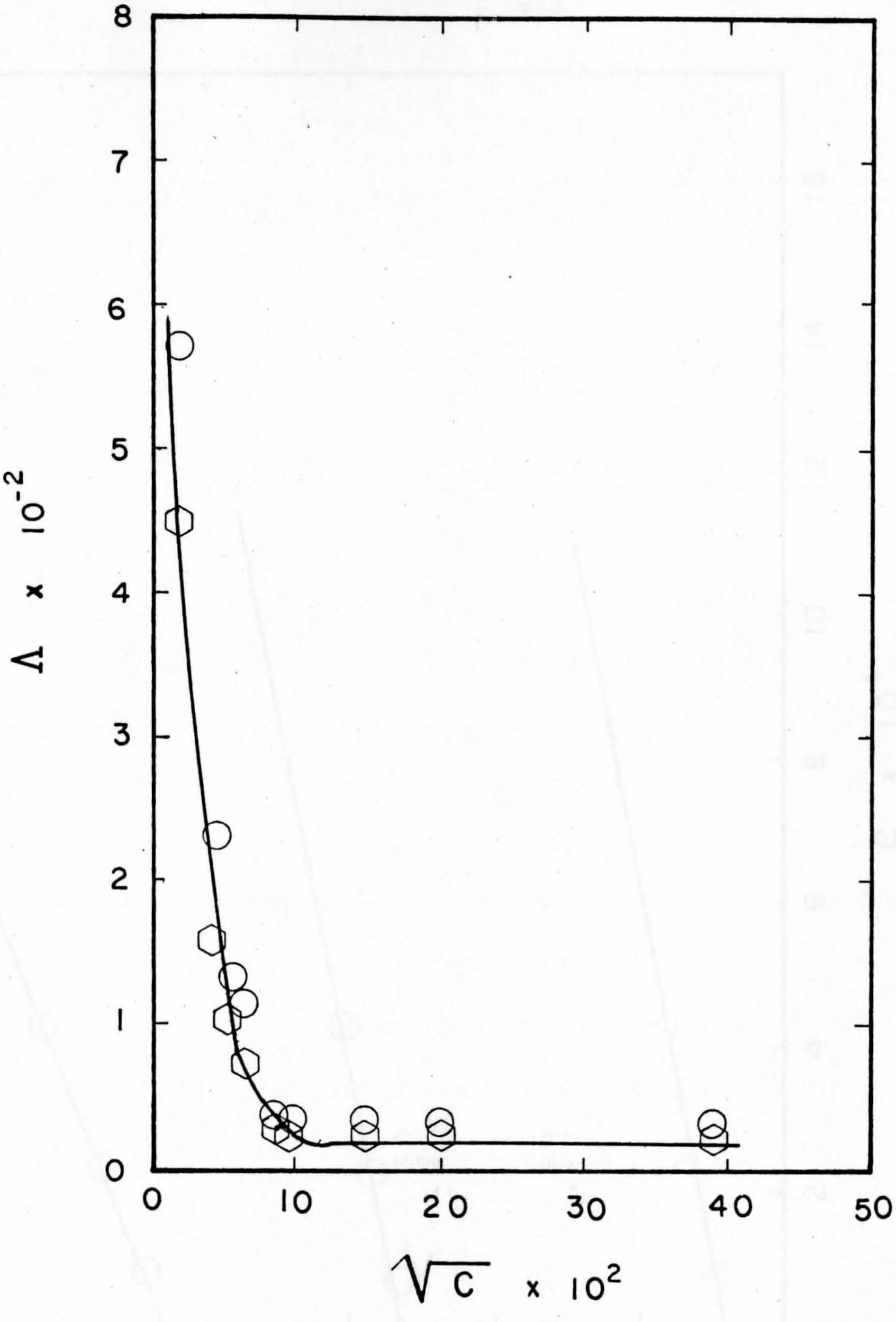


Fig.7. Kohlrausch Plots. Equivalent conductance of Potassium iodide in formamide versus square root of concentration. The hexagons and the circles correspond to 27°C and 40°C, respectively.

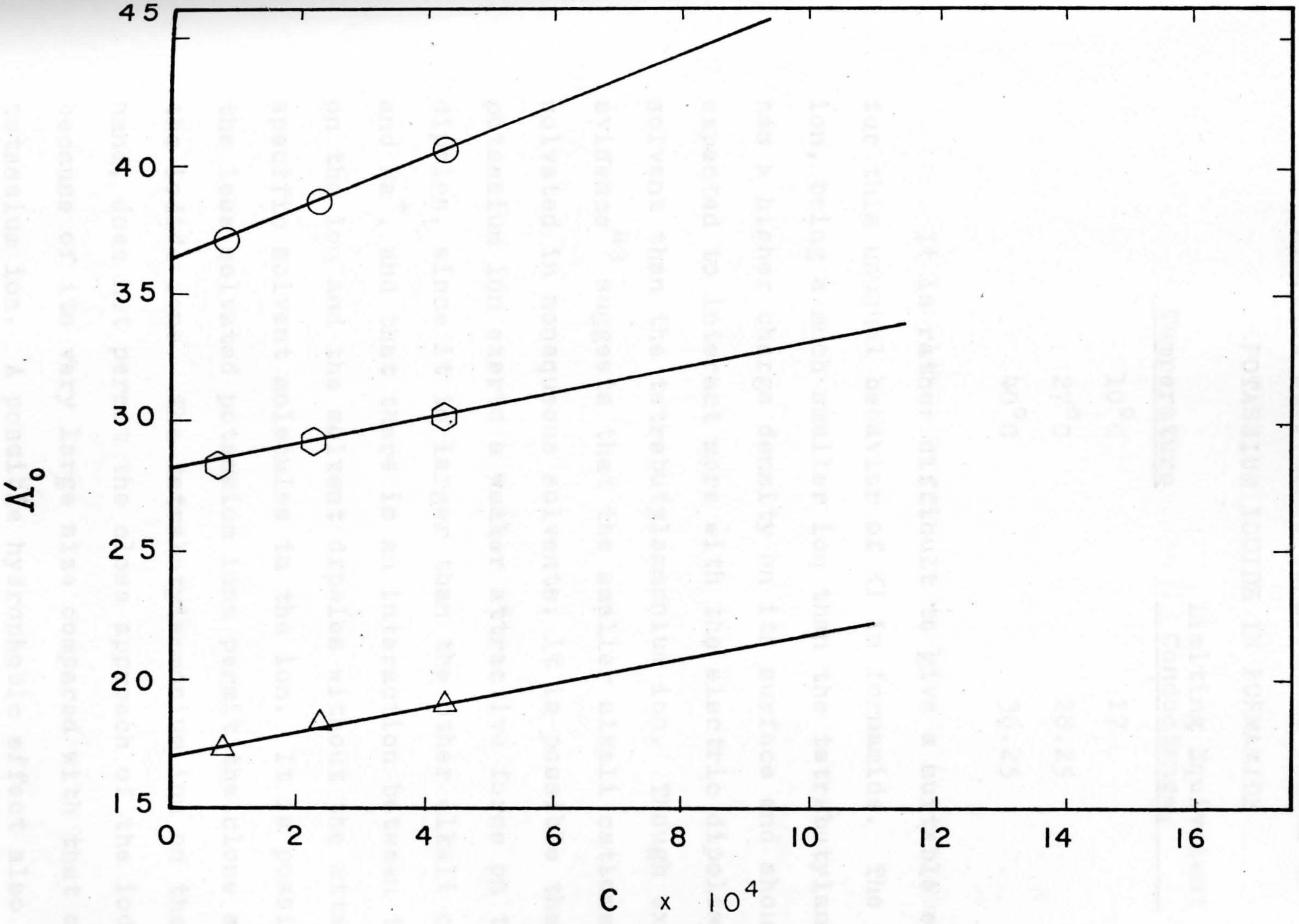


Fig. 8. Shedlovsky's Plots. Theoretical equivalent conductance of Potassium iodide in formamide versus concentration. The triangles, hexagons and the circles correspond to 10°C, 27°C and 40°C, respectively.

### TABLE 16

### LIMITING EQUIVALENT CONDUCTANCE VALUES OF POTASSIUM IODIDE IN FORMAMIDE

| Temperature | Limiting Equivalent Conductance, |
|---|---|
| 10°C | 17 |
| 27°C | 28.25 |
| 40°C | 36.25 |

It is rather difficult to give a suitable explanation for this unusual behavior of KI in formamide. The potassium ion, being a much smaller ion than the tetrabutylammonium ion, has a higher charge density on its surface and should be expected to interact more with the electric dipoles of the solvent than the tetrabutylammonium ion. Though experimental evidence[43] suggests that the smaller alkali cations are strongly solvated in nonaqueous solvents, it is possible that the potassium ion exerts a weaker attractive force on the solvent dipoles, since it is larger than the other alkali cations $Li^+$ and $Na^+$, and that there is an interaction between the charge on the ion and the solvent dipoles without the attachment of specific solvent molecules to the ion. It is possible that the less solvated potassium ions permit the close approach of the iodide ions. The tetrabutylammonium ion on the other hand, does not permit the close approach of the iodide ions because of its very large size compared with that of the potassium ion. A possible hydrophobic effect also may tend to keep tetrabutylammonium ions from iodide ions.

Products of viscosity and equivalent conductance are also not constant in the case of KI, except in the range of 0.1N to 0.15N further indicating that KI does not behave as a strong electrolyte in formamide (see Tables 17, 18, and 19, p. 44-46).

TABLE 17

CONDUCTANCE AND VISCOSITY OF POTASSIUM IODIDE IN FORMAMIDE AT 10°C

| C | $\Lambda$ | $\eta$ x10$^2$ | $\Lambda\eta$ x10 |
|---|---|---|---|
| 0.0005804 | 26.54 | 5.08 | 13.48 |
| 0.005804 | 18.37 | 5.13 | 8.398 |
| 0.0087054 | 16.28 | 5.09 | 8.285 |
| 0.011607 | 16.72 | 5.11 | 8.536 |
| 0.023214 | 16.45 | 5.16 | 8.49 |
| 0.043156 | 16.56 | 5.17 | 8.56 |
| 0.14626 | 15.63 | 5.36 | 8.38 |

C=Concentration in gm. equivalents per liter

$\Lambda$=Equivalent conductance

$\eta$=Viscosity in poises

$\Lambda\eta$=Product of viscosity and conductance (mhos cm$^2$ poise/equiv.)

## TABLE 18

## CONDUCTANCE AND VISCOSITY OF POTASSIUM IODIDE IN FORMAMIDE AT 27°C

| C | $\Lambda$ | $\eta$ x10$^2$ | $\Lambda\eta$ x10 |
|---|---|---|---|
| 0.0005804 | 453.73 | 3.2511 | 147.5 |
| 0.00174108 | 163.64 | 3.2718 | 53.51 |
| 0.0040625 | 85.6985 | 3.2308 | 27.69 |
| 0.005223 | 76.34 | 3.24 | 24.72 |
| 0.0087054 | 26.76 | 3.24 | 8.66 |
| 0.023214 | 26.52 | 3.25 | 8.63 |
| 0.043156 | 26.55 | 3.26 | 8.66 |
| 0.14626 | 24.62 | 3.39 | 8.35 |

C=Concentration in g.. equivalents per liter

$\Lambda$=Equivalent conductance (mhos cm$^2$/equiv)

$\eta$=Viscosity in poises

$\Lambda\eta$=Product of equivalent conductance and viscosity (mhos cm$^2$ poise/equiv.)

## TABLE 19

## CONDUCTANCE AND VISCOSITY OF POTASSIUM IODIDE IN FORMAMIDE AT 40°C

| C | $\Lambda$ | $\eta$ x$10^2$ | $\Lambda\eta$ x10 |
|---|---|---|---|
| 0.0005804 | 575.15 | 2.42 | 138.9 |
| 0.00174108 | 235.08 | 2.42 | 56.77 |
| 0.005223 | 104.07 | 2.42 | 25.22 |
| 0.0087054 | 34.72 | 2.425 | 8.44 |
| 0.023214 | 34.72 | 2.44 | 8.47 |
| 0.043156 | 35.45 | 2.452 | 8.70 |
| 0.14626 | 34.69 | 2.55 | 8.85 |

C=Concentration in g. equivalents per liter

$\Lambda$=Equivalent conductance (mhos cm$^2$/equi)

$\eta$=Viscosity in poises

$\Lambda\eta$=Product of viscosity and equivalent conductance (mhos cm$^2$ poise/equi).

## Viscosity Studies of KI and $Bu_4NI$ Solutions in Formamide

Viscosity studies of KI in formamide were undertaken in the concentration ranges 0.0005N to 0.15N at 10°C, 27°C, and 40°C (Tables 20, 21 and 22, p. 48-50). Plots of $\eta_r - 1/\sqrt{C}$ vs $\sqrt{C}$ showed departures from the Jones and Dole equation, equation (14) (see Figure 9, p. 51). Negative curvatures were obtained at 27°C and 40°C. These negative curvatures obtained at low concentrations are general ones.[44] Solutions of $Bu_4NI$ in formamide also showed similar behavior (see Tables 23, 24 and 25, p. 52-54 and Figure 10, p. 55) except that the curves were less steep in this case as measurements were not taken in the very dilute region. No satisfactory explanation has so far been given for this phenomenon. The explanation given by Rabinovich[45] is that associated solvent molecules dissociate into simpler molecules upon the introduction of soluble substances and the temperature has a marked effect on the depolymerization process. In the present system the effect of decrease in viscosity due to the depolymerization of solvent molecules is probably more than the effect of increase in viscosity due to the friction of ions on the solvent, with the result that there is a net decrease in viscosity at low concentrations. At higher concentrations the usual effect of friction of ions on the solvent molecules predominates, with the result there is a positive slope at higher concentrations.

## TABLE 20

## DENSITY AND VISCOSITY DATA OF POTASSIUM IODIDE IN FORMAMIDE AT 10°C

| C | d | Kinematic η Centistokes | Absolute η Centipoises | Relative η | $\eta_r - 1/\sqrt{C}$ |
|---|---|---|---|---|---|
| 0.00058036 | 1.1277 | 4.5065 | 5.082 | 0.9797 | -0.8427 |
| 0.0017411 | 1.1306 | 4.5296 | 5.1212 | 0.9873 | -0.3044 |
| 0.005223 | 1.1311 | 4.5155 | 5.1074 | 0.9846 | -0.2131 |
| 0.0087054 | 1.1297 | 4.5049 | 5.0893 | 0.9812 | -0.2020 |
| 0.011607 | 1.1297 | 4.5184 | 5.1045 | 0.9841 | -0.1476 |
| 0.023214 | 1.1318 | 4.5625 | 5.1638 | 0.9955 | -0.0295 |
| 0.043156 | 1.1333 | 4.5662 | 5.1749 | 0.9977 | -0.0110 |
| 0.14626 | 1.1458 | 4.6783 | 5.3604 | 1.0334 | 0.0873 |

C=Concentration in g. equivalents/liter

d=Density in g/ml

η=Viscosity

$\eta_r$=Relative viscosity

## TABLE 21

## DENSITY AND VISCOSITY DATA OF POTASSIUM IODIDE IN FORMAMIDE AT 27°C

| C | d | Kinematic $\eta$ Centistokes | Absolute $\eta$ Centipoises | Relative $\eta$ | $\eta_r$-1/ $\sqrt{C}$ |
|---|---|---|---|---|---|
| 0.00058036 | 1.1222 | 2.8911 | 3.2511 | 1.009 | 0.3749 |
| 0.00174108 | 1.1225 | 2.9086 | 3.2718 | 1.0154 | 0.3704 |
| 0.0040625 | 1.1233 | 2.8762 | 3.2308 | 1.0027 | 0.0429 |
| 0.0087054 | 1.1236 | 2.8792 | 3.2351 | 1.0040 | 0.0436 |
| 0.023214 | 1.1278 | 2.8851 | 3.2538 | 1.0099 | 0.0650 |
| 0.043156 | 1.1294 | 2.8896 | 3.2635 | 1.0128 | 0.0620 |
| 0.14626 | 1.1463 | 2.9568 | 3.3893 | 1.0519 | 0.1357 |

C=Concentration in g. equivalents/liter

d=Density in g./ml

$\eta$ =Viscosity

$\eta_r$ =Relative viscosity

## TABLE 22

## DENSITY AND VISCOSITY DATA OF POTASSIUM IODIDE IN FORMAMIDE AT 40°C

| C | d | Kinematic η Centistokes | Absolute η Centipoises | Relative η | $\eta_r - 1/\sqrt{C}$ |
|---|---|---|---|---|---|
| 0.00058036 | 1.1144 | 2.167 | 2.415 | 1.0037 | 0.1536 |
| 0.00174108 | 1.1145 | 2.167 | 2.415 | 1.0037 | 0.0887 |
| 0.0087054 | 1.1146 | 2.176 | 2.425 | 1.0079 | 0.0847 |
| 0.011607 | 1.1155 | 2.177 | 2.428 | 1.0091 | 0.0849 |
| 0.023214 | 1.1177 | 2.183 | 2.440 | 1.0141 | 0.0925 |
| 0.043156 | 1.1206 | 2.188 | 2.452 | 1.0191 | 0.09205 |
| 0.14626 | 1.1402 | 2.237 | 2.551 | 1.060 | 0.1577 |

C=Concentration in gm. equivalents/liter

d=Density in g/ml

η=Viscosity

$\eta_r$=Relative viscosity

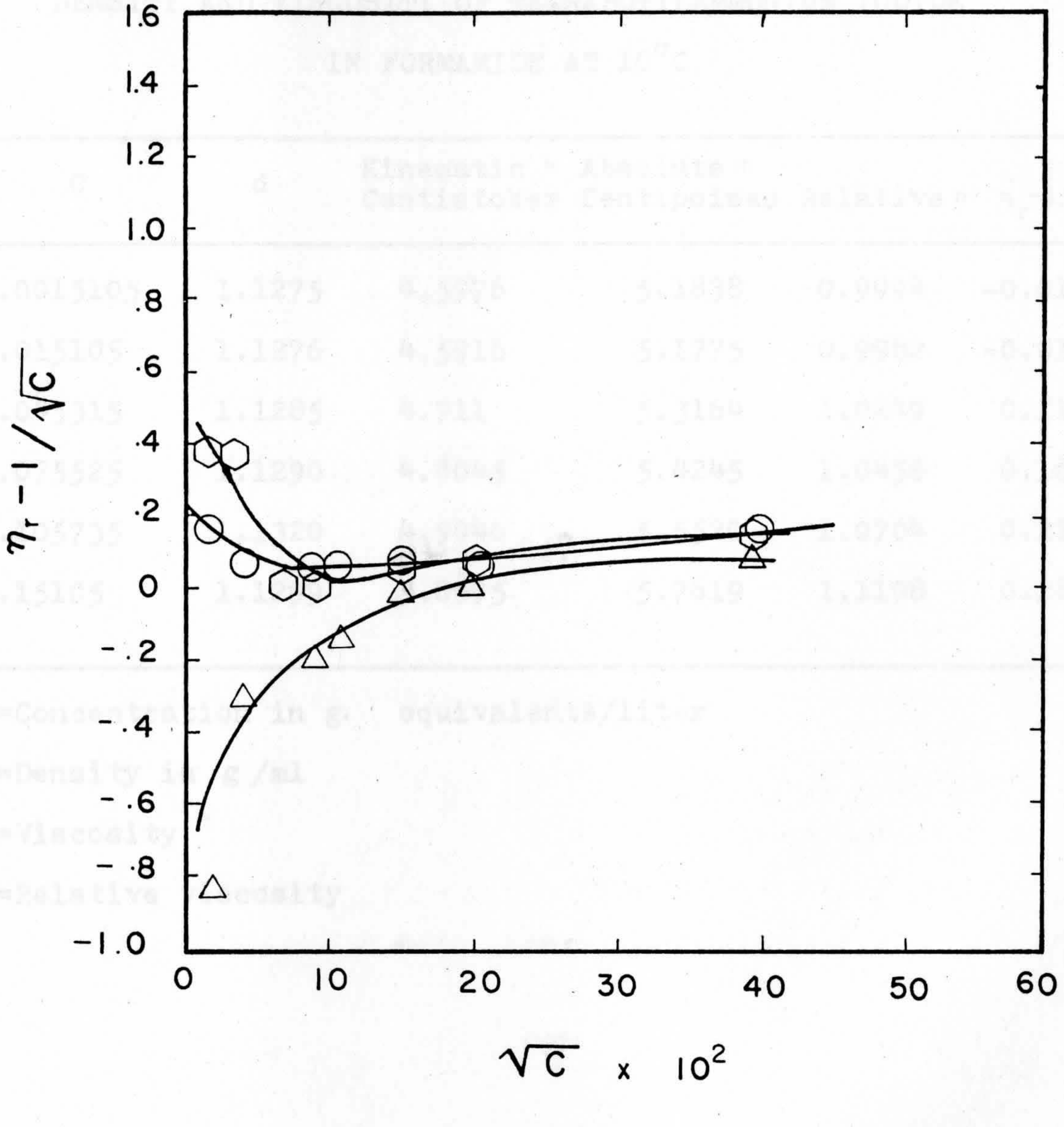


Fig. 9. Relative Viscosity of Potassium iodide in formamide versus square root of concentration. The triangles, hexagons and the circles correspond to 10°C, 27°C and 40°C, respectively.

## TABLE 23

## DENSITY AND VISCOSITY OF TETRABUTYLAMMONIUM IODIDE IN FORMAMIDE AT 10°C

| C | d | Kinematic $\eta$ Centistokes | Absolute $\eta$ Centipoises | Relative $\eta$ | $\eta_r$-1/$\sqrt{C}$ |
|---|---|---|---|---|---|
| 0.0015105 | 1.1275 | 4.5976 | 5.1838 | 0.9994 | -0.0154 |
| 0.015105 | 1.1276 | 4.5916 | 5.1775 | 0.9982 | -0.0147 |
| 0.045315 | 1.1285 | 4.711 | 5.3164 | 1.0249 | 0.1170 |
| 0.075525 | 1.1290 | 4.8045 | 5.4245 | 1.0458 | 0.1667 |
| 0.105735 | 1.1320 | 4.9046 | 5.5520 | 1.0704 | 0.2165 |
| 0.15105 | 1.1299 | 5.0995 | 5.7619 | 1.1108 | 0.2851 |

C=Concentration in g. equivalents/liter

d=Density in g /ml

$\eta$=Viscosity

$\eta_r$=Relative viscosity

## TABLE 24

## DENSITY AND VISCOSITY OF TETRABUTYLAMMONIUM IODIDE IN FORMAMIDE AT $27^{o}C$

| C | d | Kinematic $\eta$ Centistokes | Absolute $\eta$ Centipoises | Relative $\eta$ | $\eta_r$-1/$\sqrt{C}$ |
|---|---|---|---|---|---|
| 0.0015105 | 1.1228 | 2.8829 | 3.2369 | 1.0046 | 0.1190 |
| 0.015105 | 1.1234 | 2.8933 | 3.2503 | 1.0088 | 0.0715 |
| 0.045315 | 1.1225 | 2.9083 | 3.2645 | 1.0132 | 0.0620 |
| 0.075525 | 1.1235 | 2.9836 | 3.3521 | 1.0403 | 0.1469 |
| 0.105735 | 1.1243 | 3.0403 | 3.4182 | 1.0609 | 0.1873 |
| 0.15105 | 1.1263 | 3.1522 | 3.550 | 1.1018 | 0.2619 |

C=Concentration in g. equivalents/liter

d=Density in g/ml

$\eta$ =Viscosity

$\eta_r$ =Relative viscosity

## TABLE 25

## DENSITY AND VISCOSITY OF TETRABUTYLAMMONIUM IODIDE IN FORMAMIDE AT 40°C

| C | d | Kinematic η Centistokes | Absolute η Centipoises | Relative η | $\eta_r - 1/\sqrt{C}$ |
|---|---|---|---|---|---|
| 0.0015105 | 1.1126 | 2.1775 | 2.4226 | 1.007 | 0.1801 |
| 0.015105 | 1.1135 | 2.1872 | 2.4354 | 1.0122 | 0.0993 |
| 0.045315 | 1.1141 | 2.2021 | 2.4533 | 1.0197 | 0.0925 |
| 0.075525 | 1.1147 | 2.2542 | 2.5128 | 1.0444 | 0.1616 |
| 0.105735 | 1.1149 | 2.3076 | 2.5727 | 1.0693 | 0.1968 |
| 0.15105 | 1.1151 | 2.328 | 2.5960 | 1.0789 | 0.2032 |

C=Concentration in g. equivalents/liter

d=Density in g /ml

η =Viscosity

$\eta_r$ =Relative viscosity

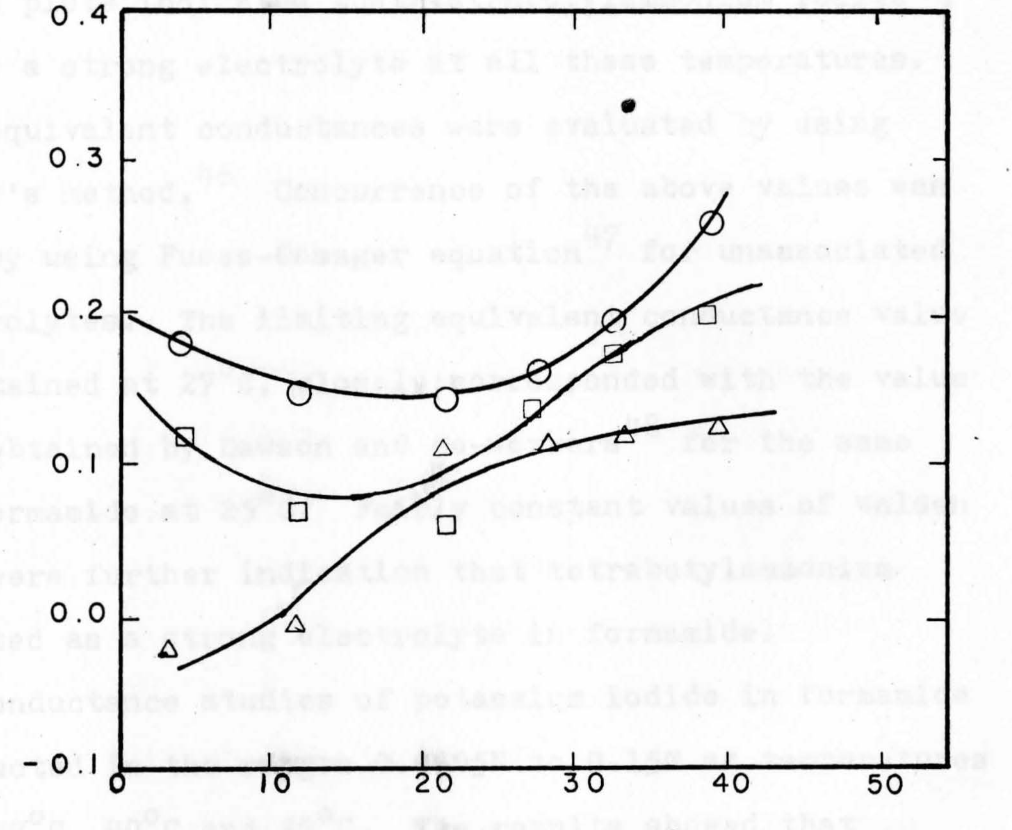


Fig.10. Relative viscosity of Tetrabutyl ammonium iodide in formamide versus square root of concentration. The triangles, squares and the circles correspond to 10°C, 27°C and 40°C, respectively.

## CHAPTER V

## SUMMARY AND CONCLUSION

Conductance studies of tetrabutylammonium iodide in formamide were done in the concentration ranges 0.0015N to 0.15N at temperatures 10°C, 27°C and 40°C. Linearity of Kohlrausch plots indicated that tetrabutylammonium iodide behaved as a strong electrolyte at all these temperatures. Limiting equivalent conductances were evaluated by using Shedlovsky's method.[46] Concurrence of the above values was obtained by using Fuoss-Onsager equation[47] for unassociated 1:1 electrolytes. The limiting equivalent conductance value of 23, obtained at 27°C, closely corresponded with the value of 23.37 obtained by Dawson and co-workers[48] for the same salt in formamide at 25°C. Fairly constant values of Walden products were further indication that tetrabutylammonium iodide acted as a strong electrolyte in formamide.

Conductance studies of potassium iodide in formamide were conducted in the ranges 0.0005N to 0.15N at temperatures of 10°C, 27°C, 40°C and 50°C. The results showed that potassium iodide acted as a weak electrolyte at all these temperatures. This observation was contrary to the earlier belief that all electrolytes are completely dissociated in solvents of high dielectric constant. Results of the present work could not, however, be ignored as the differences between the solvent and the solution conductances were too large to attribute the effect to the large solvent correction. No suitable explanation could be given to this unusual behavior.

Even though strong solvation is expected of all the alkali cations, it is possible that in the case of potassium ion, solvation is ion-solvent interaction without the attachment of specific solvent molecules. Thus the potassium ion which is not so strongly solvated permits the close approach of iodide ions. The tetrabutylammonion ion, on the other hand, does not permit the close approach of iodide ions due to its larger size. Also a possible hydrophobic effect may tend to keep it from the iodide ions. In order to verify the results it is recommended that more work is to be done in this field using more dilute solutions of a purified sample of formamide with a lower solvent conductance.

Studies of viscosity of both the salts at temperatures of 10°C, 27°C and 40°C indicated deviation from the Jones and Dole equation.[49] Negative curvatures were obtained at 27°C and 40°C, the deviation being more pronounced at low concentrations. A similar behavior was observed by several earlier workers.[50] Rabinovich[51] offered a rationale for this behavior and postulated that addition of solute particles caused depolymerization of associated solvent molecules resulting in a decrease in viscosity. In the present systems the decrease in viscosity due to depolymerization was more than the effect of increase in viscosity due to the friction of ions on the solvent with the result that there was a net decrease in viscosity. However, no specific information about the structure of the solution or ion association is gained from the data collected in this study.

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