

A STUDY OF CERTAIN PHYSICAL PROPERTIES OF AQUEOUS
SOLUTIONS OF THE SODIUM SALTS OF THE
HIGHER FATTY ACIDS

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by

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To My Family

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ABSTRACT

Equivalent conductances, densities and viscosities of aqueous solutions of sodium decanoate, sodium laurate and sodium myristate, have been determined, from extremely dilute region to high concentration, at 25°C and 35°C. The limiting conductances of these salts have been determined at 25°C and 35°C. The limiting equivalent conductances of sodium formate, sodium acetate, sodium propionate and sodium butyrate have also been determined at 35°C.

The effect of increasing chain length on the mobility is discussed. By considering the experimental and the theoretical values of slopes of plots of equivalent conductance vs square root of concentration, it was concluded that some sort of interaction, preferably, a reversible dimerisation of anions takes place even in the dilute region, which accounts for lower experimental values of slopes.

The critical micelle concentrations have been determined precisely and recent energy concepts associated with the process of micelle formation are applied to interpret the structure of the micelles. Surface tensions of the aqueous solutions of sodium octanoate, sodium decanoate, sodium laurate and sodium myristate have been measured at 25°C and 50°C and the Gibb's adsorption theory has been applied to interpret the surface phenomenon of these salts in the aqueous solutions.

Finally the conductance and viscosity behavior of these salts have been discussed in terms of structural considerations over the entire region of concentration.

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TABLE OF SYMBOLS

a, a°	Distance of closest approach between ions in solution, in cm. and \AA , 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
K	Specific conductance in mhos per cm.
n	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
a	Degree of dissociation of an electrolyte in solution
E	Charge on the electron, e.s.u.
K	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

INTRODUCTION

CHAPTER I

For several years the study of the conductance and viscosity of various electrolytes in aqueous solutions over the complete range of concentration, has been proceeding in this laboratory. Since, at the limiting dilution, the equivalent conductance of an electrolyte is the sum of the conductance of its constituent ions and since, for a univalent electrolyte, the conductance of cation or anion is solely determined by its speed and this again by its size, it was felt that it should be possible to find an anion so large that it was effectively motionless and non-conducting and therefore the conductance should be determined solely by the cation. Such a phenomenon, if it were realized, would render the theoretical study of conductance some what simpler.

With this in mind, a precise determination of the limiting equivalent conductances of the sodium salts of normal fatty acids, from hexanoic acids onwards was undertaken, since there were no reliable values for the conductances of the sodium salts of these acids. Work was carried out at 25°C and 35°C. The first part of this thesis deals with these conductance measurements.

For a long time it was commonly assumed that aqueous solutions of the salts of long chain acids, like ordinary electrolytes, where the conductance changes with concentration in accordance with Onsager's Theory, would follow the theory up to the micelle concentration where the course of conductance changes abruptly. In recent years attention has been diverted to studying in great detail in dilute region for the salts of long chain acids in aqueous solution and to finding the mechanism of the process occurring. It was partly the purpose of this work to find the extent of deviation of

conductance from the theory and to seek an explanation from some of the modern concepts of the behavior of amphiphilic (compounds having both hydrophilic and hydrophobic parts) salts in dilute solution.

It is well known that in aqueous solutions of these salts micellar formation, aggregation of ions, takes place. It was partly the aim of this work to determine the critical micelle concentrations precisely by the conductance method and with the help of recent energy concepts of micelle formation to give a structural interpretation of these micelles.

Additional support was sought for micelle formation from measurements of Surface Tension and viscosity determinations of the aqueous solutions of the salts. It was also the object of this work to seek an explanation of the peculiar surface phenomenon (surface tension values) in terms of Gibb's adsorption theory applied to solutions. Lastly, all these physical properties were measured up to very high concentrations in order to get more information regarding the internal structure of the solutions, not only just below and just above the critical micelle concentrations, but also at high concentrations where the experimental data might give a qualitative idea of the possible structural changes.

GENERAL AND THEORETICAL INTRODUCTION

CHAPTER II

It is appropriate to start this introduction with the theory of Debye - Hückel - Onsager as applied to the electrolytic conductance of low - valence type of electrolytes and the subsequent modification of the theory by later workers.

The anomalies of strong electrolytes and in particular the complete breakdown of the Ostwald dilution law, which is based on simple law of mass action (i.e. without activity co-efficients), led to numerous attempts to calculate the deviation from ideal behavior from a consideration of the electrical (coulomb) forces involved.

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 X, the degree of dissociation of an electrolyte in aqueous solution. 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

$$\frac{\Lambda}{\Lambda_0} = \alpha \frac{(u^+ + v^-)}{(u_0^+ + v_0^-)} \quad 1$$

the ratio of ionic velocities at finite concentration to those at infinite dilution remain unaltered, and equal to unity. Application of the law of mass action for a 1;1 electrolyte results in the Ostwald dilution law:

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

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. Sutherland², Noyes³, and Bjerrum⁴ 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,

$$\text{i.e. if } \alpha = 1.00, \text{ then } \frac{\Lambda}{\Lambda_0} = \frac{u^+ + v^-}{u_0^+ + v_0^-} \quad 3$$

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 Debye - Hückel⁵ marked the commencement of a new era in electrochemistry.

The Debye - Hückel Theory:

The concept of an ionic atmosphere introduced by Debye - Huckel made it possible to calculate the effect of coulombic forces upon the activity, although as far as colloidal particles are concerned the idea of a diffuse atmosphere or double layer of counter ions (gegenions) surrounding the particles or charged surface had been introduced much earlier⁶. The fundamental idea underlying the Debye - Hückel treatment is that, as a consequence of electrical attractions between positive and negative ions, there are, on the average, more ions of unlike than like sign in the neighbourhood 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 in motion under the influence of an external electrical field, however 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 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.

By taking into consideration these two effects, together with the Brownian movement of the ions, Onsager⁷ developed the following equation for the equivalent conductance of a uni-univalent electrolyte

$$\Lambda = \Lambda_0 - \left[\frac{82.4}{(D_0 T)^{1/2}} \eta_0 + \frac{8.20 \times 10^5}{(D_0 T)^{3/2}} \Lambda_0 \right] \sqrt{c} \quad 4$$

Due to the mathematical simplifications and the assumptions made, which are really valid only for the very dilute region, in the above simple form. Onsager's equation is not valid at concentrations greater than .001 N.

Later on an important extension and modification of the theory was proposed⁸ in which allowance was made for the finite size of the ions and a new expression for the relaxation effect was developed.

Wishaw and Stokes⁹ published their conductance equation in the form

$$\Lambda = \left[\Lambda_0 - \frac{B_2 \sqrt{c}}{1 + Ka} \right] \left[1 - \frac{B_1 \sqrt{c}}{1 + Ka} F \right] \quad 5$$

where

$$B_1 = \frac{8.20 \times 10^5}{(D_0 T)^{3/2}}, \quad B_2 = \frac{82.4}{(D_0 T)^{1/2} \eta_0} \quad 5a, 5b$$

$$B_1 a^0 \sqrt{c} = \frac{50.29 a^0 \sqrt{c}}{(D_0 T)^{3/2}} = Ka \quad 6$$

$$F = \frac{\exp 0.2929 Ka - 1}{0.2929 Ka} \quad 7$$

$$K = \left[\frac{\pi N e^2}{125 D_0 k T} \right]^{1/2} \sqrt{c} \quad 8$$

In the above equation the only adjustable parameter is the effective ionic diameter a^0 , if one assumes that Λ_0 is already known from suitable measurements.

The question arises whether the values for "a" as they appear in the Wishaw - Stokes equation have any physical significance. Since the values obtained for "a" are ~~not~~ 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 solutions. It must be admitted, however, that the manner in which the equation is employed to analyse experimental data forces "a" to absorb all imperfections in the theory as well as any experimental error which may have occurred. Fowler¹⁰ says, "a" is an "omnium gatherum" correction." It would seem that the values for "a" are at best only empirical.

It can be seen that in Robinson and Stokes equation 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 at higher concentration. Bernal and Fowler¹¹ 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) Inter ionic attractions cause increased shear and hence increased viscosity, and
- 3) changes in the hydration of the ions cause changes in the viscosity.

It is generally agreed, however, that some form of viscosity corrections must be applied to the conductance equations. The exact form is not known, but experience has shown that dividing the theoretical equation by the relative viscosity, seems to be very approximately correct. It is observed that these viscosity corrections often reproduce experimental data for solutions whose concentration far exceed the limits to which they are theoretically applicable. Thus Campbell et al^{12,13} found surprisingly good agreement in very many cases, especially in the case of lithium chlorate at 25°C where the agreement up to saturation is quite good.

In addition to this, Fuoss¹⁴ has recently extended the highly mathematical treatment given earlier by Fuoss and Onsager¹⁵ and by Fuoss¹⁶ and expressed the conductance equation for a uni-univalent electrolyte as

$$\Lambda = \Lambda_0 - S c^{1/2} + E c \log c + J c \quad 9$$

where the constants S , E and J are as follows:

$$S = \alpha + \beta \Lambda_0 \quad 10$$

α and β are Debye - Hückel constants defined as

$$\alpha = \frac{82.40}{(D_{0T})^{1/2} \eta_0} \quad 10a$$

$$\beta = \frac{8.20 \times 10^5}{(D_{0T})^{3/2}} \quad 10b$$

$$E = E_1 \Lambda_0 - E_2 \quad 11$$

where $0.4343 E_1 = \frac{k^2 a^2 b^2}{24c} \quad 11a$

and $0.4343 E_2 = \frac{Kab}{16c^{1/2}} \quad 11b$

with b defined by $b = \frac{\epsilon^2}{aDokT} \quad 12$

By combining equation 12 with equations 11, 11a, 11b 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 10 that S is also independent of these parameters.

J is given by

$$J = \sigma_1 \Lambda_0 + \sigma_2 \quad 13$$

where

$$\sigma_1 = \frac{k^2 a^2 b^2}{12c} \left[h(b) + 0.9074 + \ln \frac{Ka}{\sqrt{c}} \right] \quad 13a$$

and

$$\sigma_2 = \alpha\beta + \frac{11\beta Ka}{12c^{1/2}} - \frac{Ka\beta}{8c^{1/2}} \left[1.017 + \ln \frac{Ka}{c^{1/2}} \right] \quad 13b$$

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

$$h(b) = \frac{2b^2 + 2b - 1}{b^3} \quad 14$$

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 equations for these two parameters using two given values of

Λ would be extremely difficult due its complicated form. Another method is as follows: First Λ_0 is obtained by Shedlovsky's method¹⁸ to be discussed and this is used to obtain S value using equation 10 and E value using equation 12. Next another quantity Λ^i is defined by the expression

$$\Lambda^i = \Lambda_0 + Jc \quad 15$$

where

$$\Lambda_0 = \Lambda + sc^{1/2} - Ec \log c$$

A plot of Λ^i against C is linear with the intercept on the Λ^i 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 13, 13a, 13b.

In spite of the fact that the Fuoss - Onsager equation reproduced the conductance data rather accurately for many solutions, their equations are only applicable to solutions for which $Ka < 0.2$. In other words their theory cannot be extended to higher concentrations (0.05 N). The question arises of how far these conductance theories are valid in the case of colloidal electrolytes of which the salts of fatty acids belong. Since their first recognition as such, by McBain in 1913, colloidal electrolytes have received steadily increasing attention, because of their interesting departures from the behavior of ordinary electrolytes and because they embrace such large groups of substances. McBain^{17,18,19}) found that soaps were able to form colloidal particles in a reversible manner from simple ions and constitute, therefore, an important section of that class of substance intermediate between ordinary colloids,

having large particles whose charge is due to adsorption of ions and ordinary electrolytes whose ions remain distinct and of atomic dimensions. In dealing with these colloidal electrolytes which are characterised by low osmotic properties and relatively high electrolytic conductance, one has to take into consideration not only uni-valent cations and anions, but also particles of colloidal dimensions. The latter are made up of large monomeric ions, together with bound counter ions of opposite charge (gegenions) and water molecules. These are known as "micelles" or "micellar ions" and are responsible for some of the anomalous behavior of these substances, with respect to ordinary electrolytes.

In common with other strong electrolytes, some of the anomalies of colloidal electrolytes may be at least partially explicable in terms of the ionic attraction theory of Debye - Hückel, from a consideration of the inter action due to the coulomb forces between the ions and micelles at distances, which by comparison with molecular forces are very great. Since simple Debye - Huckel theory fails badly to represent the facts for electrolytes of high valence type in any but the most dilute solution, the deviations from ideality as predicted by the theory increase rapidly with increasing valence or charge of micellar ions. Hartley²⁰ has summarised the effect of the Debye - Huckel treatment on colloidal electrolytes and concluded that in order to explain the experimental results some kind of association between micelles and ions of opposite charge (gegenions) must occur. The effect of this on the equilibrium between simple long chain ions and micelles may be greater than the direct atmosphere effects and at

least it will be considerably modified by it.

It was considered for a long time, that the conductances of colloidal electrolytes follow, in general, Onsager's theory right up to the critical micelle concentration, but in recent years a number of workers^{21,22,23,24,25,26,27} reported that precise conductance measurement showed that deviation from the theory is observed even in very dilute solution. As mentioned already, it was partly the purpose of this research to test the validity of Onsager's equation for the sodium salts of fatty acids at 25°C and 35°C and to seek an explanation for the deviation, if there is any, from the theory.

As concentration increases, micelle formation takes place at a definite concentration and a sudden change of physical properties occurs.

Critical Micelle Concentration (C M C)

The sharp variation of any of the physical properties such as conductivity, turbidity, viscosity, which occurs at a definite concentration is known as the "critical micelle concentration". In solutions of amphiphilic salts the critical micelle concentration is determined by a number of factors such as size, shape of the paraffin chain and by the nature of the polar group attached to the hydrocarbon portion of the molecule.

In a recent paper William, Philips and Mysels²⁸ stressed the importance of the critical micelle concentration, which they consider to be a measure of formation of colloidal particles, and of how this is affected by changing conditions. Philips²⁹ has recently defined critical micelle concentration as the concentration at which the properties of the solution change in the most abrupt manner (i.e.)

$$\frac{d^3\phi}{dc^3} = 0$$

where ϕ is an additive property which varies linearly with the concentration of micellised and of undissociated detergent. It is, however, very difficult to determine this concentration experimentally by this method since it involves measuring third order differences. In practice the critical micelle concentration is determined as the point of intersection of the curves extrapolating the measured properties of the solution from below and from immediately above the region in which rapid change of slope is observed.

Micelle Formation:

The micelle is the kinetic unit of the disperse phase in colloidal solutions. It differs from the units in ordinary solutions - molecules and ions - in that it is much larger. It may not be completely free in its movements although apparently free from the thermodynamic (equilibrium) point of view. In some cases the micelle is known to be a statistical grouping of molecules. Nevertheless, in addition to the average size, the shape and the manner in which the micelle is built up from molecules or ions can be determined. In such case one can explain the bulk colloidal properties of the solution in terms of the individual micelle. Restraint on the free motion of the micelle is the origin of many of the peculiar properties of colloidal electrolytes.

Theory of Micelle Structure:

Although, it is true several theories^{30,31,32,33} have been developed recently to account for the micelle structure, at least semi-quantitatively, the fundamentals of these theories leave much to be desired. Most of the theories of micelle formation have emphasized

energy considerations. In the formation of the micelle two different forms of energy take part. Energy is liberated by the removal of a number of the hydrocarbon chains from the surrounding water, thus bringing them in contact and decreasing the hydrocarbon - water interface. An equally important factor, no doubt, is the strong cohesive forces (hydrogen bonding etc.) between water molecules, which tend to aggregate and expel the chains from solution. The molecular forces involved in this process are of the short range type commonly designated Van der Waals forces. Simultaneously the electrically charged polar heads are brought closer to each other. This process requires energy when ionic atmospheres overlap. Here the forces to be overcome are long range electrical (Coulombic) forces. In the formation of the micelle an equilibrium is reached between these opposing forces, with an accompanying decrease in force energy. It is the interplay of these short and long range forces which determines the structure of the micelles. The hydrophilic nature of the polar groups keeps the micelles suspended in solution.

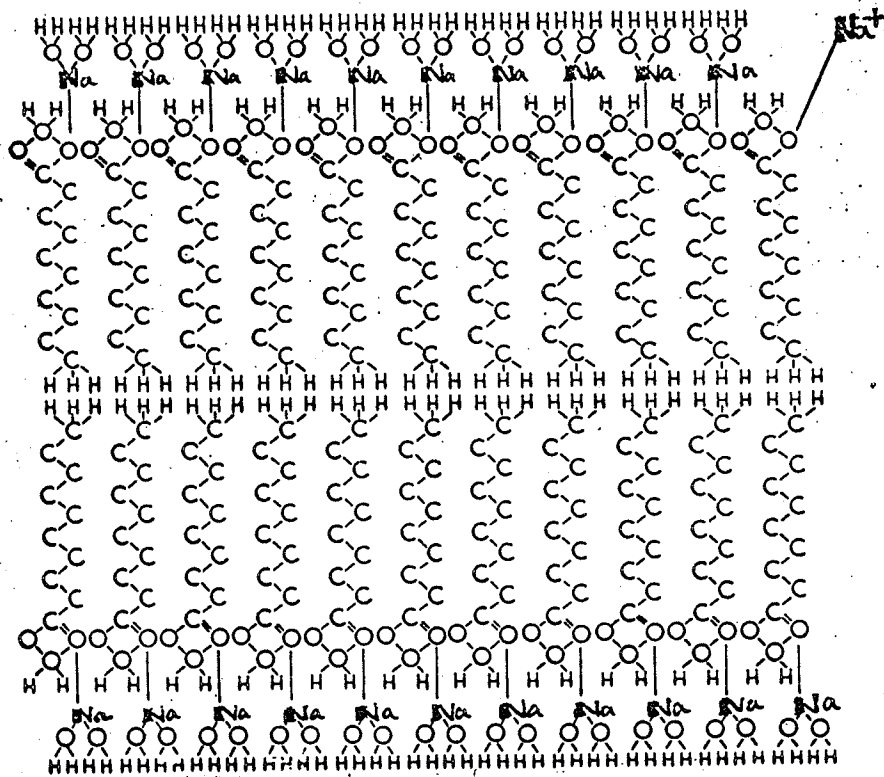
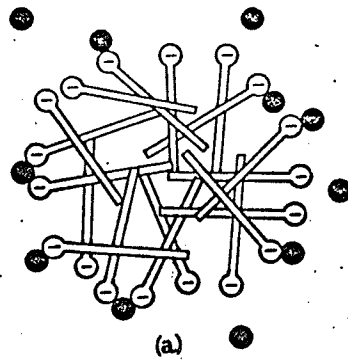
No theory of the micelle is complete which does not give due consideration to the role of the gegenion. Unfortunately reliable data for making comparisons are scarce. Various factors must influence the dissociation of the gegenion from the micelle surface. The valence (charge) evidently plays an important role.

Numerous models have been proposed for micelle structures. McBain³⁴ has postulated two kinds of micelles, ionic spherical and neutral lamellar and this view has received much support from the X - ray work of Stauff³⁵ and Hess³⁶ and more recently Harkins, Mattoon

and Corrin³⁷. Hartley³⁸, however, assumes only one type of micelle, a spherical one of variable charge. This view is supported by Vetter³⁹ from conductance and diffusion measurement of sodium disulfosuccinate. Recently, Schulman and Ridey⁴⁰ and Friend⁴¹ by means of X-ray and light scattering investigations of oilwater disperse systems conclude that a hydrocarbon spherical micelle is a better structure for aggregated soap molecules than the lamellar or the cylindrical form.

It is desirable to adopt a model which is simpler and at the same time consistent with the experimental results. There seems to be general agreement to adopt the Hartley type of micelles, in dilute solution, when there are less than 100 monomeric units aggregated into a compact spherical body on the surface of which the charged heads remain exposed to the water. Approximately two thirds of the counterions are firmly bound to the surface aggregate, due to strong electrical interactions⁴², the remaining one third being in the diffuse double layer surrounding the aggregate. For micelles containing more than 100 units, and at higher concentrations, however, experimental results indicate that micelles are asymmetric and there is very good reason to believe that spherical micelles transform into micro crystalline units of the lamellar kind as suggested by McBain. It is possible to represent, as shown in Figure 1, the two kinds of micellar structures as discussed above.

FIGURE 1. Schematic representation of a soap micelle (a) Spherical micelle of Hartley type (b) Lamellar micelle of McBain's type.



(b)

FIGURE 1

EXPERIMENTAL PROCEDURE

CHAPTER III

Preparation of the Salts:

Sodium salts of the acids, decanoic, lauric and myristic, (the acids were Fisher certified products) were prepared by neutralizing the alcoholic solution of the acids with hot alcoholic sodium hydroxide, using phenolphthalein as indicator and evaporating the resultant solution to dryness under reduced pressure. The salts thus obtained were recrystallized twice from aqueous alcohol and dried at 110°C , ground in an agate mortar and stored in an oven at 110°C . The purity of the salts was determined by converting them to sulphates and estimating the sulphates as described by Stock, Stahler, Patnode and Dennis⁴³. By this method the purity of the salts was found to vary between 99.3 to 99.6 percent, as the mean of several separate determinations. Since the most likely impurity is sodium carbonate the results should be high rather than low, because the percentage of sodium in sodium carbonate is about 43% as compared to 11.8%, 10.3%, 9.2% in sodium decanoate, sodium laurate and sodium myristate respectively. The results should also be high if sodium hydroxide were present as an impurity. The results are therefore probably within the experimental error.

The potassium chloride used in the determinations of the cell constants, a Fisher certified reagent was fused in a platinum dish, ground in an agate mortar and stored over barium oxide until needed.

Preparation of the Solutions:

Distilled water obtained from a Barnstead still, was further degassed for removal of dissolved carbon dioxide by bubbling through it

pure nitrogen, already purged through alkaline pyrogallol, sulfuric acid and 'ascarite'. Conductance water, thus obtained had a specific conductance of 0.5 to 1.5×10^{-6} mhos/cm at 25°C.

The solutions were prepared by weighing. For the extremely dilute solutions, as used in conductance measurements, successive additions of salt of about 0.02 gms, weighed accurately on a Metler 14-5 Grammatic microbalance to the nearest 2 μ gms, were made to a known amount of water and the concentrations expressed as moles/litre assuming the density of the solutions to be that of water at the respective temperatures.

Conductance Cells:

The conductance cells used for higher concentrations had the leads and filling tubes sufficiently far apart, as suggested by Jones and Bollinger⁴⁴, so that error due to the Parker effect⁴⁵ was avoided. The concentrations of potassium chloride used to determine the cell constants were those defined by Jones and Bradshaw⁴⁶. Periodic checks of these cell constants showed a variation within 0.03 %.

For the determination of the conductance of extremely dilute solution a Shedlovsky type⁴⁷ cell was used. It is shown in Figure 2. It consists of a silica vessel of a litre capacity and a hard pyrex glass bulb attached to the flask through a graded seal. Two platinum electrodes, having a thin coating of platinum black, as recommended by Jones and Christian⁴⁸ to eliminate polarisation effects, were sealed into the pyrex bulb. The cell constant of this cell was obtained by using the following equation due to Fuoss⁴⁹

FIGURE 2. The Shedlovsky type cell.

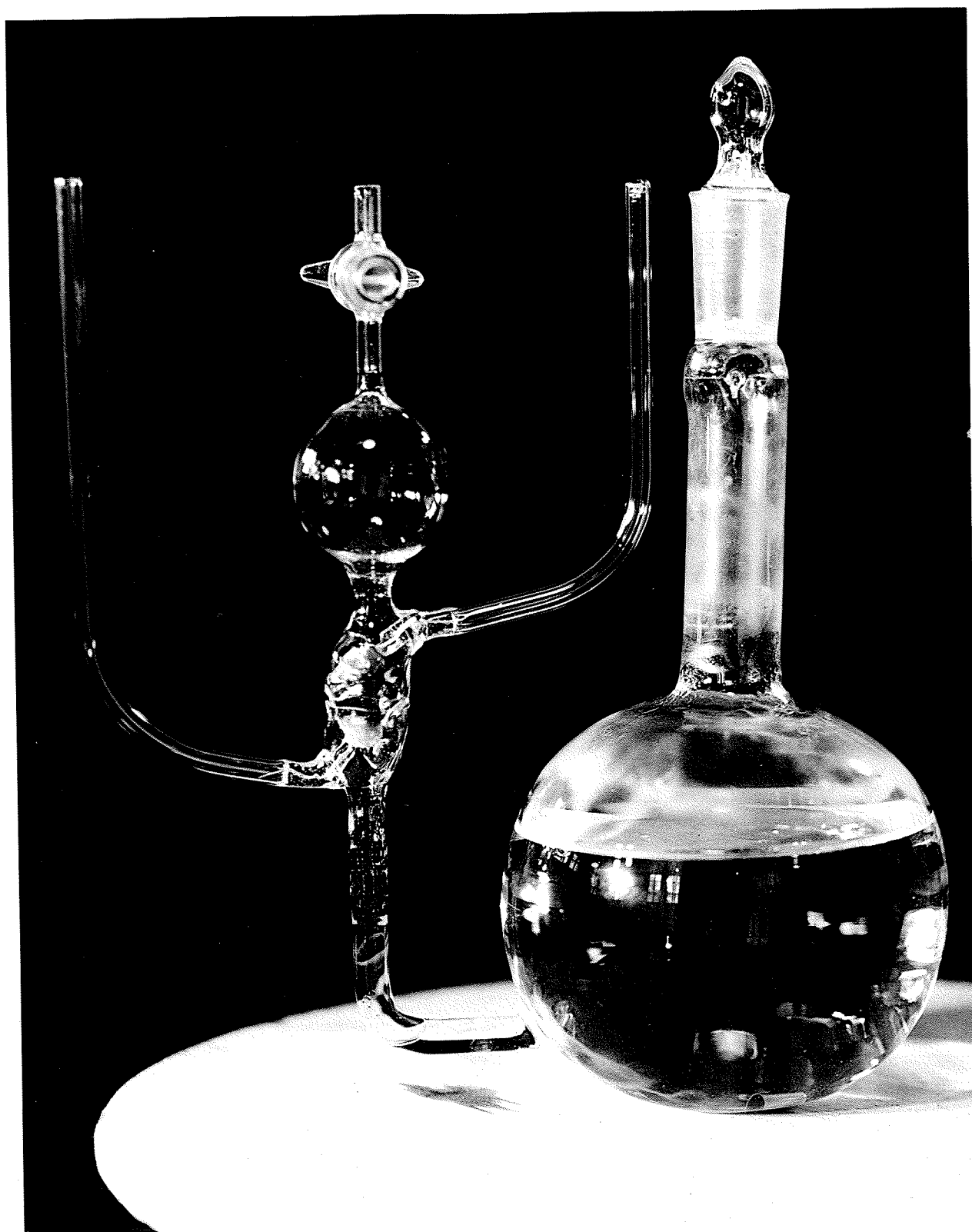


FIGURE 3.

$$\Lambda = 149.93 - 94.65c^{1/2} + 58.74c \log c + 1984c \quad 16$$

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

$$\Lambda = \frac{1000 A}{cR} \quad 17$$

where R is the measured resistance and A is the cell constant; the latter can be determined from known values of Λ at different concentrations by measuring the resistance R accurately.

There is no direct way of determining the cell constant at 35°C, but Washburn⁵⁰ has developed an equation based on the coefficient of expansion of glass,

$$\Delta A = -\beta A \Delta T \quad 18$$

showing the variation of cell constant with temperature. Here ΔA is the change in cell constant A, β is the linear coefficient of thermal expansion of glass, and ΔT is the change in temperature. The corrections were applied to the cells taking 3.5×10^{-6} units/degree centigrade as a value for β and ΔT being 10°C. The corrections, however, were scarcely significant.

The Thermostats:

The thermostat used at 25°C consisted of a steel tank of about 18 gallon capacity housed in a double-walled insulated box, filled with 'Marcol', a high boiling hydrocarbon oil and stirred by means of a pump. A top view of the thermostat is shown in Figure 3.

FIGURE 3. Top view of the thermostat at 25°C.

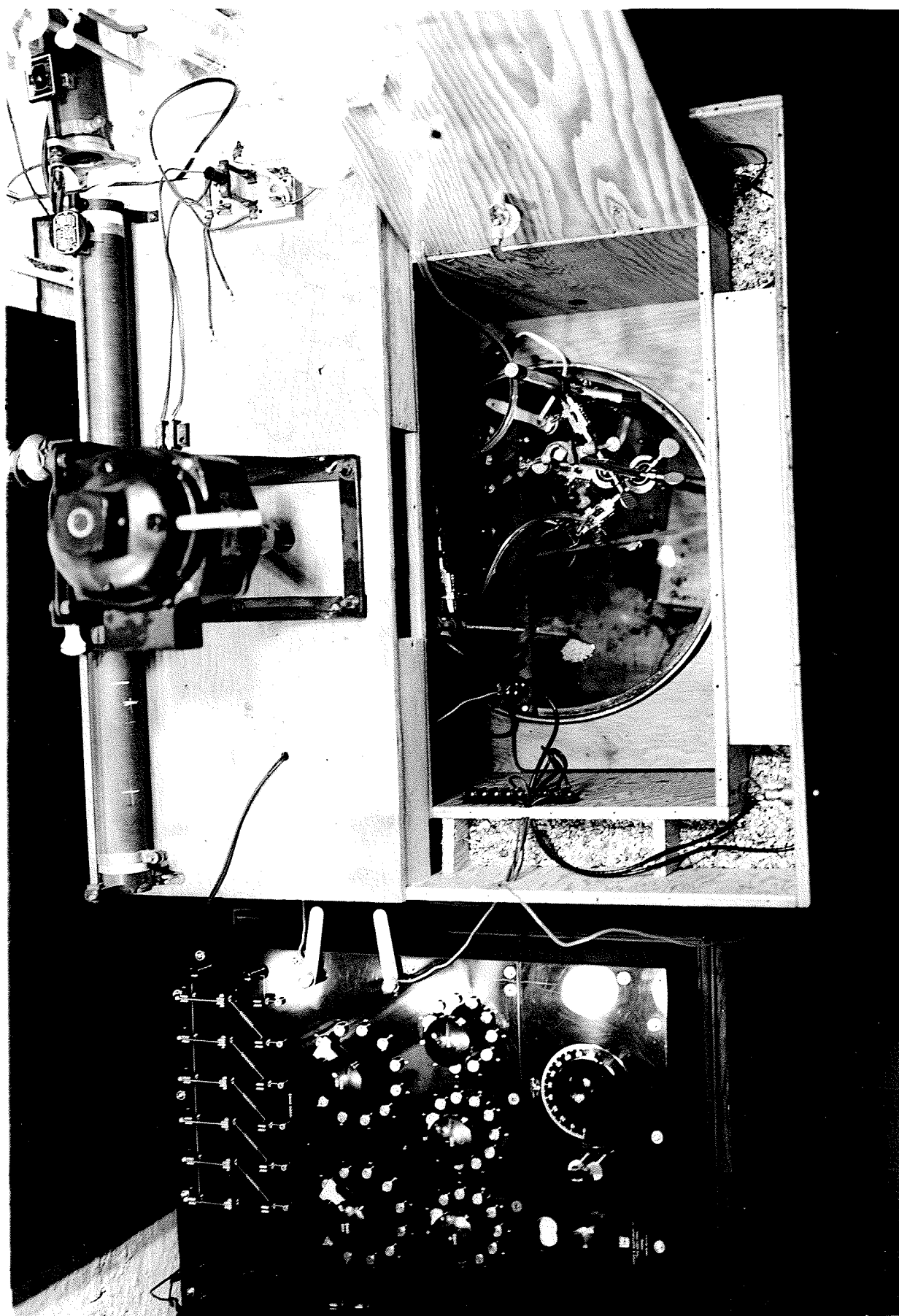


FIGURE 3

Temperature control was effected by the use of a mercury - toluene regulator and thyatron relay as described by Swineheart⁵¹. The temperature was read on a Beckmann thermometer which was frequently calibrated against a standard platinum - resistance thermometer and Müller bridge. The temperature fluctuations were well within $\pm .005$ C. It was found necessary to precool the thermostat bath so as to counteract the frictional heat generated by the stirrer. This was achieved 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 at 35°C was a square type glass vessel of about eight gallon capacity. It was lagged with half inch felt and 'marcol' was used as a thermostat 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.

For surface tension measurements the thermostats used at 25°C and 50°C contained water as thermostat liquid instead of 'marcol' in order to avoid any contamination of oil or vapors at the tip of the stalogrameter which would affect the surface tension values. The rest of the arrangements were the same.

The Conductance Bridge:

The resistances of the solutions were measured on a Leeds and Northrup Jones conductivity bridge. This is a modified version of the usual wheatstone bridge adapted to a.c. measurements.

Current leakage at the detector terminals is eliminated by inclusion of a Wagner Ground. An oscilloscope in series with a tuned amplifier and a frequency filter served as a detector. Measurements of resistance can be made well within 1 ohms in 10000. The circuit diagram of the bridge is shown in Figure 4.

The Hydrolysis Correction:

The method of Campbell and Bock⁵² was used to correct the equivalent conductance for the effect of hydrolysis. Hydrolysis of a salt of weak acid and strong base occurs as $A^- + H_2O \rightarrow HA + OH^-$ where A^- is a weak acid anion. In this method, the degree of hydrolysis α is calculated from the expression

$$\alpha = -\frac{k_h}{2c} + \sqrt{\frac{k_h^2}{4c^2} + \frac{k_h}{c}} \quad 19$$

where k_h is the hydrolysis constant and c is the Stoichiometric concentration. Assuming the equivalent conductance of the base to be equal to its limiting equivalent conductance, the true equivalent conductance, Λ_{true} , of the unhydrolysed salt is calculated from the equation.

$$\Lambda_{exp} = (1-\alpha)\Lambda_{true} + \alpha\Lambda_{base} \quad 20.$$

This hydrolysis correction was applied to all the results.

The Density Measurements:

Two pycnometers (Ostwald - Sprengel type) of 25 ml capacity were

FIGURE 4. The circuit diagram of the conductance set up.

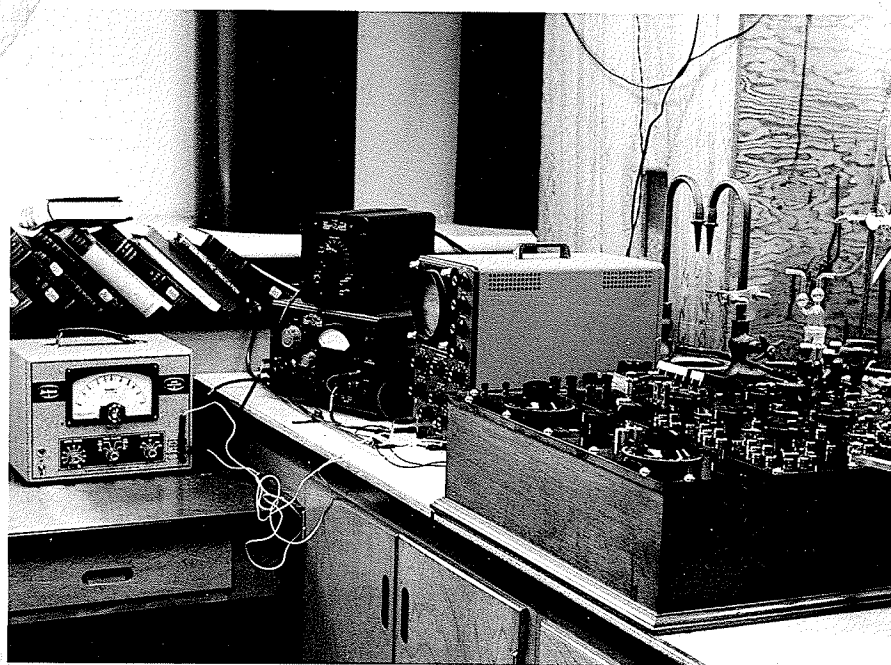


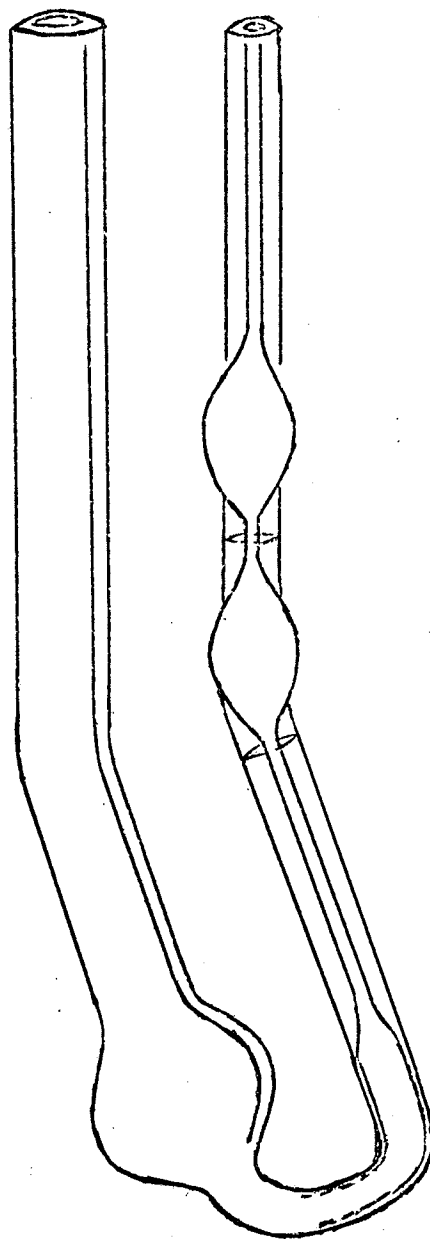
FIGURE 4

used to determine the density of the solutions at 25°C and 35°C. The pycnometer was always weighed against an empty of same capacity thus avoiding any buoyancy error. Several times during the course of the work, the pycnometers were standardized with water and agreement was well within the experimental error.

The Viscosity Determinations:

The choice of viscometer is important if viscosity determinations of these electrolytes are to be comparable in accuracy with the conductance data. An Ostwald viscometer is most commonly employed in this type of work; it has the advantage of being simple in principle and operation. On the design of viscometers innumerable papers have appeared, most notable of which are by Willihnganz, McCliver, Fenske and McGrew⁵³. After due consideration of the literature and of the viscous properties of the solution it was decided to use a viscometer of the Cannon and Fenske type⁵⁴, as shown in Figure 5, where the drainage and kinetic energy corrections to the measurement were considered to be negligible by virtue of the rather narrow capillary diameter which gave an efflux time in excess of 200 seconds for all the measurements. The bend in the viscometer causes it to be much less sensitive to the angle of tilt from the vertical and permits the viscometer to be supported in the bath by means of an ordinary clamp and clamp stand, separate from the thermostat and fixtures. The viscometer was calibrated with conductance water at 25°C and 35°C. Run times were reproducible to only 0.05 %. Measurements were done in duplicate and

unintentional and cannot be avoided.



VISCOMETER (CANNON AND FENSKE TYPE)

FIGURE 5

by preliminary experiments it was found that interchange of viscometers at both temperatures, without refilling, did not alter the efflux time. In other words the viscometer can be transferred from 25°C bath to 35°C bath without refilling it with fresh solution for a particular determination.

The Surface Tension Measurements:

The method used to determine the surface tension was the well known Stalogrameter method as described by Harkins⁵⁵. In this method the numbers of drops from a fixed volume, at constant temperature, of a standard liquid (water) and for the same volume of solution falling from a perfectly well polished tip of a capillary tube, are counted. Then, knowing the density of both standard liquid and solution and the surface tension of the standard, the surface tension of the solution at a given concentration is calculated from the formula

$$\gamma = \frac{N_0 \times d}{N \times d_0} \times \gamma_0$$

21

where N_0 = number of drops of the standard solvent (water)

N = number of drops of the solution

d_0 = density of the standard (water)

γ_0 = surface tension of the standard (water)

Because of the high viscosity of the solutions, especially the concentrated ones, the number of drops ranged between 100 - 200. To count them more accurately, an automatic counting system was devised and thus avoided the use of a hand counter. In this automatic counter

the fall of each drop from the tip of the capillary tube on the platinum cones of the receiver is counted automatically through an electronic glow counter as shown in Figure 6. The counter was previously tested several times to find possible signal pick up. The signal pick up from stray currents was eliminated by having a Faraday cage around the counter. The graduation marks on the Stalogrameter made it possible to count fractional drops. At least four sets of readings for each concentration were taken. The calibrated Stalogrameter was often checked against benzene and it was found that the agreement between the experimental value 24.11 dynes/cm at 25°C and 24.86 dynes/cm at 50°C and the literature value⁵⁶ 28.25 dynes/cm at 25°C and 24.98 dynes/cm at 50°C was good.

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FIGURE 6. Glow counter and Stalogrameter

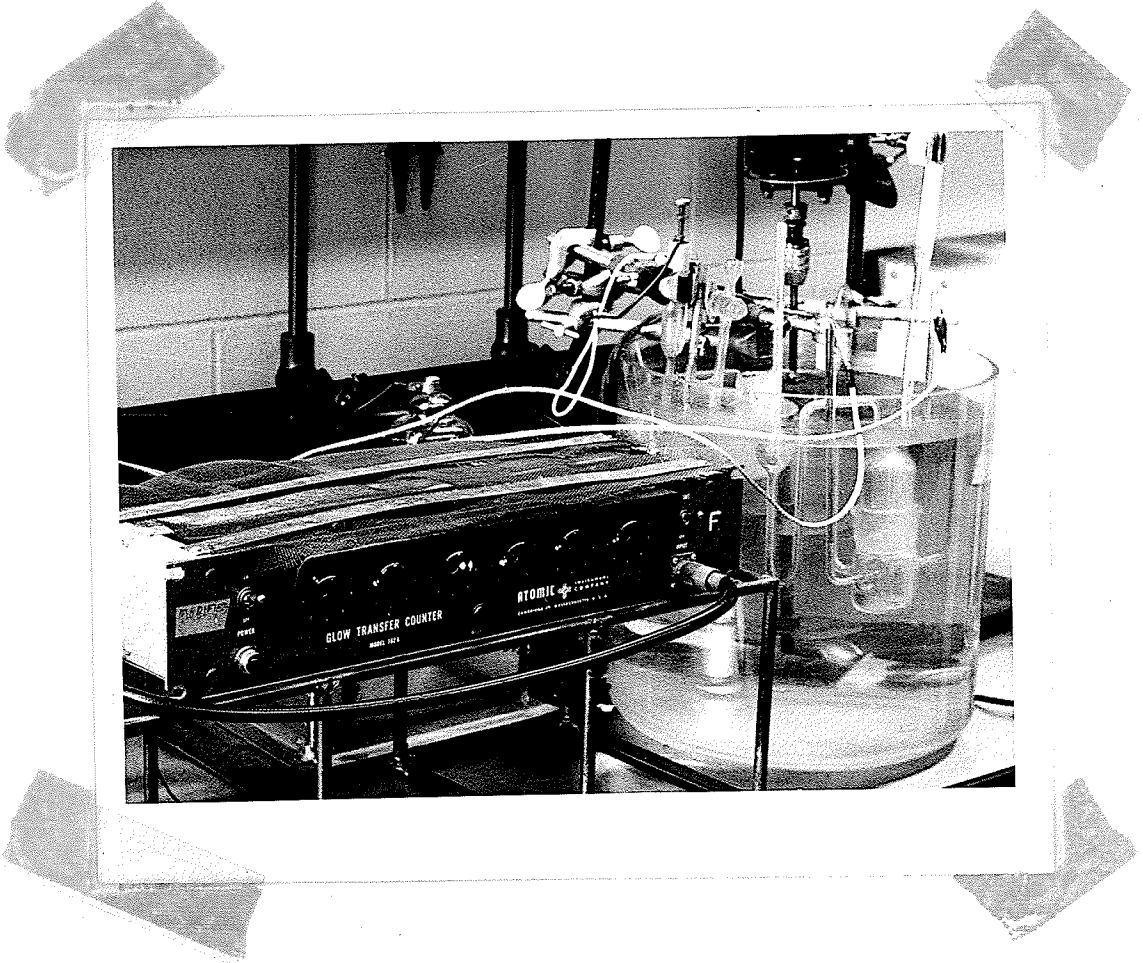


FIGURE 6

EXPERIMENTAL RESULTS

TABLE I
Formula

EQUIVALENT CONDUCTANCES (DILUTE SOLUTION) OF SODIUM DECANOATE
($\text{CH}_3(\text{CH}_2)_8\text{COONa}$)

Temperature 25°C		Temperature 35°C	
concentration (mole/litre $\times 10^4$)	Equivalent Conductance (mhos)	Concentration (mole/litre $\times 10^4$)	Equivalent Conductance (mhos)
2.46	71.35	2.45	88.21
4.36	71.20	4.35	87.95
6.78	70.99	6.76	87.61
9.11	70.73	9.08	87.48
13.00	70.51	12.97	87.10
16.16	70.34	16.11	86.85
20.40	70.01	20.34	86.59
23.86	69.84	23.78	86.42

TABLE 2

Formula
EQUIVALENT CONDUCTANCES (DILUTE SOLUTION) OF SODIUM LAURATE.
($\text{CH}_3(\text{CH}_2)_9\text{COONa}$)

Temperature 25°C		Temperature 35°C	
Concentration (mole/litre $\times 10^4$)	Equivalent Conductance (mhos)	Concentration (mole/litre $\times 10^4$)	Equivalent Conductance (mhos)
2.42	70.08	3.92	86.73
5.35	69.72	5.73	86.49
7.16	69.65	7.14	86.32
9.71	69.43	9.69	86.07
11.31	69.31	12.95	85.80
12.75	69.28	16.12	85.55
16.17	69.05	19.99	85.32
20.05	68.77	23.91	85.02
23.98	68.61	-	-

TABLE 3

EQUIVALENT CONDUCTANCES (DILUTE SOLUTION) OF SODIUM MYRISTATE.
Formula
(CH₂(CH₂)₁₂COONa)

Temperature 25°C		Temperature 35°C	
Concentration (mole/litre X10 ⁴)	Equivalent Conductance (mhos)	Concentration (mole/litre X10 ⁴)	Equivalent Conductance (mhos)
1.38	69.68	1.37	86.17
2.43	69.55	2.42	86.01
3.61	69.49	3.60	85.92
4.95	69.33	4.93	85.65
5.98	69.16	5.96	85.58
7.15	69.08	7.13	85.47
8.06	68.97	8.03	85.36
9.49	68.95	9.46	85.30

TABLE 4 **

DENSITIES, VISCOSITIES AND CONDUCTANCES OF SODIUM OCTANOATE AT 25°C
 $(\text{CH}_3(\text{CH}_2)_6\text{COONa})$

Concentration (moles/litre)	Density (gm/ml)	Relative Viscosity	Specific Conductance _{sp} (mhos/cm X10 ⁴)	Equivalent Conductance (mhos)
0.000237	-		0.17186	72.21
0.000647	-		0.46317	71.49
0.001233	-		0.87750	70.91
0.001624	-		1.1485	70.58
0.002088	-		1.4687	70.22
0.002858	-		2.0010	69.91
0.01086	0.99731	1.022	7.2143	66.38
0.07416	0.99935	1.071	44.706	60.27
0.1043	1.0024	1.095	60.652	58.17
0.1977	1.0046	1.182	107.06	54.40
0.3484	1.0084	1.332	169.64	48.69
0.5099	1.0128	1.537	220.23	42.87
0.6245	1.0159	1.723	258.71	41.42
0.8409	1.0210	2.222	320.16	38.07
1.1332	1.0277	3.460	397.01	35.04
1.6338	1.0386	8.311	491.38	30.07
2.1137	1.0495	26.027	520.35	24.62
2.8287	1.0659	65.069	501.36	17.72

** Results from Reference⁵⁹.

TABLE 5 **

DENSITIES, VISCOSITIES AND CONDUCTIVITIES OF SODIUM OCTANOATE AT 35°C
(CH₃(CH₂)₆COONa)

Concentration (moles/litre)	Density (gm/ml)	Relative Viscosity	Specific Conductance (mhos / cm X10 ⁴)	Equivalent Conductance (mhos)
0.000236			0.21265	89.51
0.000646			0.57321	88.66
0.001232			1.0868	87.93
0.001619			1.4189	87.40
0.002081			1.8189	87.19
0.002850			2.4738	86.58
0.01082	0.99418	1.020	8.9059	82.31
0.07395	0.99641	1.069	55.245	74.71
0.1040	0.99742	1.092	74.902	72.03
0.1970	1.0001	1.165	133.231	67.63
0.3472	1.0041	1.323	211.48	60.91
0.5079	1.0079	1.521	247.45	54.04
0.6223	1.0108	1.701	322.81	51.87
0.8373	1.0155	2.192	403.14	48.15
1.1280	1.0225	3.409	500.84	44.41
1.6255	1.0342	8.159	620.03	38.16
2.1021	1.0445	25.350	661.49	31.47
2.8213	1.0603	54.149	645.31	22.87

** Results from reference⁵⁹

TABLE 6

DENSITIES AND EQUIVALENT CONDUCTANCES OF SODIUM DECANOATE AT 25°C
 $(\text{CH}_3(\text{CH}_2)_8\text{COONa})$

Concentration (mole/litre)	Density (g/ml)	Specific Conductance (mhos/cm $\times 10^4$)	Equivalent Conductance (mhos)
0.0102	0.9973	6.8895	67.27
0.0326	0.9986	20.540	63.06
0.0523	0.9987	31.651	60.51
0.0758	1.0003	43.653	57.59
0.1099	1.0004	60.591	55.12
0.1372	1.0009	70.213	51.17
0.1833	1.0029	85.218	46.49
0.2299	1.0038	100.47	43.71
0.3055	1.0053	126.80	42.16
0.4449	1.0069	176.80	39.74
0.5241	1.0096	206.48	39.40
0.8452	1.0139	304.79	36.06
1.0078	1.0167	357.81	35.51
1.2072	1.0209	404.78	33.53
1.3982	1.0241	436.31	31.21
1.7254	1.0290	467.85	27.12

TABLE 7

DENSITIES AND EQUIVALENT CONDUCTANCES OF SODIUM DECANOATE AT 35°C
(CH₃(CH₂)₈COONa)

Concentration (mole/litre)	Density (g/ml)	Specific Conductance (mhos/cm X10 ⁴)	Equivalent Conductance (mhos)
0.0101	0.9943	8.4909	83.11
0.0324	0.9957	25.356	78.07
0.0521	0.9959	38.989	74.79
0.0734	0.9970	54.138	73.79
0.1093	0.9974	74.400	68.04
0.1368	0.9976	86.925	63.56
0.1827	0.9996	106.22	58.14
0.2290	0.9999	125.41	54.76
0.3044	1.0018	159.75	52.48
0.4432	1.0031	222.42	50.18
0.5221	1.0057	260.82	49.96
0.8415	1.0095	382.48	45.45
1.0038	1.0127	449.06	44.76
1.2016	1.0162	507.39	42.23
1.3907	1.0186	547.69	39.38
1.7158	1.0253	589.95	36.38

TABLE 8

DENSITIES AND EQUIVALENT CONDUCTANCES OF SODIUM LAURATE AT 25°C
(CH₃(CH₂)₁₀COONa)

Concentration (mole/litre)	Density (g/ml)	Specific Conductance (mhos/cm X10 ⁴)	Equivalent Conductance (mhos)
0.00450	0.99798	3.0422	67.56
0.00904	0.99847	5.9411	65.72
0.01398	0.99865	9.0655	64.85
0.01753	0.99898	11.150	63.61
0.0275	0.99903	16.664	60.67
0.0436	0.99910	21.544	49.46
0.0601	0.99962	25.875	43.08
0.0773	0.99979	30.877	39.96
0.1067	0.99984	39.540	37.06
0.1379	1.0007	48.847	35.42
0.1632	1.0010	55.373	33.93
0.2136	1.0019	73.928	34.61
0.2717	1.0027	94.152	34.66
0.3217	1.0035	111.42	34.64
0.3853	1.0043	132.70	34.44

TABLE 9

DENSITIES AND EQUIVALENT CONDUCTANCES OF SODIUM LAURATE AT 35°C
(CH₃(CH₂)₁₀COONa)

Concentration (mole/litre)	Density (g/ml)	Specific Conductance (mhos/cm X10 ⁴)	Equivalent Conductance (mhos)
0.00449	0.99516	3.7621	83.81
0.00901	0.99529	7.3775	81.60
0.01393	0.99556	11.143	79.93
0.01748	0.99587	13.776	78.81
0.0274	0.99596	20.428	74.58
0.0434	0.99620	26.550	61.13
0.0599	0.99638	32.246	53.86
0.0770	0.99640	38.603	50.15
0.1063	0.99646	49.739	46.78
0.1375	0.99752	62.057	45.15
0.1627	0.99783	70.122	43.10
0.2128	0.99846	93.662	44.01
0.2707	0.99923	119.47	44.13
0.3205	0.99992	142.71	44.53
0.3840	1.0009	168.93	43.99

TABLE 10

DENSITIES AND EQUIVALENT CONDUCTANCES OF SODIUM MYRISTATE AT 25°C
($\text{CH}_3(\text{CH}_2)_{12}\text{COONa}$)

Concentration (mole/litre)	Density (g/ml)	Specific Conductance (mhos/cm $\times 10^4$)	Equivalent Conductance (mhos)
0.00222	0.99781	1.5063	67.73
0.00311	0.99812	2.0942	67.30
0.00469	0.99825	3.1496	67.18
0.00536	0.99832	3.5821	66.83
0.00635	0.99849	4.1999	66.14
0.00717	0.99860	4.7266	65.97
0.00800	0.99873	5.1043	63.81
0.00890	0.99890	5.4865	61.68
0.01041	0.99896	5.7902	55.62
0.01175	0.99901	6.2515	53.20

TABLE II

DENSITIES AND EQUIVALENT CONDUCTANCES OF SODIUM MYRISTATE AT 35°C
(CH₃(CH₂)₁₂COONa)

Concentration (mole/litre)	Density (g/ml)	Specific Conductance (mhos/cm X10 ⁴)	Equivalent Conductance (mhos)
0.00221	0.99510	1.8609	83.90
0.00310	0.99519	2.5821	83.22
0.00467	0.99530	3.8712	82.81
0.00535	0.99545	4.3779	81.83
0.00632	0.99547	5.1337	81.23
0.00714	0.99550	5.6903	79.70
0.00797	0.99567	5.9739	74.92
0.00887	0.99571	6.3682	71.82
0.01038	0.99580	6.8106	65.61
0.01171	0.99584	7.3483	62.75

TABLE 12

VISCOSITIES AND FLUIDITIES OF AQUEOUS SOLUTIONS OF SODIUM DECANOATE
 $(\text{CH}_3(\text{CH}_2)_8\text{COONa})$ AS A FUNCTION OF CONCENTRATION

Concentration	Temperature 25°C		Temperature 35°C	
	Relative Viscosity	Fluidity (Rhes)	Relative Viscosity	Fluidity (Rhes)
0.1996	0.9979	112.1	0.9958	138.9
0.6336	1.0180	109.9	1.0150	136.4
1.0173	1.0379	107.8	1.0332	133.9
1.4289	1.0513	106.4	1.0485	132.0
2.1304	1.0896	102.7	1.0869	127.3
2.6620	1.1333	98.73	1.1243	123.1
3.5506	1.1943	93.70	1.1815	117.1
4.4526	1.2725	87.95	1.2698	108.9
5.9032	1.4227	78.65	1.4126	97.98
8.583	1.7316	64.63	1.7249	80.24
10.084	2.0665	54.15	1.9327	71.61
16.193	3.1660	35.35	3.1057	44.56
19.254	4.1974	26.66	4.0095	34.52
22.969	6.562	17.05	6.5488	21.13
26.522	10.267	10.90	9.909	13.97
32.557	23.878	4.69	22.992	6.02

TABLE 13

VISCOSITIES AND FLUIDITIES OF AQUEOUS SOLUTIONS OF SODIUM LAURATE
 $(\text{CH}_3(\text{CH}_2)_{10}\text{COONa})$ AS A FUNCTION OF CONCENTRATION

Concentration	Temperature 25°C		Temperature 35°C	
	Relative Viscosity	Fluidity (Rhes)	Relative Viscosity	Fluidity (Rhes)
0.2013	0.9984	112.1	0.9958	139.0
0.3112	1.0059	111.2	1.0019	138.1
0.3903	1.0102	110.8	1.0066	137.5
0.6113	1.0216	109.5	1.0177	136.0
0.9692	1.0477	106.8	1.0451	132.4
1.3356	1.0804	103.6	1.0740	128.9
1.7173	1.1097	100.8	1.1026	125.5
2.3721	1.1713	95.54	1.1701	118.3
3.0632	1.2427	90.05	1.2364	111.9
3.6251	1.2867	86.97	1.2823	107.9
4.7383	1.4241	78.68	1.4158	97.75
6.0229	1.5956	70.14	1.5636	88.52
7.1251	1.7804	62.86	1.7005	81.39



TABLE 14

VISCOSITIES AND FLUIDITIES OF AQUEOUS SOLUTIONS OF SODIUM MYRISTATE
($\text{CH}_3(\text{CH}_2)_{12}\text{COONa}$) AS A FUNCTION OF CONCENTRATION

Concentration	Temperature 25°C		Temperature 35°C	
Weight Percentage	Relative Viscosity	Fluidity (rhes)	Relative Viscosity	Fluidity (rhes)
0.078	0.99906	112.01	0.99677	138.85
0.118	0.99941	111.96	0.99783	138.70
0.135	0.99978	111.94	0.99822	138.65
0.159	1.0001	111.90	0.99915	138.52
0.180	1.0011	111.79	1.0003	138.37
0.201	1.0074	111.07	1.0029	137.99
0.223	1.0143	110.33	1.0063	137.54

TABLE 15

SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF SODIUM OCTANOATE

(CH₃(CH₂)₆COONa) AT 25°C and 50°C.

Temperature 25°C		Temperature 50°C	
Concentration (mole/litre)	Surface Tension (dyne/cm)	Concentration (mole/litre)	Surface Tension (dyne/cm)
0.0521	65.02	0.0265	59.78
-	-	0.0705	50.19
0.1421	52.09	0.1380	45.60
-	-	0.2513	39.82
0.2395	45.42	0.3675	37.75
0.3181	41.05	0.4916	36.63
0.4586	39.19	0.5114	36.46
0.6095	39.01	0.7425	36.24
0.7997	38.26	1.0980	35.67
0.9352	38.11	1.5778	33.70
1.3402	37.03	2.0333	31.64
1.6107	36.12	2.3714	29.88
1.7701	35.26	-	-
1.8342	35.09	-	-
2.3015	32.94	-	-
2.4781	31.87	-	-
2.5399	31.71	-	-

TABLE 16

SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF SODIUM DECANOATE

($\text{CH}_3(\text{CH}_2)_8\text{COONa}$) AT 25°C and 50°C

Temperature 25°C		Temperature 50°C	
Concentration (mole/litre)	Surface Tension (dynes/cm)	Concentration (mole/litre)	Surface Tension (dyne/cm)
0.0186	61.64	0.0138	54.57
0.0407	51.18	0.0216	50.01
0.0746	42.30	0.0426	43.57
0.0989	38.36	0.0559	41.55
0.1631	37.49	0.0791	38.38
0.2253	36.90	0.1274	35.92
0.2867	36.60	0.1868	35.89
0.6933	34.46	0.2511	35.84
0.8838	33.58	0.3095	35.61
1.0703	32.47	0.4200	35.11
1.3317	31.86	0.6870	33.84
-	-	1.0459	32.23
-	-	1.5586	29.72

TABLE 17

SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF SODIUM LAURATE

($\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$) AT 25°C AND 50°C .

Temperature 25°C		Temperature 50°C	
Concentration (mole/litre)	Surface Tension (dyne/cm)	Concentration (mole/litre)	Surface Tension (dynes/cm)
0.0042	52.68	0.0021	50.41
0.0076	42.70	0.0037	44.25
0.0112	36.25	0.0052	40.75
0.0165	29.07	0.0114	33.20
0.0206	26.41	0.0188	28.10
0.0236	24.03	0.0246	25.10
0.0251	24.43	0.0291	25.92
0.0288	26.78	0.0339	28.14
0.0349	29.76	0.0525	30.67
0.0394	30.22	0.0740	32.01
0.0669	32.80	0.1075	32.34
0.0913	33.52	0.1816	32.80
0.2206	34.06	0.2680	31.72
0.3326	32.67	0.4358	31.54
-	-	0.6831	30.61

TABLE 18

SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF SODIUM MYRISTATE

($\text{CH}_3(\text{CH}_2)_{12}\text{COONa}$) AT 25°C AND 50°C .

Temperature 25°C		Temperature 50°C	
Concentration (mole/litre)	Surface Tension (dyne/cm)	Concentration (mole/litre)	Surface Tension (dyne/cm)
0.00111	50.54	0.00112	41.14
0.00228	46.47	0.00167	32.90
0.00297	44.46	0.00226	29.33
0.00416	40.01	0.00315	26.43
0.00538	38.06	0.00412	22.39
0.00635	35.01	0.00532	21.76
0.00757	34.54	0.00584	20.69
0.00858	36.40	0.00749	20.04
0.00998	38.46	0.00921	21.40
-	-	0.01342	24.17
-	-	0.0174	25.36
-	-	0.0303	27.44
-	-	0.0434	28.53
-	-	0.0720	29.41
-	-	0.0994	28.84

DISCUSSION OF THE RESULTS

CHAPTER IV

The limiting Equivalent Conductances

The limiting equivalent conductance of sodium decanoate, sodium laurate and sodium myristate have been determined by the usual extrapolation techniques of Kohlrausch and Shedlovsky⁵⁷. In the Kohlrausch method plots of the equivalent conductances (Tables 1 - 3) corrected for the hydrolysis by the method of Bock and Campbell against the square root of concentrations in the very dilute region resulted in straight lines which on further extrapolation to zero concentration gave the limiting equivalent conductances of the corresponding salts. In Shedlovsky's method, Onsager's limiting conductance equation,

$$\Lambda = \Lambda_0 - (\alpha \Lambda_c + \beta) \sqrt{c} \quad 22$$

is rearranged so that Λ_c may be calculated directly from individual values of Λ , the difference between successive values of Λ_c is proportional to the difference in concentration. The value of Λ_0 thus obtained, designated as Λ_0' , is

$$\Lambda_0' = \frac{\Lambda + \alpha \sqrt{c}}{1 - \beta \sqrt{c}} = \Lambda_0 + Bc \quad 23$$

where B is a positive constant, characteristic of each electrolyte.

The plot of Λ_0' against the first power of concentration is a straight line which is then extrapolated to zero concentration to get a Λ_0 value.

In addition to these methods, Fuoss' method of obtaining the limiting equivalent conductances, as discussed in the general introduction, using equation 15, has been tried for these salts.

The plots of equivalent conductance versus square root of concentration (Kohlrausch) in the dilute regions are shown in Figures 7, 8, 9 for sodium decanoate, sodium laurate and sodium myristate at both 25°C and 35°C respectively and the limiting equivalent conductances obtained by the three different methods for all the salts, are tabulated in Table 19.

Higher values are obtained by the Shedlovsky and Fuoss methods for all the salts at both 25°C and 35°C as compared to the Kohlrausch values. Considering the facts that Shedlovsky method is empirical, that one has to make use of Shedlovsky's value of Λ_0 in the first place in the Fuoss method, and that the deviations from least square analysis by the Kohlrausch method are small, in subsequent calculations Kohlrausch values are used for the limiting equivalent conductances of the salts at 25°C and 35°C.

Since there are no reliable data available at 35°C, the limiting equivalent conductances of sodium formate, sodium acetate, sodium propionate and sodium butyrate have also been determined. The limiting equivalent conductances of fatty acid anions from formate to myristate at both 25°C and 35°C are summarized in Table 20 by subtracting the limiting equivalent conductances of sodium ion⁶³ at 25°C and 35°C from the respective limiting equivalent conductance of the salts.

FIGURE 7. Equivalent Conductance Vs square root of Concentration
at 25°C and 35°C of Sodium decanoate by Kohlrausch method.

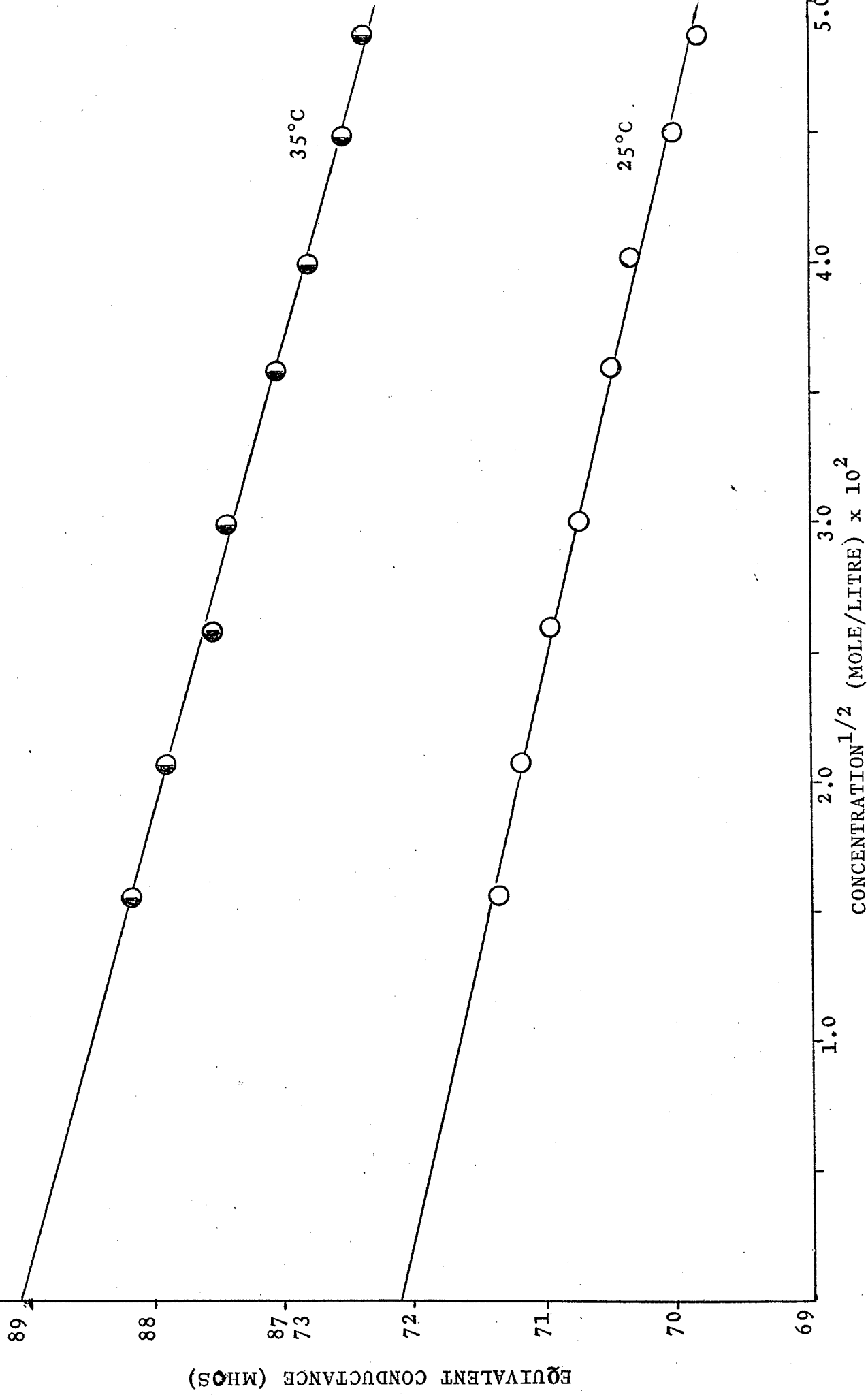


FIGURE 7

FIGURE 8. Equivalent Conductance Vs Square root of Concentration
at 25°C and 35°C of Sodium Laurate by Kohlrausch method.

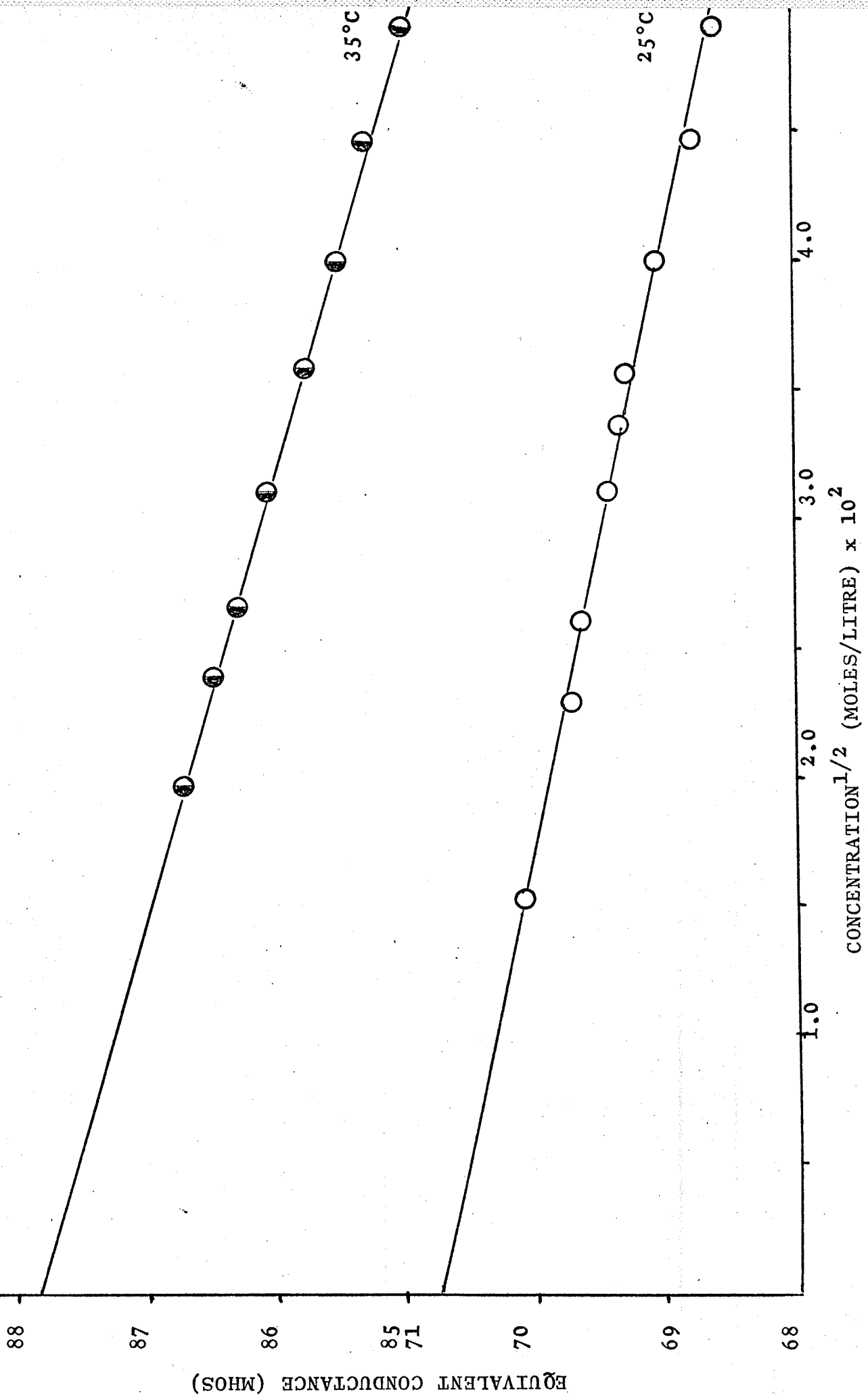


FIGURE 8

FIGURE 9. Equivalent Conductance Vs Square root of Concentration
at 25°C and 35°C of Sodium Myristate by Kohlrausch method.

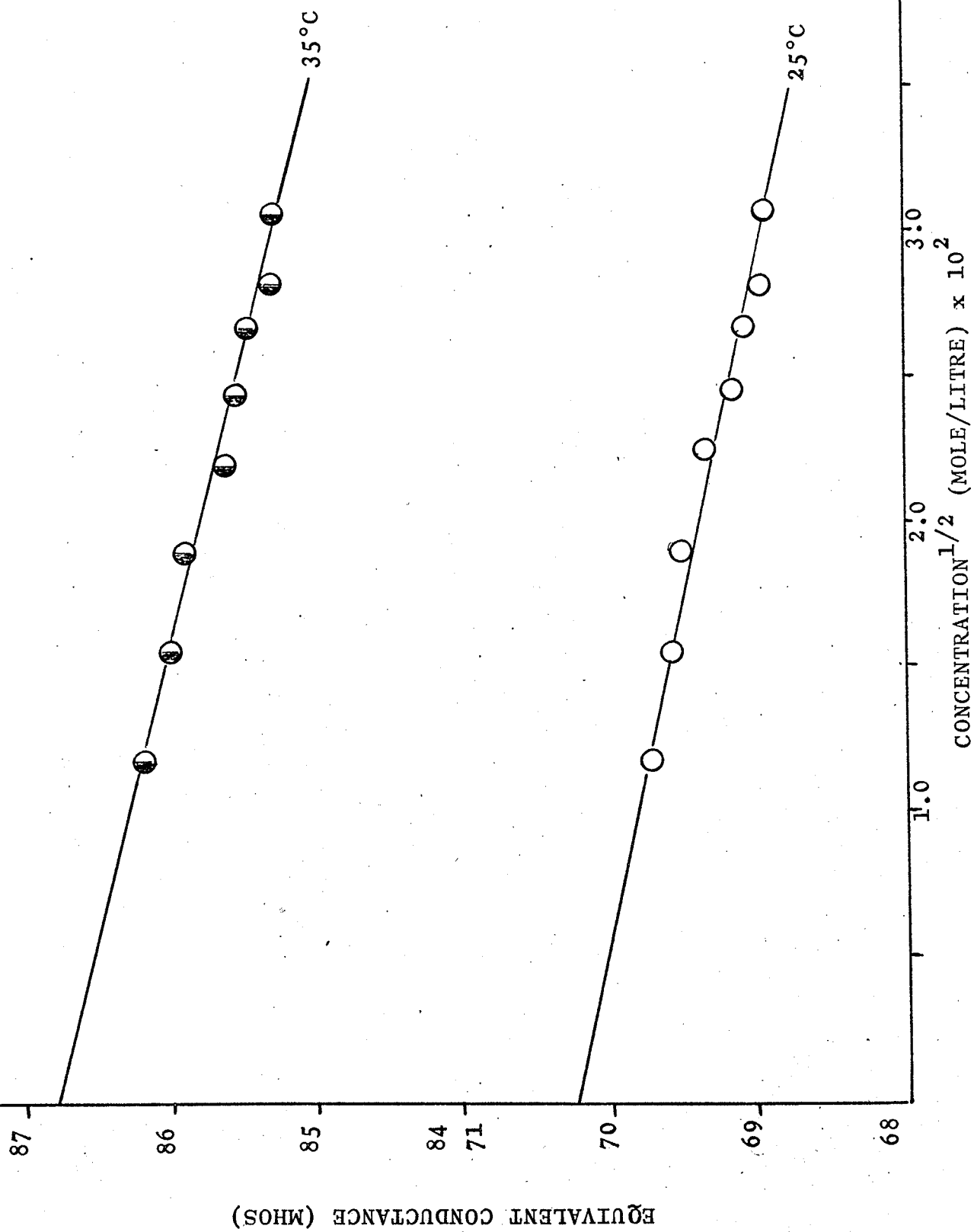


FIGURE 9

TABLE 19

LIMITING EQUIVALENT CONDUCTANCES OF SODIUM SALTS OF FATTY ACIDS
AT 25°C AND 35°C

Salt	Temperature °C	Kohlrausch	Shedlovsky	Fuoss	Reference
Hexanoate	25	77.47	77.84	-	(58)
Hexanoate	35	96.23	96.71	-	(58)
Octanoate	25	73.18	73.30	73.34	(59)
Octanoate	35	90.63	99.90	90.92	(59)
Decanoate	25	72.11	72.54	72.62	This work
Decanoate	35	89.10	89.70	89.78	"
Laurate	25	70.76	71.22	71.37	"
Laurate	35	87.86	88.39	88.50	"
Myristate	25	70.21	70.55	70.74	"
Myristate	35	86.77	87.18	87.32	"

TABLE 20

LIMITING EQUIVALENT CONDUCTANCES OF FATTY ACID ANIONS AT 25°C AND 35°C

Anions	Temperature		Reference
	25°C	35°C	
Formate (C1)	54.59 (60)	67.69	This work
Acetate (C2)	40.90 (61)	50.71	This work
Propionate (C3)	35.80 (62)	44.42	This work
Butyrate (C4)	32.60 (62)	40.29	This work
Hexanoate (C6)	27.37	34.69	(58)
Octanoate (C8)	23.08	29.09	(59)
Decanoate (C10)	22.01	27.56	This work
Laurate (C12)	20.66	26.32	This work
Myristate (C14)	20.11	25.23	This work
Na ⁺	50.10	61.54	(63)

C1, C2, C3, etc. indicates the number of carbon atoms in the chain.

A plot of the limiting equivalent conductances of fatty acid anions versus number of carbon atoms at both 25°C and 35°C is shown in Figure 10.

In the lower homolog of the series the difference of mobility between succeeding carbon atoms is fairly high while from octanoate ion onwards the mobility decreases with further increase of the chain length, the decrement becoming smaller and smaller, so that the curve tends to become horizontal. Similar results are obtained at 35°C. In other words, it appears that after decanoate (10-carbon atom in the chain) the mobility of the anion tends to become constant. Similar results, where the mobility difference between succeeding C-atoms of sodium alkyl sulphate is small, were obtained by Flockhart⁶⁴.

It should be possible to predict the value of λ_{C} from the dimensions, charges and other physical properties of the ions and the solvent molecules. In the state of infinite dilution the motion of an ion is limited solely by its interactions with the surrounding solvent molecules, there being no other ions within a finite distance. As Edward⁶⁵ points out, the carboxylate group binds an inner sheath of water molecules and causes break down in the outer zone. Ions of smaller size (in terms of crystallographic radius) like sodium, lithium, fluoride acquire, by solvent-ion interaction, a permanent hydration sheath and effectively become larger with lower mobility, whereas with carboxylate ions, since the hydrophobic part increases with increase in number of carbon atoms, the hydration effect is comparatively less. Nevertheless merely on account of their large size a mobility decrease can be expected.

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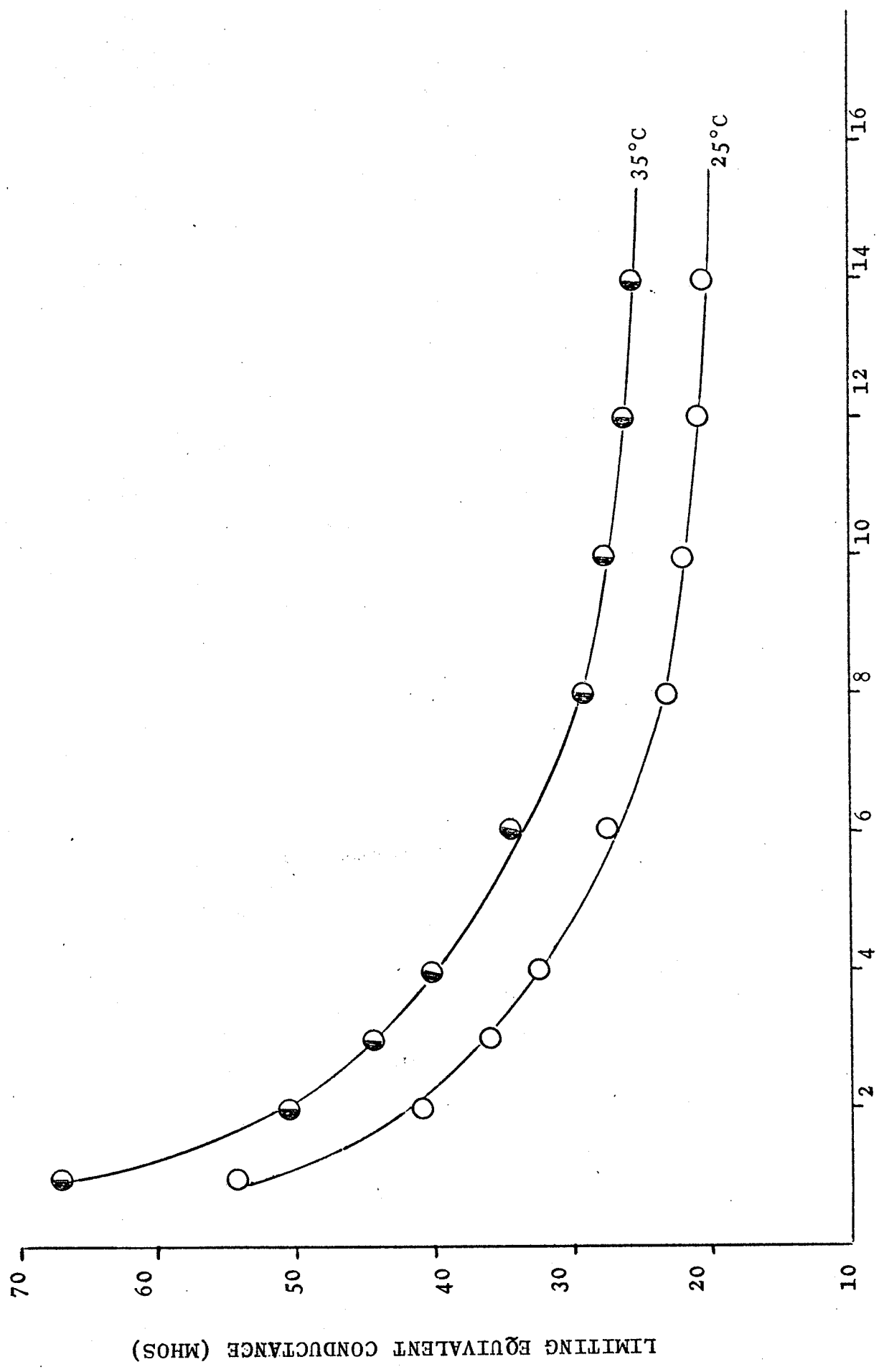
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NUMBER OF CARBON ATOMS IN THE CHAIN

FIGURE 10

LIMITING EQUIVALENT CONDUCTANCE (MHOS)

The increased mobility at 35°C is closely related to the increased fluidity of water at 35°C. The temperature effect on the limiting equivalent conductances of the sodium salts is almost the same for all the salts as shown in Table 21. For comparative purpose the fluidity ratio of water at 35°C and 25°C is also given in the same table.

Comparison of Experimental results with theoretical (Onsager's) values:

It is well known, that equivalent conductance of uni-univalent electrolytes follow Onsager's theoretical equation in the dilute region, (up to a concentration not greater than .001 N) well within the experimental error. In other words, the theoretical slope of Onsager's equation for uni-univalent electrolyte,

$$\Lambda = \Lambda_0 - \left[\frac{82.40}{(D_0 T)^{1/2} \eta_0} + \frac{8.2 \times 10^5}{(D_0 T)^{3/2}} \Lambda_0 \right] \sqrt{c} \quad 24$$

or

$$\Lambda = \Lambda_0 - [\beta + \alpha \Lambda_0] \sqrt{c} \quad 25$$

where Λ_0 is the limiting equivalent conductance of the electrolytes and α and β are constants for a given solvent at a particular temperature, agree well with the experimental slope. α and β values for water are 0.2289 and 60.19 at 25°C and 0.2333 and 75.21 at 35°C respectively⁶⁶. The experimental slopes of plots (conductance Vs square root of concentration) of sodium octanoate, sodium decanoate, sodium laurate, sodium myristate are compared with the theoretical slopes obtained using the above equation. The Experimental slopes in all cases except sodium octanoate are lower by about 40 - 45% than the theoretical slopes in the very

TABLE 21

RATIO OF LIMITING EQUIVALENT CONDUCTANCES AT 35°C AND 25°C OF
SODIUM SALTS OF FATTY ACIDS.

Conduc- tance Ratio	Sodium Salts					Fluidity Ratio $\frac{\phi_{35^\circ}}{\phi_{25^\circ}}$
	Hexanoate	Octanoate	Decanoate	Laurate	Myristate	
$\frac{\phi_{35^\circ}}{\phi_{25^\circ}}$	1.242	1.238	1.236	1.242	1.237	1.237

TABLE 22

COMPARISON OF SLOPES OF PLOTS OF EQUIVALENT CONDUCTANCES VS SQUARE ROOT OF CONCENTRATION OF SODIUM SALTS OF FATTY ACIDS AT 25°C AND 35°C.

Sodium Salts	Temperature 25°C		Temperature 35°C	
	Theoretical	Experimental	Theoretical	Experimental
Octanoate	-76.94	-66.10	-96.35	-82.05
Decanoate	-76.70	-45.02	-96.01	-54.85
Laurate	-76.39	-43.36	-95.71	-57.82
Myristate	-76.26	-41.79	-94.45	-48.72

dilute region. Attempt was made to use Robinson and Stokes equation⁶⁷,

$$\Lambda = \Lambda_0 - \frac{\alpha \Lambda_0 + \beta}{1 + Ka} \sqrt{c}$$

26

where $(1+Ka)$ term represents correction factor for deviation from Onsager's slope, to calculate the theoretical equivalent conductance values for all the four salts in the dilute region. A reasonable agreement was found between the experimental and theoretical values, with a large $\overset{\circ}{A}$ value (distance of closest approach) in the case of sodium octanoate; whereas in the cases of sodium decanoate, sodium laurate, and sodium myristate, in spite of a large $\overset{\circ}{A}$ value, the agreement was very poor even in the dilute region. At first it was thought that hydrolysis of these salts in the dilute region, which would increase the conductance and hence decrease the slope, would account for this; but the hydrolysis effect has been taken into consideration and appropriate corrections have been applied to all the conductance values according to the method described by Bock and Campbell. In spite of these corrections the experimental conductivities are higher than the theoretical values, particularly in the cases of sodium decanoate, sodium laurate and sodium myristate and hence the slopes of the curves are smaller. A higher conductance value is possible if there are more conducting ions than simple uni-univalent sodium and fatty acid anion; in other words some sort of interaction takes place between the existing ions even in the dilute solution to form a more conducting ion or radical of greater mobility.

Kraus and coworkers^{21,22,23} have shown, from their detailed study

of conductance of alkyl trimethyl quaternary salts in dilute solutions that dimerisation of cations is responsible for observed deviation from the theory. Recently Mukerjee and Mysels^{24,25,26} in a series of papers, based on new experimental data, have established the fact that lauryl sulphate ion dimerises reversibly to a certain extent in dilute solution to form LS_2^- ion and hence the conductivity is enhanced. Similar effects for some other amphiphilic ions have also been observed by the same authors²⁷. They state that dimerisation seems to be a rather general phenomenon and this makes it possible to explain numerous hitherto unexplained observations with this type of salts.

In order to explain quantitatively the observed enhanced conductance of sodium lauryl sulphate the above authors have derived equations from Onsager's theory*,

$$\Lambda_{\text{observed}} = \Lambda' (1-2\alpha) + \Lambda'' 2\alpha \quad 27$$

where α = degree of dimerisation

$$\Lambda' = (\lambda_+^0 + \lambda_-^0) - \left[\frac{5.770 \times 10^5}{(DT)^{3/2}} (\lambda_+^0 + \lambda_-^0) + \frac{57.96}{(DT)^{1/2} \eta_0} \right] \sqrt{2c(1+\alpha)} \quad 28$$

and

$$\Lambda'' = (\lambda_+^0 + \lambda_-^0) - \left[\frac{1.970 \times 10^6}{(DT)^{3/2}} \frac{v^*}{1+\sqrt{v^*}} \times 2(\lambda_+^0 + \gamma \lambda_-^0) + \frac{86.94}{(DT)^{1/2} \eta_0} \right] \sqrt{2c(1+\alpha)} \quad 29$$

* For detailed discussion consult reference 24

where $\nu^* = \frac{2}{3} \left(\frac{\lambda_0^+ + \gamma \lambda_0^-}{2 \lambda_0^+ + \gamma \lambda_0^-} \right)$ 29a

Attempts were made to apply these equations to the present results, solving them by successive approximations. Although the correct values of K_d are not known, there seems to be, in general, a certain amount of agreement between the experimental and calculated conductance values based on the above equations. Hence a possible explanation of the enhanced conductance of these salts, particularly that of sodium decanoate, sodium laurate and sodium myristate at both temperatures in dilute solution is to be found in the reversible formation of dimers of the fatty acid anions. Since the percent deviation increases with concentration in each of the three salts, the concentration of dimers probably increases with increasing concentration in the dilute region. Thus both monomers and dimers



probably exist in a reversible equilibrium and the total conductivity is then the sum of conductances of monovalent Na^+ , fatty acid anion and dimerised fatty acid anions.

Critical Micelle Concentration (CMC)

As discussed in the general introduction, the critical micelle concentration, hereafter abbreviated as CMC, is obtained by determining the concentration at which normal behavior of any of the physical properties changes sharply on account of association or aggregation of ions.

In Figures 11, 12, 13 the plots of conductance versus the square root of concentration are given for the three salts at 25°C and 35°C respectively and it is seen that at concentrations 0.101 mole/litre, 0.025 mole/litre, 0.0069 mole/litre for 25°C and at 0.103 mole/litre, .0265 mole/litre, .00705 mole/litre for 35°C the straight line behavior deviates from its course for sodium decanoate, sodium laurate, sodium myristate respectively. For sodium octanoate*, the same type of plot (Λ vs \sqrt{c}) does not show any significant break. A better method of finding the CMC is the plot of specific conductance versus concentration; abrupt change occurs at the intersection of the two nearly straight lines and this concentration is taken as the CMC. This is what has been done in Figures 14,15,16,17 for sodium octanoate, sodium decanoate, sodium laurate and sodium myristate respectively at both temperatures and the values of the CMC's (mole/litre) are tabulated in Table 23.

TABLE 23

THE CRITICAL MICELLE CONCENTRATIONS OF SODIUM SALTS OF FATTY ACIDS FROM SPECIFIC CONDUCTANCE DATA AT 25°C AND 35°C

Temperature	* Sodium Octanoate	Sodium Decanoate	Sodium Laurate	Sodium Myristate
25°C	0.34	0.094	0.0245	0.0069
35°C	0.36	0.098	0.0250	0.00695

* I regret to inform that in the previous publication⁵⁹ it was wrongly reported that sodium octanoate did not form micelles. Specific conductance Vs concentration plot does show a change of slope at the above concentration.

FIGURE 11. Equivalent Conductance Vs Square root of Concentration
of Sodium Decanoate at 25°C and 35°C.

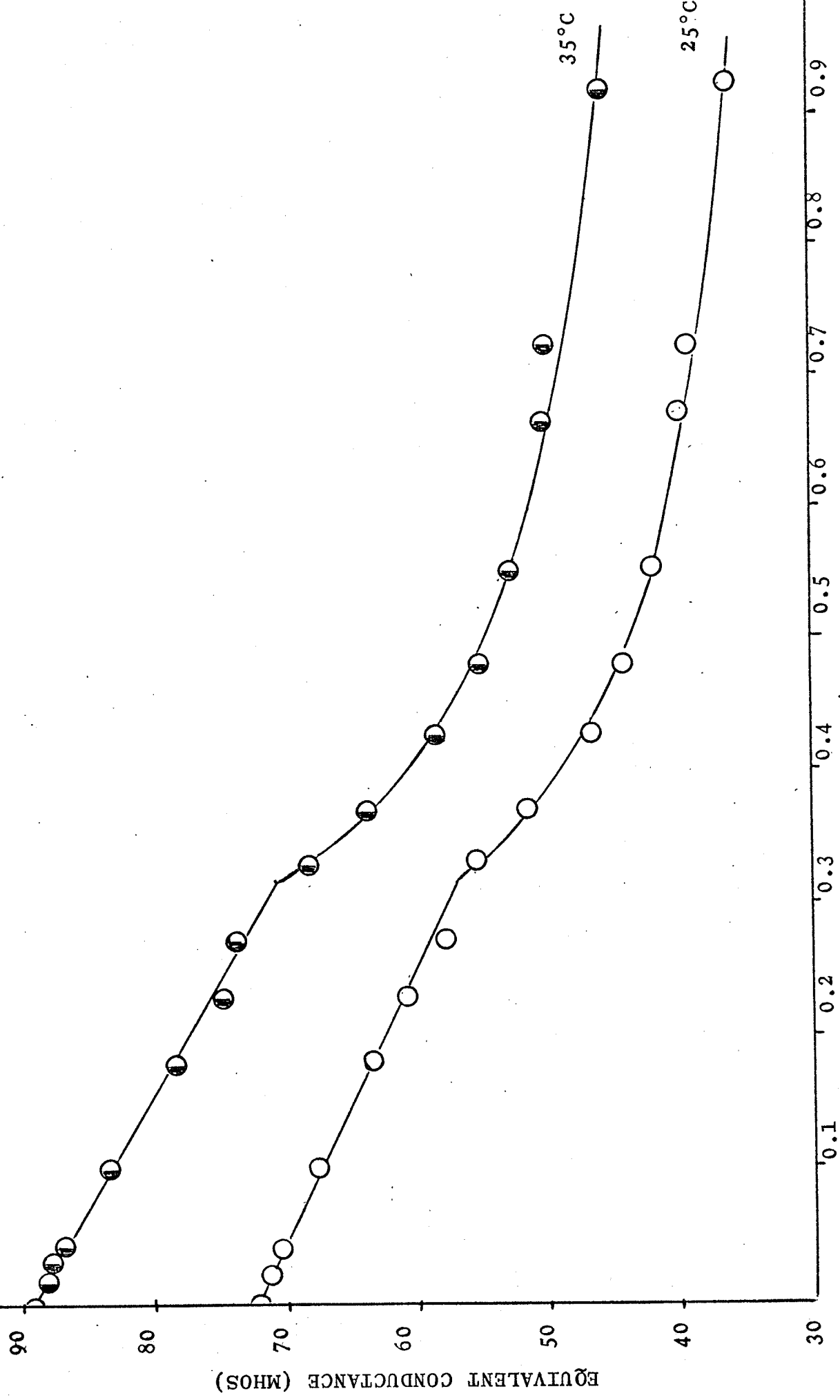


FIGURE 11
 CONCENTRATION^{1/2} (MOLE/LITRE)

FIGURE 12. Equivalent Conductance Vs Square root of Concentration of Sodium Laurate at 25°C and 35°C.

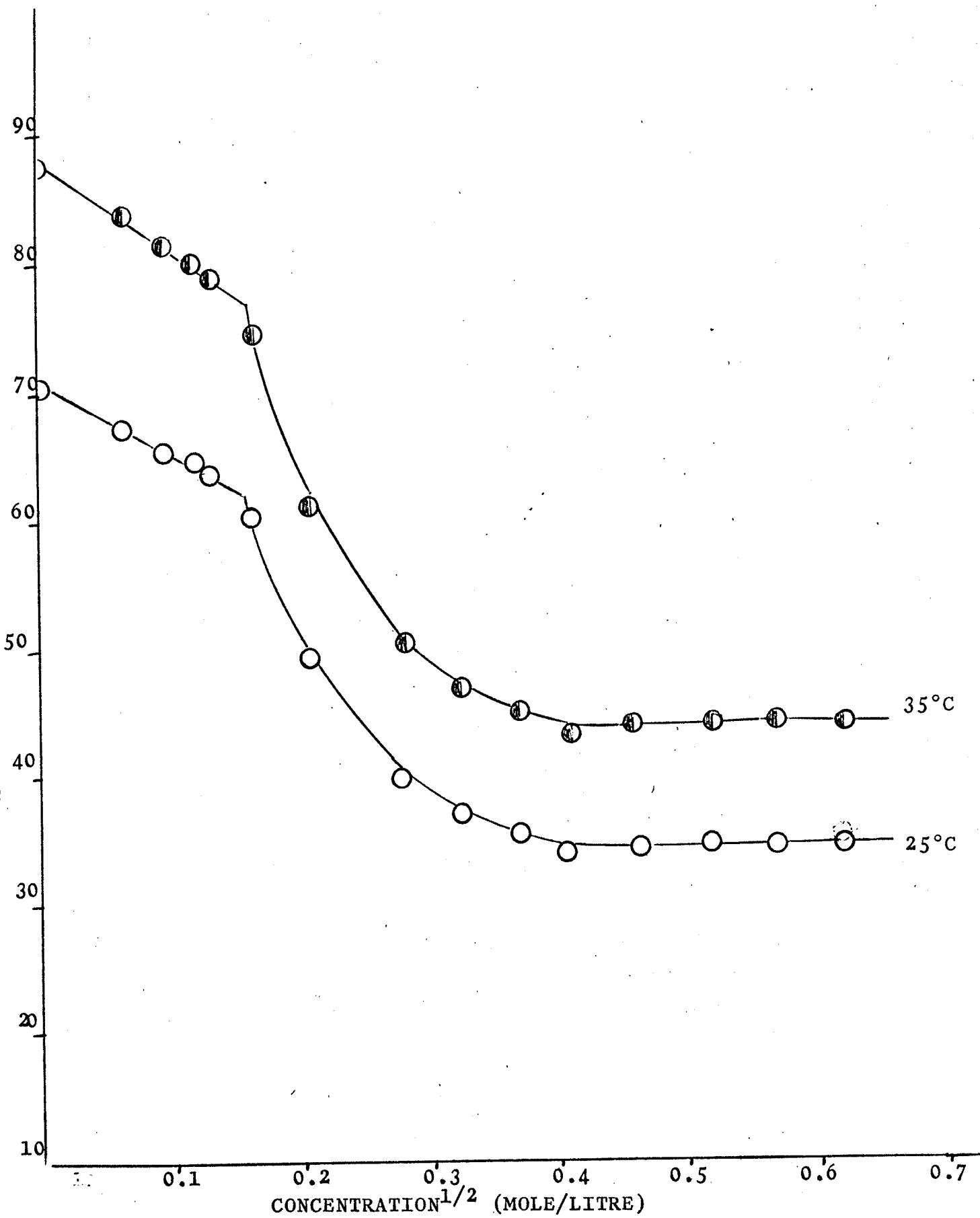


FIGURE 12

FIGURE 13. Equivalent Conductance Vs Square root of Concentration of Sodium Myristate at 25°C and 35°C.

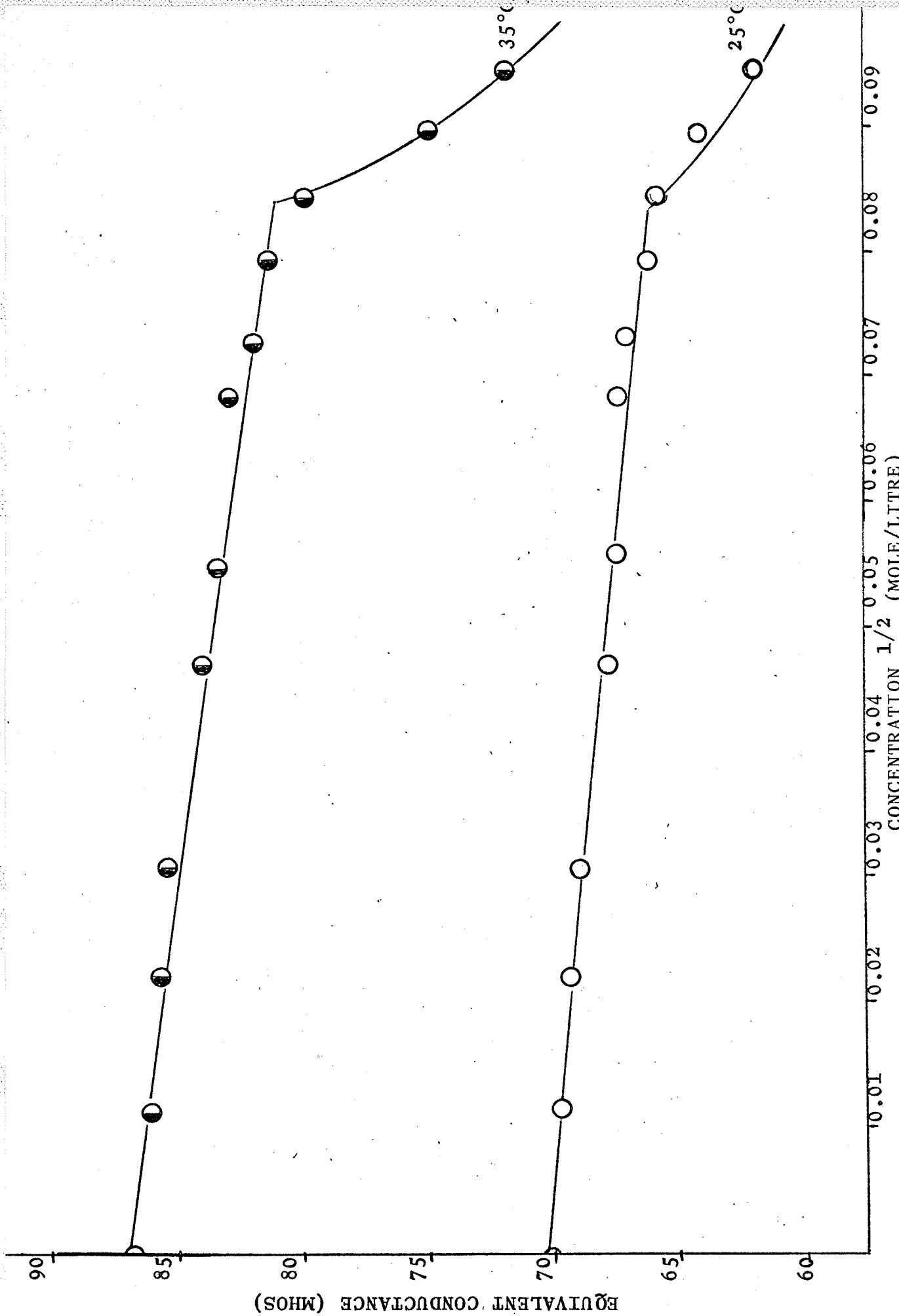


FIGURE 13

FIGURE 14. Specific Conductance Vs Concentration of Sodium Octanoate
at 25°C and 35°C.

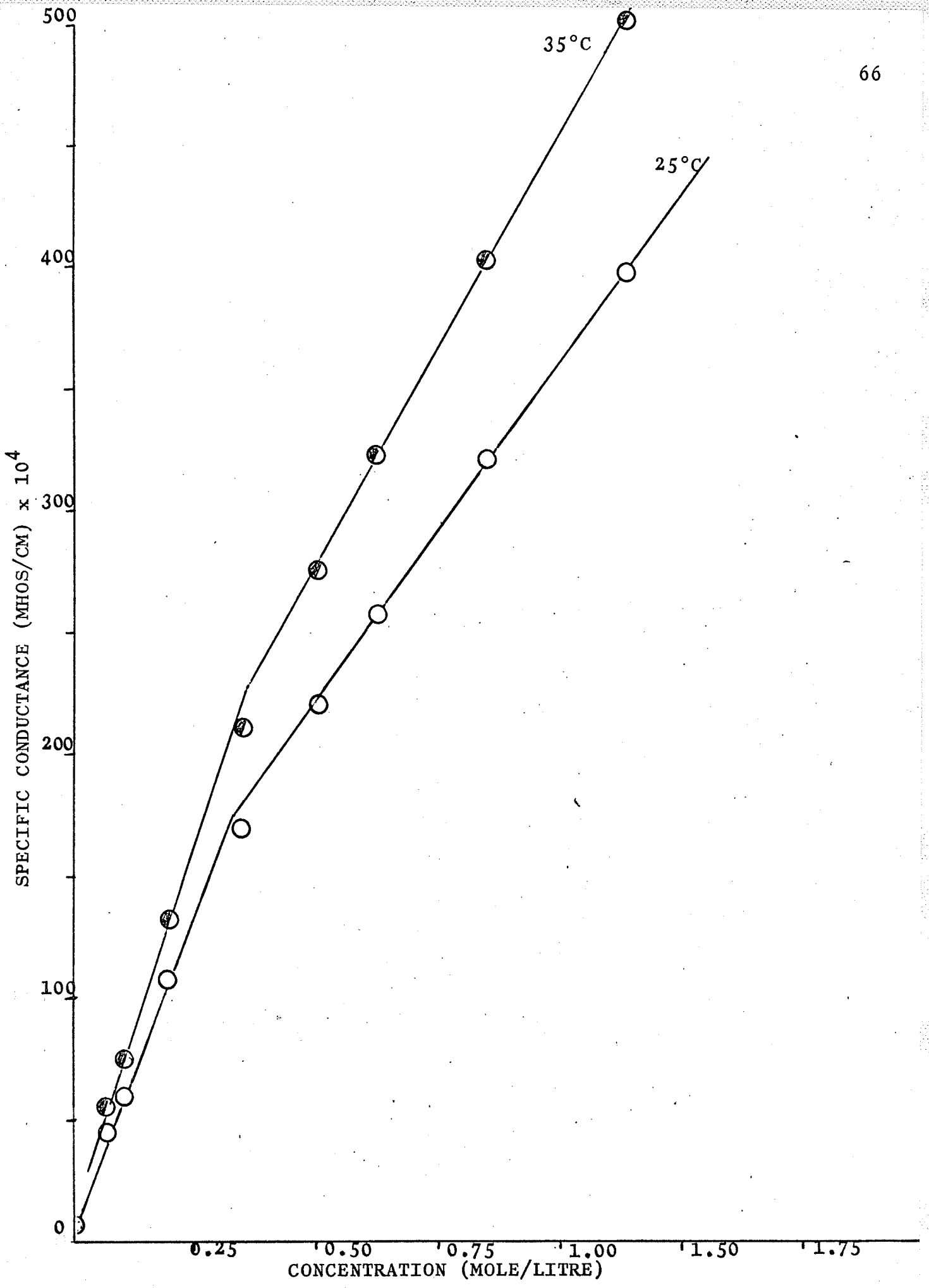


FIGURE 14

FIGURE 15. Specific Conductance Vs Concentration of Sodium Decanoate
at 25°C and 35°C.

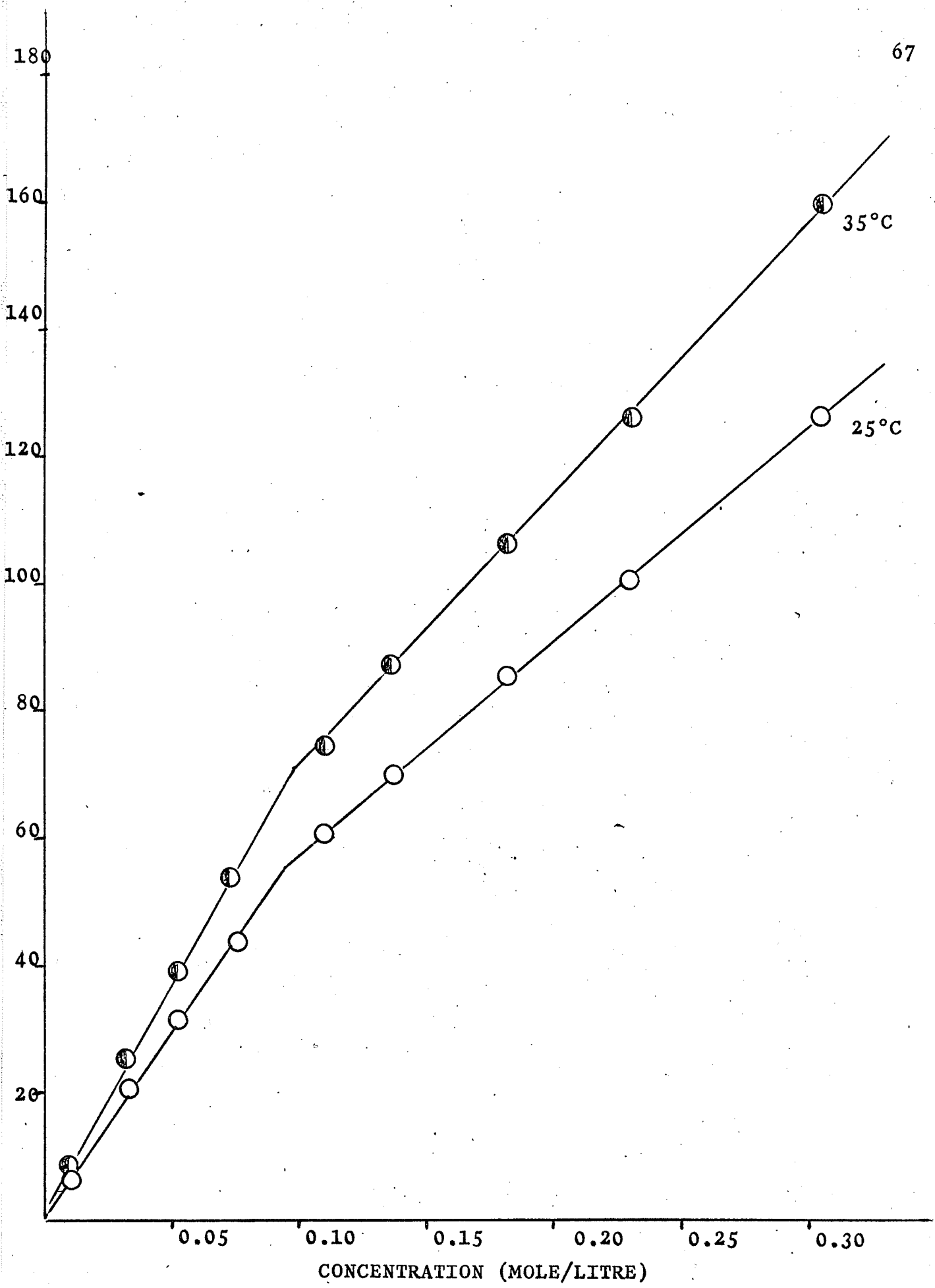


FIGURE 15

FIGURE 16. Specific Conductance Vs Concentration of Sodium Laurate
at 25°C and 35°C.

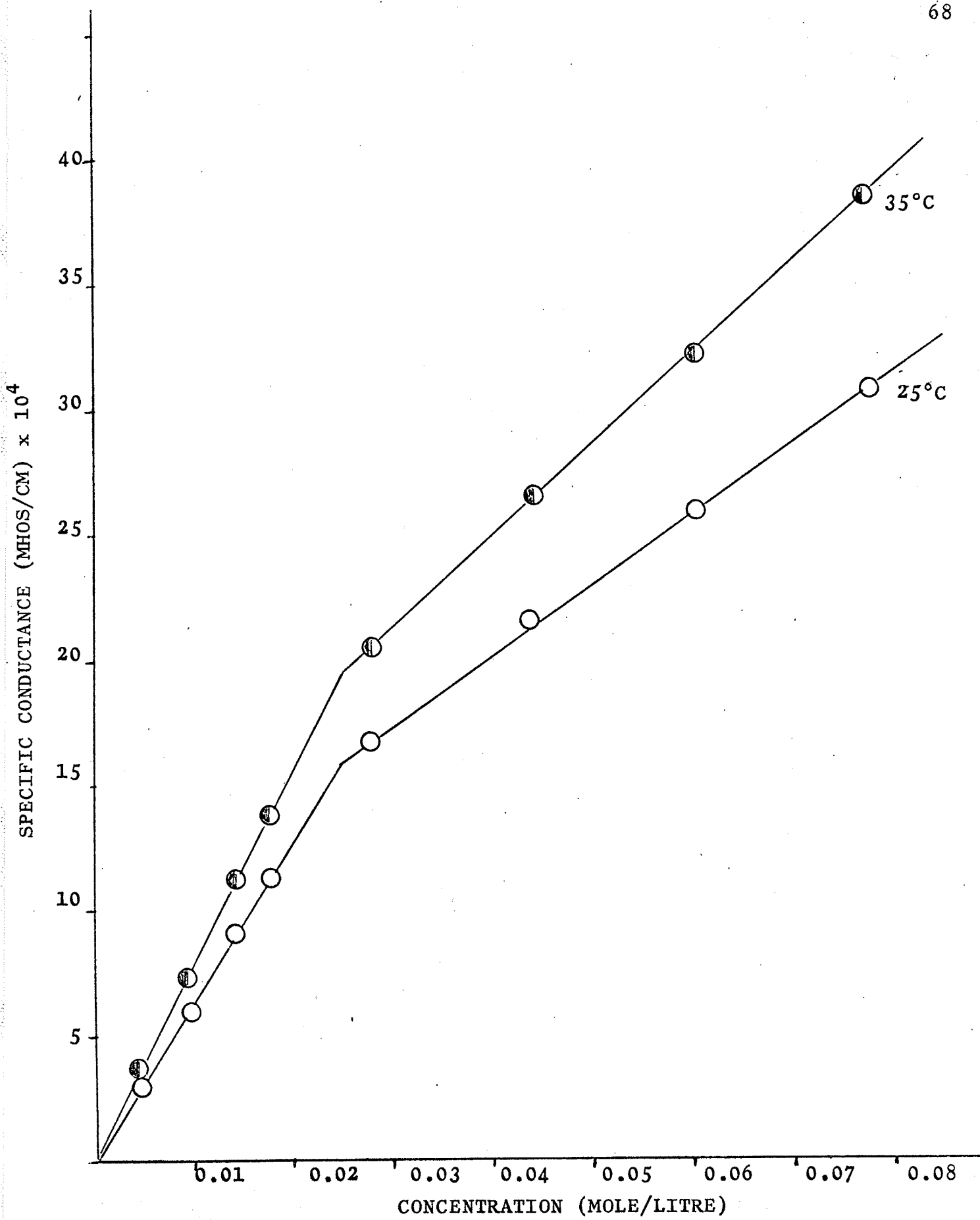


FIGURE 16

FIGURE 17. Specific Conductance Vs Concentration of Sodium Myristate
at 25°C and 35°C.

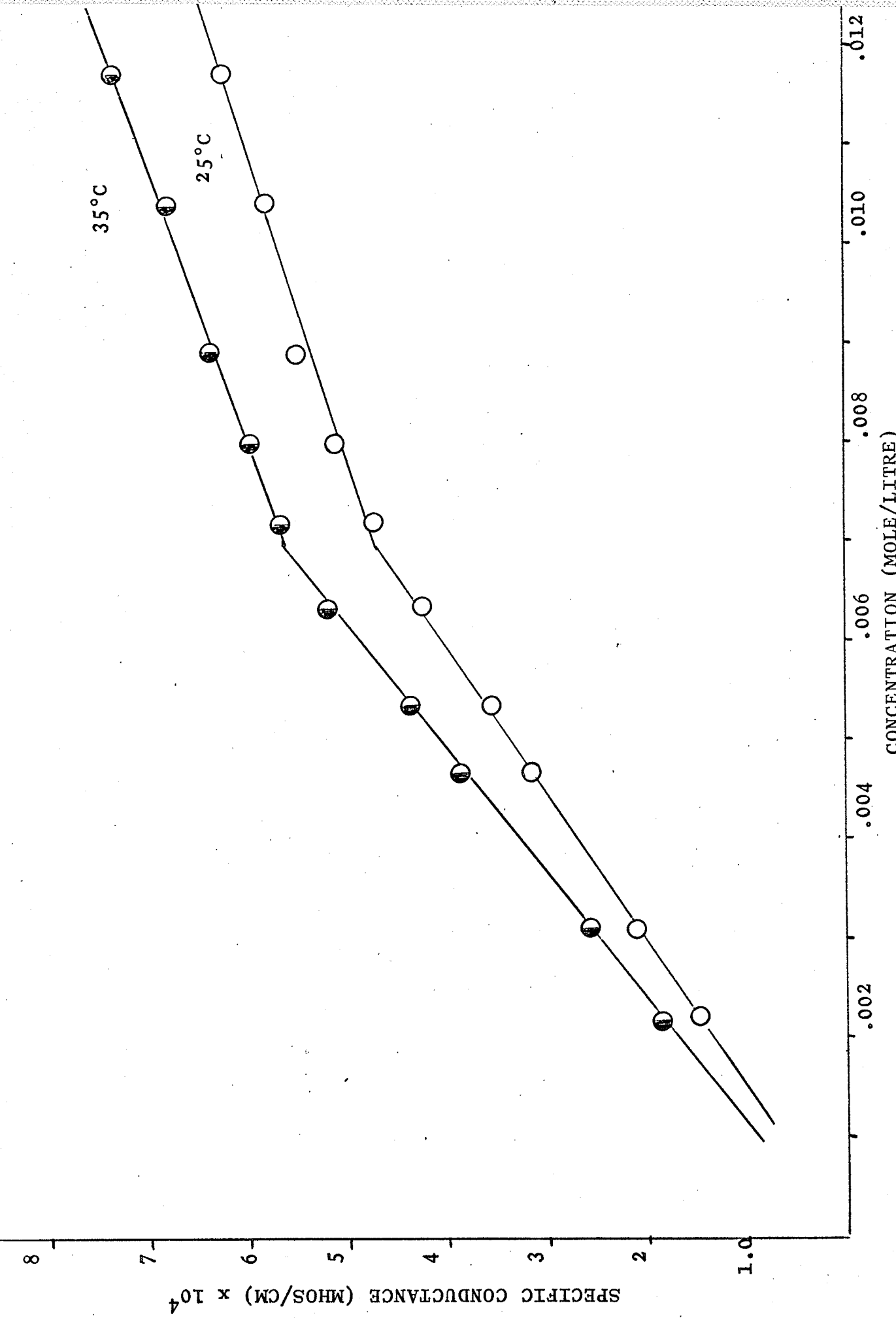


FIGURE 17

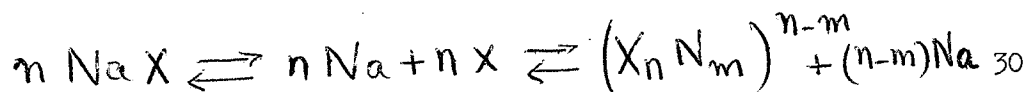
The value of the CMC at 25°C for sodium laurate agrees closely with that of 0.024 given by Huff, Brady and McBain⁶⁸.

Increase of temperature usually raises the CMC. As discussed in the introduction, micelle formation takes place when the energy released by the process of aggregation of monomeric units is sufficient enough to overcome the electrical repulsion between the ionic groups and balance the decrease in entropy of aggregation process. When the temperature is raised kinetic energy of ions is raised and hence the CMC is increased. The effect of temperature on the CMC is not very much as seen in Table 23; this means the energy involved in the process of micelleformation is not very great. The CMC decreases with increasing chain length, approximately four times from octanoate to decanoate, from decanoate to laurate and so on at both 25°C and 35°C. Similar results were obtained by Harkins⁶⁹ and Klevens⁷⁰ who found that the CMC increased by a factor of two for the removal of each - CH₂ - group from the chain.

Structure of Micelles

It is well known, that, when long chain anions aggregate together to form micelles the conductivity should increase. If n single anions aggregate together to form a homoionic micelle then the conductance of the micelle should increase to $n^{2/3}$ times that of the single ion. Generally, however, it is observed, as explained by Hartley, that because of the inclusion effect of gegenion in the micelle, the conductance actually decreases after the CMC is reached and hence the ratio of adsorbed gegenion to the number of long chain ions should be a

determining factor for the equivalent conductance of amphiphilic salts above the CMC. Evans⁷¹ has proposed an equation for the composition of the micelle from the conductance data. The equilibrium of a micelle composed of n long chain ions and m gegenions can be represented as



According to Evans the conductance of a micellar salt at concentration C above the CMC(C_0) can be considered as due to the conductance of single unassociated ions, micelles and free sodium ions - hence the specific conductance K at C can be written as

$$1000K = \epsilon_0 (\lambda_{\text{Na}} + \lambda_{\text{X}}) + \frac{C-C_0}{n} \lambda_{\text{mic}} + \frac{C-C_0}{n} (n-m) \lambda_{\text{Na}} \quad 31$$

where λ_{Na} , λ_{X} , λ_{mic} are the equivalent conductance of sodium, anion and micellar ions. At the critical micelle concentration C_0 the above reduces to

$$1000 \frac{K-K_0}{C-C_0} = \frac{1}{n} \lambda_{\text{mic}} + \frac{n-m}{n} \lambda_{\text{Na}} \quad 32$$

An approximate value of n can be calculated assuming a spherical micelle

$$n = \frac{4/3 \pi l^3 N d}{10^{24} M}$$

where l = length of the hydrocarbon portion attached to the carboxylate group, N is the Avagadro number and d = density. According to Stoke's

law the conductivity of a micelle containing n-long chain ions and of charge (n - m) is given by

$$\frac{\Lambda_{mic}}{\Lambda_x} = \frac{(n-m)^2}{n^{1/3}} \quad 33$$

$$\text{Now } \Lambda_{Na} + \Lambda_x = \frac{1000k_0}{C_0}$$

and this is the slope S_1 of the specific conductivity Vs concentration curve below the CMC and the left hand side of the above equation³² is the slope S_2 above the CMC. It follows then that

$$1000S_2 = \frac{(n-m)^2}{n^{4/3}} (1000S_1 - \Lambda_{Na}) + \frac{n-m}{n} \Lambda_{Na} \quad 34$$

where Λ_{Na} is the value at infinite dilution and m can be obtained by solving the quadratic equation taking only positive values.

Using the above equation, from the measured slopes of the specific conductance Vs concentration curves (Figures 14,15,16,17) of all four salts n and m values have been calculated at both temperatures and are summarized in Table 24.

Below the CMC the slopes (S_1) increases with increasing chain length and decreasing anion mobility and above the CMC the gegenion micelle interaction increases, as seen in the increased ratio of gegenion (m) to single ions (n) with the increasing chain length. In fact, m/n ratio, as seen in Figure 18, increases linearly with the chain length. In other words, the degree of binding of gegenions increases with the increase of the chain

length. The temperature effect, however, upon this ratio m/n over the narrow range between 25°C and 35°C is not very great.

In spite of the fact that one can arrive at the composition of a micelle by Evans procedure there are certain limitations involved in this method due to various assumptions. There are other methods available for determining the composition of micelles especially for non-hydrolysable salts among which light scattering method⁸⁸ is the one which has been widely used. Light scattering (Tyndal effect) depends primarily on an interference effect originating at the suspended particles. If the particles are small compared with the wave length of the incident light each acts as a point source and the scattering depends largely upon a microscopic heterogeneity of the solution due to fluctuations in concentration. The extent of these spontaneous fluctuations in concentration is a measure of the osmotic work necessary to produce them and it is found that a simple relation exists between the intensity of the scattered light and osmotic pressure of the solution both observed as a function of concentration.

Since its introduction by Debye, number of papers have appeared on this method and in the region of interest the results are represented⁸⁹ by the equation

$$\frac{H (C - C_0)}{\mathbb{T} - \mathbb{T}_0} = A + B (C - C_0)$$

where H is a constant involving geometric and refractive index of light scattering and \mathbb{T} is the turbidity of a solution at concentration

C. A and B are constants characteristic of the system. From a plot

$$\frac{H(C-C_0)}{T-T_0} \text{ vs Concentration}$$

the intercept A and the slope B can be obtained. Mysels and et al (89,90) have introduced correction factors for A and B and thus are able to calculate micellar weight, number of monomertic units in it and degree of association of number of amphiphilic salts.

The charge on the micelle has been determined by electrophoretic mobility method using tracers^{91,92,93} by tagging micelles with minute amount of a solubilised material such as dye. In aqueous solution of soap for example water insoluble dyes are taken up by micelles alone and the movement of the dyes and therefore of the micelles may be observed under the influence of electrical forces. The mobility is related to the charge, size and shape of the micelle and to the composition of the solution. From these measurements a reasonably accurate estimate of zeta potential and of the charge of the micelle can be obtained.

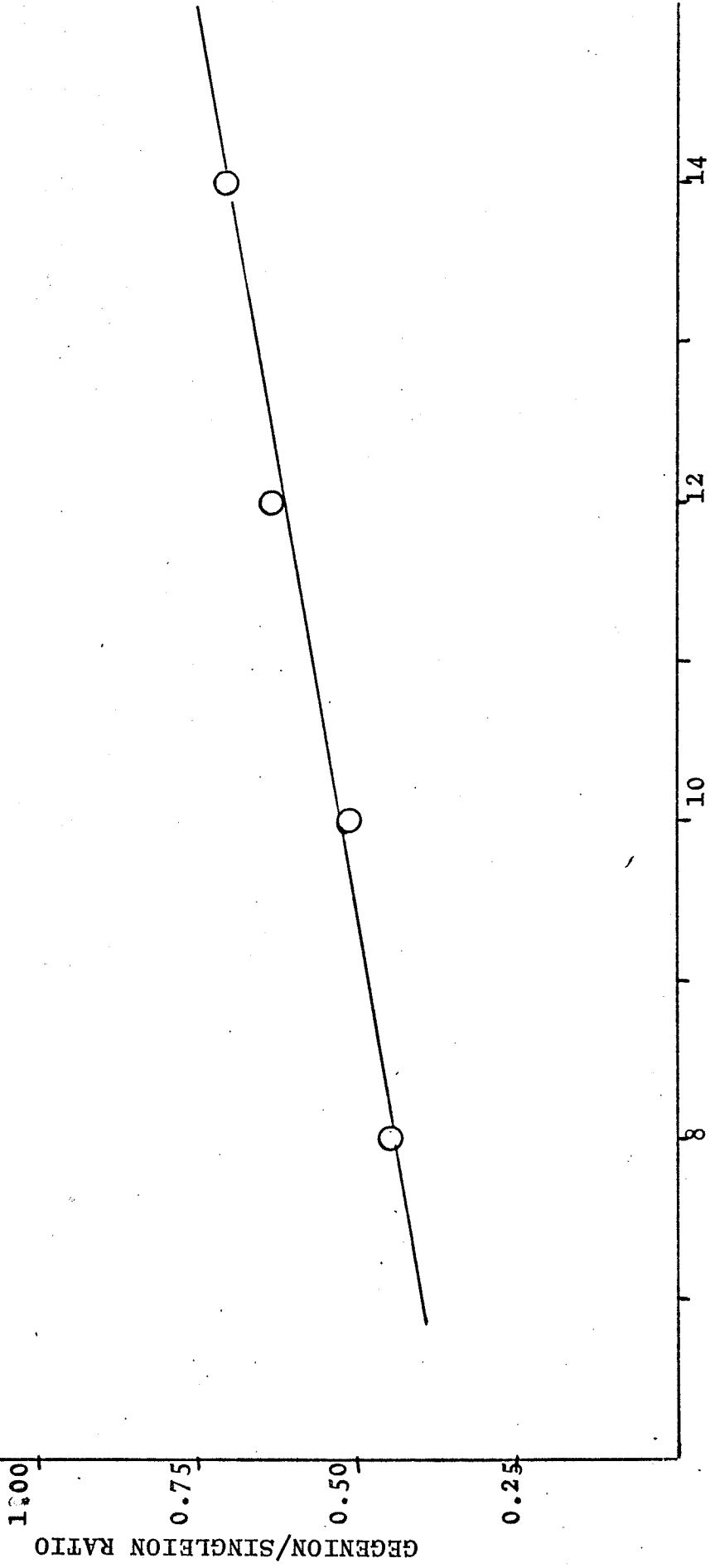
TABLE 24

DEGREE OF CATION BINDING IN FATTY ACID SALTS (SODIUM) SOLUTION FROM
SPECIFIC CONDUCTANCE DATA AT 25°C AND 35°C

Sodium Salts	Temperature °C	1000S ₁	1000S ₂	n	m	$\frac{m}{n}$	$-\frac{\Delta G^{\circ}}{RT}$
Octanoate (C ₈)	25	50.35	27.94	7	3	0.448	5.91
	35	61.74	35.25	7	3	0.456	5.86
Decanoate (C ₁₀)	25	57.88	33.78	14	7	0.516	8.71
	35	72.04	42.65	14	7	0.527	8.70
Laurate (C ₁₂)	25	64.72	28.40	23	15	0.629	11.91
	35	77.06	36.65	23	15	0.638	12.10
Myristate (C ₁₄)	25	68.03	31.90	35	24	0.702	14.79
	35	80.02	36.20	34	24	0.699	14.71

* C₈, C₁₀ etc. refers to number of carbon atoms in the chain.

FIGURE 18. Gegenion / Single ion ratio Vs number of Carbon Atoms at 25^oC.



NUMBER OF CARBON ATOMS IN THE CHAIN
FIGURE 18

GEGENION/SINGLEION RATIO

Recently, Phillips⁷² has developed an equation for the energy relationship associated with the process of micelle formation. For an anionic detergent in which a reversible equilibrium exists between single ions and micelles the standard free energy change per molecule associated with the micelle, in the absence of added electrolyte is given by

$$\Delta G^{\circ} = \frac{2.3 kT (\log_{10} 3 + 2 \log_{10} N)}{N} + \frac{2.3 kT (2N - p - 1)}{N} \log_{10} CMC$$

--- 35

here, the CMC is expressed in mole fraction so that ΔG° will refer to a mole fraction of unity (Standard State).

ΔG° values are obtained as shown in Table 24 for all the four salts at 25°C and 35°C. According to Davies⁷³ a value of 1.37 kt per molecule per -CH₂- group adsorbed at the oil - water interface is in agreement with partition data for the transfer of an additional -CH₂- group from aqueous to paraffin phase, which means that at the surface the hydrocarbon chains are completely immersed in the oil phase. The energy increment from octanoate to Myristate, as seen in Table 24, is about 8.88 kt at 25°C and 8.85 kt at 35°C and this is in close agreement with the calculated value of 8.22 kt (1.37 x 6). This means, for fatty

acid salts' micelles the liquid like character is obvious. In other words, the interior of the micelle consists of hydro-carbons of unordered, loose structure with the carboxyl polar groups at the surface of the micelle.

Viscosity and Fluidity of the Salts at 25°C and 35°C.

In Tables 12,13,14 the relative viscosities and fluidities of sodium decanoate, sodium laurate and sodium myristate at 25°C and at 35°C are summarized. Changes of slope of the fluidity versus concentration plots are observed at concentrations of 1.85 %, 0.575 %, 0.175 % at 25°C and at concentrations of 1.90 %, 0.59 %, 0.178 % at 35°C for sodium decanoate, sodium laurate and sodium myristate respectively. These changes apparently correspond to the same critical micelle concentrations as are observed in the specific conductance versus concentration plots. In the dilute region the changes of viscosity with concentration are not very great, but at higher concentrations, in general, a sudden increase of viscosity is observed in the cases of sodium decanoate and sodium laurate. In the case of sodium myristate the concentration was not high enough to notice a sudden change of viscosity. Solvation and aggregation of monomeric units are probably the most important reasons for such an increase. Solvation involves strong binding of solvent molecules, usually in a layer not more than one molecule thick, the particle plus the solvent layer thus acting as the kinetic unit in motion. An increase in volume concentration is thus clearly involved. At higher concentrations, aggregation increases rapidly and hence also the viscosity. As with macromolecules, the molecules are likely to show short range order which means, adjacent

molecules tend to lie parallel to each other. Intermolecular forces play a still greater part. The energy content and therefore the life time of a link will depend to a large extent on the number of large molecules which take part in it and this, in turn, increases with concentration with a consequent increase in viscosity.

Temperature effect:

Though not very much information can be obtained from the measurements of viscosity just at two temperatures (25°C and 35°C), it is possible to deduce an approximate general trend with rise in temperature. As long as the type of association remains the same, the viscosity - temperature relationship can be expressed as an exponential function⁷⁴

$$\eta = A e^{-E/RT}$$

where A, E constants ; Here E measuring the activation energy of flow, (i.e.) the energy necessary to destroy the mutual coherence between the molecules and thus giving the information concerning the type of association, is important. It is seen from Tables 12, 13, 14 that the relative viscosity at 25°C is higher than at 35°C for all the three salts as expected. Temperature change can affect viscosity through its effects on both degree of solvation and molecular shape. Increase of temperature usually involves decrease of solvation and decrease of monomeric units and hence causes a slight decrease in relative viscosity.

Assuming a linear relationship between 25°C and 35°C of both conductance and fluidity, temperature coefficients for these salts are evaluated at even concentrations as shown in Tables 25, 26, 27. The ratio

TABLE 25

ACTIVATION ENERGY OF CONDUCTANCE AND VISCOSITY (FLUIDITY) AND TEMPERATURE
 COEFFICIENTS OF CONDUCTANCE AND FLUIDITY BETWEEN
 25°C AND 35°C OF SODIUM DECANOATE

Concentration (mole/litre)	Activation energy of conductance (K-cal/mole)	Activation energy of fluidity (K-cal/mole)	Coefficient of		α/β
			Fluidity $\times 10^2$ (α)	Conductance (β) $\times 10^2$	
0.125	3.93	4.21	2.59	2.43	1.06
0.250	4.12	4.16	2.55	2.53	1.01
0.500	4.13	4.22	2.64	2.54	1.04
0.750	4.29	4.29	2.45	2.65	1.00
1.000	4.21	4.95	2.76	2.59	1.07
1.250	4.12	4.71	2.76	2.53	1.09
1.500	4.38	4.11	2.50	2.71	0.92

TABLE 26

ACTIVATION ENERGY OF CONDUCTANCE AND VISCOSITY (FLUIDITY) AND TEMPERATURE
 COEFFICIENTS OF CONDUCTANCE AND FLUIDITY BETWEEN
 25°C AND 35°C OF SODIUM LAURATE

Concentration (mole/litre)	Activation energy of conductance (K-cal/mole)	Activation energy of fluidity (K-cal/mole)	Co-efficient of		α/β
			Fluidity $(\alpha) \times 10^2$	Conductance $\beta \times 10^2$	
0.0125	3.93	3.96	2.42	2.40	1.01
0.0250	4.08	3.97	2.43	2.50	0.97
0.0500	3.92	4.02	2.46	2.38	1.04
0.100	4.51	4.05	2.48	2.79	0.89
0.150	4.48	4.08	2.50	2.77	0.90
0.200	4.47	5.27	3.38	2.76	1.22
0.250	4.47	3.94	2.41	2.77	0.87
0.300	4.48	4.03	2.47	2.76	0.90

TABLE 27

ACTIVATION ENERGY OF CONDUCTANCE AND VISCOSITY (FLUIDITY) AND TEMPERATURE
 COEFFICIENTS OF CONDUCTANCE AND FLUIDITY BETWEEN
 25°C AND 35°C OF SODIUM MYRISTATE.

Concentration (mole/litre)	Activation energy of conductance (K-cal/mole)	Activation energy of fluidity (K-cal/mole)	Coefficient of		α/β
			Fluidity $(\alpha) \times 10^2$	Conductance $\beta \times 10^2$	
0.002	3.91	3.94	2.40	2.39	1.00
0.003	3.88	3.92	2.39	2.36	1.01
0.004	3.83	3.93	2.39	2.33	1.03
0.005	3.83	3.91	2.39	2.33	1.03
0.006	3.83	3.91	2.38	2.33	1.02
0.007	3.45	3.90	2.38	2.09	1.14
0.008	3.18	3.90	2.42	1.90	1.27

of temperature coefficient of fluidity to the temperature coefficient of equivalent conductance is of interest and is included. The Arrhenius equation applied to the conductance figures and to the corresponding viscosities (fluidities) for the same concentrations and temperatures yields the figures of Tables 25,26,27 for the activation energies of conductance and viscosity respectively.

Since both conductance and viscosity are dynamic properties of a solution which involve the motion of molecular or ionic units relative to similar units in the solution these two properties are closely related. This is also exemplified by the appearance of an identical term for the potentials in the treatment of conductance and viscosity on the basis of inter-ionic theory. The striking similarity (almost equality) in the values of activation energies for conductance and fluidity and also the value of almost unity for the ratio of the temperature coefficients of fluidity and viscosity in all three salts (Table 29 - 31) suggest a strong fundamental resemblance of the two properties in the aqueous solution. In spite of their close relationship it should be obvious that, since conductance involves ionic migration through the bulk of the solution and viscosity involves a shearing motion of the whole of the solution, their mechanism must be quite different. The similarity of the temperature coefficients of fluidity and conductance support the idea of proportionality and this may justify the use by many workers of the relation (ionisation coefficients corrected for fluidity)

$$\alpha = \frac{\lambda_e}{\lambda_0} \frac{\phi_0}{\phi_e}$$

In any case, a close relationship is clearly demonstrated and it is

probable that any treatment of viscosity and conductance should contain an identical term for both fluidity and conductance over a complete range of concentration.

The Surface Tensions of the Aqueous Solutions of the Salts and the Application of Gibbs Adsorption Theorem:

In Tables 15,16,17,18 are summarized molarity and surface tension of sodium octanoate, sodium decanoate, sodium laurate and sodium myristate at 25°C and at 50°C. If concentration instead of activity is used and plots are made with surface tension (γ) against $\ln c$ the curves exhibit a break at the CMC. Thus the CMC's at 25°C and at 50°C are shown in Table 28 for the four salts. The CMC values obtained by different methods are also compared in the same table. The variation of surface tension with concentration of the four salts at 25°C and 50°C follow in general the same pattern. Surface tension is reduced considerably in the dilute region, leading to a minimum (except in the cases of sodium octanoate and decanoate), followed by a slow rise, but with further increase in concentration the surface tension is again gradually reduced. Because of Solubility limitations it was not possible to reach high concentrations at 25°C for sodium myristate. The minimum observed with the sodium laurate and sodium myristate is not unusual. These slight minima in the surface tension versus concentration curves appear to be characteristic of certain colloidal electrolytes, irrespective of the method by which surface tension is measured^{77,78}.

TABLE 28

COMPARISON OF THE CRITICAL MICELLE CONCENTRATIONS (MILLI MOLE/LITRE) OF
SODIUM SALTS OF FATTY ACIDS BY DIFFERENT METHODS AT 25°C, 35°C AND 50°C.

Sodium Salts	Temperature 25°C			Temperature 35°C		Temperature 50°C
	Conduc- tivity	Viscosity	Surface Tension	Conduc- tivity	Viscosity	Surface Tension
Octanoate	340.	-	351.0	360.0	-	385.0
Decanoate	94.0	96.0	95.5	98.0	97.5	106.0
Laurate	24.5	25.8	23.0	25.0	26.6	28.0
Myristate	6.9	6.97	6.9	6.95	7.06	7.1

** Values converted from percentage to milli mole/litre

From the stand point of the Gibbs adsorption theorem⁷⁹

$$\Gamma = -\frac{d\gamma}{d\mu} = -\frac{a}{RT} \cdot \frac{d\gamma}{da}$$

or approximately

$$\Gamma = -\frac{c}{RT} \cdot \frac{d\gamma}{dc}$$

where Γ is excess of surface of concentration of solute per unit area of interface, the nature of the curves (γ Vs concentration) of sodium laurate and sodium myristate at both temperatures predict that there will be a large amount of adsorption in the free surface in dilute solution, followed by no adsorption at the minimum where $\frac{d\gamma}{da} = 0$ which is then followed by negative adsorption for higher concentrations. At further higher concentration once again there is a large amount of adsorption of the solute. In other words, at the point where surface tension is greatly reduced there is no adsorption of the surface active material and at higher concentration where surface tension is slightly higher, the surface active material is negatively adsorbed. McBain and Wilson⁸⁰ made a suggestion that the minimum can be explained away as due to partly irreversible adsorption.

According to Adams⁸¹, more than one capillary active component, present or being produced, is responsible for greater irreversible adsorption and hence for the minimum. Murray⁸² has suggested that single ions are mainly responsible for the surface activity of colloidal electrolyte solutions. Traube⁸³ also holds the same view that the surface activity of a colloidal electrolyte is greatly influenced by noncolloidal particles. It was shown by Murray⁸² that with increasing solute concentrations the absolute concentration of single long

chain ions shows an initial rapid increase, followed by a decrease in concentration at higher concentrations due to micelle formation, and the concentration of counterions increases moderately slowly.

Thus it is seen that the difficulty with having such a minimum was that in the region of positive slope, a negative surface excess would be predicted by the Gibbs equation. But direct determination of Γ by the microtome method⁷⁶ gave positive values instead of negative ones by the Gibbs equation. This contradiction can be resolved by assuming that supposedly single solute consists in reality of two components, because of either an impurity or hydrolysis. Ordinary soap in bulk solution is correctly regarded as a single component even though it hydrolyses, but it can not be so regarded if the surface is considered since at certain concentrations acid soap is strongly concentrated in the surface leaving free alkali in the bulk. Similar minima are exhibited in the surface tension curves by non-hydrolysable detergents such as lauryl sulphonic acid, sodium alkyl sulphates or alkyl quaternary ammonium salts. Miles and Shedlovsky⁷⁵ have shown for certain alkyl sulphates that extensive purification of the detergent by repeated ether extraction tends to eliminate this minimum and deliberate addition of lauryl alcohol to some of these detergents greatly intensify the minimum. Similarly Brady⁹⁴ also found that on foaming sodium lauryl sulphate solution the residual solution gave no minimum, but that from the collapsed foam showed a pronounced minimum and the impurity was shown to consist of a trace of lauryl alcohol. Thus it was confirmed for non-hydrolysable salts that minimum in the surface tension curves was due to the presence of

relatively small amount of impurity. In the case of soaps, such as sodium laurate, sodium myristate, the hydrolysis products act as a third component as far as surface composition is concerned and thus have an effect of impurity in the system. This being selectively adsorbed causes the minimum. Adamson⁹⁵ has summarised these effects and stated that in the case of colloidal electrolyte solutions it seems once the micelle point is passed, impurities previously surface adsorbed may leave the surface because of being solubilised or held within the micelle structure, thus bringing about an increase in surface tension.

Thus the direct application of Gibbs adsorption equation leads to anomalous conclusions. This was considered by McBain and Mills⁸⁴ mainly due to the existence of a potential difference at the interface which was not taken into consideration when the Gibbs Theorem was derived. McBain and Wilson⁸⁰ have pointed out that the region where surface tension increases with increasing concentration, as in the case of sodium laurate and sodium myristate, apparently indicates that surface adsorption is negative while surface activity is almost at its maximum; this is mainly due to a decrease of electrical repulsions in the adsorbed layer resulting from the aggregation of anions to form micelles. Rapid aggregation to micelles results in decreasing surface active species in the bulk concentration of the surface active species. These arguments show that the Gibbs adsorption equation may be only a limiting law; it needs the inclusion of correction terms to allow for surface orientation and submerged double layer. Recently

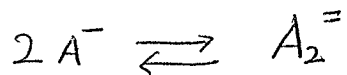
Alexander⁸⁵ has put forward an explanation which assumes that the Gibbs equation is thermodynamically rigorous and valid; he has shown that when $\frac{dr}{dc} = 0$, in colloidal electrolytes where single and micelle molecules or ions present, this does not necessarily mean that adsorption is absent. This may well mean that the concentration of single ions or molecules is independent of total concentration and this he found is in accordance with the experiments and with the results obtained by the application of the law of mass action to the single molecule micelle equilibrium, while still based on the Gibbs theorem. Therefore, in order to apply Gibbs theorem to obtain the total adsorption, one has to plot concentration (activity) of single ions or molecules, rather than stoichiometric concentration C, against surface tension.

GENERAL DISCUSSION

CHAPTER VI

With the experimental data available, it is appropriate to discuss three possible regions of concentrations (i.e.) one far below the CMC, the other that of the CMC and thirdly at high concentration of the salts, in order to see how the physical properties (conductance, viscosity and surface tension) of these colloidal solutions vary with the concentrations at different stages; this may give a clue to the internal structure of the solutions and a general picture of the association process.

At low concentrations the equivalent conductances of sodium salts of these fatty acids, particularly, sodium decanoate, sodium laurate and sodium myristate at both 25°C and 35°C show an enhanced conductance over that of the theoretical values calculated from the Onsager's equation and hence the slopes of the equivalent conductance Vs square root of concentration plots are lower than the theoretical values as seen in Table 22. This shows that there must be some sort of interaction taking place among the fatty acid anions to form a more conducting unit, even in the dilute region as discussed in the previous part. The reversible formation of dimers,



to a certain extent is probably a first step in the dilute region responsible for greater conductance.

With increasing concentration, there is always a decrease in equivalent conductance, a decrease of surface tension and a slight increase of relative viscosity, while at concentrations (CMC),

where the transition from a molecularly dispersed solution to a micellar solution occurs, the physical properties show a sudden variation. The concentrations at which these changes take place are almost the same for all the physical properties as shown in Table 28. The ease with which micelle formation takes place can be predicted from the consideration of free energy decrease for micelle formation. As seen in Table 24, the longer the chain length, the greater is the decrease of free energy for micelle formation and the lower the concentration at which micelle formation takes place. In fact, the CMC is reduced by a factor of two per CH_2 - group increase in the chain length.

When specific conductances are plotted against concentrations over the entire region of concentration for these salts variation of slopes occur at concentrations as shown in Table 29.

These changes of slope indicate that some sort of structural change takes place at about these concentrations as mentioned in Table 29 which is probably responsible for variations in slopes. McBain has already pointed out that marked changes take place in the physical properties of colloidal electrolytes in the concentration region. Some German workers^{86,87} also claim that diffraction measurements on colloidal electrolytes in the concentrated region show a definite indication of the appearance of new properties and structural changes. Fluidity Vs concentration plots of these salts also indicate change of slopes of the curves at about the same concentrations as that of the plots of specific conductance Vs concentration. The concentrations of which the slope changes may be termed as the second critical micelle concentration and the third critical micelle

TABLE 29

THE CRITICAL MICELLE CONCENTRATIONS OF
SODIUM SALTS OF FATTY ACIDS AT
25°C AND 35°C

Sodium Salts	Temperature °C	1 st CMC (mole/litre)	2 nd CMC (mole/litre)	3 rd CMC (mole/litre)
Octanoate	25	0.34	1.11	1.84
	35	0.36	1.13	1.86
Decanoate	25	0.094	0.55	1.125
	35	0.098	0.575	1.25
Laurate	25	0.0245	0.178	-
	35	0.0250	0.182	-
Myristate	25	0.0069	-	-
	35	0.00695		

concentration zones respectively. Second critical micelle concentration region is observed in the case of sodium laurate. It can not be said from the present experimental data alone how a structural effect would influence the course of conductance and the other physical properties in these regions, but qualitatively one can say that at higher concentrations the spherical micelle of the Hartley type is transformed into the lamellar type of micelles around the second and third critical zones and these are probably responsible for the variations of physical properties observed in these salts.

SUMMARY AND CONCLUSION

CHAPTER VII

1. The limiting equivalent conductances of the sodium salts of decanoic, lauric and myristic acids at 25°C and 35°C are found to be 72.11, 70.76, 70.21 (mhos) and 89.10, 87.86, 86.77 (mhos) respectively. Also the limiting equivalent conductances of sodium formate, sodium acetate, sodium propionate and sodium butyrate at 35°C are found to be 128.63, 112.25, 105.96, and 101.83 respectively. From the trend of mobility with the number of carbon atoms in the anion, it appears that further increase of chain length beyond ten carbon atom (decanoic acid) produces only a slight decrease in mobility, (i.e.) the limiting ionic conductance of fatty acid anions seem to approach a constant value.
2. The enhanced conductance, even in the dilute solution of these salts over the theoretical (Onsager's) value suggests a possible interaction between anions leading to reversible dimerisation and hence increased conductance.
3. For a given salt the critical micelle concentration is found to be the same, no matter what method is used for the determination (see Table 28). This shows that the CMC is a real physical entity.
4. From the free energy calculations for micelle formation it is shown that the interior of the micelle is liquid like. Also the ease with which micelles are formed increases with increase of chain length.

5. Activation energy values of conductance and viscosity and the temperatures coefficients of these properties are found to be almost the same for all the three salts.

6. The minima observed in the surface tension measurements are probably mainly due to adsorption of the hydrolysis products (acids or acid soap) on the surface. A discussion is given of how Gibbs theorem can be used to explain the surface phenomena of these colloidal electrolytes in aqueous solution.

7. Lastly, it is suggested qualitatively, that at higher concentrations, judging by the change of slope of specific conductance versus concentration, and of fluidity versus concentration, there are other concentration regions which can be called second and third micelle concentration regions where there may be change in the physical properties and internal structure of the solution.

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CHAPTER VIII

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