

CONDUCTANCES OF AQUEOUS SOLUTIONS
OF SODIUM OCTANOATE

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ABSTRACT

Equivalent conductances, densities and viscosities of aqueous solutions of sodium octanoate have been determined at 25°C. and 35°C. at concentrations ranging from 0.0002 molar to 3.0 molar. The limiting equivalent conductances of the octanoate ion have been determined at 25°C. and 35°C.

Comparison of the experimental equivalent conductances with the values calculated by the Robinson-Stokes and the Falkenhagen-Leist equations, showed a reasonable agreement only in the dilute region of concentrations. It was also found necessary to use large values of α in the theoretical equations to have this reasonable agreement.

From the general conductance behavior of aqueous solutions of sodium octanoate it has been concluded that the micelle formation does take place with the octanoate ion.

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TABLE OF SYMBOLS

$a, \overset{\circ}{a}$...	Distance of closest approach between ions in solution, in cm. and $\overset{\circ}{A}$, respectively
A ----	Empirical constant
B ----	Fuoss-Onsager constant
B_1, B_2, B_3	Theoretical constants
C ----	Concentration in moles per litre
D ----	Dielectric constant of a pure solvent
E ---	Fuoss-Onsager constant
f ----	Mean ionic activity coefficient of an electrolyte
F ----	Value of the Faraday coulombs
J ----	Fuoss-Onsager constant
k ----	Boltzmann's constant
K_a --	Association constant for ion pair formation
κ ---	Specific conductance in mhos per cm.
η ---	Concentration in ions per unit volume
N ----	Avogadro's number in molecules per gram mole
N_1, N_2 --	Reciprocal of the volume of ions 1 and 2
S ----	Fuoss-Onsager constant
T ----	Temperature in degrees absolute
V ----	Volume in ml.
α, β ---	Debye-Hückel constants
α ----	Degree of dissociation of an electrolyte in solution

e Charge on the electron, e.s.u.

κ ... Reciprocal of the radius of the ionic
atmosphere

Λ, Λ_0 Equivalent conductance and limiting equivalent conductance in mhos

η, η_0 Viscosity of solution and pure solvent, poises

σ_1, σ_2 Fuoss-Onsager constants

THEORETICAL INTRODUCTION

THEORETICAL INTRODUCTION

The Theory of Electrolytic Solutions

The theory of electrolytic solutions, particularly that of uni-univalent and uni-divalent or di-univalent, has developed to a very great extent ever since Arrhenius' theory of electrolytic dissociation appeared in the late nineteenth century. It is not possible to discuss them all in a short thesis like this. Hence an attempt to describe the gradual growth of the theory, with the main stress on our present work, has been made.

In his theory of electrolytic dissociation Arrhenius¹ assumed that an equilibrium existed between the undissociated molecules and the ions, and that the current was carried through the solution by these ions. Arrhenius, assuming complete dissociation at infinite dilution, expressed the conductance ratio $\frac{\Lambda}{\Lambda_0}$ as equal to α , the degree of dissociation of an electrolyte in aqueous solution. In this case the ions were assumed to move independently of one another and their velocities were considered to be constant over a range of concentration. That is, in the expression

$$\frac{\Lambda}{\Lambda_0} = \alpha \frac{(u_+^+ + v_-^-)}{(u_0^+ + v_0^-)} \dots\dots\dots(1)$$

the ratio of ionic velocities at a definite concentration to those at infinite dilution remains unaltered. Application of the law of mass action results in the Ostwald dilution law:

$$\frac{\alpha^2 c}{(1-\alpha)} = k \quad \dots\dots\dots(1A)$$

The Arrhenius theory was successful in accounting for the properties of weak electrolytes but, when applied to strong electrolytes, the values of k were not constant with respect to concentration.

Following the suggestion of Van Larr² that the properties of solutions of strong electrolytes could not be independent of concentration, Sutherland (1902), Noyes (1904), and Bjerrum (1906) adopted the view that the behavior of strong electrolytes in dilute solution could be accounted for by the hypothesis of complete dissociation and an adequate consideration of the effects of interionic attraction. Studies of the crystal structure of electrolytes, which seemed to indicate a regularly arranged aggregation of ions rather than molecules with binding force largely electrostatic in character, strengthened the hypothesis of complete dissociation. Changes in conductivity are thus ascribed to changes in ionic mobility and not to the changes in the degree of dissociation.

The well known Kohlrausch relationship,

$$\Lambda = \Lambda_0 - A\sqrt{c} \quad \dots\dots\dots(2)$$

where A is the slope of the straight line, is strictly empirical, and is valid only for the dilute range of concentration. Any theory, however, should supply a mathematical expression that will simplify to this form for the region of high dilution.

The Debye-Hückel Theory

An attempt to treat the interionic attraction theory of electrolytes quantitatively was made by J. C. Ghosh (1918), with relatively little success, but the work of P. Debye and E. Hückel³ marked the commencement of a new era in electrochemistry. The fundamental idea underlying their deductions is that as a consequence of electrical attractions between positive and negative ions there are, on the average, more ions of unlike than of like sign in the neighborhood of any ion. Every ion may, therefore, be regarded as being surrounded by an ionic atmosphere of opposite charge. When the ion is static the ionic atmosphere has a spherical symmetry. When the ion is made to move under the influence of an external electrical field, there is a distortion of the ionic atmosphere in such a way that the charge density

of its oppositely charged atmosphere becomes greater behind the ion than in front. The rate at which the atmosphere on one side forms and that on the other side dies away is expressed in terms of a quantity called the time of relaxation of the ionic atmosphere. The result is a retardation of the ion; this influence is called the Relaxation Effect.

In addition when an electrical potential is applied the ionic atmosphere itself, along with its associated solvent molecules, moves in a direction opposite to that of the ion, thus reducing the speed of its motion. In other words the viscous resistance of the medium has been increased. This viscous drag on the moving ion is known as the Electrophoretic Effect.

Taking into consideration these two effects together with the Brownian movement of the ions, Onsager developed the following equation for the equivalent conductance:

$$\Lambda = \Lambda_0 - \left[\frac{82.4}{(D_0 T)^{1/2} \eta_0} + \frac{8.20 \times 10^5}{(D_0 T)^{3/2}} \Lambda_0 \right] \sqrt{c} \dots\dots\dots(3)$$

For uni-univalent electrolytes in water at 25°C., equation 3 assumes the simplified form

$$\Lambda = \Lambda_0 - (0.2273 \Lambda_0 + 59.78) \sqrt{c} \dots\dots\dots(4)$$

which is of the form of the empirical Kohlrausch law.

Due to the mathematical simplifications and the assumptions made, which are really valid only for the dilute region, Onsager's equation is not valid at concentration greater than 0.005N. Among the various reasons which render the theory unsuitable at concentrated region are the following:

1. In the potential distribution function,

$$e^{-\frac{\psi_{0j} l_i}{kT}} = 1 - \frac{\psi_{0j} l_i}{kT}$$

the potential ψ_{0j} is assumed to be a linear function of charge density; i.e., only the linear terms in the Boltzmann distribution law are taken into account. Since an exponential term is involved for the distribution, this assumption necessarily restricts the applicability of the equation to low concentration.

2. The ionic size is neglected, and this may introduce serious errors in the evaluation of the relaxation term at higher concentration.

3. The dielectric constant is considered to remain unchanged. But Hasted, Ritson and Collie⁴ have shown that the dielectric constant D of an electrolytic solution of concentration C can be found from the following expression:

$$D = D_0 + 2 \bar{\delta} C$$

where $\bar{\delta}$ represents the average contribution of the ions to the dielectric constant. They have also determined

$\overline{\delta}$ for various electrolytes up to a concentration of 2N. 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.

4. The viscosity effect is not taken into account.

The Wishaw-Stokes Equation

For some twenty years after the appearance of Onsager's theory, no further major progress was made with the relaxation effect. In 1952, however, Falkenhagen, Leist, and Kelbg⁵ published an important extension and modification of the theory, in which allowance was made for the finite size of the ions and a new expression for the relaxation effect was developed. At the same time they used the Eigen-Wicke⁶ distribution function, which also considered the ions to be finite in size, and obtained an expression,

$$\frac{\Delta x}{x} = \frac{\epsilon^2}{3D_0RT} \cdot \frac{0.2929}{1+Ka} \cdot \frac{\exp(0.2929Ka - 1)}{0.2929Ka} \dots\dots\dots(5)$$

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 opposite sense.

K is defined by the following expression:

$$K = \left[\frac{\pi N \epsilon^2}{125 D_0 R T} \right]^{\frac{1}{2}} \sqrt{C} \left[1 - \frac{\ln_1}{2N_1} - \frac{\ln_2}{2N_2} \right] \dots\dots\dots(6)$$

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 Stokes⁷ modified Falkenhagen's expression for the relaxation effect to allow retention of the Boltzmann function and published their conductance equation in the form:

$$\Lambda = \left[\Lambda_0 - \frac{B_2 \sqrt{c}}{1 + Ka} \right] \left[1 - \frac{B_1 \sqrt{c} F}{1 + Ka} \right] \quad \dots(7)$$

where $B_1 = \frac{8.20 \times 10^5}{(D_0 T)^{3/2}} \quad \dots(8)$

$$B_2 = \frac{82.5}{(D_0 T)^{1/2} \eta_0} \quad \dots(9)$$

$$B a \sqrt{c} = \frac{50.29 a \sqrt{c}}{(D_0 T)^{3/2}} = Ka \quad \dots(10)$$

$$F = \frac{\exp(0.2929 Ka - 1)}{0.2929 Ka} \quad \dots(11)$$

and $K = \left[\frac{\pi N e^2}{125 D_0 k T} \right]^{1/2} \sqrt{c} \quad \dots(12)$

In the above equation the only adjustable parameter is the effective ionic diameter a° , if one assumes that Λ_0 is already known from suitable measurements.

The Falkenhagen-Leist Equation

Consideration of the fact that the ions, being impenetrable, must be displaced during migration led Falkenhagen⁸ to evaluate the relaxation effect as

$$\Delta_I = \frac{0.2929 B_2 \Delta_o K}{(1+Ka) \left(1 + \frac{1}{2}\sqrt{2} Ka + \frac{1}{6} K^2 a^2\right)} \dots\dots(13)$$

and the electrophoretic effect as

$$\Delta_{II} = \frac{B_3 K}{1+Ka} \dots\dots(14)$$

where K is defined by equation 12. The constant B_3 is defined by

$$B_3 = \frac{\epsilon^2 N}{27\pi\eta_0 10''} \dots\dots(15)$$

Falkenhagen's general conductance equation is

$$\Delta = \Delta_o - \Delta_I - \Delta_{II} \dots\dots(16)$$

instead of the product type proposed by Wishaw and Stokes. Here, too, "a" is the only adjustable parameter and has the same meaning.

The question arises whether the values for "a" as they appear in the Wishaw-Stokes and 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 7 and 16 are employed to analyze experimental data forces "a" to absorb all imperfections in the theory as well as any experimental error which may have been incurred. Fowler⁹ says, "a" is an 'omnium gatherum' correction." It would seem that the values for "a" are at best only qualitative.

It can be seen that in equations 7 and 16, 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 Fowler¹⁰ have shown that ions in solution affect the viscosity in at least three different 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) change in the hydration of the ions cause changes in the viscosity.

Walden¹¹ studied the relationship between viscosity and equivalent conductance for tetra-ethyl ammonium picrate and found that, for a variety of solvents and for a temperature range of fifty degrees,

$$\Lambda_0 \eta_0 = \text{Constant}$$

Attempts to extend this to solutions of finite concentrations so that

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

have usually failed. Kraus¹² found that the plot $\Lambda \eta$

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, however, that some form of viscosity correction should be applied to the conductance equations. The exact form is not known, but experience has shown that dividing both the Robinson-Stokes and Falkenhagen-Leist equations by the relative viscosity, thus,

$$\Lambda = \frac{\eta_0}{\eta} \left[\Lambda_0 - \frac{B_2 \sqrt{c}}{1 + B_2 \sqrt{c}} \right] \left[1 - \frac{B_1 \sqrt{c}}{1 + B_1 \sqrt{c}} F \right] \dots (17)$$

and
$$\Lambda = \frac{\eta_0}{\eta} \left[\Lambda_0 - \Lambda_I - \Lambda_{II} \right] \dots (18)$$

seems to be very approximately correct. It is observed that these viscosity corrected equations often reproduce experimental data for solutions whose concentration far exceeds the limits to which they are theoretically applicable. Thus, Campbell and Paterson¹³ found surprisingly good agreement right up to saturation for aqueous solutions of lithium chlorate at 25°C. and 131.8°C. Similar results were obtained by Campbell and Bock¹⁴ for ammonium nitrate at 25°C.

The Fuoss-Onsager Equation

Fuoss¹⁵ has recently extended the highly mathematical treatment given earlier by Fuoss and Onsager¹⁶ and by Fuoss¹⁷. In this theory the relaxation effect and the electrophoretic effect have been evaluated to include terms up to the order of $c^{3/2}$. The resulting conductance equation for a uni-univalent electrolyte is expressed as follows:

$$\Lambda = \Lambda_0 - S c^{1/2} + E c \log c + J c \quad \dots\dots(19)$$

In equation 19, S, E and J are constants which are defined as follows:

$$S = \alpha + \beta \Lambda_0 \quad \dots\dots(20)$$

where α and β are the Debye-Hückel constants defined

$$\text{as } \alpha = \frac{82.50}{(D_0 T)^{1/2} \eta_0} \quad \beta = \frac{8.205 \times 10^5}{(D_0 T)^{3/2}}$$

The constant E is expressed by the following three expressions:

$$E = E_1 \Lambda_0 - E_2 \quad \dots\dots(21)$$

$$\text{where } 0.4343 E_1 = \frac{K^2 a^2 b^2}{24 c} \quad \dots\dots(22)$$

$$\text{and } 0.4343 E_2 = \frac{K a b}{16 c^{1/2}} \quad \dots\dots(23)$$

$$\text{with } b \text{ defined by } b = \frac{e^2}{a D_0 k T} \quad \dots\dots(24)$$

By combining equation 24 with equations 21, 22 and 23, it is evident that the constant E is independent of concentration as well as "a", the distance of closest approach. It is seen from the equation 20 that S is also independent of these two parameters.

J is given by

$$J = \sigma_1 \Lambda_0 + \sigma_2 \dots\dots(24)$$

where

$$\sigma_1 = \frac{K^2 a^2 b^2}{12c} \left[h(b) + 0.9074 + \ln \frac{Ka}{c^{1/2}} \right] \dots\dots(25)$$

and

$$\sigma_2 = \gamma\beta + \frac{11\beta Ka}{12c^{1/2}} - \frac{Ka\beta}{8c^{1/2}} \left[1.017 + \ln \frac{Ka}{c^{1/2}} \right] \dots\dots(26)$$

The function h(b) in the equation 25 is defined by,

$$h(b) = \frac{2b^2 + 2b - 1}{b^3} \dots\dots(28)$$

where b is again expressed by equation 24.

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. A different method is used to obtain the two parameters. This will be outlined briefly.

Shedlovsky¹⁸ has devised a method to obtain a first approximation for Λ_0 . This consists in plotting Λ'_0 , defined by the function

$$\Lambda'_0 = \frac{\Lambda + \alpha c^{1/2}}{1 - \beta c^{1/2}} \quad \dots\dots(29)$$

against c . The resulting plot is usually linear up to 0.1N and extrapolation to zero concentration gives a good approximation for Λ_0 , say Λ_{01} . Knowing Λ_{01} , it is now possible to determine S using equation 20 and E using equation 21. Next another quantity Λ' is defined by the expression,

$$\Lambda' = \Lambda_0 + Jc \quad \dots\dots(30)$$

where $\Lambda_0 = \Lambda + Sc^{1/2} - Ec \log c$. A plot of Λ' against c is linear with the intercept on the Λ' axis giving Λ_0 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 24, 25 and 26.

In spite of the fact that 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 can not 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. Bjerrum¹⁹, 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 $\frac{\epsilon^2}{2 D o k T}$.

The first attempt of Fuoss and Kraus²⁰ 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 the concept of ion pair described the behavior of the electrolyte satisfactorily. The same concept 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 Onsager¹⁶ obtained their conduc-

tance equation, equation 19, that a satisfactory general equation was developed. A new definition of an ion pair was also used. Fuoss²¹ 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 concentric with the reference cation." Equation 19 was now modified in the following manner to make it generally applicable:

$$\Lambda = \Lambda_0 - S(c\gamma)^{1/2} + Ec\gamma \log c\gamma + Jc\gamma - K_a c\gamma f^2 \Lambda \quad \text{.....(31)}$$

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.

In order to determine the three parameters Λ_0 , γ , and K_a , several new quantities are defined. First γ must be known and a first approximation is obtained from the expression,

$$\gamma = \frac{\Lambda}{\Lambda_0 - S c^{1/2} \Lambda^{1/2} \Lambda_0^{1/2}} \quad \text{.....(32)}$$

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

$$\Lambda' = \Lambda + S(c\gamma)^{1/2} - Ec\gamma \log c\gamma \quad \text{.....(33)}$$

Two other quantities are defined:

$$y = \frac{\Lambda' - \Lambda_0}{c \alpha} \dots\dots(34)$$

and $x = f^2 \Lambda \dots\dots(35)$

Consideration of equations 34 and 35 shows that a plot of y against x should give a straight line, provided Λ_0 has been chosen correctly. From the equation 34 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 Ka and the intercept on the Y-axis is equal to J . Thus Ka 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 $Ka < 0.2$. Fuoss and Onsager¹⁶ mention several reasons why their equation can be expected to be in error in linear and higher order terms:

- (1) The change of viscosity with concentration and the change of dielectric constant are neglected.

- (2) Linear superposition of fields is assumed.
- (3) The volume occupied by the ions is neglected and the solvent is assumed to be continuous.
- (4) The fact that colliding ions have finite velocity is ignored.

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."

NATURE OF THE PROBLEM

NATURE OF THE PROBLEM

The work here described of conductance measurements of sodium octanoate is a part of the project of measuring the electrical conductance of sodium salts of higher fatty acids from a very low concentration to very high concentration. It is reasonable to suppose that, as one proceeds up the homologous series from acetate onwards, an increase of anion size would lead to a stage where the anion may become almost motionless and nonconducting. On the other hand, it is also known that after a certain number of carbon atoms in the chain is reached, occurrence of micelle formation, i.e. aggregation of anions to form a large kinetic unit of greater charge, does take place and thus even the largest anion can show a reasonable conductance property.

The object of the present work was therefore,

(1) To find out the extent of concentration to which the experimental values of equivalent conductance at 25°C . and 35°C . agree with the theoretical equations of Robinson-Stokes and Falkenhagen-Leist,

(2) To study the general conductance behavior of sodium octanoate at various concentrations,

and lastly, (3) to enquire into the existence or non-existence of ionic micelles at higher concentrations.

EXPERIMENTAL PROCEDURE

EXPERIMENTAL PROCEDURE

1. Preparation and Purity of the Salts

The n-octanoic acid, otherwise known as caprylic acid, was obtained from the Eastman Kodak Company and purified by redistillation. To prepare the salt the acid was neutralized with an alcoholic solution of sodium hydroxide and the resulting solution concentrated by slow evaporation. To the concentrated solution was added a mixture of acetone and alcohol in the ratio 2:1 when the sodium salt of octanoic acid was thrown out. The precipitate was filtered on a Buchner funnel, dried in a vacuum oven, ground in an agate mortar and stored in a desiccator over barium oxide.

The purity of the salt was determined by converting the sodium octanoate to the sulphate as described by Stock, Staehler, Patnode and Dennis²². Analysis of four samples established the purity of the salt to be 99.5%. The only possible impurity could be sodium carbonate and if this is present a higher percentage of sodium sulphate would be expected since the percentage of sodium in sodium carbonate is about 43 as compared to 13.7% sodium in sodium octanoate. The results should also be high if sodium hydroxide were present as an impurity.

A set of **pH** measurements of the salt at different concentrations agreed remarkably well with those calculated from the standard equations for the hydrolysis of the salt of a weak acid and strong base. For the determination of the cell constant, potassium chloride, Mallinckrodt analytical reagent, was fused in a platinum dish, ground in an agate mortar, and stored over barium oxide.

2. The Conductance Water

Water obtained from a Barnstead electric still with a block tin condenser had a specific conductance of less than 5×10^{-6} mhos/cm at 25°C . It was further purified by bubbling nitrogen through it for several hours. The nitrogen, however, was purified by bubbling it through alkaline pyrogallol, sulphuric acid and "ascarite". In this way water having a specific conductance of $2-3 \times 10^{-7}$ mhos/cm was obtained.

3. Preparation of the Solutions

a. Concentration range from 0.02N to Saturation:

At least 2.3 gms of salt was weighed to 0.2 mg. The salt was then washed into a flask and made up approximately to the desired weight. The resulting solution was weighed on an analytical balance to the nearest 0.2 mg when the total weight was less than 120 gms. The more dilute solutions were weighed on a large balance to the nearest 10 mg. Since these always weighed more than 200

gms, the weight concentration was always known to at least 0.01%. All weighings were corrected to vacuum.

b. Dilute Solutions:

Following the technique of Shedlovsky 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 MC-5 Grammatic micro-balance to the nearest 2μ gms. A maximum of six additions was made so that the weight concentrations for these solutions was also known to at least 0.01%.

4. The Conductance Bridge

A Leeds and Northrup Jones conductivity bridge was used to measure the resistance of the solutions. The Jones Bridge is a modified version of the familiar Wheatstone resistance bridge adapted to alternating current measurements. The chief modification consists in utilizing resistors designed for alternating current use and of the inclusion of the "Wagner Ground"; a device which eliminates current leakage at the detector terminals. An oscilloscope in series with a tuned amplifier served as a detector. The sensitivity of the bridge was better than one part in 10^5 . A circuit diagram of the set-up is shown in Figure 1.

5. The Conductance Cells

The conductance cells employed in this work had the leads and filling tubes sufficiently far apart, as suggested by Jones and Bollinger²³, so that errors due to the Parker effect²⁴ would be avoided.

The solutions of potassium chloride used to determine the cell constants were made up according to the specifications of Jones and Bradshaw²⁵. Periodic determination of cell constants were found to be constant within 0.04% and cell constant determinations with different demineral solutions agreed very well.

For the measurement of conductance of very dilute solutions a special type of cell, of the design recommended by Shedlovsky²⁶, was used. It is shown in Figure 1A. The cell constant of this cell was obtained by using the following equation recommended by Fuoss²⁷ et al.

$$\Delta = 149.93 - 95.65C^{1/2} + 58.74C \log C + 198.4C \dots\dots(36)$$

From this equation Δ for KCl at 25°C. can be calculated for a given concentration. From the equation defining the equivalent conductance

$$\Delta = \frac{1000A}{CR} \dots\dots(37)$$

where R the measured resistance of the KCl solution, C the concentration in equivalents per litre, and A the cell constant, it is possible to calculate the only unknown A,

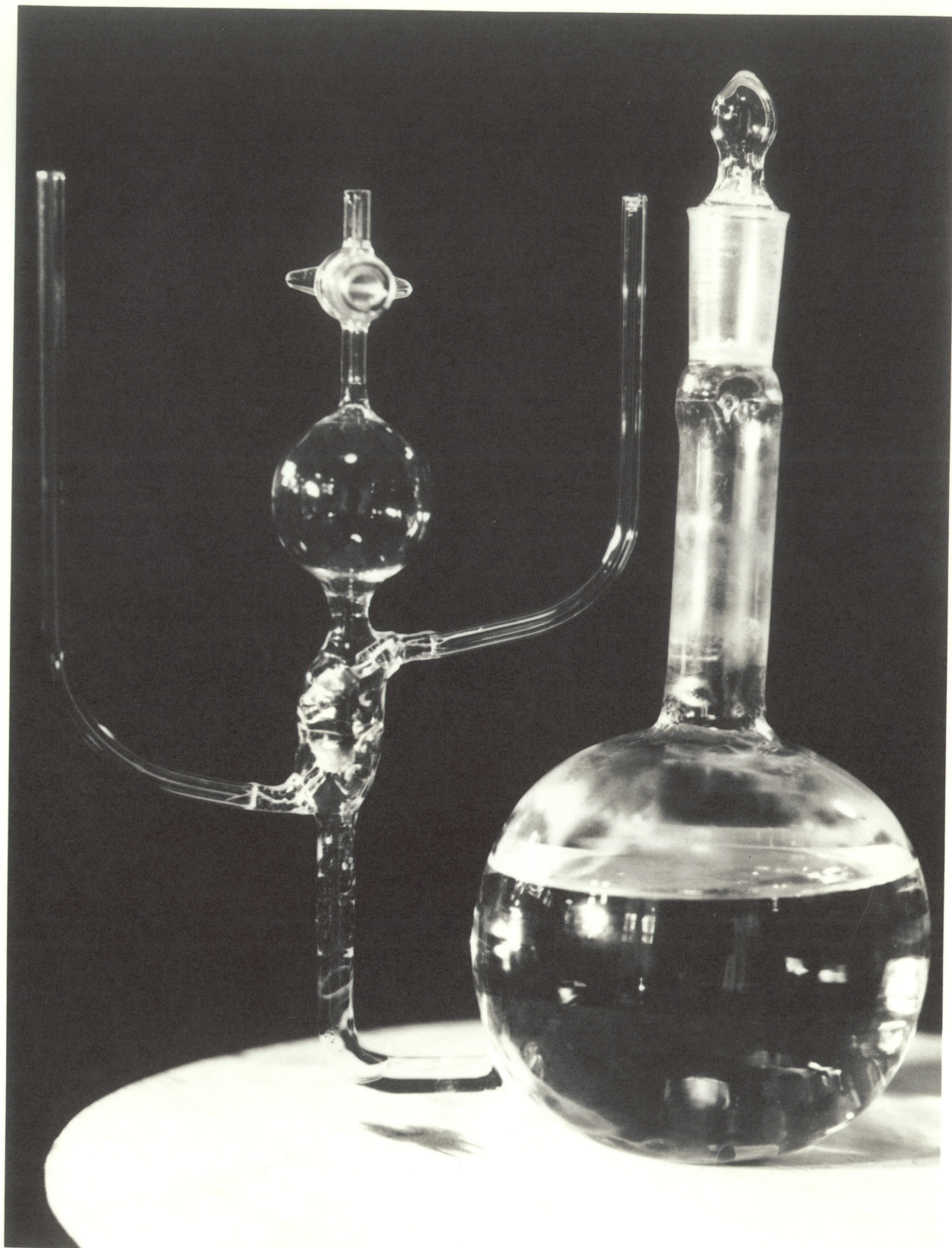


FIGURE 1A

once Δ is obtained from equation 36.

In the absence of a standard method of determining cell constants at higher temperatures an appropriate correction, as recommended by Washburn²⁸, was employed. The difference in cell constant at higher temperature is essentially due to geometry changes in the cell. For cell constant correction the expression employed is as follows:

$$\Delta A = - \beta A \Delta t \quad \dots\dots(38)$$

where β is about 3.5×10^{-6} units per degree centigrade and Δt in this case is 10°C . The corrections were applied to each cell.

6. The Thermostats

The thermostat used at 25° was the one constructed by Bock²⁹ and shown in Figure 2. The steel tank of eighteen gallon capacity was housed in a double walled insulated box. Stirring was accomplished by means of a pump. The thermostat was filled with "Marcol", a high boiling hydrocarbon oil, as recommended by Davis.³⁰ Temperature control was effected through the use of a mercury-toluene regulator and thyatron relay as described by Swinehart³¹. A Beckmann thermometer, used to record the temperature, was frequently calibrated against a standard platinum resistance thermometer by means of a "Muller Bridge. The constancy of temperature of the

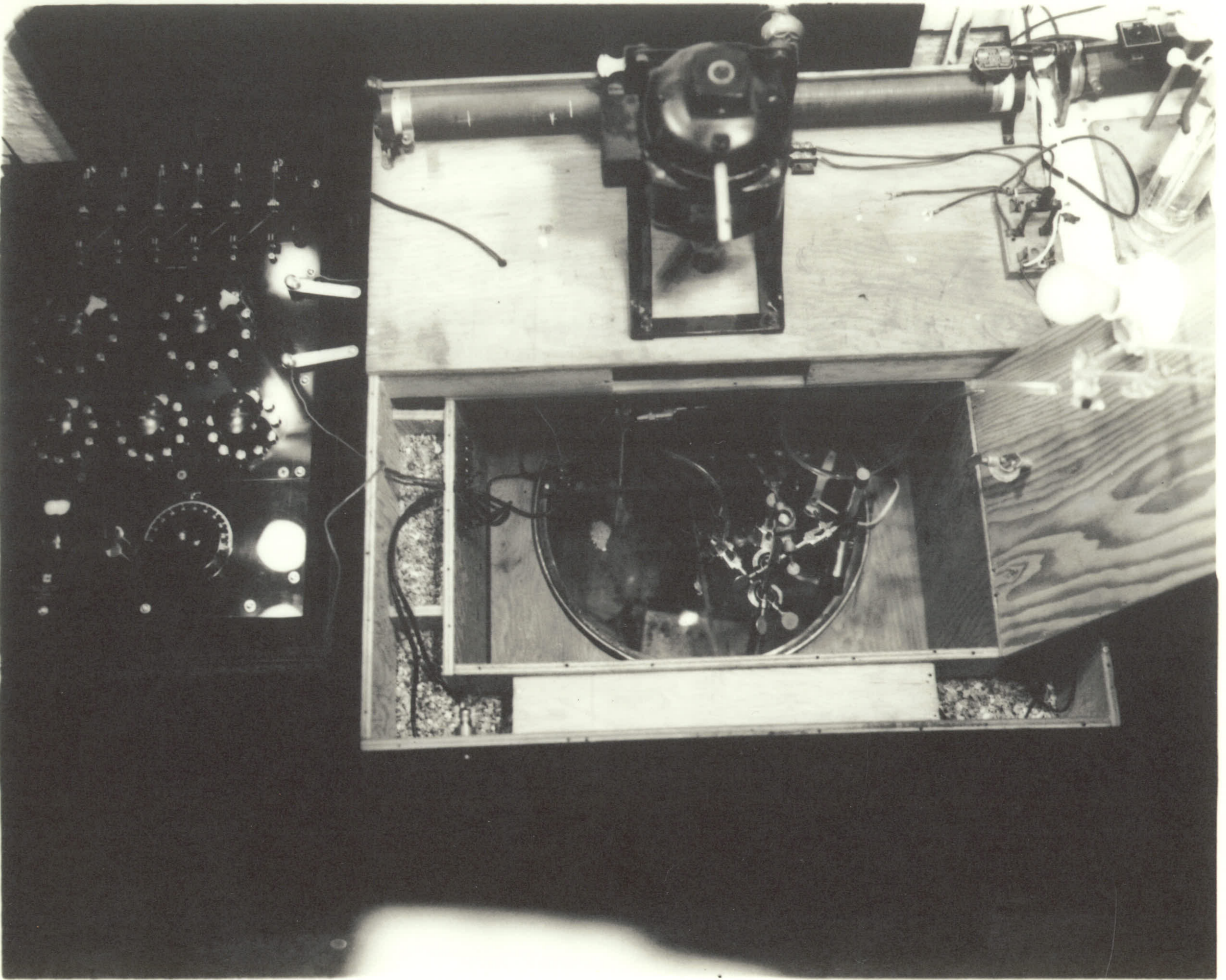


FIGURE 2

thermostat was well within $\pm .005^{\circ}\text{C}$. For 25°C . measurements it was found necessary to precool the thermostat bath so as to counteract the frictional heat generated by the stirrer. This was accomplished by passing water, the temperature of which, in turn, was regulated by means of an auxiliary thermostat to a desired value, through a copper coil immersed in the thermostat bath.

The other thermostat used at 35°C . was a thick walled square type glass vessel of about eight gallon capacity. It was lagged with half-inch felt and Marcol GX petroleum oil was used as the bath liquid. To ensure uniform temperature throughout, two propeller-type stirrers were used. The other arrangements employed to secure a good temperature control were the same as described above.

7. The Viscosity Measurements

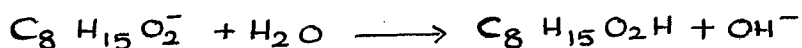
Viscosity measurements were made in a viscometer of the Cannon and Fenske³² type which has negligible drainage and kinetic energy corrections. Calibration with water at 25°C . and 35°C . was first done by filling through the capillary arm to a reference mark on the capillary portion by applying a gentle suction to the opposite arm. The viscometer was left in the bath at least half an hour before taking a reading. Run times were reproducible only to 0.05%.

8. The Density Measurements

Two pyknometers of 45 mls. capacity were filled and left in thermostat for at least 30 minutes. The solution meniscus in one capillary arm was adjusted to a reference mark by withdrawing solution with filter paper through the opposite arm. The pyknometers were rinsed with acetone, dried, and left in the balance case for an hour before weighing. Several times during the research the pyknometers were calibrated with water at both temperatures. Vacuum corrections were applied to all weighings.

9. The Hydrolysis Correction

The method of Campbell and Bock³³ was used to correct the equivalent conductance for the effect of the hydrolysis. Hydrolysis of sodium octanoate occurs as follows:



In this procedure the degree of hydrolysis α is calculated from the expression

$$\alpha = -\frac{K_h}{2c} + \sqrt{\frac{K_h^2}{4c^2} + \frac{K_h}{c}}$$

where K_h is the hydrolysis constant and c is the stoichiometric concentration. Assuming the equivalent conductance of the free acid or base to be equal to its limiting equivalent conductance, the true equivalent conductance, Δ_{true} of the unhydrolyzed salt is calculated from

the equation

$$\Lambda_{\text{expt}} = (1-x) \Lambda_{\text{true}} + x \Lambda_{\text{base}}$$

The hydrolysis constants were obtained from the data of ionization constant of octanoic acid given by Dippy³⁴.

The hydrolysis correction was applied to all the results.

Determinations of specific conductance, density, and viscosity were made in duplicate. Measurements at 35°C. were done without refilling the instruments. In case of specific conductance measurements, over a certain range of concentration, it was found that the resistance changed continuously with time. To obtain the true resistance of the solution, the resistance was measured at different intervals of time and then extrapolated to zero time.

EXPERIMENTAL RESULTS

TABLE 1

DENSITY, VISCOSITY, CONDUCTANCE OF OCTANOATE SOLUTIONS AT 25°C.

Concentration (mole/litre)	Density (gm/ml)	Specific Conductance (mho/cm x 10 ⁶)	Equivalent Conductance (mhos)	Relative Viscosity
0.000227	-	0.15131	67.36	-
0.000601	-	0.40266	66.75	-
0.001059	-	0.70235	66.16	-
0.001713	-	1.12681	65.69	-
0.002433	-	1.5899	65.18	-
0.003001	-	1.9468	64.78	-
0.01072	0.99736	6.7047	62.53	1.01081
0.02193	0.99771	13.2671	60.49	1.02507
0.04465	0.99855	26.0587	58.35	1.04331
0.09781	0.99978	50.4895	51.62	1.0820
0.16427	1.00179	74.1909	45.03	1.3428
0.21637	1.00324	79.9285	36.94	2.6895
0.24081	1.00378	70.9978	29.48	2.9195
0.29844	1.00515	82.3379	27.59	4.2175
0.36352	1.00703	98.9591	27.22	4.7630
0.41102	1.00791	128.7064	31.26	1.8449
0.44813	1.00840	176.8616	39.46	1.4952
0.55250	1.01098	205.9242	37.27	1.5934
0.73839	1.01478	256.2426	34.70	1.9275
0.99697	1.01956	321.8321	32.28	2.6749
1.2881	1.02339	374.2342	29.05	4.0938
1.9305	1.0348	465.4078	24.11	12.9046
2.1640	1.0378	473.0467	21.86	19.2350
2.6392	1.0470	453.9779	17.20	39.9242
2.7736	1.0493	443.2024	15.98	44.1941

TABLE 2
DENSITY, VISCOSITY AND CONDUCTANCE OF OCTANOATE SOLUTIONS AT 35°C.

Concentration (mole/litre)	Density (gm/ml)	Specific Conductance (mho/cm x 10 ⁶)	Equivalent Conductance (mhos)	Relative Viscosity
0.000226	-	0.18852	82.75	-
0.000599	-	0.49387	81.99	-
0.001055	-	0.86204	81.35	-
0.001706	-	1.38105	80.68	-
0.002425	-	1.94316	79.91	-
0.002998	-	2.38979	79.47	-
0.01069	0.99473	8.0903	75.68	1.0094
0.02187	0.99511	15.9858	73.09	1.2086
0.04450	0.99588	32.1299	72.21	1.0356
0.09756	0.99722	61.1226	62.65	1.0621
0.16407	0.99884	83.8768	51.05	1.3097
0.21587	1.00031	93.8012	43.46	2.6017
0.24007	1.00064	86.7853	36.15	2.7057
0.29746	1.00185	99.0119	33.29	4.0098
0.36210	1.00337	136.4044	37.66	2.3116
0.40967	1.00462	206.9265	50.51	1.3732
0.44671	1.00519	221.2373	49.53	1.4217
0.55051	1.00738	258.5473	46.97	1.5712
0.73570	1.01108	323.5117	43.97	1.9124
0.99280	1.0153	407.0278	40.99	2.6687
1.2823	1.0187	472.8888	36.88	4.0054
1.9110	1.0295	587.4016	30.74	12.5037
2.1535	1.0328	598.8653	27.81	18.8859
2.6249	1.0413	608.1890	23.17	37.5121
2.9947	1.0472	579.5834	19.35	54.1011

DISCUSSION OF THE RESULTS

DISCUSSION OF THE RESULTS

1. The Experimental Accuracy

The calibrations of the pyknometers were constant within 0.002% and hence an accuracy of 0.004% may be expected in the density determinations even if we assume the errors to be additive. The temperature control was well within $\pm 0.005^{\circ}\text{C.}$, and the errors in concentration were less than .01%. The measurements of the resistances were known to one part in 10000. Hence, assuming that the various errors are additive, an overall error of 0.1% could be expected in the actual calculation of results, the equivalent conductances, which depend essentially on the forementioned factors.

2. The Limiting Equivalent Conductances

The limiting equivalent conductance of sodium octanoate has been determined by the usual extrapolation techniques of Kohlrausch and Shedlovsky. In the Kohlrausch method a plot of the equivalent conductance against the square root of the concentration in the very dilute region resulted in a straight line which, on further extrapolation to zero concentration, gave the limiting equivalent conductance of the salt.

Shedlovsky's method requires the calculation of Λ_0° , based on the expression,

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

and then the plot of Λ_o' against the first power of the concentration which resulted in a linear plot. Extrapolating the straight line to zero concentration the desired result is obtained.

In both of these methods, only the first six measurements were used at each temperature to determine

Λ_o . The plots of Kohlrausch method at 25°C. and 35°C. are shown in the Figures 3 and 4. The method of least square analysis was employed to calculate the deviation from the straight line and it was found, in both cases, that the maximum deviation was well under 0.04%. The limiting equivalent conductances of sodium octanoate were 68.35 mhos at 25°C. and 84.02 mhos at 35°C.

Figures 5 and 6 represent the Shedlovsky extrapolation technique for 25°C. and 35°C. respectively. In this case the limiting equivalent conductances, at both temperatures, being 68.49 at 25°C. and 84.13 at 35°C., are slightly greater than those obtained by the Kohlrausch method. Considering the facts that the Shedlovsky method is empirical and the deviations from the straight line were small, the limiting equivalent conduc-

tances obtained by the Kohlrausch method, were the ones chosen to use in the theoretical equations of Robinson-Stokes and Falkenhagen-Leist.

The limiting equivalent conductances of the octanoate ion, 18.25 at 25°C. and 22.48 at 35°C., are obtained by the subtraction of the limiting equivalent conductances of the sodium ion from the extrapolated values obtained for sodium octanoate. For sodium ion, the reported values³⁵ are 50.10 mhos at 25°C. and 61.54 mhos at 35°C.

3. Application of the Conductance Equations

An attempt has been made to show the extent to which the experimental values agree with the viscosity corrected forms of the Robinson-Stokes and the Falkenhagen-Leist equations. 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 parameter a^0 , the distance of closest approach between ions, is so chosen in each series of temperature that a good agreement between experimental values and theoretical values is obtained, at least in the dilute regions.

(i) Sodium Octanoate and the Robinson-Stokes Equation

Columns 3 and 4 of Table 3 represent the calculated equivalent conductances at 25°C., using two

FIGURE 3 Λ vs $\sqrt{c}$ (AT 25°C)
KOHLEBAUSCH METHOD

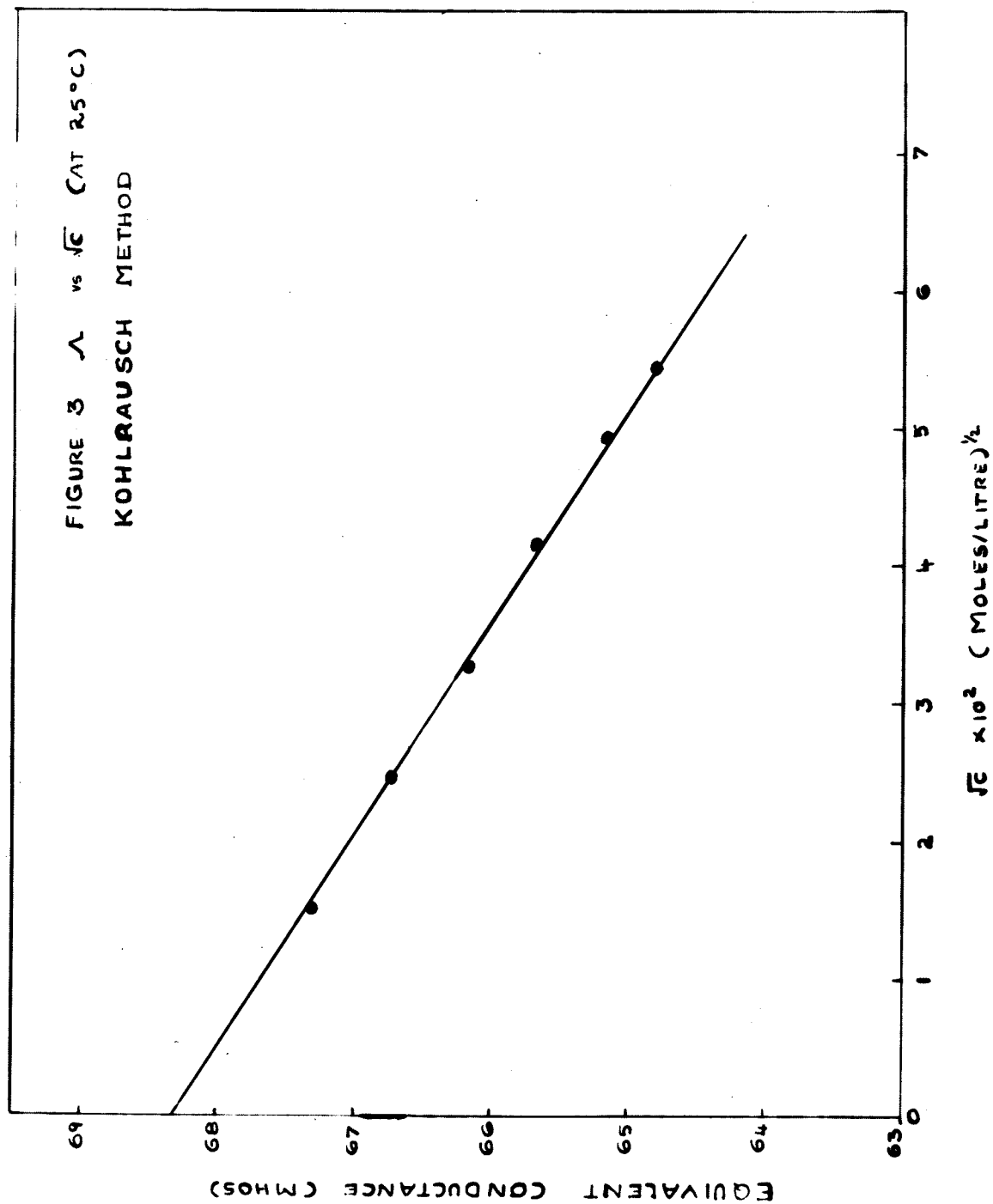


FIGURE 4 Λ vs $\sqrt{C}$ (AT 35°C)
KOHLEBAUSCH METHOD

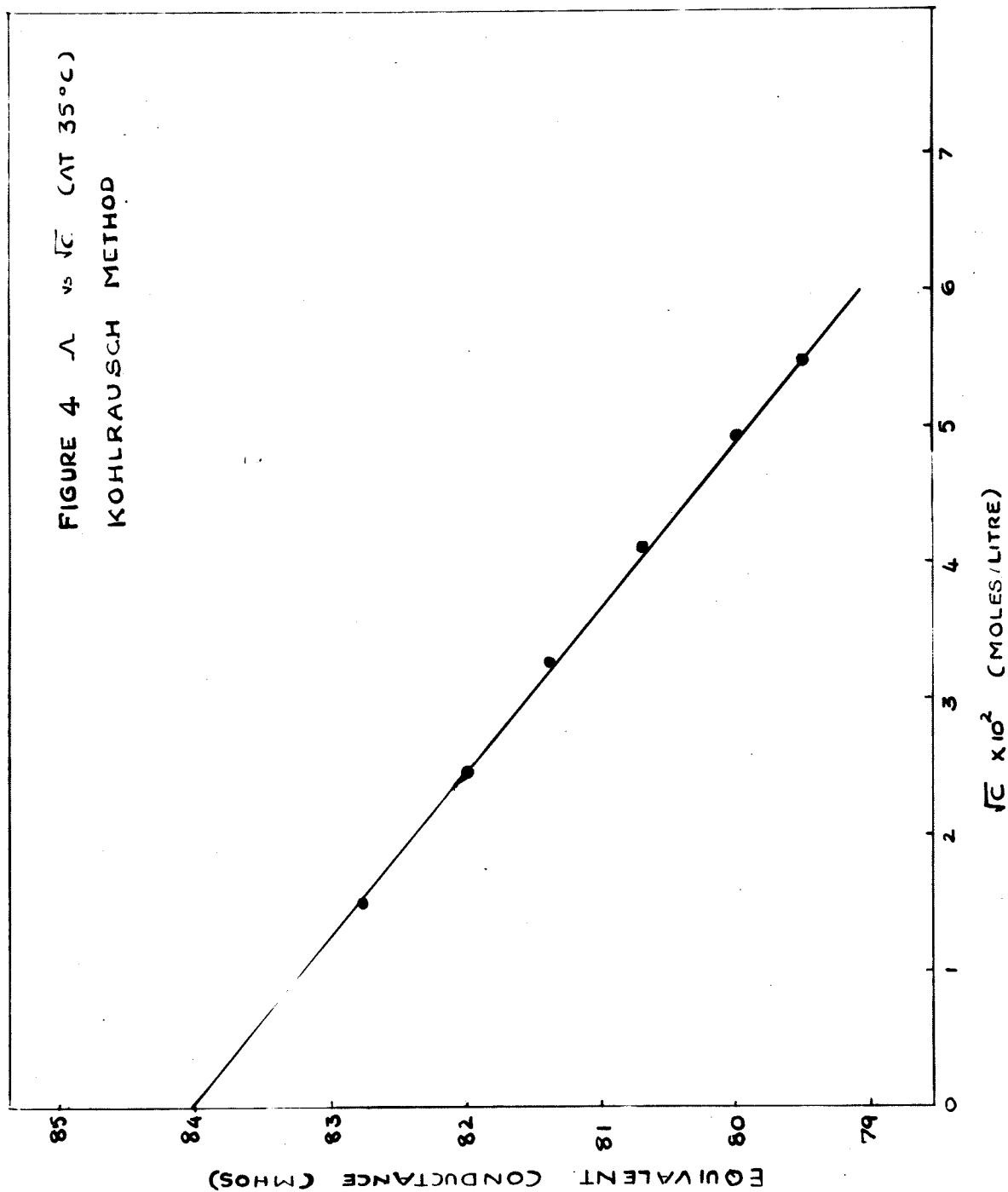


FIGURE 5 Λ vs C (AT 25°C)
SHEDLOVSKY METHOD

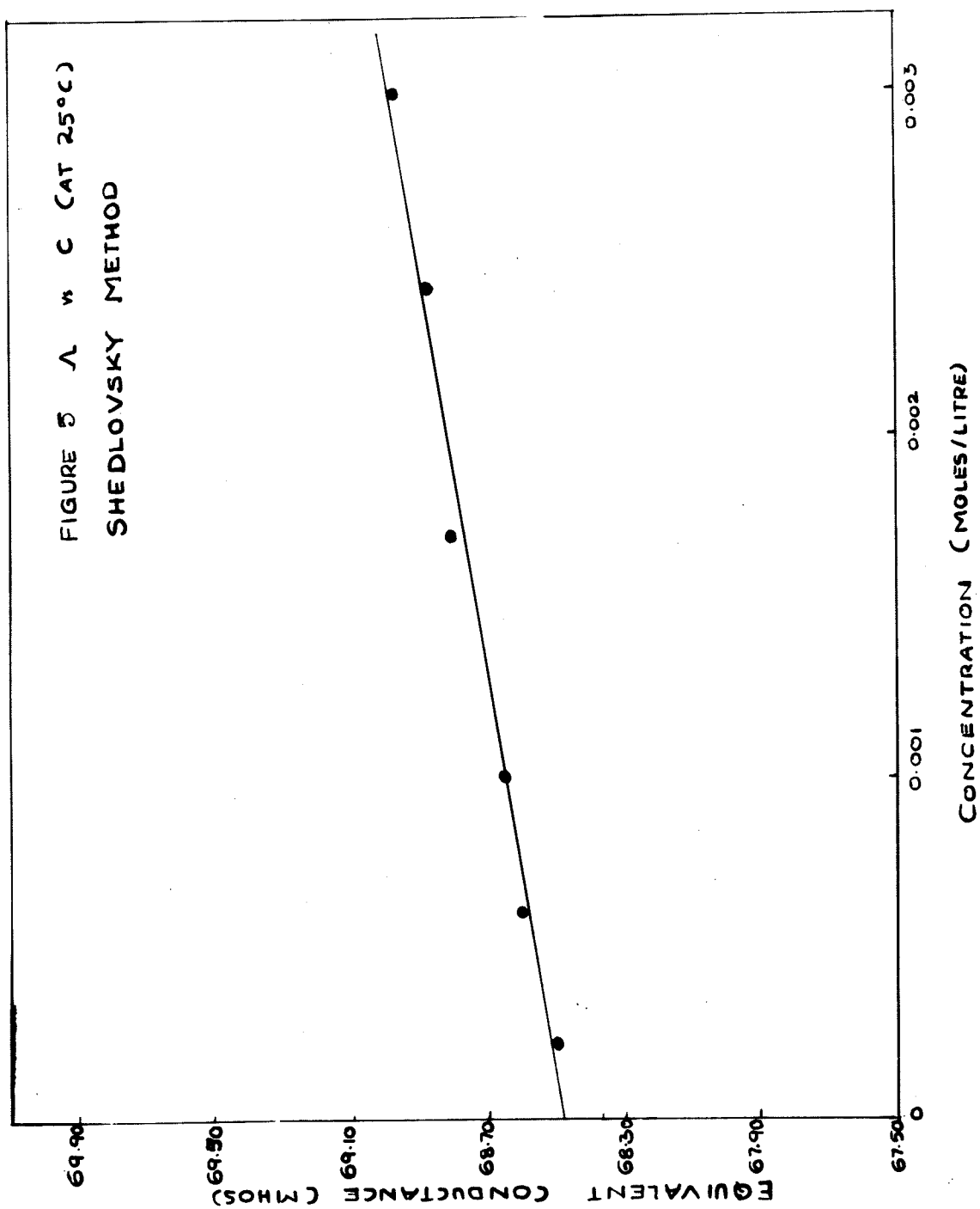
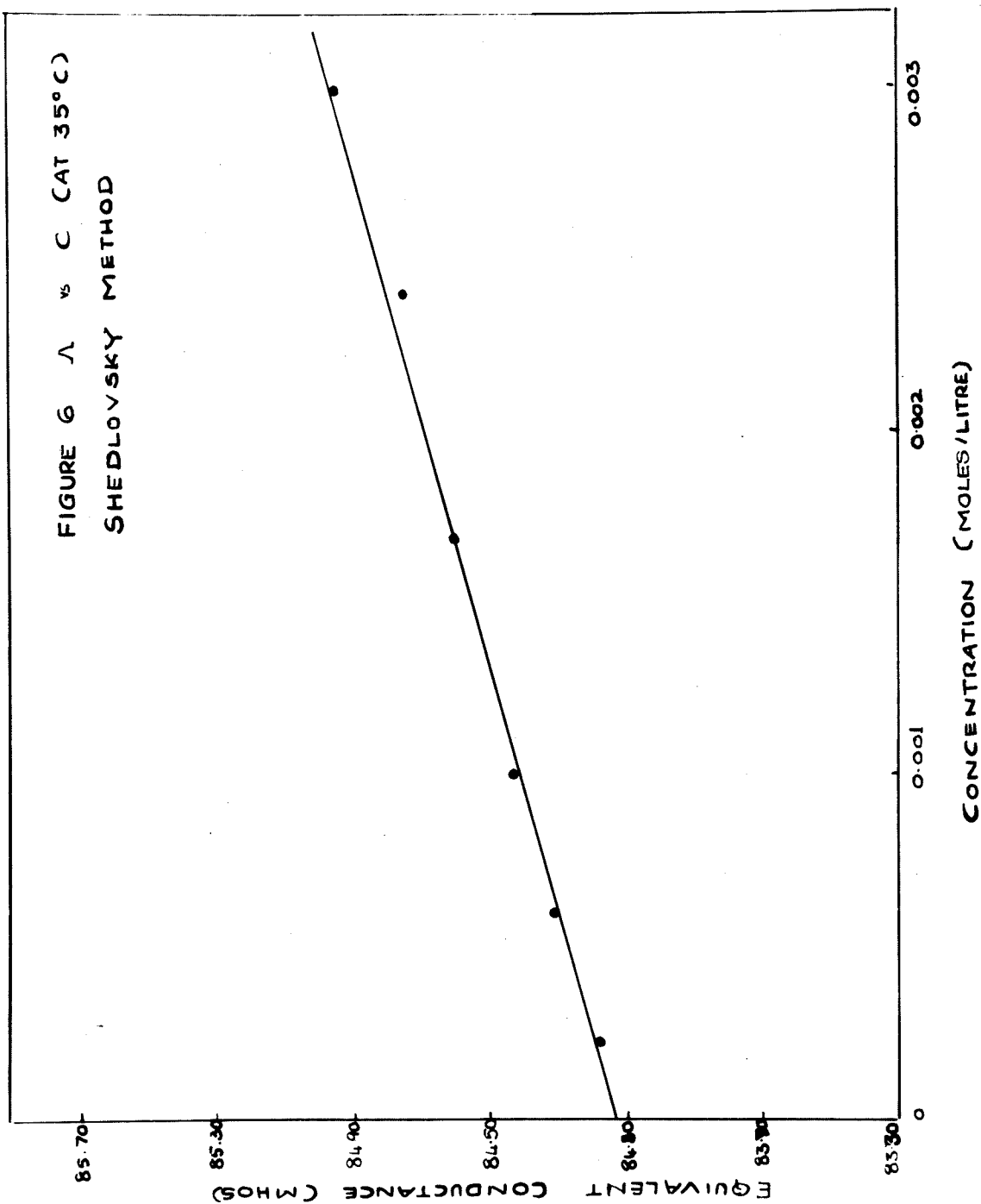


FIGURE 6 Λ vs C (AT 35°C)
SHEDLOVSKY METHOD



values of $\bar{a}$, namely $\bar{a} = 15\text{\AA}$ and $\bar{a} = 21.5\text{\AA}$, in the Robinson-Stokes equation. It is observed that the experimental values do not differ by more than 0.2 mhos at least in the very dilute region. With the parameter $\bar{a} = 15\text{\AA}$, there is a reasonable agreement within 0.5 mhos up to a concentration of 0.04 molar between theoretical and experimental values. At higher concentrations a marked difference is observed. In case of $\bar{a} = 21.5\text{\AA}$, the deviations become large for concentrations beyond 0.01 molar. It seems that the equation is less sensitive for changes in $\bar{a}$ at lower concentrations than for those at higher concentrations. An almost similar conclusion could be drawn from the table 4 of column 3 and 4 which represent the values calculated at 35°C. using $\bar{a} = 13.5\text{\AA}$ and $\bar{a} = 19\text{\AA}$ in the Robinson-Stokes equation. There is no better agreement beyond 0.01 molar between the experimental and calculated values.

(ii) Sodium Octanoate and the Falkenhagen-Leist Equation

The theoretical values of conductances based on the Falkenhagen-Leist equations are recorded in columns 5 and 6 of Table 3 for 25°C. and in columns 5 and 6 of Table 4 for 35°C. In this equation a slightly lower value of $\bar{a}$ is chosen to have results in a good agreement between calculated and experimental values. At 25°C., with $\bar{a} = 8.5\text{\AA}$ and $\bar{a} = 10.0\text{\AA}$, there is a reasonable reproducibility within 0.6 mhos up to a concentration of .05 molar.

TABLE 3
CALCULATED EQUIVALENT CONDUCTANCES AT 25° C.

Concentration (mole/litre)	Equivalent Conductance (mhos)	E. Conductance R.S. Equation		E. Conductance F.L. Equation	
		a = 15A	a = 21.5A	a = 8.5A	a = 10.0A
0.000227	67.36	67.29	67.32	67.27	67.28
0.000601	66.75	66.70	66.76	66.63	66.65
0.001059	66.16	66.06	66.19	65.98	66.04
0.001713	65.69	65.57	65.79	65.56	65.71
0.002433	65.18	65.14	65.21	64.95	65.07
0.003001	64.78	64.84	65.12	64.61	64.70
0.01072	62.53	62.74	63.84	61.85	62.05
0.02193	60.49	60.30	61.34	60.27	60.54
0.04465	58.35	57.89	58.15	56.51	57.14
0.09781	51.62	54.78	56.41	51.87	52.76
0.16427	45.03	42.93	44.44	41.28	42.35
0.21637	36.94	20.60	21.48	20.33	21.01
0.24081	29.48	19.42	20.25	18.64	19.12
0.29844	27.59	13.37	13.81	12.78	13.01
0.36352	27.22	11.74	12.23	11.22	11.57
0.41102	31.26	30.17	31.44	28.84	29.75
0.44813	39.46	37.69	38.62	35.44	36.61
0.55250	37.27	34.27	35.90	32.95	33.94
0.73839	34.70	28.07	29.21	26.98	27.93
0.99697	32.28	19.49	20.24	19.24	19.95
1.2881	29.05	12.76	13.12	12.17	12.99
1.9305	24.11	3.89	3.90	3.90	4.08
2.1640	21.86	2.58	2.56	2.61	2.74
2.6392	17.20	1.31	1.28	1.28	1.34
2.7736	15.98	1.14	1.09	1.20	1.26

TABLE 4
CALCULATED EQUIVALENT CONDUCTANCES AT 35°C.

Concentration (mole/litre)	Equivalent Conductance (mhos)	E. Conductance R.S. Equation		E. Conductance F.L. Equation	
		a = 13.5A	a = 19.0A	a = 6.5A	a = 8.5A
0.000226	82.75	82.71	82.73	82.65	82.66
0.000599	81.99	81.96	82.03	81.83	81.87
0.001055	81.35	81.24	81.42	81.04	81.11
0.001706	80.68	80.64	80.81	80.45	80.55
0.002425	79.91	80.05	80.29	79.51	79.63
0.002998	79.47	79.71	79.95	79.24	79.43
0.01069	75.68	75.97	76.38	75.39	75.87
0.02187	73.09	74.08	75.15	72.39	73.11
0.04450	72.21	71.10	72.52	68.22	69.60
0.09756	62.65	66.02	67.99	62.04	63.99
0.16027	51.05	53.40	54.89	50.27	51.92
0.21587	43.46	26.56	27.61	24.65	25.75
0.24007	36.15	25.68	26.65	22.86	24.90
0.29746	33.29	17.26	17.73	15.65	16.49
0.36210	37.66	30.06	31.52	26.81	28.37
0.40967	50.51	49.00	50.64	50.67	52.47
0.44671	49.53	47.07	48.44	45.74	47.95
0.55051	46.97	41.71	44.12	41.11	42.49
0.73570	43.97	34.14	35.69	33.20	34.47
0.9928	40.99	23.94	25.01	23.81	24.54
1.2823	36.88	15.72	16.35	15.63	16.30
1.9110	30.74	4.95	4.98	4.96	5.18
2.1535	27.81	3.02	3.21	3.27	3.41
2.6249	23.17	1.55	1.54	1.55	1.64
2.9947	19.35	1.04	1.05	1.02	1.13

At 35°C., it seems only in the very dilute region of concentration there is a fair agreement between calculated and experimental values.

4. General Discussion

Both the Robinson-Stokes and Falkenhagen-Leist equations failed when applied to the more concentrated solutions and also it became necessary to choose a fairly large α value even for dilute region if any agreement is sought between the experimental and calculated values. This is particularly true in case of the Robinson-Stokes equation where α values are fairly high.

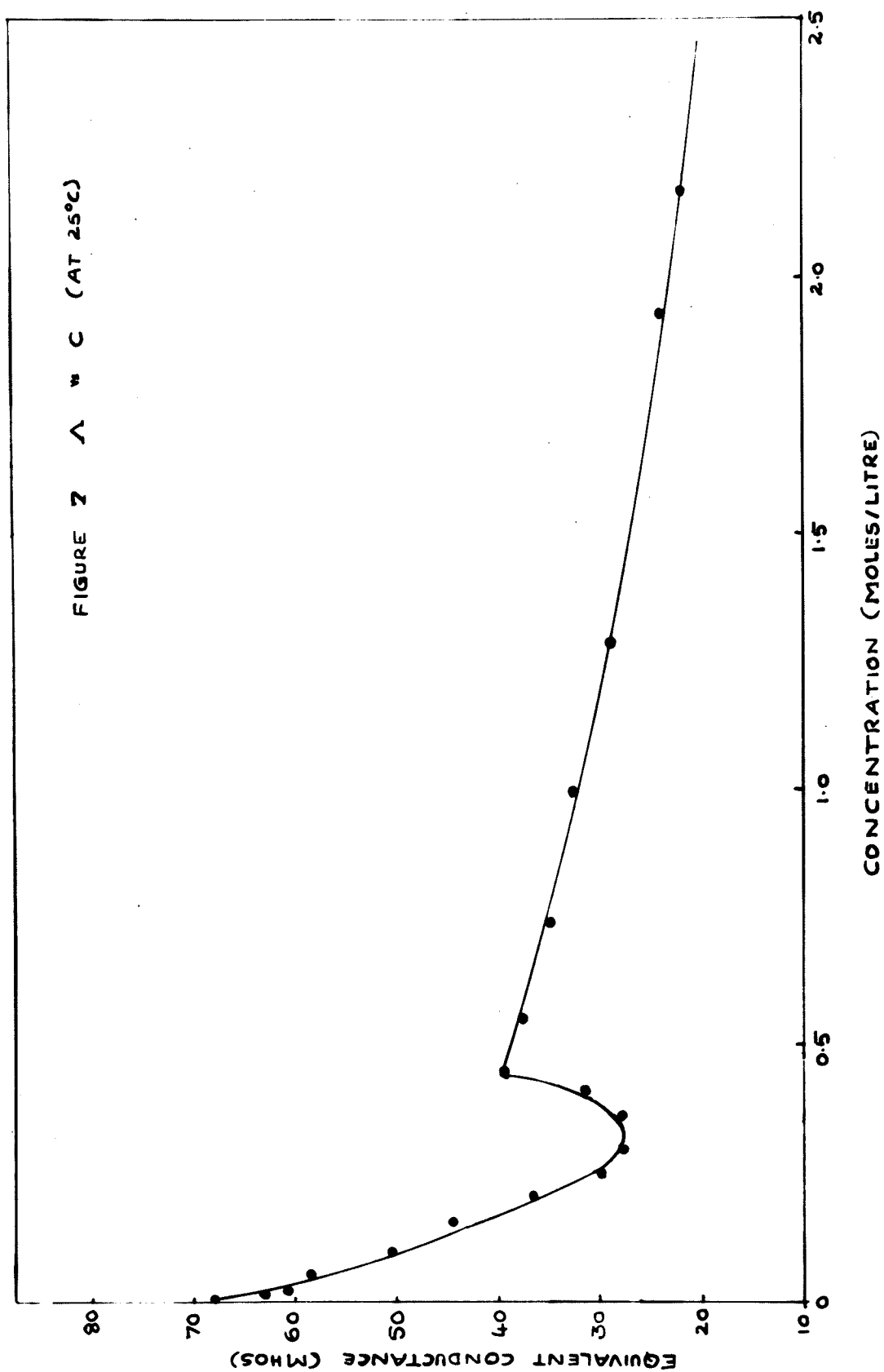
It is but reasonable to expect the failure of these equations in the concentrated region where micelle formation takes place as explained below. Moreover, the viscosity changes of this type of electrolyte is very abrupt and hence a fractional power of viscosity, rather than the first power of relative viscosity as used in the above calculations, could reproduce the results better than observed now.

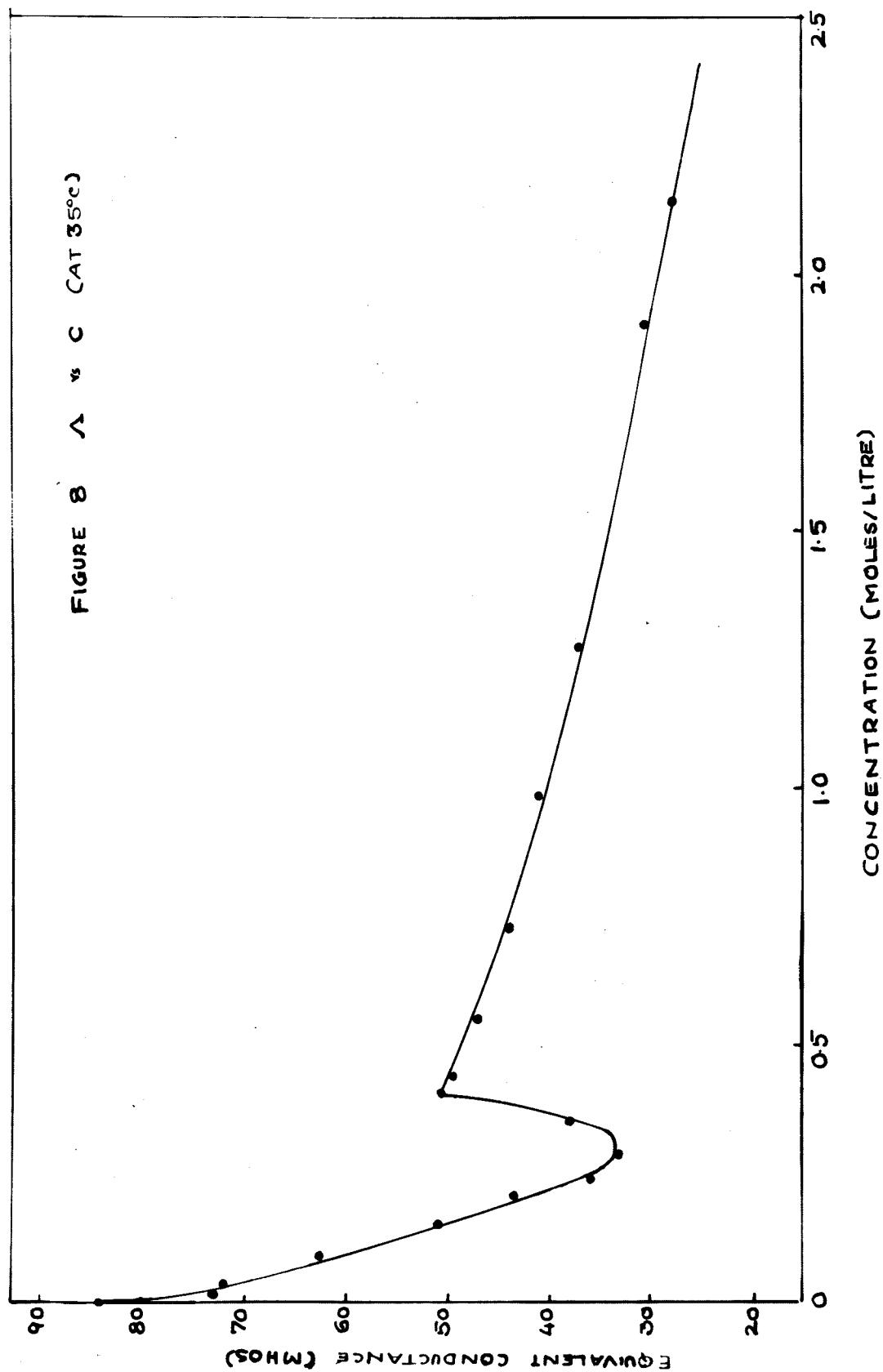
J. W. McBain developed the idea that very dilute aqueous solutions of colloidal electrolytes, to which alkali salts of fatty acids belong, behave like ordinary salts and are highly ionized into alkali metal cation and fatty acid anion. At appreciable concentrations, referred

to as the critical micelle concentration, a marked deviation from ideal behavior sets in and this is mainly due to aggregation of anions with appreciable number of water molecules to form ionic micelles. Formation of micelles causes a change in the number of particles which in turn causes a change in the colligative properties of the solutions. For the same reason a sudden change in the electrical conductance behavior can also be expected.

As can be seen from the plot of equivalent conductance as a function of concentration for sodium octanoate, there is clear evidence of the formation of ionic micelles which are mainly responsible for the observed variation of equivalent conductance. It can be seen that in the region of dilute concentration of about 0.01 molar, sodium octanoate behaves like a typical uni-univalent electrolyte obeying the Debye-Hückel theory as evidenced from the agreement between calculated values and experimental values (refer Table 3 and 4). The onset of micelle formation causes a sudden decrease in conductance to a minimum value around the region of 0.30 molar to 0.35 molar, followed by a gradual increase in conductance, due to the greater charge of micelles and hence their mobility. The gradual increase of conductivity reaches a maximum around 0.45 molar which is then followed by a slow decrease of conductance at further concentrations.

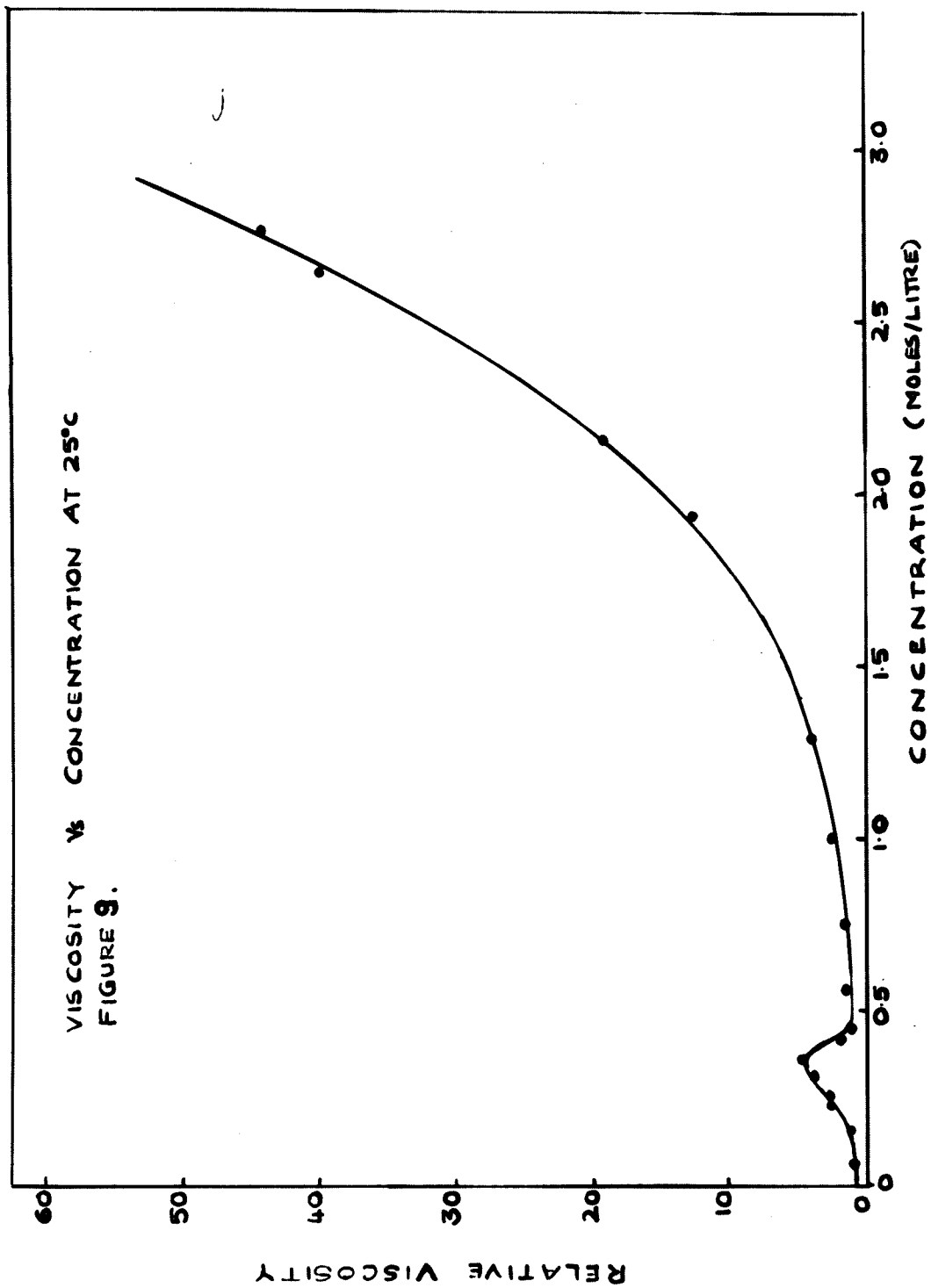
FIGURE 2 $\Lambda^{\infty} C$ (AT 25°C)

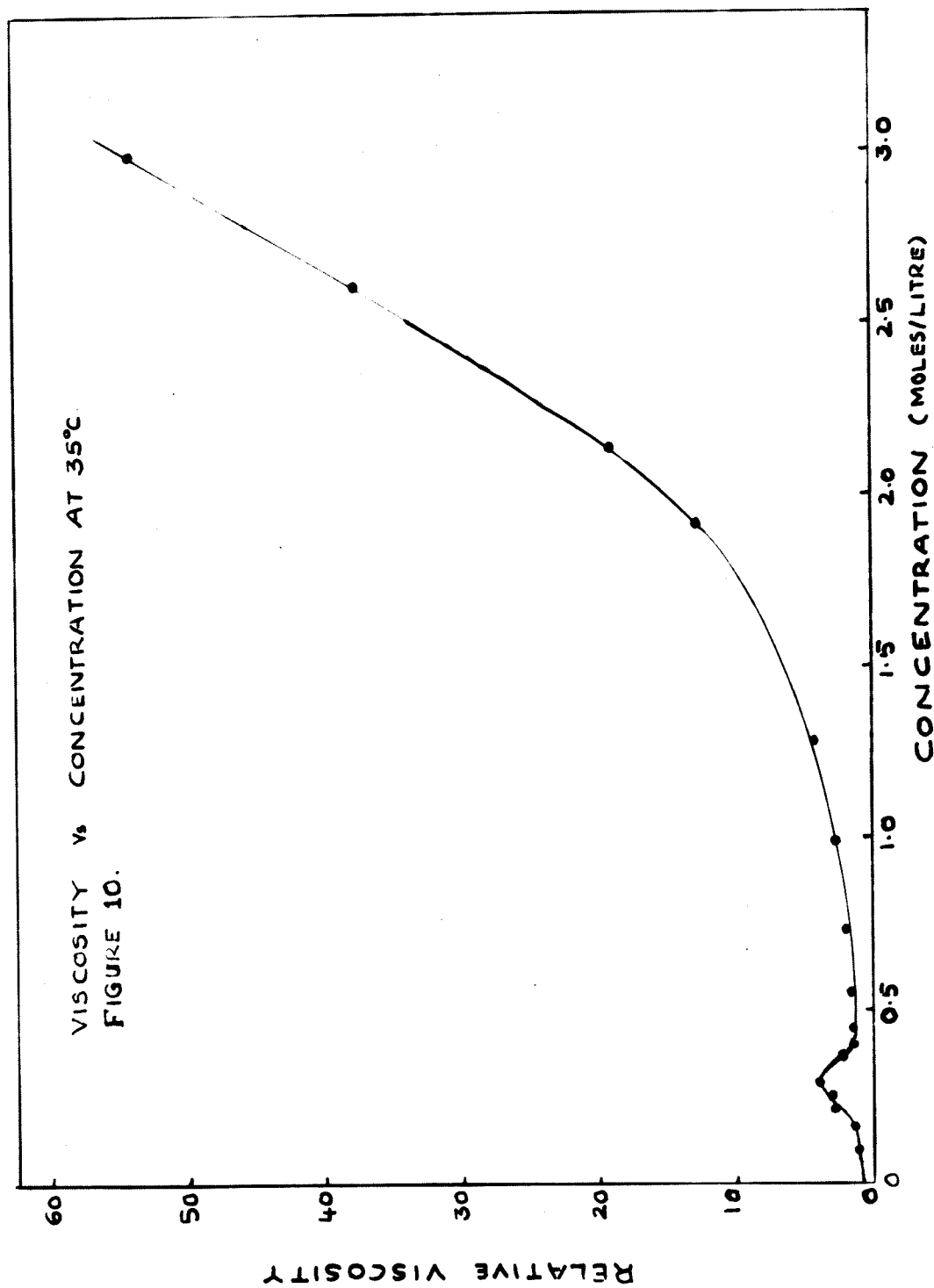




One might anticipate that the increase of concentration would result in the increase of micelle formation and hence an increase of conductance. But at higher concentrations, as explained by G. M. Hartley and others, the ionic atmosphere of oppositely charged "gegenions" (in this case the univalent sodium ions) exerts a much increased screening effect; and also, some of the "gegenions" would adhere to the micelles owing to the high charge of the micelles and thus be forced to travel in the opposite direction to that of free gegenions. The adhering gegenions, therefore, not only lower the charge of the micelle, but also cease to play their normal part in the conduction process and carry their charges in the direction opposite to that of free gegenion. This is the main reason for the shape of the conductivity-concentration plot as in Figure 7 at 25°C. and 8 at 35°C. In the initial stage of the micelle formation, the effect due to high charge of micelle predominates and hence an increase of conductance results; whereas in the concentrated region the other two effects, as explained above, outweigh the former effect and hence a general fall in conductance is observed at higher concentrations.

The viscosity measurements (Figures 9 and 10) show an abrupt increase in viscosity around the concentration of onset of micelles, followed by a decrease in viscosity and then further increase at higher concentrations.





The initial increase is due to sudden aggregation of anions into a micelle of comparatively large size which causes a disturbance in the solvent flow. The increase at higher concentrations is probably due to extreme hydration and increased formation of micelles.

An attempt was made to determine the apparent molecular weight of sodium octanoate around the region of critical micelle concentration using the vacuum flask freezing point depression technique. In this method fine shaved ice and the solution of sodium octanoate were thoroughly stirred until an equilibrium was established.

The temperature was noted and an analysis of the two withdrawn samples was done by evaporation of water. The following table shows the variation of the apparent molecular weight at different concentrations.

TABLE 5

Concentration gms of salt/ 100 gms of H ₂ O	Apparent Molecular Weight
0.8269	75.56
1.1756	83.21
1.7934	87.51
4.3411	101.33
8.9512	126.08
10.4634	150.09

As seen from the above table the increase of the apparent molecular weight with increase of concentration is essentially due to the formation of micelles which increase with concentration.

Thus the results of this work on the conductivity and the apparent molecular weight determinations of sodium octanoate show a definite proof of formation of ionic micelles of greater charge and thus we are in agreement with Smith and Robinson³⁶ who claim, by the isopiestic vapor pressure method, that there is micelle formation for sodium octanoate.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

The equivalent conductances, densities and viscosities of aqueous solutions of sodium octanoate have been determined at 25°C. and 35°C. at concentrations ranging from 0.00025 molar to 3.0 molar. The limiting equivalent conductances of the octanoate ion have been determined as 18.25 mhos at 25°C. and 22.48 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 0.5 mhos up to 0.04 molar at 25°C. when $\overset{\circ}{a} = 15.0\overset{\circ}{\text{A}}$. At 35°C. an agreement within 0.3 mhos up to 0.01 molar concentration is found. The Falkenhagen-Leist equation reproduces the data at 25°C. within 0.6 mhos up to 0.05 molar with $\overset{\circ}{a} = 8.5\overset{\circ}{\text{A}}$. At 35°C. the agreement between the calculated and experimental values is found to be only in the region of extreme dilutions with $\overset{\circ}{a} = 6.5\overset{\circ}{\text{A}}$.

From the conductance behavior of aqueous solutions of sodium octanoate and the apparent molecular weight determinations of sodium octanoate by freezing point method, it was concluded that micelle formation does take place in case of sodium octanoate.

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