CONDUCTANCES OF AQUEOUS SOLUTIONS OF SODIUM HEXANOATE

A THESIS SUBMITTED TO THE COMMITTEE ON POST-GRADUATE
STUDIES AT THE UNIVERSITY OF MANITOBA IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

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MARCH 1960

To My Parents

ABSTRACT

Equivalent conductances, densities and viscosities of aqueous solutions of sodium hexanoate have been determined at 25°C and 35°C at concentrations ranging from 0.0003 molar up to saturation.

The limiting equivalent conductances of the hexanoate ion have been determined at 25°C and 35°C.

The experimental conductances have been compared with the values calculated by the Robinson-Stokes and the Falkenhagen-Leist equation. It was found that the å values necessary to give a reasonable reproduction of the experimental data in the dilute region were very large; 10Å or larger for the Robinson-Stokes equation and 4.0Å or larger for the Falkenhagen-Leist equation.

It has also been concluded that micelle formation does not occur with the hexanoate ion.

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ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the advice and assistance of Dr. A.N. Campbell and Mr. E. Bock in discussing and planning this research.

The author is also indebted to Mr. G. Epp for constructing the glass apparatus and for his assistance in preparing the figures for this thesis.

Thanks are also due to Arlene Hetherington who programmed the calculations for the computer and also spent much time in carrying out these calculations.

Finally, the financial assistance of the National Research Council is gratefully acknowledged.

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THEORETICAL INTRODUCTION

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The nature of electrolytic solutions has interested investigators for a very long time. Careful investigation of the behavior of strong electrolytes led Kohlrausch (1) to conclude that in very dilute solutions the equivalent conductance was related to the concentration by the empirical relationship,

$$\Lambda = \Lambda_0 - A\sqrt{C} \qquad \ldots\ldots \quad 1)$$

where Λ is the equivalent conductance at concentration C, Λ_0 is the equivalent conductance at infinite dilution and A is an empirical constant. It can also be shown that the velocities of the ions are related to the equivalent conductance in the following manner:

$$\frac{\Lambda}{\Lambda_0} = \frac{\alpha\,(v_+ + v_-)}{(v_+^0 + v_-^0)} \qquad \ldots\ldots \quad 2)$$

Here α is the degree of dissociation of the electrolyte and v_+ and v_- are the velocities of the positive and negative ions respectively, at a given concentration. v_+^0 and v_-^0 refer to the velocities of the respective ions at infinite dilution.

Various early theories regarding the nature of electrolytic solutions were presented, but the first workable theory was that due to Arrhenius (2). He postulated that electrolytes dissociated into ions in solution and that the equilibrium existing between the ions and the undissociated electrolyte would be governed by the law of mass action.

Regarding conductance, he assumed that the velocities of the ions at a finite concentration were the same as at infinite dilution and that a change in conductance was solely due to a change in α, the degree of dissociation. If this is correct then it follows from equation 2) that,

$$\alpha = \Lambda/\Lambda_0 \qquad \ldots\ldots \quad 3)$$

since $(v_+ + v_-) = (v_+^0 + v_-^0)$.

Applying the mass action law to equation 3) leads to the Ostwald dilution law which can be expressed as follows:

$$K = \frac{(\Lambda/\Lambda_0)^2 C}{1 - \Lambda/\Lambda_0} \qquad \ldots\ldots \quad 4)$$

This can be rearranged to the straight line form:

$$1/\Lambda = 1/\Lambda_0 + C\Lambda/K\Lambda_0 \qquad \ldots\ldots \quad 5)$$

Equation 5) was found to be applicable to weak electrolytes, but for strong electrolytes the plot of $C\Lambda$ against $1/\Lambda$ was no longer linear. Therefore, a new approach to the conductance problem was necessary.

1. The Debye-Hückel Theory.

By assuming that strong electrolytes were completely dissociated into ions in solution and that any departure from ideality was due to ionic interactions, Milner (3) was able to calculate the thermodynamic properties of electrolyte solutions. Debye and Hückel applied this model to the problem of conductance.

The Debye-Hückel theory calculates the potential ψ at a point in solution in terms of the concentrations of the ionic species and their charges and the properties of the solvent. For a spherical distribution of charges the Poisson equation can be expressed as follows:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = -\frac{4\pi\rho}{D} \qquad \text{.....}\ 6)$$

where D is the dielectric constant of the medium and ρ is the charge density at the point in question.

Debye and Hückel now assumed that the distribution of charges was given by the Boltzmann distribution law. Then the charge density at any given point is given by,

$$\rho = \sum_i n_i z_i \epsilon \; exp\left(\frac{-\epsilon\psi}{kT}\right) \qquad \text{.....}\ 7)$$

Equations 6) and 7) refer to a moving co-ordinate system with the origin at some reference ion, say the jth ion.

The principle of linear superposition of fields requires that a linear relationship exist between ρ and ψ. In equation 7), however, ρ varies exponentially with ψ. To resolve this difficulty Debye and Hückel expanded the exponential terms and retained only the linear terms. Then equation 7) can be written as follows:

$$\rho = -\sum_i n_i z_i \frac{\epsilon^2\psi}{kT} \qquad \text{.....}\ 8)$$

Substitution of equation 8) into equation 6) and solution of the resulting differential equation leads to the Debye-Hückel expression for the potential:

$$\psi = \frac{z_i \epsilon}{D} \cdot \frac{e^{Ka}}{1 + Ka} \cdot \frac{e^{-Kr}}{r} \qquad \text{.....} \quad 9)$$

Here "a" is the distance of closest approach and K is defined by:

$$K^2 = \frac{4\pi\epsilon^2}{D} \sum_i n_i z_i^2 \qquad \text{.....} \quad 10)$$

Debye and Hückel now assumed that a decrease in conductance with an increase in concentration was due to a change in the ionic mobilities. These in turn are influenced by two effects; the electrophoretic effect and the relaxation effect. The relaxation effect arises from the fact that each ion will be surrounded by an ionic atmosphere of oppositely charged ions. When no external field is present the ionic atmosphere will be spherically symmetrical about the central ion, but application of an external field will distort the atmosphere and the central ion will experience a net retarding force. The electrophoretic effect arises from the fact that the ions will drag solvent molecules with them as they move through the solution. Consequently, other ions are not moving through a stationary medium but through one which either aids or opposes their motion.

On the basis of the foregoing discussion Debye and Hückel were able to make a good first approximation to the conductance problem. Later Onsager (4) modified the Debye-Hückel treatment to include the Brownian motion of the reference ion. This resulted in a conductance equation which, for uni-univalent electrolytes, can be expressed in the following form:

$$\Lambda = \Lambda_0 - \frac{82.49}{(D_0T)^{1/2}\eta_0} + \frac{8.204 \times 10^5 \Lambda_0}{(D_0T)^{3/2}\eta_0} \sqrt{C} \qquad \ldots\ldots \quad 11)$$

where D_0 and η_0 are the dielectric constant and the viscosity respectively, of the pure solvent. The constants, 82.49 and 8.204 x 10^5 are derived from combinations of such physical quantities as the Faraday, the charges on the ions and Avagadro's number.

When equation 11) is expressed in the form

$$\Lambda = \Lambda_0 - (\alpha + \beta\Lambda_0)\sqrt{C} \qquad \ldots\ldots \quad 12)$$

where

$$\alpha = \frac{82.49}{(D_0T)^{1/2}\eta_0} \qquad \ldots\ldots \quad 13)$$

and

$$\beta = \frac{8.204 \times 10^5}{(D_0T)^{3/2}\eta_0} \qquad \ldots\ldots \quad 14)$$

it is immediately evident that equation 12) becomes identical with the Kohlrausch expression, provided the temperature and solvent are specified.

It must be remembered, however, that the Debye-Hückel-Onsager equation is really only a limiting law which can be expected to apply only to extremely (strictly, infinitely) dilute solutions. There are several reasons for this. Among them are the following:

1. It has been assumed that the dielectric constant of the solution is essentially that of the solvent. Due to the enormous field strength in the immediate vicinity of an ion (Hückel (5) has calculated the field strength of a univalent ion in a medium of dielectric constant of 80 to be 2×10^6 volts/cm. at a distance of 3×10^{-8} cm. from the center of the ion) the dielectric constant will be altered markedly. Hasted, Ritson and Collie (6) have shown that the dielectric constant D of an electrolytic solution of concentration C can be found from the following expression:

$$D = D_0 + 2\bar{\delta}C \qquad \ldots\ldots 15)$$

where $\bar{\delta}$ represents the average contribution of the ions to the dielectric constant. They have also determined $\bar{\delta}$ for various electrolytes up to a concentration of 2M. These values vary from -7 to -15. Thus it is obvious that the dielectric constant of a solution may be markedly different from that of pure solvent.

2. It has been assumed that the interionic potential energy is negligible relative to the thermal energy of the ions. This assumption was necessary because the theorem of linear superposition of fields requires that a linear relationship

exist between the charge density ρ and the potential ψ. The Boltzmann distribution function, however, gives an exponential relationship. Thus, according to this law,

$$dn_+ = n \exp\left(\frac{-\epsilon\psi}{kT}\right) dV \qquad \ldots\ldots 16)$$

and

$$dn_- = n \exp\left(\frac{\epsilon\psi}{kT}\right) dV \qquad \ldots\ldots 17)$$

dn_+ and dn_- are the number of positive and negative ions respectively, in a volume dV, ϵ is the electronic charge and k is the Boltzmann constant. The charge density at a distance r from a selected ion is now given by,

$$\rho = \frac{(dn_+ - dn_-)\epsilon}{dV} \qquad \ldots\ldots 18)$$

which becomes

$$\rho = n\epsilon\left[\exp\left(\frac{-\epsilon\psi}{kT}\right) - \exp\left(\frac{\epsilon\psi}{kT}\right)\right] \qquad \ldots\ldots 19)$$

upon substitution of equations 16) and 17). As has already been pointed out, to obtain the necessary linear relationship between ρ and ψ Debye and Hückel expanded the exponential terms into a power series and neglected all second order and higher terms. In essence, this assumes that $\epsilon\psi \ll kT$, an assumption which is not justified in concentrated solutions where ions approach each other more and more closely.

3. Ions have been represented by point charges and the size

of the ions is assumed to be negligible relative to the distance between ions. In concentrated solutions the interionic distance decreases and the size of the ions becomes important.

2. The Wishaw-Stokes Equation.

Several attempts have been made to extend the Debye-Hückel-Onsager theory into the region of finite concentrations by taking the finite size of the ions into account. Thus, Falkenhagen (7) and co-workers considered ions to have finite size and developed a new expression for the relaxation effect. At the same time they used the Eigen-Wicke (8) distribution function, which also considered the ions to be finite in size, and obtained the expression,

$$\Delta X = \frac{\epsilon^2}{3 D_0 kT} \cdot \frac{0.2929}{1 + Ka} \cdot \frac{\exp (0.2929\, Ka) - 1}{0.2929\, Ka} \qquad \ldots\ldots 20)$$

where "a" is the distance of closest approach, X represents the intensity of the field acting on the ion and ΔX is the relaxation field which acts in the opposite sense. K is defined by the following expression:

$$K = \left[\frac{\pi N \epsilon^2}{125 D_0 kT} \right]^{1/2} \sqrt{C} \left[1 - \frac{1\, n_1}{2 N_1} - \frac{1\, n_2}{2 N_2} \right] \qquad \ldots\ldots 21)$$

In the definition of K, n_1 and n_2 are the number of cations and anions per cubic centimeter and N_1 and N_2 are the reciprocal volumes of the cations and the anions.

Wishaw and Stokes (9) modified Falkenhagen's expression for the relaxation effect to allow retention of the Boltzmann function and published their conductance equation in the form:

$$\Lambda = \left[\Lambda_0 - \frac{B_2\sqrt{C}}{1 + Ka}\right]\left[1 - \frac{B_1\sqrt{C}}{1 + Ka} \cdot F\right] \qquad \text{.....} \quad 22)$$

where

$$B_1 = \frac{8.20 \times 10^5}{(D_0 T)^{3/2}} \qquad \text{.....} \quad 23)$$

$$B_2 = \frac{82.5}{(D_0 T)^{1/2}\eta_0} \qquad \text{.....} \quad 24)$$

$$B\mathring{a}\sqrt{C} = \frac{50.29\,\mathring{a}\sqrt{C}}{(D_0 T)^{1/2}} = Ka \qquad \text{.....} \quad 25)$$

$$F = \frac{\exp(0.2929\,Ka) - 1}{0.2929\,Ka} \qquad \text{.....} \quad 26)$$

and

$$K = \left[\frac{\pi N \epsilon^2}{125 D_0 k T}\right]^{1/2} \sqrt{C} \qquad \text{.....} \quad 27)$$

In equation 22) $\mathring{a}$ is the only adjustable parameter once Λ_0 is known.

3. The Falkenhagen-Leist Equation.

Falkenhagen's considerations that ions had a finite size led him to conclude that they must be impenetrable and hence must be displaced during migration. He also used the

Eigen-Wicke distribution function to describe the distribution of charge in the ionic atmosphere surrounding any given ion. These considerations led to the Falkenhagen-Leist conductance equation (10), which can be expressed as follows:

$$\Lambda = \Lambda_0 - \Lambda_{I} - \Lambda_{II} \qquad \text{.....} \; 28)$$

where Λ_{I} is the relaxation term and is defined by

$$\Lambda_{I} = \frac{0.2929\; K \Lambda_0 B_2}{(1 + Ka)(1 + \frac{1}{2}\sqrt{2}\, Ka + \frac{1}{6} K^2 a^2)} \qquad \text{.....} \; 29)$$

and the electrophoretic term, Λ_{II}, is given by

$$\Lambda = \frac{B_3 K}{1 + Ka} \qquad \text{.....} \; 30)$$

B_2 and B_3 are constants; B_2 being defined by equation 24) and B_3 given by,

$$B_3 = \frac{\epsilon^2 N}{27 \pi \eta_0 10^{11}} \qquad \text{.....} \; 31)$$

The other symbols have their usual meaning. Here, too, "a" is the only adjustable parameter.

The question arises whether the values for "a" as they appear in the Wishaw-Stokes and the Falkenhagen-Leist equations have any physical significance. Since the values which are obtained for "a" are usually not less than the sum of the crystallographic radii of the ions, it could be argued that "a" does give a measure of ionic diameters in solution. It must be admitted, however, that the manner in which equations 22) and 28) are employed to analyse experimental data forces "a" to absorb all imperfections in the theory as well as any experimental error which may have been incurred. Fowler (11) says, "a is an 'omnium gatherum' correction". It would seem that the values for "a" are at best only qualitative.

4. The Viscosity Correction.

It is observed that in equations 22) and 28) η_0, the viscosity of the pure solvent is the only viscosity term which appears. The viscosity of the solution will, in general, be quite different from that of the solvent. Bernal and Fowler (12) have shown that ions in solution affect the viscosity in at least three ways: 1. They impart momentum to the solvent molecules by colliding with them and thus cause changes in the viscosity.
2. Interionic attractions cause increased shear and hence increased viscosity, and 3. changes in the hydration of the ions cause changes in the viscosity.

Walden (13) studied the relationship between viscosity and equivalent conductance for tetra-ethylammonium picrate and found that, for a variety of solvents and for a temperature range of fifty degrees,

$$\Lambda_0 \eta_0 = \text{constant} \qquad \text{.....} \ 32)$$

Attempts to extend this to solutions of finite concentrations so that

$$\Lambda \eta = \text{constant}$$

have usually failed. Kraus (14) found that the plots of $\Lambda\eta$ versus concentration usually passed through a minimum and then increased continually. He explained this on the basis of ion pair formation.

It is generally agreed, therefore, that some form of viscosity correction should be applied to the conductance equations. The exact form of the correction is not known, but experience has shown that dividing equations 22) and 28) by the relative viscosity is approximately correct. When this is done, it is observed that the Robinson-Stokes and the Falkenhagen-Leist equations often reproduce experimental data for solutions whose concentration far exceeds the limit to which they are theoretically applicable. Thus, Campbell and Paterson (15) found surprisingly good agreement right up to saturation for aqueous lithium chlorate solutions at 25°C and 131.8°C. Similar results were obtained by Campbell and Bock (16) for ammonium nitrate at 25°C.

5. The Fuoss-Onsager Equation.

The most recent treatment of the conductance problem is due to Fuoss and Onsager (17). In a recent publication Fuoss (18) has summarized the highly mathematical treatment. A detailed treatment is also given in a book by Fuoss and Accascina (19).

In this theory the relaxation effect and the electrophoretic effect have been evaluated to include terms up to order of $C^{3/2}$. The resulting conductance equation for a uni-univalent electrolyte is expressed as follows:

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec\log c + Jc \qquad \ldots\ldots 33)$$

In equation 33) S, E and J are constants which are defined as follows:

$$S = \alpha + \beta\Lambda_0 \qquad \ldots\ldots 34)$$

where α and β are the Debye-Hückel constants defined by equations 13) and 14). The constant E is defined by the following three expressions:

$$E = E_1\Lambda_0 - E_2 \qquad \ldots\ldots 35)$$

where

$$0.4343\,E_1 = \frac{K^2a^2b^2}{24C} \qquad \ldots\ldots 36)$$

and

$$0.4343\,E_2 = \frac{Kab\beta}{16C^{1/2}} \qquad \ldots\ldots 37)$$

with b defined by

$$b = \frac{\epsilon^2}{aD_0kT} \qquad \ldots\ldots 38)$$

By combining equation 38) with equations 35, 36) and 37) it is evident that the constant E is independent of concentration as well as "a", the distance of closest approach. It is seen from equation 34) that S is also independent of these two parameters.

J is given by

$$J = \sigma_1 \Lambda_0 + \sigma_2 \qquad \ldots\ldots 39)$$

where

$$\sigma_1 = \frac{K^2 a^2 b^2}{12 C^{1/2}} \left[h(b) + 0.9074 + \ln \frac{Ka}{C^{1/2}} \right] \qquad \ldots\ldots 40)$$

and

$$\sigma_2 = \alpha\beta + \frac{11\beta K a}{12 C^{1/2}} - \frac{K a \beta}{8 C^{1/2}} \left[1.0170 + \ln \frac{Ka}{C^{1/2}} \right] \qquad \ldots\ldots 41)$$

The function h (b) in equation 40) is defined by,

$$h(b) = \frac{2b^2 + 2b - 1}{b^3} \qquad \ldots\ldots 42)$$

where b is again given by equation 38).

Examination of these expressions shows that the conductance of an electrolyte in a given solvent and at a fixed temperature is a function of the two parameters Λ_0 and "a". Simultaneous solution of the equation for these two parameters using two given values of Λ would be extremely difficult due to its complicated form. Another method is used to obtain the two parameters. This will be outlined briefly.

Shedlovsky (20) has devised a method to obtain a first approximation for Λ_0. This consists in plotting Λ_0', defined by the function

$$\Lambda'_o = \frac{\Lambda + \alpha C^{1/2}}{1 - \beta C^{1/2}} \qquad \text{..... 43)}$$

against C. The resulting plot is usually linear up to o.1 N and extrapolation to zero concentration gives a good approximation for Λ_o, say Λ_{o1}. Knowing Λ_{o1}, it is now possible to determine S using equation 34) and E using equation 35). Next another quantity Λ' is defined by the expression,

$$\Lambda' = \Lambda_o + Jc \qquad \text{..... 44)}$$

where $\Lambda_o = \Lambda + Sc^{1/2} + Ec \log c$. A plot of Λ' against C is linear with the intercept on the Λ'- axis giving Λ_o and having a slope equal to J. Once the slope J is known, the distance of closest approach can be calculated by means of equations 39), 40) and 41).

Although the Fuoss-Onsager equation reproduced conductance data rather accurately for many solutions, an anomaly still seemed to exist for the strong electrolytes. It was observed that electrolytes which obeyed the Fuoss-Onsager equation in aqueous solution behaved like weak electrolytes in solvents which had a low dielectric constant. It cannot be assumed that part of the electrolyte exist as neutral molecules in these solvents, since it is now generally accepted that these salts are ionic even in the crystalline state. Bjerrum (21), in 1926, suggested that ion association could take place in these solvents. He reasoned that in a medium of low dielectric constant the Coulombic potential energy could become large enough to overcome the thermal energy of the ions and thus ions could associate to form non-conducting ion pairs. The question now arises, "When can two ions be considered as an ion pair?" Bjerrum considered two ions to be an ion pair when the distance between them was less than $\frac{\epsilon^2}{2D_0kT}$.

Fuoss and Kraus' (22) first attempt to develop a general theory of conductance using the ion pair idea to explain the behavior of strong electrolytes in a medium of low dielectric constant was only partially successful. In media of low dielectric constant it described the behavior of the electrolyte satisfactorily. It also reduced to the Debye-Hückel-Onsager equation for media of high dielectric constant, but it failed in the intermediate range. In part at least, this was due to the fact that Fuoss and Kraus had assumed that the Debye-Hückel-Onsager equation applied to solutions having finite concentrations, and it was not until Fuoss and Onsager (17) obtained their conductance equation, equation 33), that a satisfactory general equation was developed. A new definition of an ion pair was also used. Fuoss (19) defined an ion pair as follows: "An ion pair will be defined as an anion and a cation separated by a distance between r and r + dr , provided that no other unpaired anion is located inside the sphere of radius r concentric with the reference cation." Equation 33) was now modified in the following manner to make it generally applicable:

$$\Lambda = \Lambda_o - S(c\gamma)^{1/2} + Ec\gamma \log c\gamma + Jc\gamma - K_a c\gamma f^2 \Lambda \quad \ldots\ldots 45)$$

Here $(1 - \gamma)$ represents the fraction of the ions which are associated to form ion pairs and f is the mean ionic activity coefficient for the electrolyte. K_a is the association constant for ion pair formation.

To facilitate determination of the three parameters Λ_o, γ and K_a, several new quantities are defined. First γ must be known and a first approximation is obtained from the expression,

$$\gamma = \frac{\Lambda}{\Lambda_o - Sc^{1/2}\Lambda^{1/2}/\Lambda_o^{1/2}} \quad \ldots\ldots 46)$$

This now permits evaluation of the quantity Λ' where Λ' is given by

$$\Lambda' = \Lambda + S(c\gamma)^{1/2} - Ec\gamma \log c\gamma \quad \ldots\ldots 47)$$

Two other quantities are defined:

$$y = \frac{\Lambda' - \Lambda_o}{c\gamma} \quad \ldots\ldots 48)$$

and

$$x = f^2 \Lambda \quad \ldots\ldots 49)$$

Consideration of equations 48) and 49) shows that a plot of y against x should give a straight line, provided

Λ_0 has been chosen correctly. From equation 48) it is evident that the numerator of y will be positive if Λ_0 is too small, and since the denominator tends to zero as C becomes smaller, the curve will become concave upwards for low concentrations. Similarly, it is seen that the curve will become concave downwards if Λ_0 is too large. For the proper choice of Λ_0, however, both numerator and denominator tend to zero for low concentrations and the plot will be linear. The slope of this straight line will be equal to K_a and the intercept on the y-axis is equal to J. Thus K_a is known and the parameter "a" can be calculated from the value of J.

Theoretically the Fuoss-Onsager equations are only applicable to solutions for which $\kappa a < 0.2$. This is due to the mathematical approximations which were made in deriving the equations. Furthermore, the model used to represent the system was essentially that of Debye and Hückel, which assumed a continuous distribution of charge in the ionic atmosphere surrounding any given ion. In the more concentrated solutions the ions are closer together and the continuous charge picture is no longer a good approximation. Fuoss, in fact, maintains that this theory cannot be extended to higher concentrations. To use Fuoss own words, "It therefore seems futile to look for a solution to the problem of higher concentrations by an extension of the present theory which is, however, valid for low concentrations." (19)

NATURE OF THE PROBLEM

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Much work has been done in the past in this laboratory on the conductanse of inorganic salt solutions. This research, in which the conductanse of sodium hexanoate has been determined, is part of a program in which it is intended to measure the conductances of the salts of the fatty acids. Proceeding up the homologous series, the increasing size of the anions might eventually lead to a situation where the anion is essentially non-conducting. On the other hand, the formation of ionic micelles could give rise to a situation where the increased charge on the micelles would counterbalance the effect of increased size and thus even the larger anions would exhibit appreciable conductances.

During the course of the research the limiting equivalent conductances of the hexanoate ion was determined and the applicability of the Robinson-Stokes and Falkenhagen-Leist equations was tested.

EXPERIMENTAL PROCEDURE

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1. Preparation and Purity of the Salts.

The n-hexanoic acid was obtained from the Eastman Kodak Company and was purified by redistillation. The purity of the acid was checked by measuring the refractive index on a Pulfrich Refractometer. It was found to be 1.41502 at 25.4°C for the Na_D line as compared to 1.4149 at 25°C as reported in the literature (23).

To prepare the salt the acid was neutralized with an alcoholic solution of sodium hydroxide and the resulting solution was evaporated slowly until the salt crystallized out. It was then recrystallized twice from alcohol, dried at 110°C, ground in an agate mortar and stored in an oven at 110°C.

An attempt was made to establish the purity of the salt by titration with HCl using a Fisher titrimeter, but the "breaks" in the curves were not sharp enough to give accurate results. The results obtained for a series of six trials ranged from 97.5% sodium caproate to 102%. Therefore, this method was abandoned and the sodium caproate was converted to the sulfate as described by Stock, Stähler, Patnode and Dennis (24). This established the salt to be at least 99.9% pure. Since the most likely impurity that one would expect is sodium carbonate, a moments reflection will reveal that the results should be high rather than low because the percentage of sodium in sodium carbonate is about 43% as compared to 16.6% sodium in sodium hexanoate. The results should also be high if sodium hydroxide were present as an impurity. Furthermore, the results are probably within the experimental error since only a limited amount of salt was available for the analysis.

The potassium chloride used in the determination of the cell constants was Mallinckrodt analytical reagent grade. It was fused in a platinum dish, ground in an agate mortar and stored over sulfuric acid until needed.

2. Preparation of the Solutions.

a. Concentration range from 0.02N to saturation:

At least 2.3 grams of salt was weighed to 0.2 mg. The salt was then washed into a tared flask and made up approximately to the desired weight. The resulting solutions were weighed on an analytical balance to the nearest 0.2 mg. when their total weight was less than 120 grams. The more dilute solutions were weighed on a large balance to the nearest 10 mg. Since these always weighed more than 200 grams, the weight concentration was always known to at least 0.01%. It should also be pointed out that all weighings were corrected to vacuum.

b. Dilute Solutions

These solutions were prepared by successive additions of salt to a known amount of water. At least 0.02 grams of salt were weighed on a Mettler M-5 Grammatic micro-balance to the nearest 2 μgms. A maximum of six additions was made so that the weight concentrations for these solutions was also known to at least 0.01%.

3. The Conductance Water.

A Barnstead still with a block tin condenser was used to supply the conductance water. The water obtained from this still usually had a specific conductance less than 5×10^{-6} mhos/cm. at 25°C and it was used without further purification for the more concentrated solutions.

In the medium concentration range the water from the Barnstead still was first passed through an Amberlite M-3 mixed bed ion - exchange resin and then "equilibrated" with the carbon dioxide of the atmosphere by shaking for at least half an hour. The specific conductance was now about $2 - 3 \times 10^{-6}$ mhos/cm. at 25°C.

In the very dilute region the water from the still was further purified by bubbling nitrogen through it for several hours. Before the nitrogen was bubbled through the water, however, it was purified by bubbling it through alkaline pyrogallol, sulfuric acid and ascarite and finally saturated by bubbling it through two tall water saturators which were situated right in the thermostat. In this way water having a specific conductance of $2 - 3 \times 10^{-7}$ mhos/cm. was obtained.

4. The Conductance Bridge.

A model 200 C Hewlett-Packard Oscillator was used to supply the 1000 cycles per second alternating current. The other components of the bridge were, a No. 4750 resistance box, a variable condenser and a No. 1553 Leeds and Northrup shielded ratio box. The resistances in the No. 4750 resistance box were calibrated for internal consistency by comparison with a Jones bridge. A pair of headphones served as a detector. In order to avoid heating of the solution a low voltage output from the oscillator was used and the signal was amplified, after it had passed through the cell, by means of a Heathkit EA - 2 12 watt amplifier.

5. The Conductance Cells.

The conductance cells which were used all had the leads and filling tubes sufficiently far apart, as suggested by Jones and Bollinger (25), so that errors due to the Parker effect (26) would be avoided.

The solutions used to determine the cell constants were those defined by Jones and Bradshaw (27) as follows:

Solution	Gms KCl/1000 gms sol'n all wts. corr. to vac.	Sp. Cond. at 25°C.
1.0 Demal	71.1352	0.111342 mhos/cm.
0.1 Demal	7.41913	0.0128560
0.01 Demal	0.745263	0.00140877

The cell constants were determined periodically and were found to be constant within 0.03%. The cell constants were 1.4409, 18.229, 61.18, 181.34 and 443.76.

For the determination of Λ_0 the conductance of the very dilute solutions was measured in a cell of the Shedlovsky type (28) shown in Figure 1, and using the apparatus assembled by Bock (29), shown in Figure 2. The cell constant for this cell was obtained by using the following equation, published by Fuoss (30) et al.

$$\Lambda = 149.93 - 94.65c^{1/2} + 58.74c\log c + 198.4c \qquad \text{.....} \ 50)$$

From this equation Λ for KCl at 25°C can be calculated for a given concentration. But,

$$\Lambda = \frac{1000A}{CR} \qquad \text{.....} \ 51)$$

where R is the measured resistance of the KCl solution and A is the cell constant. A is the only unknown in equation 51) and can thus be calculated. In this way the cell constant for the Shedlovsky cell was found to be 0.43246.

Since no solutions for the determination of cell constants at 35°C have been defined, it was impossible to determine them at this temperature. Washburn (31), however, has shown that the expression,

$$\Delta A = -\beta A \Delta T$$

gives the change of cell constant with change in temperature

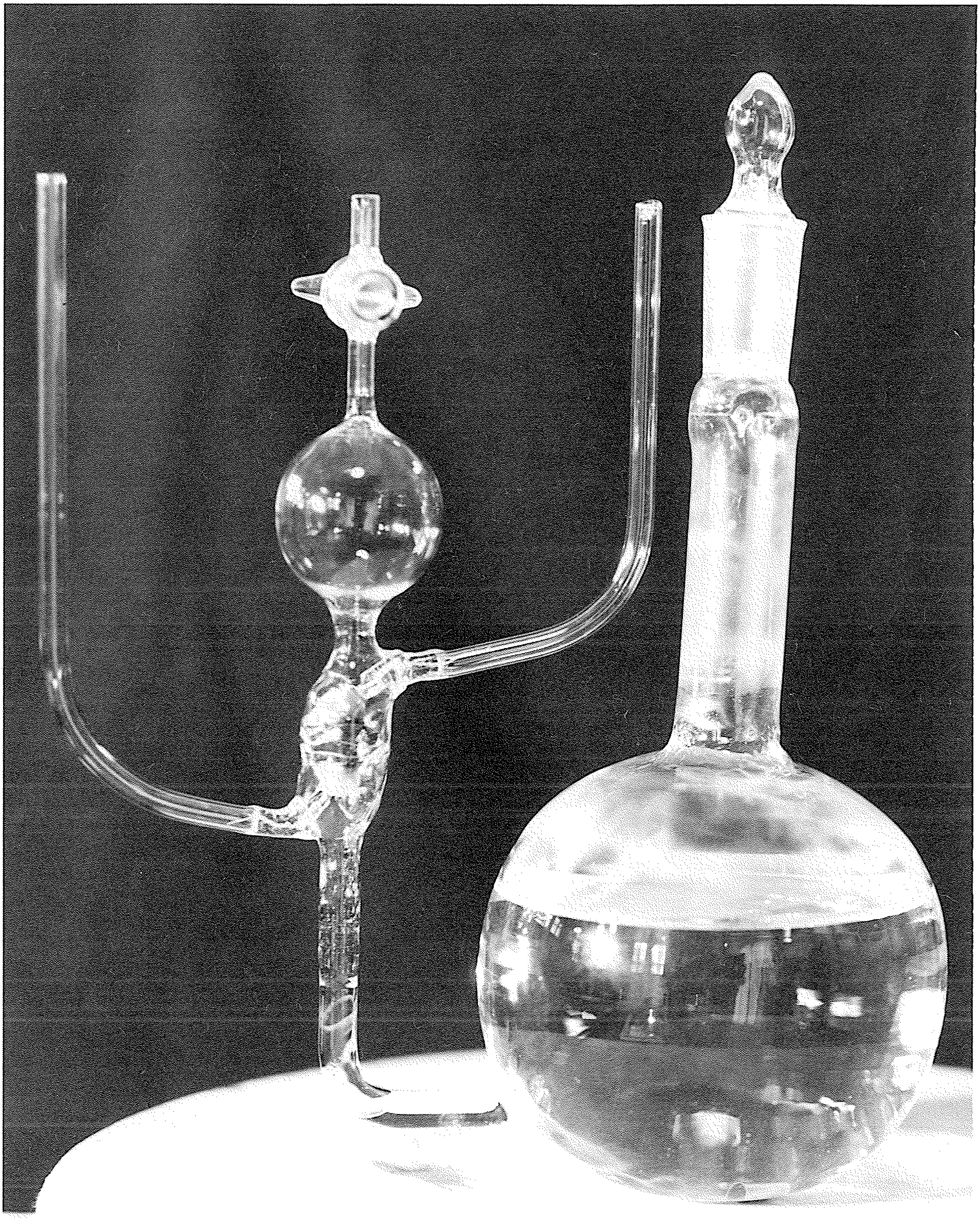

FIGURE 1
The Shedlovsky-type Cell

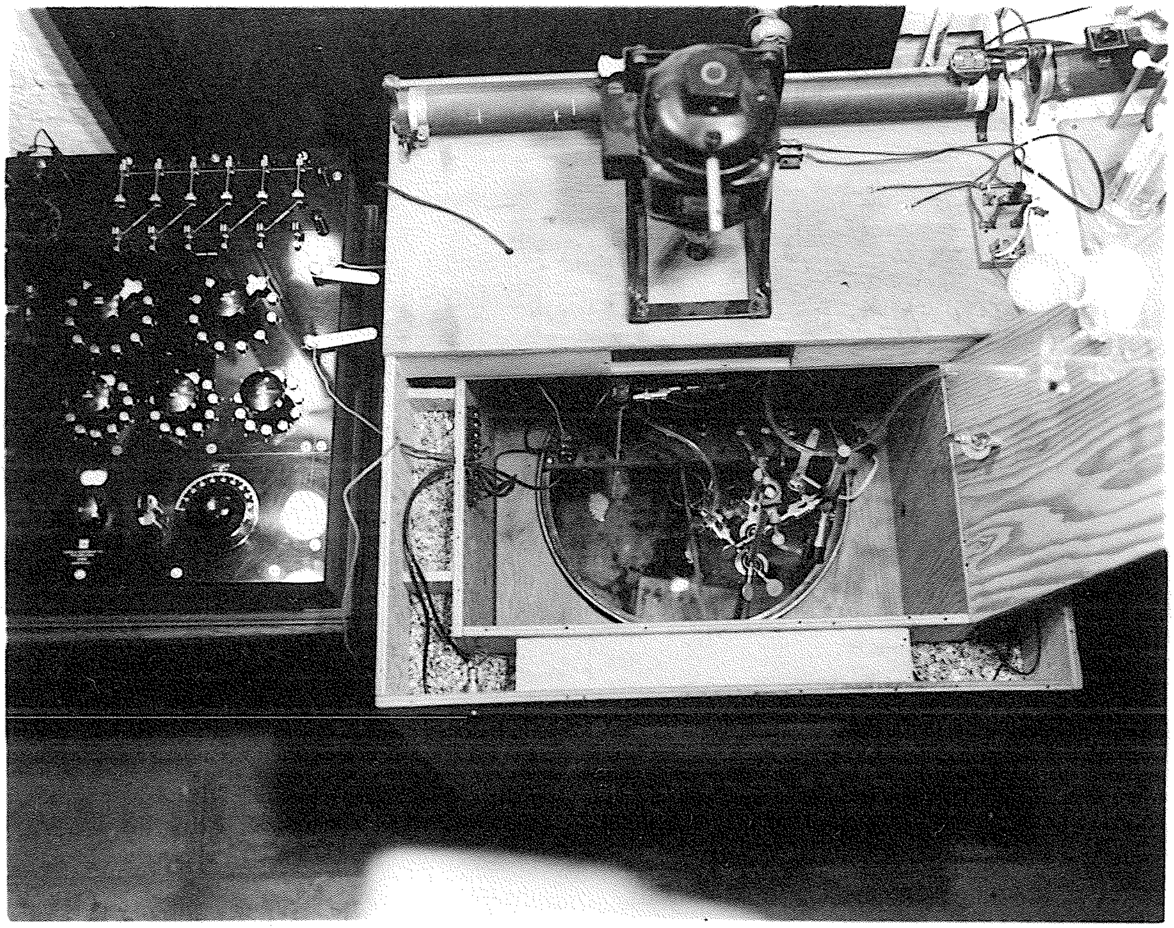

FIGURE 2

Thermostat for Dilute Solutions

for cells with large electrode separation. Here ΔA is the change in cell constant A, β is the linear coefficient of thermal expansion for glass and ΔT is the change in temperature. In this work ΔT was 10°C and since β is about 3.5×10^{-6} units per degree centigrade $\Delta A/A$ is less than 0.004%. This is well within the experimental error and therefore the cell constants were assumed to be the same at both temperatures.

6. The Thermostats.

The thermostat used for the very dilute solutions was the one assembled by Bock (29) and shown in Figure 2. The tank, containing about six gallons of bleached petroleum oil, was housed in a double-walled insulated box. Stirring was accomplished by means of a pump. The temperature, which was controlled by a mercury-toluene regulator and thyratron relay as described by Swinehart (32), was read on a platinum resistance thermometer that had been calibrated by the National Research Council. The temperature was known to about 0.005°C and was constant within 0.002°C.

When the bath was operated at 35°C the temperature of the air above the bath was maintained just above 35°C to prevent distillation of solvent into the exposed section of the cell.

The other two baths were thick-walled Pyrex vessels of about four gallon capacity. Each vessel was lagged with half inch felt and Marcol GX petroleum oil was used as the bath liquid. Two propeller-type stirrers were used in each bath to insure uniform temperature throughout. In addition the 25°C bath contained a copper cooling coil so that the bath could be cooled whenever necessary. Mercury-toluene regulators were used in conjunction with electronic relays and the temperature was read on Beckmann thermometers which were calibrated periodically against a platinum resistance thermometer. Here, too, the temperature was known within 0.005°C, while constancy was maintained within 0.002°C.

7. The Viscosity Measurements.

The two viscometers used were of the Cannon and Fenske (33) type in which drainage and kinetic energy corrections are negligible. They were calibrated with water at 25°C and 35°C. To fill the viscometer the capillary arm was inverted into the solution and gentle suction was applied to the wide arm until the liquid rose to the mark on the capillary arm. The two arms were then connected by means of rubber tubing to prevent loss by evaporation while the viscometers came to temperature in the bath. They were left in the bath at least half an hour before readings were taken. Run times were reproducible to only 0.05%.

8. The Density Measurements.

Two pycnometers, each having a capacity of approximately

45mls. were used in this research. They were calibrated with water at each temperature. Periodical calibrations were constant within at least 0.002%.

The pycnometers were filled completely and were than placed in the thermostat, where they were left at least half an hour. After this time the excess solution was removed by holding a filter paper to one arm until the liquid was adjusted to the mark on the other arm. The arms were capped and the pycnometers were removed from the bath, rinsed with acetone and dried. They were then left in the balance case at least half an hour before they were weighed.

Density and viscosity measurements were not made on the six most dilute solutions since these were made up by successive additions of salt to the Shedlovsky-type cell. The measurement of density, viscosity and conductance at 35°C was done without refilling the instruments.

9. The Hydrolysis Correction.

Hydrolysis of the sodium hexanoate will occur according to the following equation:

$$C_6H_{11}O_2^- + H_2O \longrightarrow C_6H_{11}O_2H + OH^-$$

The method of Campbell and Bock (34) was used to correct the equivalent conductance for the effect of the hydrolysis. This method calculates x, the degree of hydrolysis from the expression,

$$x = -\frac{K_h}{2C} + - \frac{K_h^2}{4C^2} + \frac{K_h}{C}$$

where K_h is the hydrolysis constant and C is the stoichiometric concentration, and then assumes that the equivalent conductance of the free acid or base will be the limiting equivalent conductance. Then it follows that,

$$\Lambda_{exp't} = (1 - x)\Lambda_{true} + x\Lambda_{o\,acid}$$

Thus Λ_{true}, the equivalent conductance of the unhydrolyzed salt can be calculated.

The hydrolysis constants were obtained from the data of Everett, Landsman and Pinsent (35). At 25°C $K_h = 7.25 \times 10^{-10}$ and at 35°C $K_h = 1.57 \times 10^{-9}$. The value of K_h at 35°C was obtained by a graphical interpolation of the above data. The hydrolysis correction was applied to all the results.

EXPERIMENTAL RESULTS

TABLE I

DATA FOR SODIUM HEXANOATE AT 25°C

Concentration (moles/liter)	Density (gm/ml.)	Relative Viscosity	Specific Conductance (mhos/cm.x10^4)	Equivalent Conductance (mhos)
0.000250	-	-	0.19197	76.56
0.000632	-	-	0.48207	76.04
0.000968	-	-	0.73337	75.65
0.001579	-	-	1.1889	75.16
0.002320	-	-	1.7350	74.69
0.003249	-	-	2.4128	74.18
0.019937	0.99788	1.014	13.876	69.57
0.049792	0.99896	1.035	32.648	65.55
0.099588	1.00075	1.067	61.299	61.54
0.50023	1.01527	1.374	231.01	46.18
0.98536	1.03233	1.875	350.52	35.57
2.0019	1.05917	4.606	498.53	24.89
2.6215	1.07242	11.654	531.99	20.29
2.9987	1.08127	21.64	521.35	17.38
3.4487	1.09058	39.27	477.78	13.85

TABLE II

DATA FOR SODIUM HEXANOATE AT 35°C

Concentration (moles/liter)	Density (gm/ml)	Relative Viscosity	Specific Conductance, (mhos/cm$\times10^4$)	Equivalent Conductance (mhos)
0.000611	-	-	0.5782	94.31
0.001164	-	-	1.0925	93.64
0.001604	-	-	1.4973	93.16
0.002241	-	-	2.0783	92.60
0.002926	-	-	2.6983	92.08
0.003014	-	-	3.5845	91.45
0.019875	0.99480	1.015	17.087	85.91
0.049637	0.99585	1.033	40.204	80.96
0.092732	0.99759	1.064	-	-
0.49838	1.01152	1.341	288.06	57.79
0.98092	1.02768	1.778	455.42	45.40
1.9909	1.05335	4.202	643.49	32.31
2.6061	1.06612	10.14	688.89	26.43
2.9803	1.07473	17.46	682.15	22.88
3.4238	1.08270	30.26	635.93	18.57

DISCUSSION OF THE RESULTS

DISCUSSION OF THE RESULTS

1. Estimation of the Possible Error.

It has already been pointed out that the calibrations of the pycnometers were constant within 0.002%. A similar error must be assumed for the density measurements themselves, and allowing for the fact that the errors may be additive would restrict the density determinations to an accuracy of 0.004%.

The accuracy of the equivalent conductances depends on the accuracy of the various measurements involved in determining them, namely; concentration, resistance, temperature and cell constants. The temperature coefficient of conductance is usually between 2 and 3 percent per degree centigrade and since the temperature was known within 0.005°C, the error incurred would be less than 0.02%. The error due to the concentration measurements would be less than 0.01%, as has been pointed out earlier. The more significant sources of error are those due to an inconsistency in the resistances and an error in the determination of the cell constants. The latter were constant within 0.03%. The resistances were calibrated for internal consistency against a Jones bridge, ascertaining consistency within 0.02%. At this point it should be mentioned that accurate absolute values of the resistance are unnecessary since all measurements are relative to the equivalent conductance of the potassium chloride used for the determination of the cell constants and a small error in the cell constant will be compensated for by a similar error in the determination of the specific conductance.

Now it must again be assumed that all these errors may be additive and thus a limit of 0.1% would have to be imposed on the accuracy of the equivalent conductances.

2. The Limiting Equivalent Conductances.

The limiting equivalent conductance is a quantity which cannot be determined by direct experimental measurement and it is generally determined by either the Kohlrausch method or the Shedlovsky (20) extrapolation technique. In the Kohlrausch method the equivalent conductance is plotted as a function of the square root of the concentration. In the very dilute region a straight line is obtained, which can be extrapolated to zero concentration to get the limiting equivalent conductance.

Shedlovsky observed that a plot of Λ_o', where Λ_o' is defined by the expression,

$$\Lambda_o' = \frac{\Lambda + \alpha\sqrt{C}}{1 - \beta\sqrt{C}}$$

against the first power of the concentration usually resulted in a linear plot up to a concentration of about 0.1N. This plot could again be extrapolated to zero concentration to get the desired quantity.

Both of these methods were used in this research. Only the first six measurements at each temperature were used to determine Λ_0. The results of the Kohlrausch extrapolation method are shown graphically in Figure 3 for 25°C and in Figure 4 for 35°C. In both cases the maximum deviation from the straight line, calculated by the method of least squares, did not exceed 0.05%. At 25°C this method gave a value of 77.47 ± 0.04 mhos for the limiting equivalent conductance. At 35°C the limiting equivalent conductance was found to be 96.23 ± 0.05 mhos.

Figures 5 and 6 give the results for the Shedlovsky extrapolation method for 25°C and 35°C respectively. From these graphs the limiting equivalent conductances were found to be 77.84 mhos at 25°C and 96.71 mhos at 35°C. In both cases the values are higher than those obtained by the Kohlrausch method. Similar results were observed by Bock (36) for the various ammonium salts. In view of the facts that the Shedlovsky method is empirical and the deviations from the straight line were small, it was decided in this research to use the values of the limiting equivalent conductance obtained by the Kohlrausch method. These are the values used in the calculations.

The limiting equivalent conductances of the sodium ion, as reported by Benson and Gordon (37), are 50.10 mhos at 25°C and 61.54 mhos at 35°C. Subtracting these values from

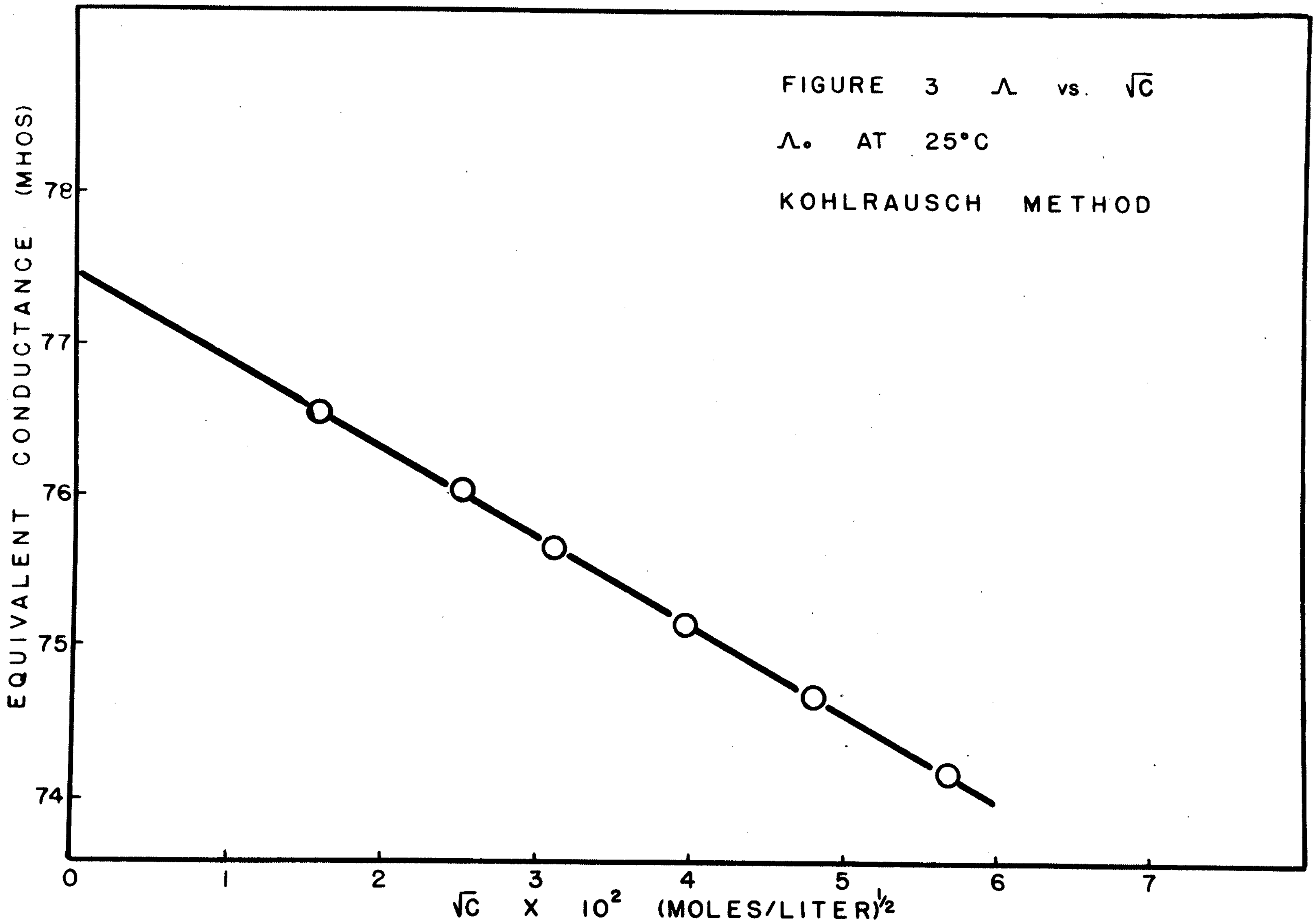

FIGURE 3 Λ vs. $\sqrt{C}$

Λ_0 AT 25°C

KOHLRAUSCH METHOD

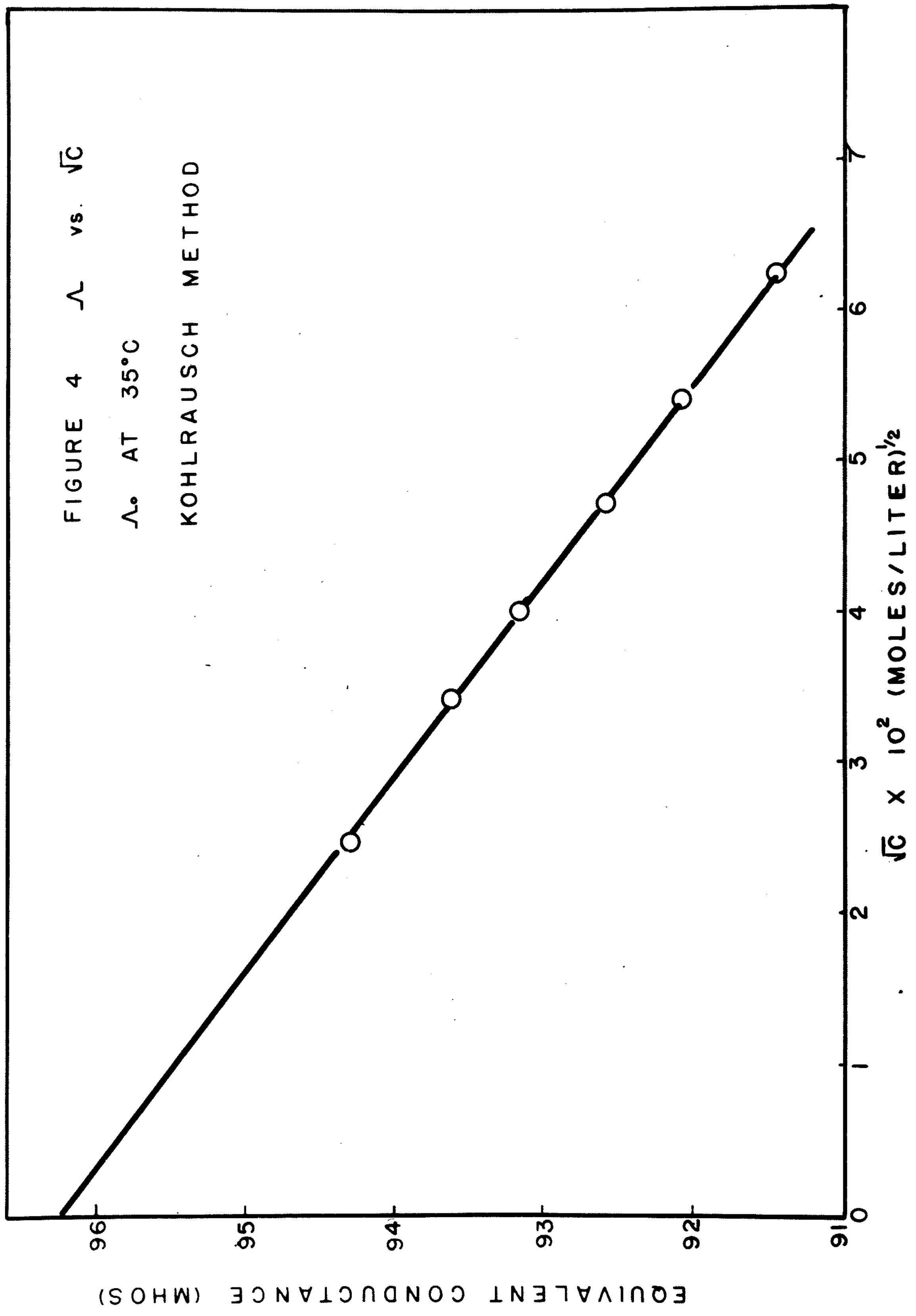

FIGURE 4 Λ vs. $\sqrt{C}$

Λ_0 AT 35°C

KOHLRAUSCH METHOD

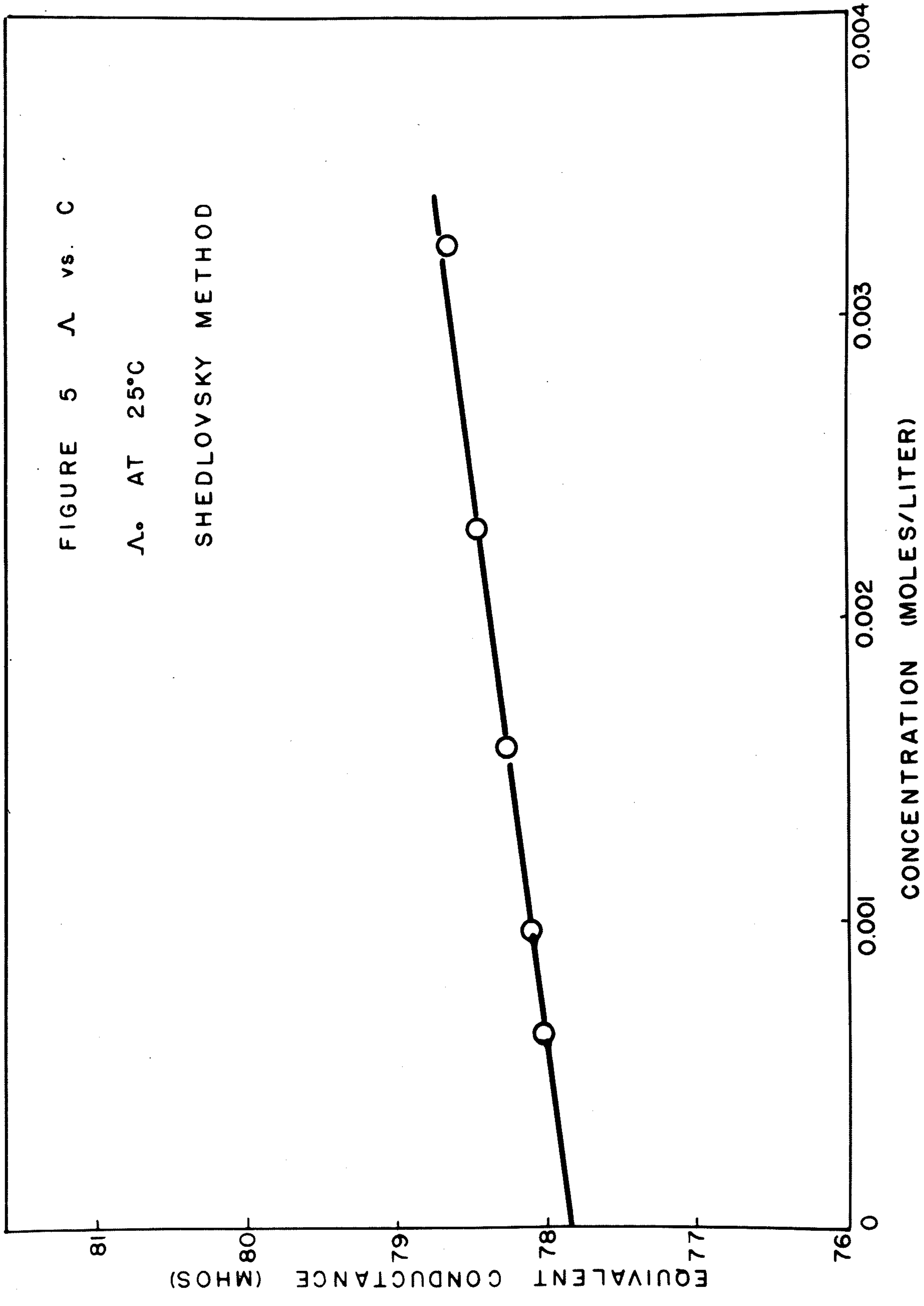

FIGURE 5 Λ vs. C

Λ_0 AT 25°C

SHEDLOVSKY METHOD

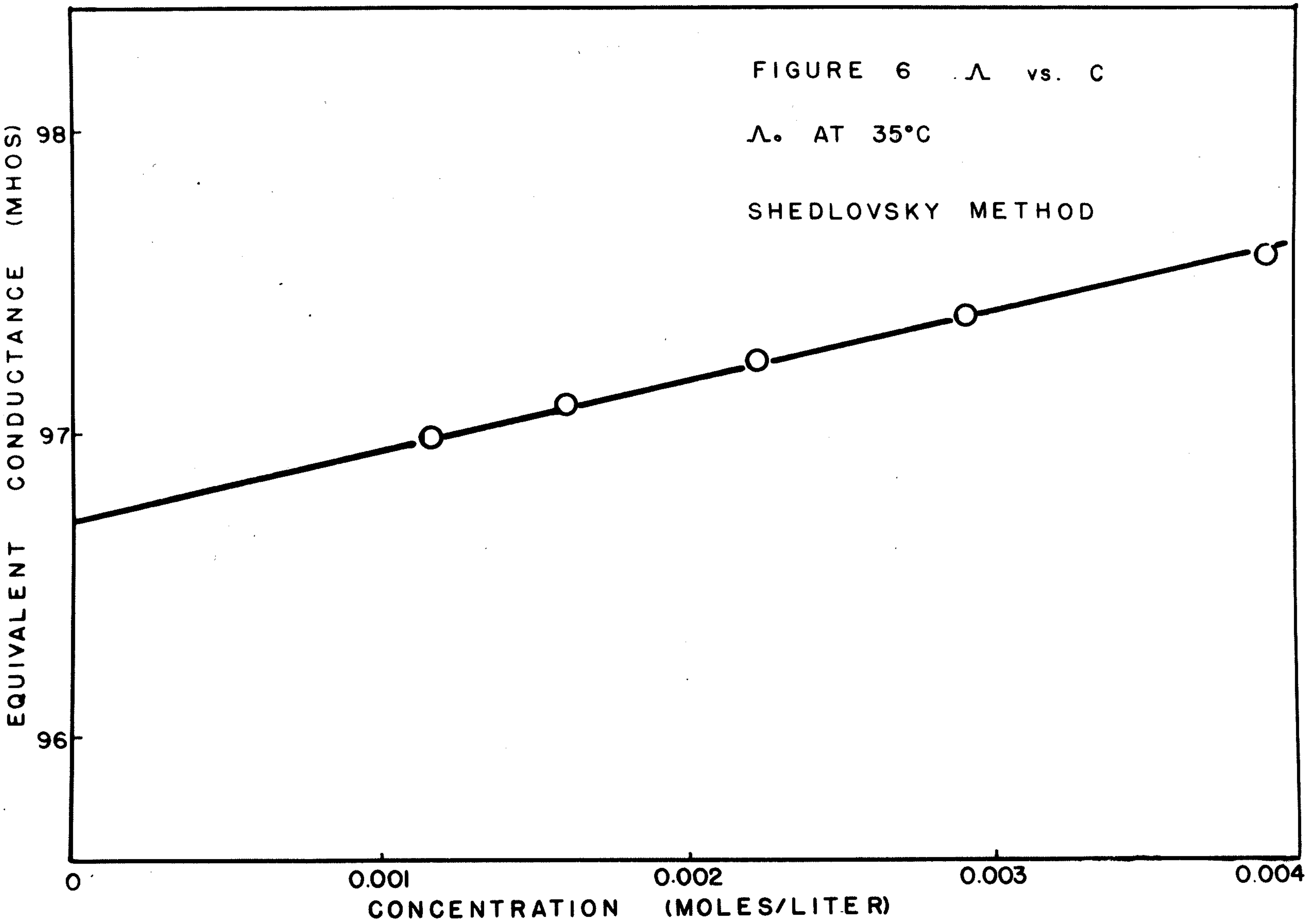

FIGURE 6 Λ vs. C

Λ_0 AT 35°C

SHEDLOVSKY METHOD

the values obtained for sodium hexanoate by the Kohlrausch method establishes the limiting equivalent conductances of the hexanoate ion as 27.37 ± 0.04 mhos and 34.69 ± 0.05 mhos at 25°C and 35°C respectively.

3. Application of the Conductance Equations.

The viscosity corrected forms of the Robinson-Stokes and Falkenhagen-Leist equations have been used in the following calculations. Since, however, viscosity determinations were not made for the six most dilute solutions these values were estimated for purposes of the calculations by means of a graphical interpolation.

The conductance equations were programmed for a Bendix G-15D computer in such a way that the best $\mathring{a}$ was found for each concentration. Then an $\mathring{a}$ was chosen in the dilute region, usually about 0.1N, and this $\mathring{a}$ was then used to calculate a conductance value for each concentration. This calculation was also done on the computer.

(1) Sodium Hexanoate and the Robinson-Stokes Equation.

The 25°C data based on the Robinson-Stokes equation are given in columns 3 and 4 of Table III. The two values $\mathring{a} = 13\text{Å}$ and $\mathring{a} = 20\text{Å}$ were used in these calculations and the results for $\mathring{a} = 13\text{Å}$ have been plotted in Figure 7.

Several points are to be noted. It is observed that even in the very dilute region the calculated and observed conductances differ by as much as 0.3 mhos. When $\mathring{a} = 13\text{Å}$ is used, the calculated and observed conductances agree within 0.7 mhos up to a concentration of 0.5 molar, but for higher concentrations the calculated values differ markedly from the experimental results.

For $\overset{\circ}{a} = 20\text{Å}$ the deviations become large for a concentration of 0.02 molar. Below this concentration the agreement is similar to that observed for $\overset{\circ}{a} = 13\text{Å}$. The reason for the similarity in the dilute region using two different values for $\overset{\circ}{a}$ is that the equation becomes less sensitive to a change in $\overset{\circ}{a}$ at lower concentrations. Friesen (38) has shown that the Falkenhagen-Leist equation reproduces experimental data for a 0.001N solution whose conductance is known to an accuracy of 0.01%, even if the $\overset{\circ}{a}$ values differ by as much as 25%. Since conductances are usually not known to 0.01%, an even larger deviation in $\overset{\circ}{a}$ would still reproduce the experimental value within the error.

The results obtained with the Robinson-Stokes equation at 35°C are given in columns 3 and 4 of Table IV. The results for $\overset{\circ}{a} = 17\text{Å}$ are shown graphically in Figure 8.

Again it is observed that the agreement between observed and calculated values in the dilute region is only within 0.5 mhos. For $\overset{\circ}{a} = 10\text{Å}$ the conductance values are reproduced within 0.5 mhos up to a concentration of 0.05 molar. For $\overset{\circ}{a} = 17\text{Å}$ the agreement is somewhat better in the dilute region but it extends only to 0.004 molar. The calculated values for the higher concentrations again deviate very

TABLE III

CALCULATED EQUIVALENT CONDUCTANCES AT 25°C

Concentration (moles/liter)	Equivalent Conductance (mhos)	Calculated E. Conductance Robinson-Stokes (mhos)		Calculated E. Conductance Falkenhagen-Leist (mhos)	
		$\mathring{a}$ = 13.0Å	$\mathring{a}$ = 20.0Å	$\mathring{a}$ = 5.5Å	$\mathring{a}$ = 7.0Å
0.000250	76.56	76.31	76.34	76.52	76.52
0.000632	76.04	75.67	75.75	75.96	75.98
0.000968	75.65	75.28	75.40	75.62	75.64
0.001579	75.16	74.73	74.91	75.11	75.15
0.002301	74.69	74.23	74.48	74.63	74.69
0.003249	74.18	73.72	74.04	74.13	74.20
0.019937	69.57	69.56	70.63	69.59	69.95
0.049792	65.55	66.17	67.81	65.50	66.19
0.099588	61.54	62.58	64.65	61.14	62.18
0.50023	46.18	45.52	47.78	42.65	44.49
0.98536	35.57	32.19	33.69	29.81	31.53
2.0019	24.89	12.39	12.55	11.58	12.45
2.6215	20.29	4.739	4.622	4.503	4.867
2.9987	17.38	2.500	2.362	2.406	2.608
3.4487	13.85	1.342	1.208	1.315	1.430

TABLE IV

CALCULATED EQUIVALENT CONDUCTANCES AT 35°C

Concentration (moles/liter)	Equivalent Conductance (mhos)	Calculated E. Conductances Robinson-Stokes (mhos)		Calculated E. Conductances Falkenhagen-Leist (mhos	
		$\mathring{a} = 10\mathring{A}$	$\mathring{a} = 17\mathring{A}$	$\mathring{a} = 4.0\mathring{A}$	$\mathring{a} = 6.0\mathring{A}$
0.000611	94.31	93.97	94.07	94.37	94.40
0.001164	93.64	93.17	93.37	93.69	93.74
0.001604	93.16	92.67	92.93	93.24	93.31
0.002241	92.60	92.14	92.45	92.71	92.81
0.002926	92.08	91.58	91.99	92.21	92.34
0.003914	91.45	90.94	91.46	91.60	91.77
0.019875	85.91	85.58	87.21	85.98	86.64
0.049637	80.96	81.04	83.54	80.48	81.78
0.49838	57.79	55.65	59.82	51.18	55.21
0.98092	45.40	40.31	43.52	35.90	39.94
1.9909	32.31	16.16	17.14	14.06	16.24
2.6061	26.43	6.514	6.755	5.661	6.638
2.9803	22.88	3.721	3.786	3.240	3.827
3.4238	18.57	2.106	1.620	1.842	2.194

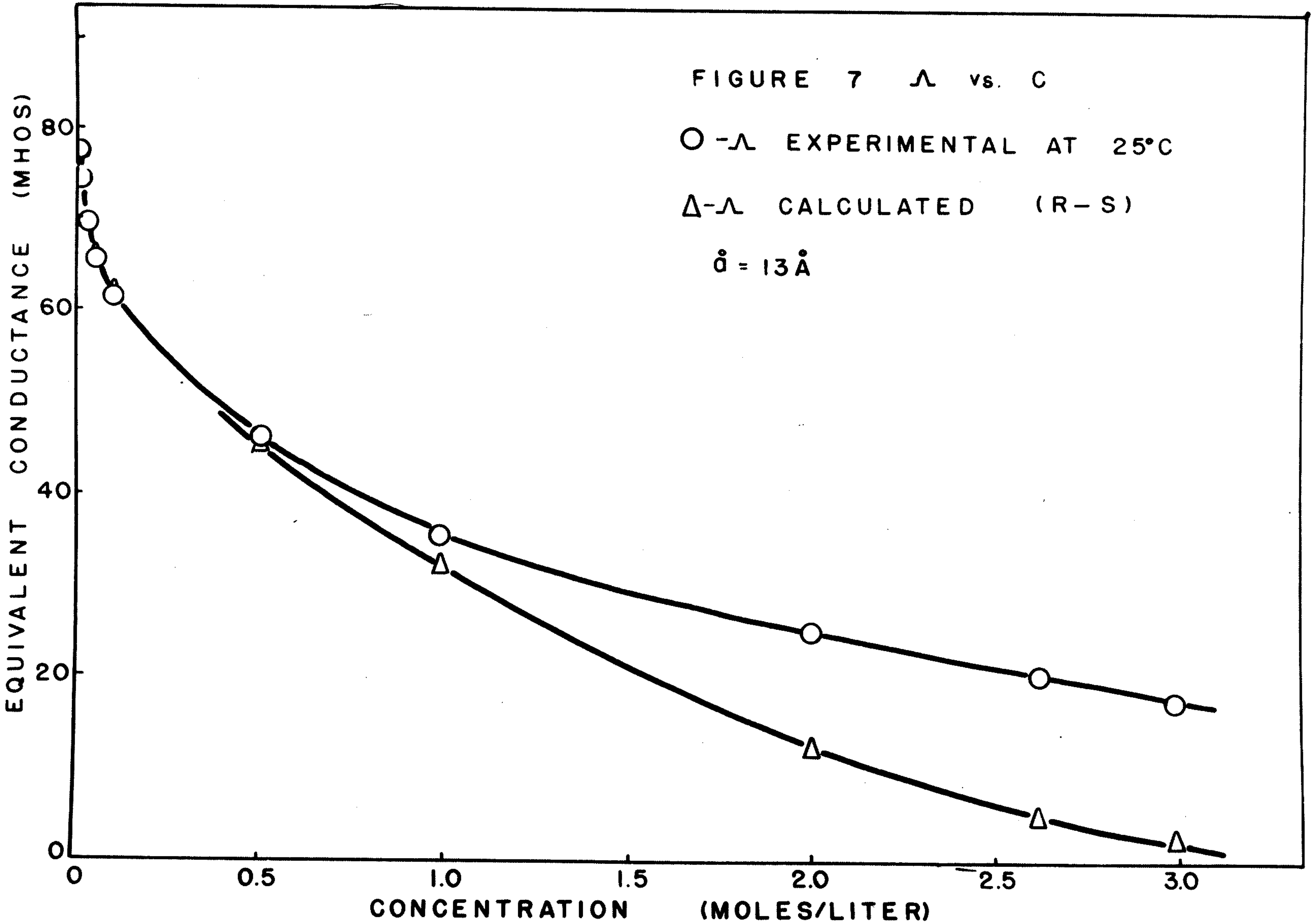

FIGURE 7 Λ vs. C

markedly from the experimental values.

(ii) Sodium Hexanoate and the Falkenhagen-Leist Equation.

a.) At 25°C.

The results of the calculations at 25°C based on the Falkenhagen-Leist equation are given in columns 5 and 6 of Table III. Figure 9 gives a graphical comparison of the experimental results with the calculated values using $\mathring{a} = 5.5\,\text{Å}$.

In the dilute region this equation reproduces the data rather well, the deviations being less than 0.1 mhos up to 0.05 molar and 0.4 mhos at a 0.1 molar when $\mathring{a} = 5.5\,\text{Å}$. For the larger value, $\mathring{a} = 7.0\,\text{Å}$, the deviations become appreciable at 0.02 molar. Above 0.1 molar the equation fails rather badly.

b.) At 35°C.

Columns 5 and 6 of Table IV give the 35°C data obtained with the Falkenhagen-Leist equation. These are compared with the experimental results in Figure 10, using $\mathring{a} = 4.0\,\text{Å}$. Behavior similar to that observed at 25°C was also observed at 35°C. The data are reproduced within 0.5 mhos up to 0.05 molar when $\mathring{a} = 4.0\,\text{Å}$ and within 0.8 mhos when $\mathring{a} = 6.0\,\text{Å}$.

4. General Discussion.

Several points must be noted when the results presented in the foregoing discussion are considered. First of all, it

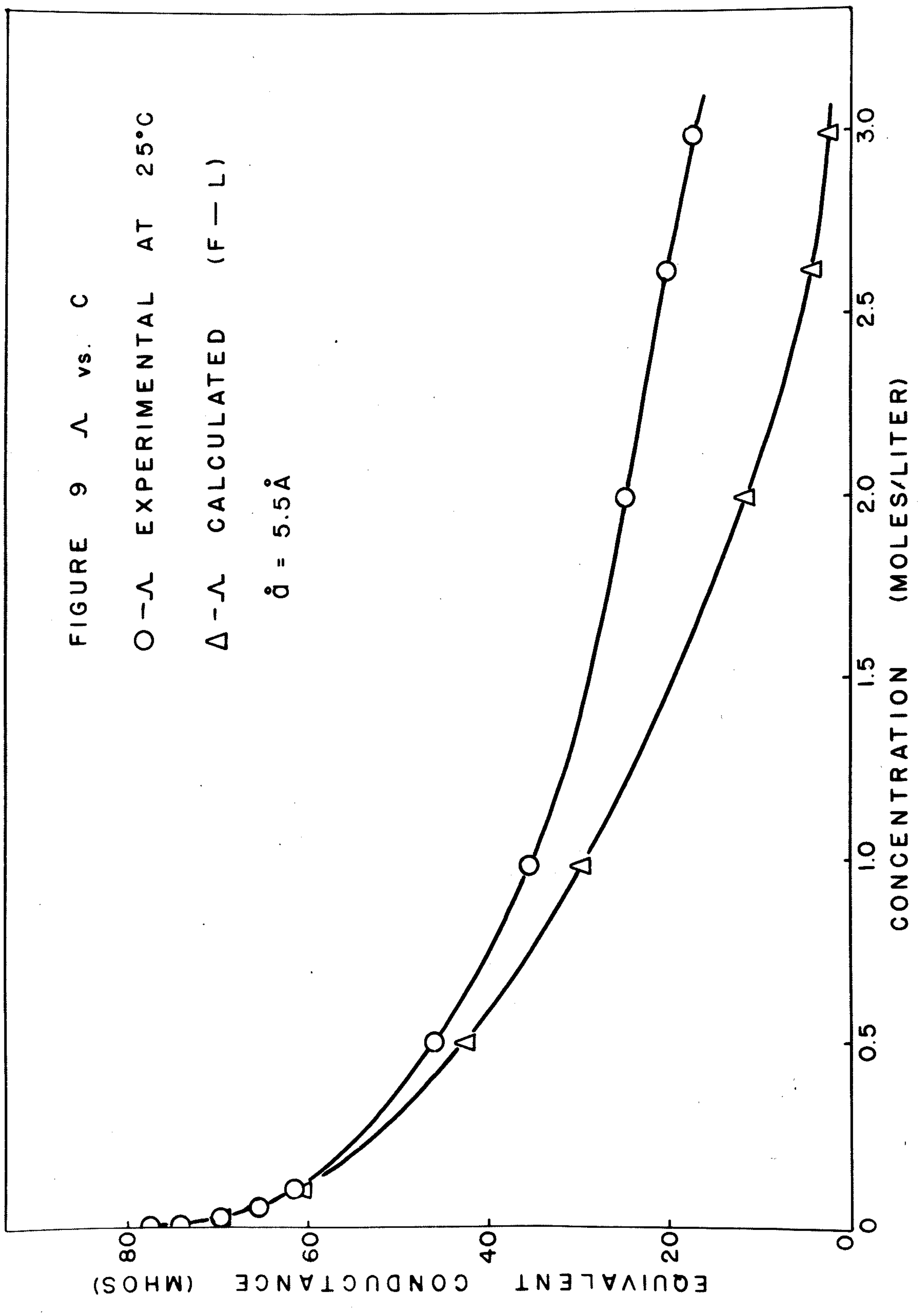

FIGURE 9 Λ vs. C

○ - Λ EXPERIMENTAL AT 25°C

Δ - Λ CALCULATED (F — L)

å = 5.5Å

must be noted that the Robinson-Stokes, as well as the Falkenhagen-Leist equations fail when applied to the more concentrated solutions, and secondly it is noted that the å values necessary to reproduce the data even in the dilute region are rather large. This latter observation is especially true of the Robinson-Stokes equation where å's of 10Å or greater had to be assumed.

One reason for the failure of the equation when applied to the concentrated solutions may be the empirical nature of the viscosity correction. The viscosity rises rather rapidly for these solutions and using some fractional power of the viscosity could bring these results closer to the observed values. Furthermore, it must be remembered that theoretically these equations are not expected to apply in this region.

The reason for the large å values was sought in terms of micelle formation. According to McBain (39) solutions of colloidal electrolytes exhibit approximate ideal behavior until a certain concentration characteristic of the substance is reached. Then marked deviation from ideal behavior sets in rather suddenly and the narrow concentration region where this occurs is referred to as the critical micelle concentration. The deviation from ideal behavior is attributed to an aggregation of the particles to form charged micelles.

The fatty acids belong to the class of compounds which exhibit this behavior. Formation of micelles causes a change in the number of particles which in turn causes a change in the colligative properties of the solution. Smith and Robinson (40) employed the isopiestic vapor pressure method to obtain the osmotic coefficients for the sodium salts of the fatty acids at 25°C. From these they calculated the molal vapor pressure lowering and found that the butyrate ion was the first member of the series which exhibited any tendency toward micelle formation. Micelle formation was also observed for the hexanoate ion.

The change in the number of particles should also be evident in the conductance curves. McBain (41) and co-workers measured the conductance of the potassium salts of the fatty acids at 18°C and at 90°C and observed that anomalous curves were obtained beginning with the potassium laurate (C_{12}).

It will be observed from the figures showing equivalent conductance as a function of concentration for sodium hexanoate (Figures 7 - 10) that these do not show the minimum exhibited by salts which form micelles, viz. potassium laurate. In Figure 11 the specific conductance is plotted as a function of concentration. If micelle formation occurred these curves should show a "break" corresponding to the critical micelle concentration. Since these "breaks" are absent it must be concluded that micelle formation does not occur.

The same conclusions were reached on the basis of an apparent molecular weight determination using the vacuum flask freezing point depression method. In this method finely shaved ice and the solution of the sodium hexanoate

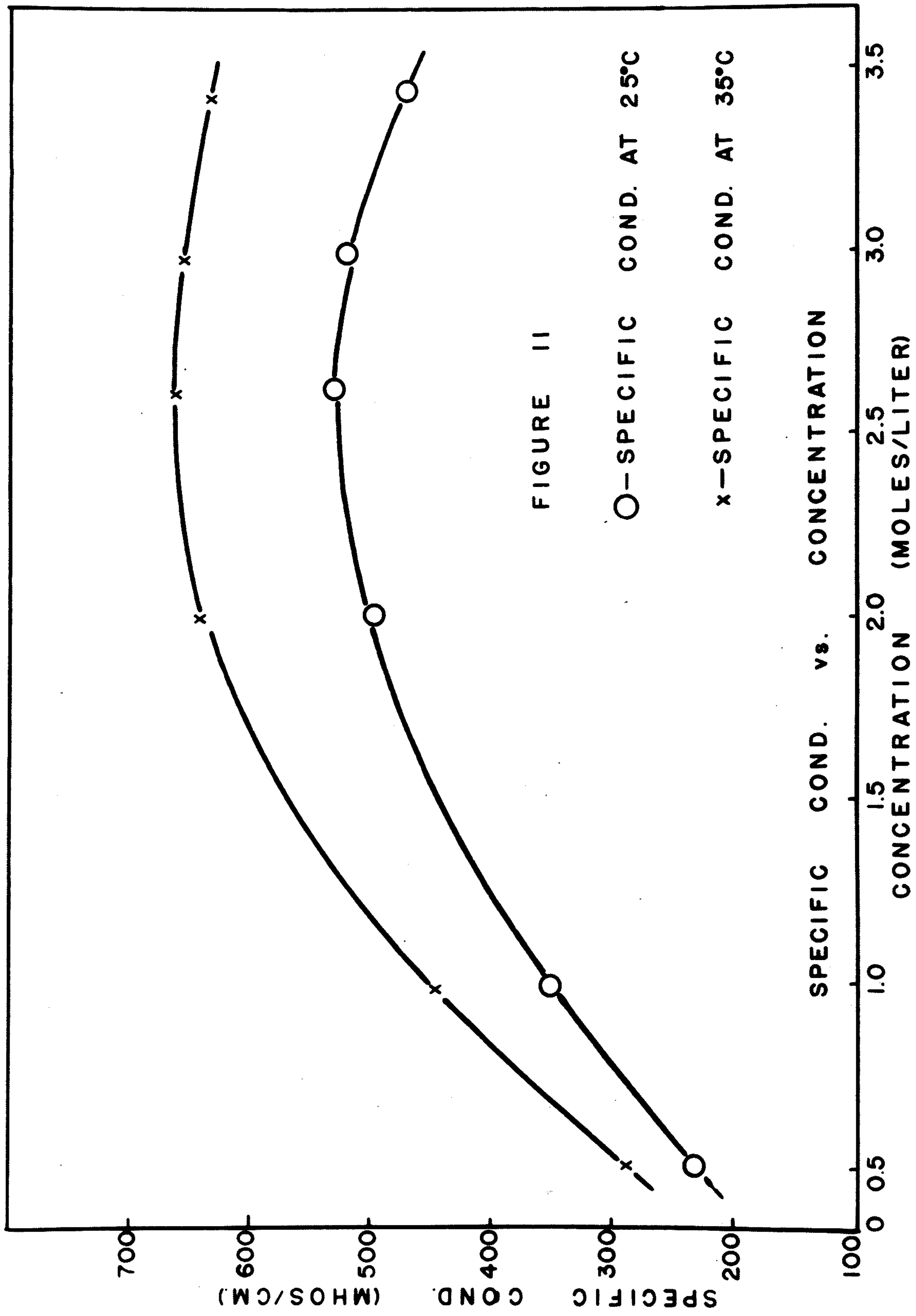

FIGURE II

SPECIFIC COND. vs. CONCENTRATION

were thoroughly stirred until equilibrium was reached. The temperature was noted, two samples were withdrawn and the solution was analyzed by evaporation of the water. The results are tabulated in Table V below.

TABLE V

Concentration gms. of salt/ 100 gms. H_2O.	Apparent Molecular Weight
1.0517	69.2
5.1895	67.0
10.287	63.0
17.298	59.5

From the above data it is seen that the apparent molecular weights correspond approximately to the complete dissociation of the salt and they do not give any evidence for micelle formation.

The results of this research are thus seen to be in agreement with the conclusions reached by McBain (41) that the hexanoate anion does not form charged micelles.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

The equivalent conductances, densities and viscosities of aqueous solutions of sodium hexanoate have been determined at 25°C and 35°C at concentrations ranging from 0.0003 molar to saturation.

The limiting equivalent conductances of the hexanoate ion have been determined as 27.37 ± 0.04 mhos at 25°C and 34.69 ± 0.05 mhos at 35°C.

The Robinson-Stokes and the Falkenhagen-Leist equations have been applied to the data. The Robinson-Stokes equation reproduces the data within 0.7 mhos up to 0.5 molar at 25°C when $\mathring{a}$ = 13Å. At 35°C the data are reproduced within 0.5 mhos up to 0.05 molar for $\mathring{a}$ = 10Å. The Falkenhagen-Leist equation reproduces the data at 25°C within 0.4 mhos up to 0.1 molar with $\mathring{a}$ = 5.5Å. An $\mathring{a}$ = 4.0Å reproduces the 35°C data with 0.5 mhos up to 0.05 molar.

From the form of the conductance curves and from an estimation of the apparent molecular weight it was concluded that the hexanoate ion does not form ionic micelles.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Kohlrausch, F.W. and Holborn, L., Das Leitvermoegen der Elekrolyte. Teubner, Leipzig, (1916).

2. Arrhenius, S., Z. physik. Chem., 1, 63, (1887).

3. Milner, S.R., Phil. Mag., 23, 551, (1912).

4. Onsager, L., Physik. Zeit., 27, 388, (1926).
   28, 277, (1927).

5. Hückel, E., Physik. Zeit., 26, 93, (1925).

6. Hasted, J.B., Ritson, D.M. and Collie, C.H., J. Chem. Phys., 16, 1, (1948).

7. Falkenhagen, H., Leist, M. and Kelbg, G., Ann. Physik, 11, 51, (1952).

8. Wicke, E. and Eigen, M., Naturwiss., 38, 153, (1951).

9. Wishaw, B.F. and Stokes, R.H., J. Am. Chem. Soc., 76, 2065, (1954).

10. Falkenhagen, H., private communication to Dr. A.N. Campbell, (1957).

11. Fowler, R.H., Statistical Mechanics, Cambridge University Press, (1929), p. 322.

12. Bernal, J.D. and Fowler, R.H., J. Phys. Chem., 58, 673, (1954).

13. Walden, P., Ulich, H. and Busch, G., Z. Physik. Chem., 123, 429, (1926).

14. Kraus, C., J. Phys. Chem., 58, 429, (1926).

15. Campbell, A.N. and Paterson, W.G., M. Sc. Thesis, University of Manitoba, Chem. Dept., (1957).

16. Campbell, A.N. and Bock, E., Can. J. Chem., 36, 337, (1958).

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

18. Fuoss, R.M., J. Am. Chem. Soc., 80, 3163, (1958).

19. Fuoss, R.M., and Accascina, F., Electrolytic Conductance, Interscience Publishers, Inc., New York, (1959).

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

21. Bjerrum, N., Kgl. Danske Videnstab. Selskab., 1, No. 9, (1926).

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

23. Beilsteins Handbuch der organischen Chemie Zweites Ergänzungswerk II, 282. Simon, Bl. Soc. Chem. Belg. 38,(1959).

24. Stock, Staehler, Patnode and Dennis, *Quantitative Chemical Analysis*, McGraw-Hill Book Co., Inc., New York and London, 1st Ed., (1935).

25. Jones, G. and Bollinger, G.M., J. Am. Chem. Soc., 53, 411, (1931).

26. Parker, H.C., J. Am. Chem. Soc., 45, 1366, (1923).

27. Jones, G. and Bradshaw, B.C., J. Am. Chem. Soc., 55, 1780, (1933).

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

29. Bock, E., Can. J. Chem., 37, 889, (1959).

30. Lind, J.E., Jr., Zwolenik, J.J. and Fuoss, R.M., J. Am. Chem. Soc., 81, 1557, (1959).

31. Washburn, E. W., J. Am. Chem. Soc., 38, 2431, (1916).

32. Swinehart, D.F., Anal. Chem., 21, 1577, (1949).

33. Cannon, M.J. and Fenske, M.R., Ind. Eng. Chem., Anal. Ed., 10, 299, (1938).

34. Campbell, A.N. and Bock E., Can. J. Chem., 36, 330, (1958).

35. Everett, D.H., Landsman, D.A and Pinsent, B.R.W., p. 403, Proc. Roy. Soc., A215, (416).

36. Bock, E., M. Sc. Thesis, University of Manitoba, Chem. Dept., (1957).

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

38. Friesen, R.J., M. Sc. Thesis, University of Manitoba, Chem. Dept., (1959).

39. McBain, M.E.L. and Hutchinson, E., Solubilization and Related Phenomena, Academic Press Inc., Publishers, New York, (1955).

40. Smith, E.R.B. and Robinson, R.A., Trans. Far. Soc., 38, 70, (1942).

41. McBain, J.W., Laing, M.E. and Titley, A.F., J. Chem. Soc., 115, 1279, (1919).