A PHYSICO-CHEMICAL AND ELECTROCHEMICAL STUDY OF AQUEOUS BARBITURIC ACID AND SODIUM BARBITAL AT 25°C

By

Deogratius Jaganyi

This thesis has been submitted to the College of Biological and Physical Sciences, University of Nairobi in partial fulfilment of the requirements for the degree of Master of Science.

July, 1988

DECLARATION

This work is completely original and has not been presented in any other University.

Signed:---------------------------
DEOGRATIUS JAGANYI

Date:---3rd August 1988---

This work has been presented for examination with my approval as the Project Supervisor.

Signed:---M. Shamim---
DR. MOHAMMED SHAMIM

Date:---04-08-1988---

DEDICATION

TO MY PARENTS

ACKNOWLEDGEMENTS

I wish to express my appreciation to Dr. M. Shamim, my Supervisor, who initiated this work, for his guidance, patience and invaluable advice during the carrying out of this investigation. My sincere thanks are also due to Dr. V.D. Nair (Co-supervisor), for her stimulating comments and suggestions throughout the work.

I would like to thank Moses Njau, Khalifa Said and Othako for their technical assistance, and to render my sincere gratitude to all the staff of the Department of Chemistry whose help made this study possible.

I am indebted to the (DAAD), German Academic Exchange Services for the Scholarship and financial assistance. I wish to express my appreciation also to the University of Nairobi for use of its facilities and equipments.

Finally, special thanks are due to Mrs. Mary Kihara who kindly typed the manuscript.

CONTENTS

CHAPTER 1: OBJECTIVE, CHEMISTRY OF COMPOUNDS, THEORY OF EXPERIMENTAL PROCEDURES

PAGE

PAGE

CHAPTER II: EXPERIMENTAL

CHAPTER III:

ABSRACT:

Derivatives of Barbituric Acid like Barbitone, Phenobarbitone, Soneryl, Numbutal and Amytal etc. have long been used as a powerful hypnotic and soporitic medicine for the treatment of epilepsy and other ailments which warrant sedation.

In spite of age-long use of these compounds, it was surprising to note that physico-chemical data on these chemicals are rather meagre in the literature. It thus became the objective of the present project to produce precise physico-chemical data of such pyrimidines so as to have a better understanding of the mode of physiological action of these medicinal compounds.

Accordingly density, viscosity, refractive index, conductance and diffusion coefficient measurements were undertaken in aqueous Barbituric Acid and Sodium Barbital solutions at 25°C.

The investigation has produced equations which describe the concentration dependence of density, refractive index and relative viscosity in a wide range of concentration. Partial molal volume $\bar{V}$, for Barbituric Acid and Sodium Barbital have been found to be 74.3 and 125.2 cm^3 mol^{-1} respectively. An important observation in this

connection is that Sodium Barbital produces a decrease in effective volume.

Conductance measurements have yielded Λ^o = 372.31 $\pm$ 0.5 Scm^{2}equiv.$^{-1}$ and K_a = (1.01$\pm$.01) x 10^{-4} mol l.$^{-1}$ for Babituric Acid; and Λ^o = 89.91 $\pm$ 0.05 and λ^o_- = 39.80 $\pm$ 0.5 Scm^2 equiv.$^{-1}$ as limiting conductance values for the salt and diethyl-Barbiturate ion. Likewise the diffusion studies have given D^o = (1.196 $\pm$ .0 2) x 10^{-5} cm^{2}Sec^{-1} for the undissociated acid and D^o_i = (0.599 $\pm$ .02) 10^{-5} cm^{2}sec^{-1}. for an isolated ion. The diffusion coefficient of the salt has been found to be (1.181 $\pm$ 0.02)10^{-5} cm^2 sec.$^{-1}$. All these results indicate a strong ion-ion and ion-solvent interactions.

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

OBJECTIVE, CHEMISTRY OF COMPOUNDS AND THEORY OF EXPERIMENTAL PROCEDURES

1-1 THE OBJECTIVE:

Derivatives of 2:4:6-trihydroxypyrimidine (Bartiburic acid) e.g. Barbitone, Phenobarbitone, Soneryl, Numbutal and Amytal etc. have long been used as a powerful hypnotic and soporitic medicine to treat epilepsy and other ailments which warrant for sedation. The 5,5-disubstituted derivatives are well known chemotherapeutic agents. Accordingly a great deal of work on the medicinal and therapeutic aspects of these compounds has been reported in literature.

It is surprising that physico-chemical data on these substances and its parent compound, Barbituric acid, are rather meagre. An up-to-date literature (1907-1988) review reveals that no physico-chemical work has been reported on aqueous Barbituric acid. Sodium Barbital has been investigated by some workers but within narrow limits. Robert Taft and Helen M. Patton(1) have studied conductance, viscosity, density and refractive index of this compound in aqueous solutions at 30°C. The solubility(1,2) of the salt has been reported as 17.3% by weight at 30°C and 17.18% at 25°C. The limiting equivalent conductance(1) of the salt has been reported to be 82.5 S cm^2 equiv.$^{-1}$ at 30°C and hence a limiting conductance of the diethyl barbiturate ion has been deduced as 26.3 cm^2 equiv.$^{-1}$.

The density(3) ρ, of solid Sodium Barbital has been found to be 1.202 g cm^{-3}. Data on diffusion coefficient and partial molal volume is non-existant. It seems, at this stage, adequate enough to just describe the type of investigations carried out. Nevertheless, the work, mentioned above, have been critically analysed at proper places in the thesis

The scarcity of basic but important physico-chemical data thus made it desirable to study such aspects of these pyrimidines. Barbituric acid and its Sodium diethyl derivative (Barbitol) were chosen to investigate their behaviour in aqueous solutions at 25°C.

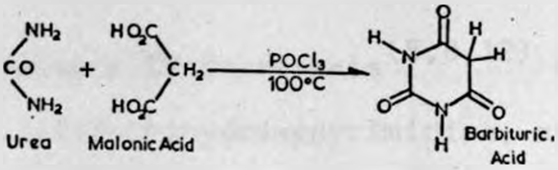
As with most organic acids and their salts, it was expected that these compounds will show a strong ion-ion and ion-solvent interactions and might even undergo complex ion formation. If it is so, the information will give a better insight of the structural nature of the individual ions in solutions and hence their mode of physiological action.

Before embarking on the discussion of the results of the present work, a brief, but pertinent, discription of the purely chemical aspects of the two compounds would not be out of place.

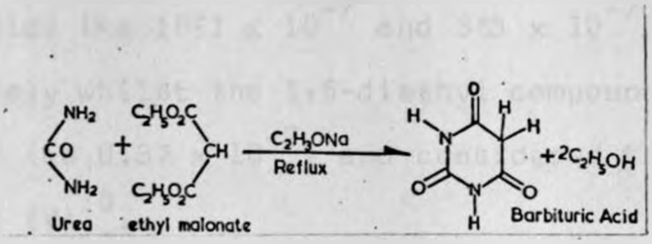
1-2 CHEMISTRY OF THE COMPOUNDS

1-2-1 BARBITURIC ACID

Barbituric acid, 2:4:6-trihydroxypyrimidine (malonglurea), was originally prepared by condensing urea with malenic acid with either phosphoryl chloride at 100°C(4,5,6,7,8) or acetic anhydride(9).

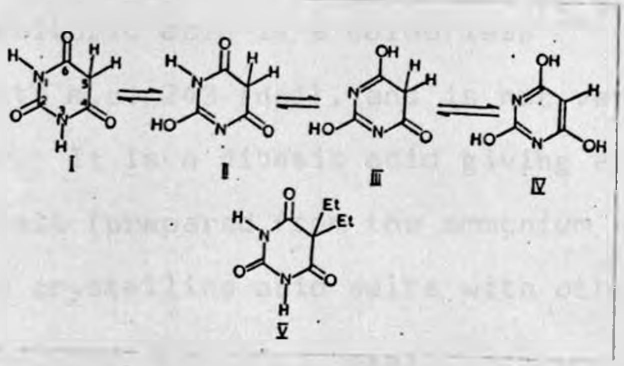


A much better synthesis is to reflux ethyl malonate with urea in ethanolic solution in the presence of sodium ethoxide as condensing agent(5,6,10,11).



Barbituric acid(5) is also obtained from 2:4:6-aminohydroxy-and-triamino-pyrimidines by hydrolysis of the amino groups by hot mineral acid.

Structure IV represents(5,8,12) barbituric acid as 2:4:6-trihydroxypyrimidine, and this structure has been proposed because of the acidic nature of barbituric acid.



This is supported by early work which shows(5) that barbituric acid and its 5-ethyl compound are strong acids (Ka 1051 x 10^{-7} and 383 x 10^{-7} respectively whilst the 5:5-diethyl compound is a weak acid (Ka 0.37 x 10^{-7}) and considered to have structure (V)[10].

On the other hand barbituric acid(8) contains an active methylene group, since it readily forms an oximino derivative with nitrous acid. Thus barbituric acid behave as if it had structure I, II, or III.

Spectroscopy and X-ray crystallography have confirmed the predominance of the trioxo-form. It is planar but does not contain a cyclic conjugate π-electron system.

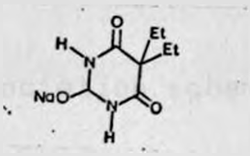
Barbituric acid is a colourless(5,7) crystalline solid with m.p. 243 (deg), and is not very soluble in water, It is a dibasic acid giving an insoluble silver salt (prepared from the ammonium salt) and it forms crystalline acid salts with other metals.

Important derivatives(13) of the acid have substituents on the N-atoms or at position 5, or both. From the various substituted urea, N-substituted derivatives are directly prepared. The O-methyl derivatives are formed from 2:4:6-trichloroprimidine and sodium methodixed by successive replacement. O-Alkyl compounds tend to rearrange to the more stable N-alkyl isomers when heated with the appropriate alkyl halide.

1-2-2 SODIUM BARITIAL

Sodium Barbital (medicinal)(14)

The structure is as shown below:



Tee dry salt itself is very light and fine. Aqueous solutions of sodium barbital are clear, colourless, alkaline liquids. The salt undergoes hydrolysis in aqueous solutions and are also very unstable at a temperature above 90°C, decomposing rapidly to give ammonia.

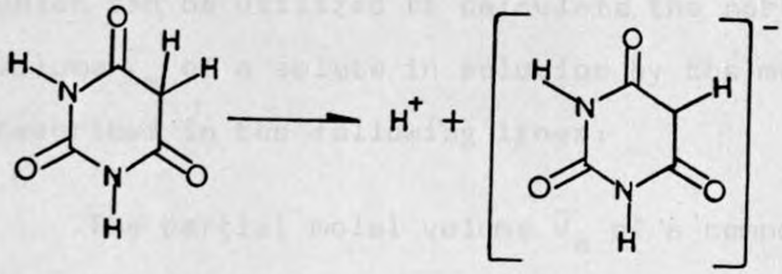
Sodium barbitale is a sodium derivative of bartibane (veronal)(15) which is prepared by condensing ethyl malonate with ethyl iodide in the presence of sodium ethoxide to give ethyl diethyl-malonate. Upon allowing the latter to react with urea in the presence of an alcoholic solution of sodium ethoxide veronal (diethylbarbituric acid or diethylmalonylurea) is produced.

$$CH_2(COOC_2H_5)_2 + 2NaOC_2H_5 + 2C_2H_5I \rightarrow$$

$$(C_2H_5)_2C(COOC_2H_5)_2 + 2NaI + 2C_2H_2OH$$

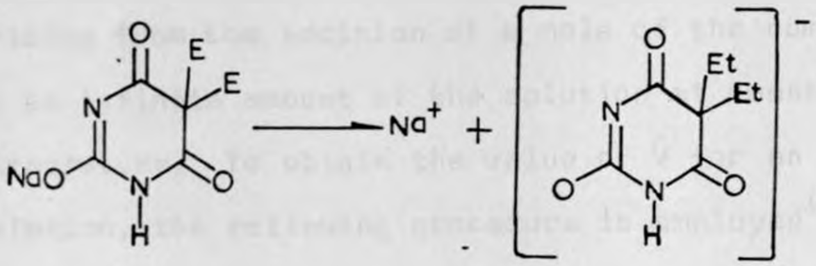
Since the anion of the two compounds differs, the author has used B^- to represent anion of Barbituric acid as $\{B^- = |C_4H_3N_2O_3|^-\}$ and $B^{\bullet}$ for the anion of sodium barbital i.e. $\{B^{\bullet} = |(C_2H_5)_2C_4HN_2O_3|^-\}$, in his work.

The dissociation scheme can thus be represented as



Or HB ——————— H+ + B-

Likewise, for Sodium Barbital



or NaB* $\longrightarrow$ $\overset{+}{Na}$ + $\overset{*}{B}^{-}$

1-3 PARTIAL MOLAR VOLUME: BASIC CONCEPTS AND DEFINITIONS.

Density of any substance, solid, liquid or a solution, is defined by the equation

$$\rho = \frac{\text{mass}}{\text{volume}} \qquad (1\text{-}1)$$

which can be utilized to calculate the partial molal volume $\bar{V}_a$ of a solute in solution by the method described in the following lines:

The partial molal volume $\bar{V}_a$ of a component 'a' in a solution, present at the molality m_a, can be defined by the expression(16).

$$\bar{V}_a = \left|\frac{\partial V}{\partial m_a}\right|_{T,b,c.....} \qquad (1\text{-}2)$$

in which V is the volume of the solution, the concentrations of the other components of the solution, b, c,.... and the temperature T being kept constant. Physically, partial molal volume may be regarded as the increase or decrease of volume arising from the addition of a mole of the component to an infinite amount of the solution at constant temperature. To obtain the value of $\bar{V}$ for an aqueous solution, the following procedure is employed(17).

Let ϕ be the apparent molal volume of the solute defined by the equation

$$\phi = \frac{V - Vo}{m} \qquad (1\text{-}3)$$

in which V is the volume of an m molal solution containing 1000g of water and V_o is the corresponding volume of pure water. Differentiating equation (1-3) with respect to m we get

$$\frac{d\phi}{dm} = \frac{1}{m}\left(\frac{\partial v}{\partial m} - \frac{v}{m} + \frac{Vo}{m}\right) = \frac{1}{m}\frac{\partial v}{\partial m} - \phi \qquad (1\text{-}4)$$

from which

$$\bar{V} = \frac{\partial v}{\partial m} = m\left(\frac{d\phi}{dm} + \phi\right) \qquad (1\text{-}5)$$

Values of ϕ may be computed from equation (1-3). Using V and V_o defined by the equations

$$V = \frac{100 + Mm}{\rho} \qquad (1\text{-}6)$$

and

$$V_o = \frac{1000}{\rho_o} \qquad (1\text{-}7)$$

Where M is the molecular weight of the solute; ρ and ρ_0 are the densities of solution and solvent respectively.

The theory of electrolyte solutions provides the following limiting equation which is valid in the low concentration(18) range.

$$\phi = \phi^o + am^{\frac{1}{2}} \qquad (1\text{-}8)$$

where ϕ^o and 'a' are constants which can be determined graphically by constructing a plot of ϕ against $m^{\frac{1}{2}}$. Equation (1-8) is known as Masson's equation which, together with (1-5), yields

$$\bar{V} = \frac{\partial v}{\partial m} = \phi^o + \frac{3}{2} am^{\frac{1}{2}} \qquad (1\text{-}9)$$

The author has used his density measurements in the above equations to calculate the partial molal volume of Barbituric Acid and Sodium Barbital in aqeous solutions.

In the following pages Barbituric Acid would be represented as HB where $B = |C_4H_3N_2O_3|^-$, and likewise Sodium Barbital as NaB* where

$B^* = |(C_2H_5)_2C_4HN_2O_3)|^-$.

1-4 VISCOSITY: BASIC CONCEPTS AND DEFINITIONS.

The viscosity of a liquid is a fundamental property and related to intermolecular forces in the liquid state. On macro scale the viscosity is a dynamic non-equilibrium property and is defined as the ratio of the shear stress per unit area at any point to the velocity gradient. The viscosity of a liquid is a measure of its resistance to flow, due to its internal frictional forces.

The absolute viscosity, η, of a fluid can be defined as the force per unit area required to maintain unit difference in velocity between two parallel layers of the fluid which are unit distance apart. It can be written as follows(19)

$$\tau = \frac{\partial u}{\partial y}\,\eta \qquad (1\text{-}10)$$

$$\eta = \tau\frac{\partial y}{\partial u} \qquad (1\text{-}11)$$

where η is the absolute viscosity, τ is the force per unit area or shear stress and $\frac{\partial u}{\partial y}$ is the velocity gradient normal to the planes of flow. Because η appears as a proportionality factor between shear stress and velocity gradient, it is usually termed the coefficient of viscosity. The dimensions of absolute viscosity are $ML^{-1}T^{-1}$

which in c.g.s. units will be g cm^{-1} $sec.^{-1}$.
The unit of 1 g cm^{-1} $sec.^{-1}$ corresponds to 1 poise (P) which is the absolute unit of viscosity. Poise (P) is defined as the viscosity of a fluid which requires a shearing force of 1 dyne per cm^2 to maintain a velocity gradient of 1 cm $sec.^{-1}$ between two planes 1 cm apart. In practice the centipoise (cP), which is equal to 0.01P, is commonly used. The absolute viscosity of water at 20°C being approximately 1 cP.

Certain other terms are in frequent use, particularly with reference to the viscosity of solutions; these are:

Kinematic Viscosity:

Kinematic viscosity, ν, is defined as the ratio of absolute viscosity to density, ρ,

$$\nu = \frac{\eta}{\rho} \qquad (1\text{-}12)$$

The dimensions of kinematic viscosity are L^2T^{-1} which in c.g.s. units will be $cm^2sec.^{-1}$. The unit of 1 $cm^2sec.^{-1}$ is known as 1 Stoke. Kinematic viscosity is widely used throughout the petroleum industry and has application in fluid mechanics, where viscosity-density ratio appears in many flow problems.

Relative Viscosity

Relative viscosity, η_{rel}, is the ratio of the viscosity of solution to that of pure solvent under the same conditions, i.e.

$$\eta_{rel} = \frac{\eta}{\eta^{o}} = \frac{\rho t}{\rho_o t_o} \qquad (1\text{-}13)$$

where η and η^o are the viscosities of solution and solvent respectively; ρ, ρ_o, t and t_o are the densities and times of flow of solution and solvent respectively. In this work equation (1-13) has been used to determine the η_{rel} in aqueous HB and NaB* solutions at 25°C.

Specific Viscosity

The specific viscosity, η_{sp}, is the ratio of the difference between the solution and solvent viscosities to the solvent viscosity.

$$\eta_{sp} = \frac{\eta - \eta^o}{\eta^o} = \eta_{rel} - 1 \qquad (1\text{-}13)$$

Fluidity

The fluidity, ϕ', is defined as the reciprocal of the absolute viscosity.

$$\phi' = \frac{1}{\eta} \qquad (1\text{-}14)$$

Intrinsic Viscosity

The intrinsic viscosity of a solution of concentration C is given by

$$\lim_{c \to o} (\eta - \eta_o)/(C\eta_o)$$

$$\text{or} \quad \lim_{c \to o} \frac{1}{C} \ln\left(\frac{\eta}{\eta_o}\right) \qquad (1\text{-}15)$$

1-4-1 JONES-DOLE EQUATION

Electrical forces between ions in adjacent layers of an electrolyte solution will increase its viscosity. The mathematical treatment of this effect was first given by Falkenhagen *et el.*(20) who showed that the limiting law is of the form

$$\frac{\eta}{\eta^o} = 1 + AC^{\frac{1}{2}} \qquad (1\text{-}16)$$

But later Jones and Dole(21) extended this equation to the form

$$\frac{\eta}{\eta^o} = 1 + AC^{\frac{1}{2}} + BC \qquad (1\text{-}17)$$

where A and B are coefficients which have great significance, and C is the concentration of solution expressed both as mol l^{-1} or mol kg^{-1}. Equation (1-17) is valid for concentration up to about 0.2M for uni-univalent electrolytes.(22)

1-4-2 A-COEFFICIENT

The A-coefficient is a function of solvent properties, ionic charges, mobilities and temperature. The $AC^{\frac{1}{2}}$ term is attributed to charge-charge interactions between the ions.

The A-coefficient has a non-zero value only for electrolytes where it is always positive. It has been interpreted theoretically on the basis of deformation of the Debye-Huckel spherical ion-atmosphere under a shearing stress. It accounts for the increase in viscosity produced by the long range coulombic forces between the ions(23). The increased viscosity contributed by the $AC^{\frac{1}{2}}$ term is small compared to BC term. Thus more attention is focused on B-coefficient rather than A-coefficient.

The A-coefficient was given theoretical treatment by Falkenhagen and Vernon. They showed that(24)

$$A = \frac{\Lambda^{o}\ 0.2577}{\eta(\varepsilon T)^{\frac{1}{2}}\lambda_{+}^{o}\lambda_{-}^{o}}\left[1-0.6863\left(\frac{\lambda_{+}^{o}-\lambda_{-}^{o}}{\Lambda^{o}}\right)^{2}\right] \qquad (1\text{-}18)$$

where λ_{+}^{o} and λ_{-}^{o} represent the limiting conductance of the subscripted ions and Λ^{o} stands for the limiting conductance of the electrolyte as a whole; η, ε, and T are the viscosity, dielectric constant and absolute temperature respectively. They attempted to calculate A-coefficient by including the parameter a°-the distance of closest approach-of the ions. All the equations are given by Stokes and Mills (35) and excellent agreements have been obtained between the theoretical and experimental A-coefficient. The A-coefficients have been shown to be nearly constant over a wide temperature range[26].

1-4-3 B-COEFFICIENT

The B-coefficient in equation (1-17) is known as viscosity B-coefficient. Todate, the viscosity B-coefficient has not been given a theoretical treatment. But many workers have related it in a qualitative manner to ion-solvent interactions. In aqueous solutions, the viscosity B-coefficients are positive for non-electrolytes, and can be positive or negative for electrolytes.

Negative viscosity B-coefficients are confined to highly associated solvents, e.g. water. The ions present in water exert a "structure breaking" effect on water, e.g. Rb^+, I^-, Cs^+. Such negative values become less negative or change to positive as the temperature is raised. The reason is that at higher temperature, the water structure is already broken down by thermal agitation. The ions can hardly make the condition worse. The negative B-coefficient seldom causes a decrease of more than 10% in viscosity. Positive B-coefficients are assumed to exert a "structure making" effect.

An important feature of the B-coefficient is its additive property of the constituent ions(27). For example, the B values for pairs of salts with the same anion but different cations have constant difference. Additivity is thus deduced for the separate ions. Gurney(28) and Kaminsky(29) have computed the ionic B-coefficient contributed by both potassium and chloride ions at different temperatures. Mandal *et al.*(30) tried this additive principle on weak acids and their salts.

Apart from being a property of ion-solvent interactions, B-coefficients can also be due to the effect of solute size. The B-coefficient is said to be a measure of the effective hydrodynamic volume of the solvated ions(31). From hydrodynamic theories applicable to particles in a fluid continuum, the increase in viscosity is due to the presence of these particles lying across the fluid stream-lines. Since these particles are subjected to torsional forces, they tend to rotate and absorb energy which results in an increased viscosity for the solution.

1-5 CONDUCTANCE:- BASIC CONCEPTS AND DEFINITIONS.

Both solids and electrolyte solutions conduct electricity and obey Ohm's law i.e.

$$I = \frac{V}{R} \qquad (1\text{-}19)$$

where V is the potential difference in volts across the resistance R (ohm) carrying a current I (ampere).

The resistance of an electrical conductor, whether solid or electrolyte solution, is directly proportional to its length and inversely proportional to its cross-sectional area A; so that

$$R \propto \frac{l}{A}$$

or

$$R = \rho . \frac{l}{A} \qquad (1\text{-}20)$$

ρ-the proportionality constant-is known as the specific resistivity of the conductor. In the study of electrolyte solutions it is the conductivity rather than resistivity which is more important. The specific conductivity K is defined as the reciprocal of resistivity

$$K = \frac{1}{\rho} \qquad (1\text{-}21)$$

from equation (1-20) and (1-21) one gets

$$K = \frac{1}{R} \cdot \frac{L}{A} \qquad (1\text{-}22)$$

In the measurement of conductivities of electrolyte solutions L is the fixed distance between the two electrodes having an area A. The quantity $\frac{L}{A}$ is, therefore, a constant and is called the cell constant of the conductance cell. Consequently equation (1-22) can be written as

$$K = \frac{J^{*}}{R} \qquad (1\text{-}23)$$

The units of cell constant J^{*} and specific conductivity K are, obviously, cm^{-1} and S cm^{-1} respectively.

To compare the specific conductivities of solutions containing different amounts of the same electrolyte or of solutions having different electrolytes, a quantity Equivalent or Molar Conductance, Λ, has been defined by the following equation

$$\Lambda = \frac{1000K}{(\chi)} \qquad (1\text{-}24)$$

where (χ) represents the concentration of electrolyte under study in gram equivalent or gram mole per litre.

1-5-1 KOHLRAUSCH'S EQUATIONS

As a result of extensive studies of the equivalent conductances of various electrolytes Kohlrausch proposed two very valuable relationships which are frequently used in the study of conductances of electrolyte solutions. The two relationships are as under:

(a) Law of Independent Migration of Ions.

According to this law the equivalent conductance of an electrolyte AB at infinite dilution, Λ^{o}_{AB}, is equal to the sum of the equivalent conductances of ions A^{+} and B^{-},

$$\Lambda^{o}_{AB} = \lambda^{o}_{A^{+}} + \lambda^{o}_{B^{-}} \qquad (1\text{-}25)$$

where λ^{o} is the equivalent conductance of the subscripted ion at infinite dilution.

(b) Empirical Conductance Equation.

Kohlrausch proposed an empirical equation connecting observed equivalent conductance to the concentration. The equation is

$$\Lambda = \Lambda^{o} - K'\sqrt{C} \qquad (1\text{-}26)$$

where K' is a constant and C the concentration in g equivalent per litre.

Although Kohlrausch could not assign any specific physical meanings to the constant K' the equation did explain very well the concentration dependence of equivalent conductances, in dilute solutions, of most strong 1:1 electrolytes.

It is evident from the equation that the observed Λ should decrease with the increase in concentration. The first attempt to explain this decrease was made by Arrhenius and a brief account of his theory is given in the following section.

1-5-2 THEORY OF ELECTROLYTIC DISSOCIATION.

According to this theory, a portion of the electrolyte molecules is reversibly broken down into ions, the degree of ionization may often be very large and it always increases with dilution approaching completion as the dilution becomes increasingly great.

The conductance of a solution depends upon

(a) the total number of ions,

(b) the charge on the ions; and

(c) the speed of the ions.

Arrhenius assumed that the speed of the ions does not vary with concentration. Hence for the same electrolyte the variation of equivalent conductance with dilution is due to the change in the total number of ions resulting from the dissociation of electrolyte. The assumption has been found to be approximately true for weak electrolytes but not for strong ones.

To calculate the degree of dissociation, α, Arrhenius proposed the following expression:

$$\alpha = \frac{\Lambda}{\Lambda^{o}} \qquad (1\text{-}27)$$

The so calculated proportion of ions did explain very well the concentration dependence of equivalent conductance in weak electrolyte solutions. The data of strong electrolytes, however, did not find any explanation because these electrolytes were known to undergo complete ionization at all reasonable concentrations. A theory was, therefore, needed, which could explain the concentration dependence of conductance in both types of solutions.

1-5-3 INTERIONIC THEORY

The present view is that strong electrolytes undergo complete ionization at all reasonable concentrations. The decrease in equivalent conductance with increasing concentration must, therefore, be attributed to the diminution in the ionic velocity. This fact has been explained by the interionic theory.

A simple picture of the theory is that with increasing concentration the ions get closer together and the force of attraction between oppositely charged ions results in a decrease of their speeds and hence in the equivalent conductance of the solution.

The quantitative treatment of the theory of interionic attraction is due mainly to the work of Debye, Huckel and Onsager(32,33,34). The fundamental idea underlying the deductions is that due to the electrical attraction, every ion, on the average, has more ions of opposite sign in its vicinity than ions of the same charge. Each ion may, therefore, be regarded as being surrounded by a centrally symmetrical ionic atmosphere with a charge opposite to that of the ion itself. When an e.m.f is applied the ions are caused to move in one direction and the oppositely charged ionic atmosphere in the other and the symmetry of the ionic atmosphere is disturbed. Hence the ion experiences a backward pull and its velocity decreases. The ions remain under this dragging effect for that length of time which the atmosphere takes to readjust itself. This effect is termed as the asymmetry or the time of relaxation effect.

Besides the relaxation effect, there is another effect which results from the ion-solvent interaction. This is known as the electrophoretic effect. The applied potential drags the ionic atmosphere with its solvent molecules in a direction opposite to that in which the central ion is moving. Thus the atmosphere exerts a dragging force on the ion causing a further retardation in its velocity.

By expressing the magnitude of these two effects in terms of the physical properties of the ions and the solvent the following equation(35) results for the equivalent conductance of an ion

$$\lambda_i = \lambda_i^o - \left[\frac{2.801 \times 10^6 Z_+ Z_- q \lambda_i^o}{(\varepsilon T)3/2(1 + \sqrt{q})}\right] + \left[\frac{41.25 Z_i}{\eta\sqrt{\varepsilon T}}\sqrt{I}\right] \tag{1-28}$$

where

$$q = \frac{Z_+ Z_- \left(\lambda_+^o + \lambda_-^o\right)}{(Z_+ + Z_-)(Z_- \lambda_+^o + Z_+ \lambda_-^o)} \tag{1-29}$$

and the ionic strength

$$I = \tfrac{1}{2}\Sigma C_i Z_i^2 \tag{1-30}$$

in which λ_i and λ_i^o have the meanings defined earlier; Z_+ and Z_- represent the valencies of the positive and negative ions respectively. ϵ and η are the dielectric constant and the viscosity of the solvent respectively at absolute temperature T. The first term in the brackets in equation (1-28) accounts for the time of relaxation effect and the second for the electrophoretic effect.

For a uni-univalent electrolyte, equation (1-28) becomes

$$\lambda_i = \lambda_i^o - (B_1\lambda_i^o + \tfrac{1}{2}B_2)\sqrt{C} \qquad (1\text{-}31)$$

By adding two such terms-one for anion and another for cation respectively - we get an equation for the equivalent conductance of completely ionized electrolyte. Thus for a 1:1 electrolyte the equation takes the form

$$\Lambda = \Lambda^o - (B_1\Lambda^o + B_2)\sqrt{C} \qquad (1\text{-}32)$$

which is Onsager conductance equation. A comparison of equations (1-32) and (1-26) shows that the constant K in Arrhenius equation is equal to $(B_1\Lambda^o + B_2)$.

For aqueous solutions at 25°C $B_1 = 0.2300$ (36) and $B_2 = 60.65$ (36), these are based on the value of $\eta = 0.008903$ (36) P and $\epsilon = 78.35$ (36). According to equation (1-32) a plot of Λ against $\sqrt{C}$ should give a straight line of slope $(B_1\Lambda + B_2)$. This has been found to be the case for dilute solutions of strong uni-univalent electrolytes.

In concentrated solutions, however, deviation from the equation becomes prominent. The reason for this departure is that the derivation of equation (1-32) involves a number of simplifying assumptions and mathematical approximations which can only be applied to very dilute solutions. Hence the equation is valid only as a limiting equation. When $(\Lambda^o - \Lambda)$ is 10% of Λ^o(37). Onsager has found that the error introduced in the calculation of Λ from equation (1-32) is about 1%.

This equation however agrees very well with experimental data for many 1:1 electrolytes in water up to 0.002M and also for 1:2 and 1:3 electrolytes at lower concentrations.

1-5-4 EQUATIONS FOR HIGHER CONCENTRATIONS.

Various empirical extensions of Onsager equation have been proposed in the literature(38) to accommodate the deviation in concentrated solutions. Among those Shedlovsky(38) proposed the equation

$$\Lambda = \Lambda^o - (B_1\Lambda^o + B_2)\sqrt{C} + bc \qquad (1\text{-}33)$$

where b is constant.

This equation fits very well for many electrolytes in relatively higher concentrations.

Robinson and Stokes (39) have given, neglecting the cross-product of the relaxation and electrophoretic terms, the following equation

$$\Lambda = \Lambda^{o} = \frac{(B_1\Lambda^{o} + B_2)\sqrt{C}}{1 + B_3a^{o}\sqrt{C}} \qquad (1\text{-}34)$$

where B_3 is a constant having a value of 0.329×10^{8} (36) and a^{o} is the distance of closest approach of the ions in Angstrom A^{o}. The equation gives a fair account of the conductances of aqueous 1:1 electrolytes up to 0.1M and at the same time provides reasonable values for the parameter a^{o}. The equation, however, fails to account for the concentration dependence of conductance in non-aqueous solutions(40).

1-5-5 CONDUCTANCE EQUATION FOR WEAK ELECTROLYTES.

In the case of weak electrolytes only a fraction α of the electrolyte undergoes dissociation and the conductance equation, therefore, corresponding to the Onsager equation (1-32) is (41)

$$\Lambda = \alpha(\Lambda^{o}-\{B_1\Lambda^{o} + B_2\}\sqrt{C\alpha}) \qquad (1\text{-}35)$$

which gives

$$\alpha = \frac{\Lambda}{\Lambda^o(1-\{B_1\Lambda^o + B_2\}\sqrt{C\alpha}/\Lambda^o)} \qquad (1\text{-}36)$$

Equation (1-35) in which Cα is the ionic strength of solution provides a method to calculate the degree of dissociation α by successive approximations. In the limit C→0, the equation reduces to

$$\alpha = \frac{\Lambda}{\Lambda^o}$$

which is the Arrhenius equation.

Shedlovsky [42] has used the quadratic equation

$$\Lambda = \alpha\Lambda^o - \frac{\Lambda}{\Lambda^o}\{B_1\Lambda^o + B_2\}\sqrt{C\alpha} \qquad (1\text{-}37)$$

which is much simpler to solve than the equation (1-35) which is cubic in $\sqrt{\alpha}$. The equation yields

$$\alpha = \frac{\Lambda}{\Lambda^o} + \left(\frac{B_1\Lambda^o + B_2}{(\Lambda^o)^2}\right) \Lambda\sqrt{C\alpha} \qquad (1\text{-}38)$$

Equation (1-37), along with the mass action equation

$$K_a = \frac{C\alpha^2}{1-\alpha} f_\pm^2 \qquad (1\text{-}39)$$

in which the mean activity coefficient $f_\pm$ can be calculated using Debye-Huckel law in the form

$$\log f_\pm = -A|Z_+Z_-|\sqrt{I}/(1 + B_3a^o\sqrt{I})$$

$$\text{or} \quad \log f_\pm = \frac{-0.5098\sqrt{C\alpha}}{1 + B_3a^o\sqrt{C\alpha}} \qquad (1\text{-}40)$$

Where $A = 0.5098$ at 25°C, Z_+, Z_- are the valencies of the subscrepted ions and I the ionic strength of the solution given by equation (1-30). Equation (1-38) gives simultaneously the dissociation constant K_a and the limiting equivalent conductance Λ^o by a graphical method explained in the following lines.

Solving equation (1-38) for α in terms of a variable Z, defined as

$$Z = (B_1\Lambda^o + B_2)\sqrt{C\Lambda}\,(\Lambda^o)^{-\frac{3}{2}}$$

one obtains

$$\alpha = \frac{\Lambda}{\Lambda^o}\left[\frac{Z}{2} + \sqrt{\{1 + (Z/2)^2\}}^{\,2}\right]$$

$$= \frac{\Lambda}{\Lambda^o} S(Z) \qquad (1\text{-}41)$$

The term in brackets can be used in expanded form

$$S(Z) = 1 + Z + \frac{Z^2}{2} + \text{-------} \qquad (1\text{-}42)$$

for small value of Z.

From equations (1-41) and (1-38) one obtains

$$\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda^o} + \frac{C\Lambda f_\pm^2 S(Z)}{K_a(\Lambda^o)^2} \qquad (1\text{-}43)$$

Thus a plot of $1/\Lambda S(Z)$ against $C\Lambda f_\pm^2 S(Z)$ would give $1/\Lambda^o$ as the intercept and the slope equal to $1/K_a(\Lambda^o)^2$. The author has used this method to obtain Λ^o and K_a values in aqueous Barbituric Acid solutions.

The corresponding Robinson and Stokes equation for weak electrolytes solution is

$$\frac{\Lambda}{\alpha} = \Lambda^o - \frac{(B_1\Lambda^o + B_2)\sqrt{C\alpha}}{1 + B_3 a^o \sqrt{C\alpha}}$$

This equation could have been used[(43)] obtain (fit) Λ^o values if the dissociation constant K_a is known with certainity. The author has preferred the afore-method because it yields Λ^o and K_a values simultaneously.

1-5-6 HYDROLYSIS (44)

Hydrolysis is a partial reversal of neutralization i.e it is a reaction between water and the acid and base conjugate taking part in the neutralization.

When the salt of a strong base and a strong acid, e.g, NaCl, is dissolved in water, the ions produced, viz., Na^+ and Cl^-, have no detectable tendency to interact with the solvent, and the solution remains neutral. If acid or base is weak, however, there is appreciable hydrolysis.

WEAK ACID AND STRONG BASE (44)

If the acid HA is weak, the conjugate base A^- will be fairly strong, and interaction with the solvent, acting as an acid, will take place to a definite extent. It follows, also, that when the salt of a weak acid and strong base e.g., NaA, is dissolved in water the A^- ions produced on dissociation will establish an equilibrium with water molecules.

$$\underset{\text{unhydrolysed salt}}{A^-} + \underset{\text{Excess}}{H_2O} \rightleftharpoons \underset{\text{Free base}}{OH^-} + \underset{\text{Free acid}}{HA} \qquad (1\text{-}44)$$

resulting in the partial re-formation of the free weak acid (HA) and the strong base (OH^-) from which the salt was constituted. The production of free OH^- ions supresses the concentration of hydrogen ions which ultimately renders the aqueous solution of such salts alkaline. Applying the equilibrium law to the above mentioned hydrolytic reaction, the hydrolysis constant, K_h, of the salt can be written as

$$K_h = \frac{a_{OH^-} \times a_{HA}}{a_{A^-}} = \frac{C_{OH^-} \times C_{HA}}{C_{A^-}} \cdot \frac{f_{OH^-} \times f_{HA}}{f_{A^-}} \qquad (1\text{-}45)$$

which reduces to

$$K_h = \frac{C_{OH^-} \times C_{HA}}{C_{A^-}} \qquad (1\text{-}46).$$

Since $f_{A^-} = f_{OH^-}$ and f_{HA} can be taken as unity. In a C molar aqueous solution of salt NaA, with a degree of hydrolysis x, the concentrations of various species would be

$$\left.\begin{aligned} C_{A^-} &= C(1-x) \\ C_{HA} &= C_{OH^-} = Cx \end{aligned}\right\} \qquad (1\text{-}47)$$

Substituting these concentration values in (1-46) one gets

$$K_h = \frac{Cx^2}{(1-x)} \qquad (1\text{-}48)$$

or the degree of hydrolysis

$$x = -\frac{K_h}{2C} + \sqrt{\frac{K_h^2}{4C^2} + \frac{K_h}{C}} \qquad (1\text{-}49)$$

provided the hydrolysis constant K_h is known. If, however x is small, then (1-48) reduces to

$$K_h \simeq Cx^2$$

and hence

$$x \simeq \sqrt{\frac{K_h}{C}} \qquad (1\text{-}50)$$

Since the relationships

$C_{H^+} \times C_{OH^-} = K_w$ and

$C_{H^+} \times C_{A^-}/C_{HA} = K_a$

must hold in the same solution, it follows that

$$K_h = K_w/K_a \tag{1-51}$$

and so the hydrolytic constant is related to the ionic product of water and the dissociation constant of the acid. If K_h, from (1-51), is substituted in (1-50), one gets

$$x = \sqrt{\frac{K_w}{K_a C}} \tag{1-52}$$

Since $C_{OH^-} = Cx$ and $C_{H^+} \times C_{OH^-} = K_w$

It follows that

$$C_{H^+} = K_w/Cx$$

Introducing the value of x from (1-52), we get

$$C_{H^+} = \sqrt{K_w K_a/C} \tag{1-53}$$

or

$$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a - \tfrac{1}{2}\log C \tag{1-54}$$

It follows, therefore, that the pH, or alkalinity, of the solution increases with increasing concentration of the salt, although the degree of hydrolysis x decreases.

Hydrolysis considerations, explained above, were applied to the conductance equation to represent the true physical picture in NaB^* solutions. The subsequent section explains the need and the derivation of such an equation.

1-5-7 CONDUCTANCE EQUATION FOR NaB* SOLUTIONS

The pH measurements were carried out in the entire range of concentration of NaB* solutions and in each case the solution was found to be alkaline. It was therefore inferred that the salt is undergoing hydrolysis. The equilibrium reactions for such a process can be represented by the following equation:

$$NaB^* \longrightarrow Na^+ + B^{*-} \text{------ (a)}$$

$$B^{*-} + \underset{\text{(Excess)}}{H_2O} \rightleftharpoons B^*H + OH^- \text{----(b)}$$

If α^* is the degree of hydrolysis in a C molar NaB* solution the concentration of various species would be

$$[Na^+] = C; \ [B^{*-}] = C(1-\alpha^*)$$

$$[B^*H] = C\alpha^*; \ [OH^-] = C\alpha^*;$$

and the ionic strength

$$I = \tfrac{1}{2}\Sigma C_i Z_i^2$$

$$I = \tfrac{1}{2}\{C_{Na^+} Z^2_{Na^+} + C_{B^*-} Z^2_{B^*-} + C_{OH^-} Z^2_{OH^-}\} = C \qquad (1\text{-}55)$$

Equation (b) yield the following equation for the hydrolysis constant

$$K_h = \frac{C_{B^*H} \cdot f_{B^*H} \times C_{OH^-} \cdot f_{OH^-}}{C_{B^*-} \cdot f_{B^*-} \times C_{H_2O} f_{H_2O}}$$

$$K_h = \frac{C\alpha^* f_{B^*H} \times C\alpha^* f_{OH^-}}{C(1-\alpha^*) f_{B^*-}}$$

which reduces to

$$K_h = \frac{C\alpha^{*2}}{(1-\alpha^*)} \qquad (1\text{-}56)$$

Since $f_{B^*H} = f_{H_2O} = 1$, and $f_{OH^-} = f_{B^*-}$

The fact that hydrolysis introduces a very mobile and conductive OH^- species makes it desirable to obtain a conductance equation which takes into account the ionic species produced by the reactions (a) and (b).

Now the observed conductance Λ_{OBS} in a C molar NaB* solution is defined by

$$\Lambda_{OBS} = \frac{1000K}{C_{NaB^*}} \qquad (1\text{-}57)$$

$$C_{NaB^*}\Lambda_{OBS} = 1000K = \Sigma C_i\lambda_i$$

$$= C_{Na^+}\lambda_{Na^+} + C_{B^{*-}}\lambda_{B^{*-}} + C_{OH^-}\lambda_{OH^-}$$

$$= C_{NaB^*}\lambda_{Na^+} + C_{NaB^*}(1-\alpha^*)\lambda_{B^*-} + C_{NaB^*}\alpha^*\lambda_{OH}$$

$$\Lambda_{OBS} = (\lambda_{Na^+} + \lambda_{B^*-}) + \alpha^*(\lambda_{OH^-} - \lambda_{B^*-})$$

$$\Lambda_{OBS} = \Lambda_{NaB^*} + \alpha^*(\lambda_{OH^-} - \lambda_{B^*-}) \qquad (1\text{-}58)$$

From Robinson and Stokes equation the conductance of NaB* solution, if it behaves as a strong 1:1 electrolyte, is

$$\Lambda_{NaB^*} = \Lambda^o_{NaB^*} - \frac{(B_1\Lambda^o_{NaB^*} + B_2)\sqrt{I}}{1 + B_3a^o\sqrt{I}}$$

which when substituted in (1-58) gives

$$\Lambda_{OBS} = \Lambda^{o}_{NaB^*} - \frac{(B_1\Lambda^{o}_{NaB^*} + B_2)\sqrt{C}}{1 + B_3a^{o}\sqrt{C}} + \alpha^*(\lambda_{OH^-} - \lambda_{B^{*-}}) \qquad (1-59)$$

Equation (1-59) thus represents the conductance of Sodium Barbital solutions in presence of the products of hydrolysis namely OH^- and B^{*-} ions. The author has utilized equation (1-59) to explain the experimental conductance values in NaB* solutions. The concentration dependence of conductance of OH^- and B^{*-} ions were calculated using equations

$$\lambda_{OH^-} = \lambda^{o}_{OH^-} - \frac{(B_1\lambda^{o}_{OH^-} + \frac{1}{2}B_2)\sqrt{C}}{1 + B_3a^{o}\sqrt{C}}$$

and

$$\lambda_{B^{*-}} = \lambda^{o}_{B^{*-}} - \frac{(B_1\lambda^{o}_{B^{*-}} + \frac{1}{2}B_2)\sqrt{C}}{1 + B_3a^{o}\sqrt{C}}$$

respectively.

1-6 DIFFUSION: BASIC CONCEPTS AND DEFINITIONS.

Diffusion is the term used to describe the macroscopic process by which relative motion takes place between the components of a system. It is an irreversible process which causes transport of material within a system until a final stage of equilibrium is established. Whenever there is a difference of concentration of a solute in different regions of a container holding the solution this process automatically sets in and the phenomenon continues to reduce the concentration difference between different zones of the solution and ceases to operate when the concentration of the solute becomes uniform throughout the solution. Thus diffusion causes a spontaneous flow of solute from higher concentration region to the lower concentration region and that of solvent in the opposite direction.

1-6-1 DEFINITIONS AND LAWS

(a) FLUX OF MATTER, J:

The flux of matter J is defined as the amount of material (in grams or moles) crossing a unit area of a plane placed perpendicular to the direction of flow in unit time.

(b) CONCENTRATION GRADIENT, $\partial c/\partial x$:

The concentration gradient $\frac{\partial c}{\partial x}$ is the rate of the increase in concentration with distance measured in the direction of flow. The direction of flow is usually taken as the positive direction of distance x. Accordingly, if J is expressed in mol $cm^{-2}sec.^{-1}$ and x in cm, C will be expressed in mol cm^{-3}.

(c) DIFFUSION COEFFICIENT, D:

The diffusion coefficient D is defined by the equation

$$J = - D\frac{\partial c}{\partial x} \qquad (1\text{-}60)$$

The partial differential being necessary because C is generally dependent on both time and distance. The negative sign in equation (1-60) is introduced in order to make diffusion coefficient, D, a positive quantity. The quantity $\frac{\partial c}{\partial x}$ is negative because the concentration decreases as the distance increases. Thus diffusion coefficient would have units of $cm^2 sec.^{-1}$.

Another equation which relates the change of concentration with time to the rate of change of flux is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right) \qquad (1\text{-}61)$$

Equation (1-60) and (1-61) are known as Fick's First and Second Laws of Diffusion. The two laws thus summarise D as a constant for a given system; the constancy is, however, not strictly followed and, as a matter of fact, it varies with concentration. The main interest of diffusion studies lies in the variation of diffusion coefficient D with concentration.

The process of diffusion and conductance both involve migration of the ions. In the latter the positive and negative ions move in opposite directions while in diffusion the movement is in the same direction. At infinite dilution the ions move independently of one another while conducting current through the solution. The case with diffusion is, however, entirely different. Both ions must move with the same speed otherwise separation of electrical charge would result. The forces that make the ions move with the same speed are (a) The concentration gradient $\frac{\partial c}{\partial x}$ or more accurately the gradient of chemical potential $\frac{\partial \mu}{\partial x}$ for that ionic species and

(b) The electrical force $Z_i eE$ which results from the tendency of the more mobile ions to move faster than the less mobile ones when a charge separation, on microscopic scale, or a gradient of electrical force $Z_i eE$ is developed. Thus an electrical force $Z_i eE$- where Z_i and e are the valence of ions under consideration and e the electronic charge respectively-causes slower ions to move faster and the faster ones to move slow. The resultant speed of both the ions thus become identical(45). The equality of the speed of ions eliminates the relaxation effect which is associated with the conducting ions.

1-6-2 NERNST-HARTLEY EQUATION.

In order to express the two forces mentioned above, acting on the diffusing ions, in terms of their electrical and physical properties, the following equation has been arrived at (46).

$$D = \frac{(\nu_+ + \nu_-)}{\nu_+|Z_+|} \cdot \frac{\lambda_+^o \lambda_-^o}{\lambda_+^o + \lambda_-^o} \cdot \frac{RT}{F^2}\left(1 + \frac{d\ln f_\pm}{d\ln C}\right) \qquad (1\text{-}62)$$

where ν_+ and ν_- stand for the number of positive and negative ions of valency Z_+ and Z_- respectively produced by one molecule of the electrolyte; λ_+^o and λ_-^o refer to the equivalent conductance of the subscrepted ions at infinite dilution; R, T and F represent the gas constant, absolute temperature and faraday constant respectively. The quantity $f_\pm$ represents the mean activity coefficient at concentration C defined by equation (1-40). The limiting value of diffusion coefficient D^o (at infinite dilution) is given by equation (1-63) when

$$\frac{d\ln f_\pm}{d\ln C} \rightarrow 0 \qquad \text{i.e}$$

$$D^o = \frac{\nu_+ + \nu_-}{\nu_+|Z_+|} \cdot \frac{\lambda_+^o \lambda_-^o}{\lambda_+^o + \lambda_-^o} \cdot \frac{RT}{F^2} \qquad (1\text{-}63)$$

which is an expression derived by Nernst. Using the conditions of electrical neutrality

$$|\nu_+ Z_+| = |\nu_- Z_-|$$

equation (1-62) can be written as

$$D = \frac{|Z_+|+|Z_-|}{|Z_+Z_-|} \cdot \frac{\lambda_+^o\lambda_-^o}{(\lambda_+^o + \lambda_-^o)} \cdot \frac{RT}{F^2} (1 + \frac{d\ln f_\pm}{d\ln c}) \qquad (1-64)$$

From equations (1-62) and (1-63), one gets

$$D = D^o\left(1 + \frac{d\ln f_\pm}{d\ln C}\right) \qquad (1-65)$$

which is known as Nernst-Hartley equation.

Equations (1-62) or (1-64) are composed of two main parts, i.e. the mobility factor

$$\frac{|Z_+|+|Z_-|}{|Z_+Z_-|} \cdot \frac{\lambda_+^o\ \lambda_-^o}{\lambda_+^o + \lambda_-^o} \cdot \frac{RT}{F^2}$$

and the activity factor

$$(1 + \frac{d\ln f_\pm)}{d\ln C}$$

The two factors can be worked out from independent measurements and the equations can be tested.

1-6-3 DIFFUSION COEFFICIENT IN STRONG ELECTROLYTE SOLUTIONS.

In concentrated solutions, considerations must be given to the motion of the solvent and solute molecules. However in very dilute solutions the motion of solvent molecules can be disregarded and the experimental diffusion coefficients can be regarded as describing the motion of the solute particles through a stationary solvent.

The variation of the D with concentration in various 1:1 and 1:2 electrolytes is many times, greater than that of the quantity $D/\left(1 + C \frac{d\ln f_{\pm}}{dc}\right)$. Thus the greater part of the change in D is attributed to the non-ideality in the thermodynamic behaviour which is allowed for by the activity factor. In general, the actual mobilities of the different ions vary slightly with concentration which is mainly due to the interionic effects.

1-6-4 DIFFUSION COEFFICIENT IN WEAK ELECTROLYTE SOLUTIONS.

Let us consider a weak electrolyte HA having α as the degree of dissociation. The concentration of various species present in a C molar solution would be then

$$(H^{+}) = C\alpha;\ (A^{-}) = C\alpha;\ (HA) = C(1-\alpha) \qquad (1\text{-}66)$$

Denoting the observed diffusion coefficient by D, the total flux by J and the stoichiometric concentration by C we get

$$J = -D\frac{dc}{dx} = J_{HA} + J_{A^-} = -D_{HA}\frac{d(HA)}{.dx} - D_{A^-}\frac{d(A^-)}{dx}$$

or

$$D = D_{HA}\frac{d(HA)}{dc} + D_{A^-}\frac{d(A^-)}{dc} \qquad (1\text{-}67)$$

$$D = D_{HA}\frac{d(1-\alpha)C}{dc} + D_{A^-}\frac{d\alpha C}{dC} \qquad (1\text{-}68)$$

$$D = D_{HA}\left(1-\alpha-\frac{Cd\alpha}{dc}\right) + D_{A^-}\left(\alpha + \frac{Cd\alpha}{dc}\right) \qquad (1\text{-}69)$$

Now

$$K_{HA} = \frac{(H^+)(A^-)}{(HA)} = \frac{C\alpha^2}{1-\alpha} \qquad (1\text{-}70)$$

(neglecting activity coefficient) which on differentiating with respect to C gives

$$C\frac{d\alpha}{dc} = \frac{1-\alpha}{2-\alpha} \qquad (1\text{-}71)$$

Putting $C\frac{d\alpha}{dc}$ from equation (1-71) into equation (1-69) we have

$$D = D_{HA}\cdot\frac{2(1-\alpha)}{(2-\alpha)} + D_{A^-}\cdot\frac{\alpha}{2-\alpha} \qquad (1\text{-}72)$$

Equation (1-72) relates the observed diffusion coefficient D to D_{HA} and D_{A^-}. This equation has been used by the author to obtain an extrapolation function[47] for determining the diffusion coefficient of undissociated Barbituric Acid molecules (see chapter III).

1-7 MEASUREMENTS OF DIFFUSION COEFFICIENTS.

Various methods for the determination of diffusion coefficients have been described in the literature[48]. Basically they can be classified into absolute and relative methods. Examples of absolute methods are gouy interference and conductometric methods. Stokes diaphragm cell method is a relative method. The diaphragm cell method has been universally accepted for measuring diffusion coefficients above 0.05M[49]. Although this is a relative method, because it requires calibration with a known solute, it has the great advantage over other absolute methods of being inexpensive and easy to install and calibrate. Furthermore this method can be successfully employed to determine diffusion coefficients at elevated temperatures[50]. Besides, this method is also considered to be capable of yielding diffusion coefficient with a relative precision of 0.2%(51) since this method was employed to study diffusion coefficients of aqueous Barbituric Acid and Sodium Barbital solutions, the theory of this method would be discussed in detail.

1-7-1 THEORY OF DIAPHRAGM CELL METHOD.

The method of determining diffusion coefficient by diaphragm cell was first introduced by Northrup and Anson (52). Later on it underwent modifications by Hartley and Runnicles[53], McBain and Dawson[54], Mouguin and Cathcart[55] and Gordon[56]. Stokes[57], (43) has made important improvements in the theory and practice of this method.

The diaphragm cell, shown in Figure 1-7-1, has two compartments A and B which are separated

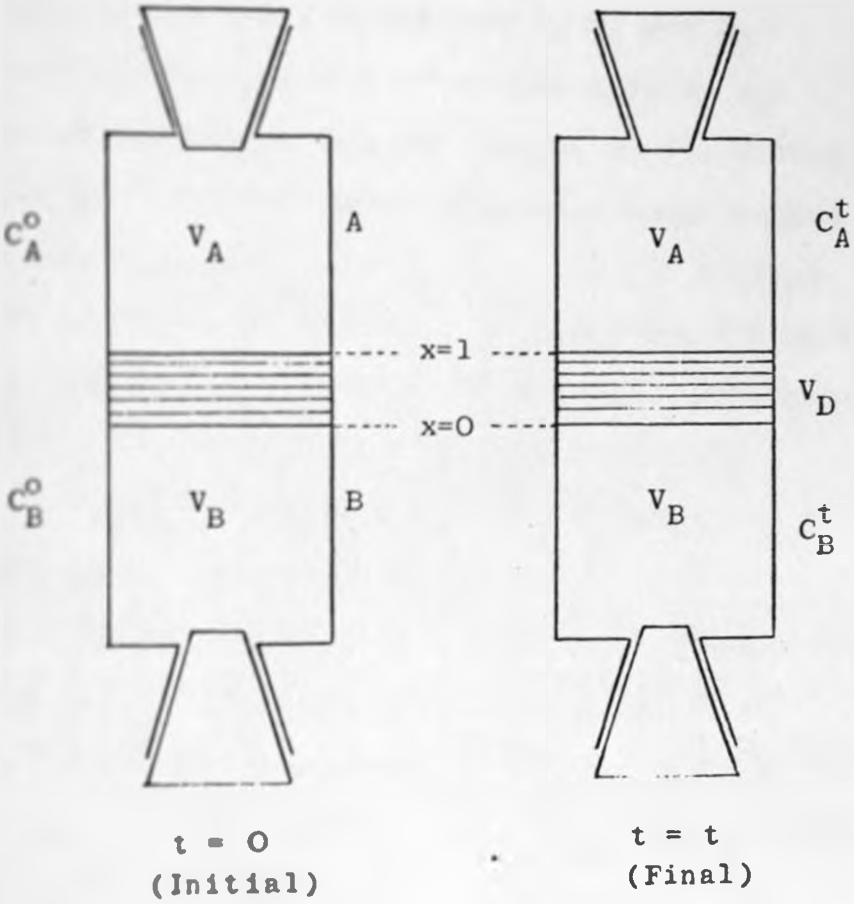


FIGURE I-7-1 GENERAL DIAPHRAGM CELL

by a porous glass disc of number 4 porosity (average size = 15μ). The volume of the two compartments are represented by V_A and V_B respectively and that of porous disc by V_D. Let the effective average length of the diffusion path be L and the total effective cross-section of the diaphragm pores be A. Let the initial concentration of solution in compartment B be C_B^o and that of A be C_A^o. C_B^o is always kept greater than C_A^o to ensure gravitational stability.

Various assumptions(59) are made in developing theory for this method:

(a) the diffusion is without convection and occurs only within the confines of the glass disc,

(b) the solutions in compartment A and B are well stirred so that there is no concentration gradient in either compartment,

(c) at any time t, the flux J is independent of distance x, but only depends on t[to stress this fact, J is represented as J(t)]; and

(d) the Fick's first law describes the diffusion occuring within the disc of the diaphragm cell.

The assumption about the space and time dependence of J is called the "pseudo-steady state". There is no material accumulation in the diaphragm during the time when transport by diffusion is taking place.

Now the rate of change of solute concentrations in the top and bottom compartments are related to the flux J(t) by the following equations[45].

$$dC_A^o = J(t) \frac{A}{\bar{V}_A}$$

$$\frac{dC_B^o}{dt} = -J(t) \frac{A}{\bar{V}_B}$$

Hence

$$\frac{d(C_B^o - C_A^o)}{dt} = J(t) \left[\frac{1}{\bar{V}_B} + \frac{1}{\bar{V}_A} \right] A \qquad (1-73)$$

Now let us define the average value of the differential diffusion coefficient D over the concentration range C_B^o and C_A^o existing at the time considered. This integral diffusion coefficient $\bar{D}$ is also time dependent and let us denote it by $\bar{D}(t)$. Then we have [60]

$$\bar{D}(t) = \frac{1}{C_B^o - C_A^o} \int_{C_A^o}^{C_B^o} D dc \qquad (1-74)$$

$$= - \frac{1}{C_B^o - C_A^o} \int_{x=o}^{L} D(\frac{dc}{dx}) dx \qquad (1-75)$$

$$= \frac{L\ J(t)}{C_B^o - C_A^o} \qquad (1-76)$$

Since $J(t) = -D \frac{dc}{dx}$ is constant at all points within the porous disc at time t, x being the distance of the plane considered from x=0. From equations (1-73) and (1-76) another equation is derived:

$$-\frac{d\ln(C_B^o - C_A^o)}{dt} = \frac{A}{L}\left(\frac{1}{V_B} + \frac{1}{V_A}\right)\bar{D}(t) \qquad (1\text{-}77)$$

Hence integrating between the initial and final conditions shown in figure (1-5-1), we get

$$\ln\frac{C_B^o - C_A^o}{C_B^t - C_A^t} = \frac{A}{L}\left(\frac{1}{V_B} + \frac{1}{V_A}\right)\int_{t=o}^{t=t}\bar{D}(t)dt \qquad (1\text{-}78)$$

Let $\bar{D} = \int_o^t \bar{D}(t)dt$

and $\beta = \frac{A}{L}\left(\frac{1}{V_B} + \frac{1}{V_A}\right)$ = cell constant

the equation (1-78), is thus represented as

$$\bar{D} = \frac{1}{\beta t}\ln\frac{\Delta C^o}{\Delta C^t} \qquad (1\text{-}79)$$

where $\Delta C^o = C_B^o - C_A^o$, and

$\Delta C^t = C_B^t - C_A^t$.

The value of integral diffusion coefficient $\bar{D}$ which is calculated directly from the initial and final solute concentrations in the top and bottom cell compartments, the time t and cell constant β using equation (1-79), is therefore a rather complicated double average of both concentration and time and is called "Diaphragm cell integral coefficient". The integral diffusion coefficient $\bar{D}$ so obtained can be converted into the real or differential diffusion coefficient D by the method described in the following section.

1-7-2 CALCULATION OF DIFFERENTIAL DIFFUSION COEFFICIENT D FROM $\bar{D}$

It has been shown by Gordon[61] that integral diffusion coefficient $\bar{D}$ is related to the true or differential diffusion coefficient D by the equation

$$\bar{D} = \frac{1}{\bar{C}_B - \bar{C}_A} \int_{\bar{C}_A}^{\bar{C}_B} D \, dc \qquad (1\text{-}80)$$

where $\bar{C}_B = \dfrac{C_B^o + C_B^t}{2}$, and

$\bar{C}_A = \dfrac{C_A^o + C_A^t}{2}$

within 0.02%. To compute differential diffusion coefficients at particular concentrations from the $\bar{D}$ values, an analytical expression with arbitrary coefficients is usually assumed for D. If a new integral diffusion coefficient $\bar{D}^o$ is defined which would be found in an experiment of vanishingly short duration with initial concentrations C and zero on the lower and upper sides of diaphragm respectively. Thus from equation (1-80) we get

$$\bar{D}^o = \frac{1}{C}\int_o^C D_{dc} \qquad (1\text{-}81)$$

We will represent $\bar{D}^o(\bar{C}_B)$ and $\bar{D}^o(\bar{C}_A)$ as the values of $\bar{D}^o$ in such a hypothetical experiment with initial concentration $\bar{C}_B$ and $\bar{C}_A$. Under these conditions, we have

$$\bar{D}^o(\bar{C}_B) = \bar{D} - \frac{\bar{C}_A}{\bar{C}_B}\left[\bar{D} - \bar{D}^o(\bar{C}_A)\right] \qquad (1\text{-}82)$$

Thus from the experimental $\bar{D}$ value one can calculate $\bar{D}^o$ for the concentration $(\bar{C}_B)$ provided we know it for the lower concentration (C_A).

Fortunately it has been found that the plots of $\bar{D}^o(\bar{C}_B)$ against $\sqrt{\bar{C}_B}$ and $\bar{D}$ against $\sqrt{C_B^o}$ lie within 1%. Stokes (62) has developed a graphical method of successive approximations which converges rapidly to give excellent results for the differential diffusion coefficients which is done in the following manner.

(a) a plot of $\bar{D}$ against $(C_B^o)^{\frac{1}{2}}$ is constructed and extrapolated to the Nernst limiting value at infinite dilution. From this curve, as a first approximation, $\bar{D}^o$ $(\bar{C}_A)$ is read for each experiment and the values are substituted in equation (1-82). Then $\bar{D}^o$ $(\bar{C}_B)$ values are calculated.

(b) These $\bar{D}^o(\bar{C}_B)$ values are then plotted against $(\bar{C}_B)^{\frac{1}{2}}$ from which, as a second approximation, $\bar{D}^o(\bar{C}_A)$ values are read and again substituted in equation (1-82) to calculate new values of $\bar{D}^o(\bar{C}_B)$ for each run.

(c) The resulting second values of $\bar{D}^o(\bar{C}_B)$ do not make any change if the process is continued and

(d) Finally the $\bar{D}^o(\bar{C}_B)$ values obtained in step (b) are plotted against $(C_B^o)^{\frac{1}{2}}$ to calculate the slope, at each concentration, for the equation

$$D = \bar{D}^o(\bar{C}_B) + \frac{(C_B^o)^{\frac{1}{2}}}{2} \cdot \frac{d\bar{D}^o}{d(C_B^o)^{\frac{1}{2}}} \qquad (1\text{-}83)$$

obtained from the differentiation of equation (1-81). Thus the differential diffusion coefficient D can be worked out. When the slope is read from the graph for each concentration, certain amount of subjectivity is introduced. Since the second factor in equation (1-83) is the product of two factors, subjectivity in the reading of slope will not produce a very pronounced effect on the final value of D.

The author has employed this method to calculate the differential diffusion coefficients D in aqueous Barbituric acid and Sodium Barbital solutions at 25°C.

CHAPTER II

EXPERIMENTAL

2-1 APPARATUS AND EQUIPMENT

2-1-1 THE TANK

Like most irreversible processes, density, viscosity, conductance and diffusion coefficients are both concentration and temperature dependent. As the intention was to study the concentration dependence of these properties in aqueous Barbituric Acid and Sodium Barbital solutions, the temperature was held constant and the measurements were carried out in a thermostatted bath, set at 25^{0}C.

For precise work in viscosity, temperature control should be better than a hundredth of a degree. A change of 0.01^{0}C causes approximately 0.02% change in the viscosity of water;(63) likewise for water and aqueous solutions, the density decreases by 0.03% per degree rise in temperature(64). Refractive indices of liquids and solutions also show a temperature dependence; diffusion coefficients undergo a change of 1% per degree change in temperature.

A thermostatted bath, made in the University Science Workshop, was used in the present work.

The dimensions of the tank were 37 cm wide, 34 cm high and 69 cm long. All the five sides were made of glass which enabled an easy inspection of pyknometer, viscometer and diffusion cell.

The tank was placed on a working bench of convenient height. It was filled with water and maintained at 25°C ± 0.02°C. The temperature fluctuations were monitored on a Beckmann thermometer. In order to compensate for water loss due to evaporation, water was added from time to time.

An additional motor for rotating the diffusion cell was mounted on to a separate steel structure so as to minimise the vibration of the bath liquid and the cell itself. The meniscus adjustment of the volumetric flask, pyknometer, and flow-time in viscosity measurements and inspection of the diffusion cell were done against a light source of 40-watt bulb fixed above the tank at one corner. This facilitated the observations which were otherwise very streneous. The bulb also served to warm the air above the oil-bath used for conductance measurements.

2-1-2 PYKNOMETER.

A flask-type pyknometer was used to determine the density of each Barbituric Acid and Sodium

Barbital solution. The neck of the 25 cm^3 volumetric flask was replaced by a tubing with internal diameter of 3mm. The etch-mark was made very close to the stopper's position. This enabled easy removal of any liquid above the mark.

2-1-3 VISCOMETER

In this work, an Ubbelohde-type (three-necked) all glass viscometer, shown in figure (2-1-3), was used for the determination of viscosities. All the openings had B-10 sockets. It was actually a type of kinematic viscometers. The viscometer was mounted on an iron frame-work and was always held in a vertical position in the thermostatted bath. To prevent the iron frame-work from rusting, it was painted with aluminium paint. The basic operation in the viscometer was to load the bulbs above the capillary with test liquid and allow it to flow through the capillary. The time taken by the liquid to pass from one mark to another was carefully recorded using a digital watch capable of reading 0.01 sec.

The Ubbelohde-type viscometer used had long flared capillaries to minimize kinetic energy losses[66] . Moreover, this viscometer is reputed to eliminate the static and dynamic surface tension

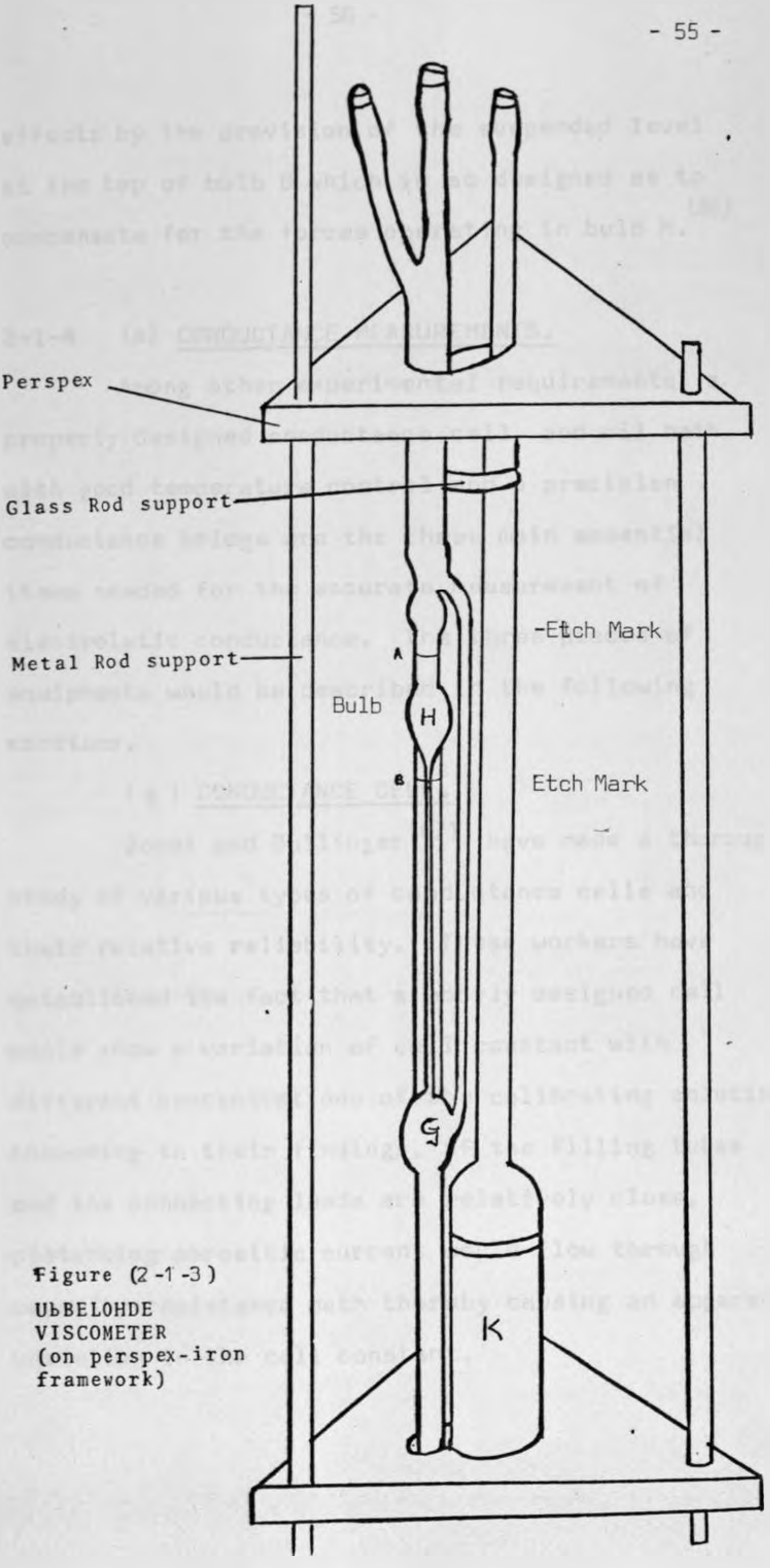


Figure (2-1-3)
UBBELOHDE
VISCOMETER
(on perspex-iron
framework)

effects by the provision of the suspended level, at the top of bulb G which is so designed as to compensate for the forces operating in bulb H.(66)

2-1-4 (a) CONDUCTANCE MEASUREMENTS.

Among other experimental requirements, a properly designed conductance cell, and oil bath with good temperature control and a precision conductance bridge are the three main essential items needed for the accurate measurement of electrolytic conductance. The three pieces of equipments would be described in the following sections.

(b) CONDUCTANCE CELL.

Jones and Bollinger(67) have made a thorough study of various types of conductance cells and their relative reliability. These workers have established the fact that a poorly designed cell would show a variation of cell constant with different concentrations of the calibrating solution. According to their findings, if the filling tubes and the connecting leads are relatively close, disturbing parasitic current would flow through capacity-resistance path thereby causing an apparent variation in the cell constant.

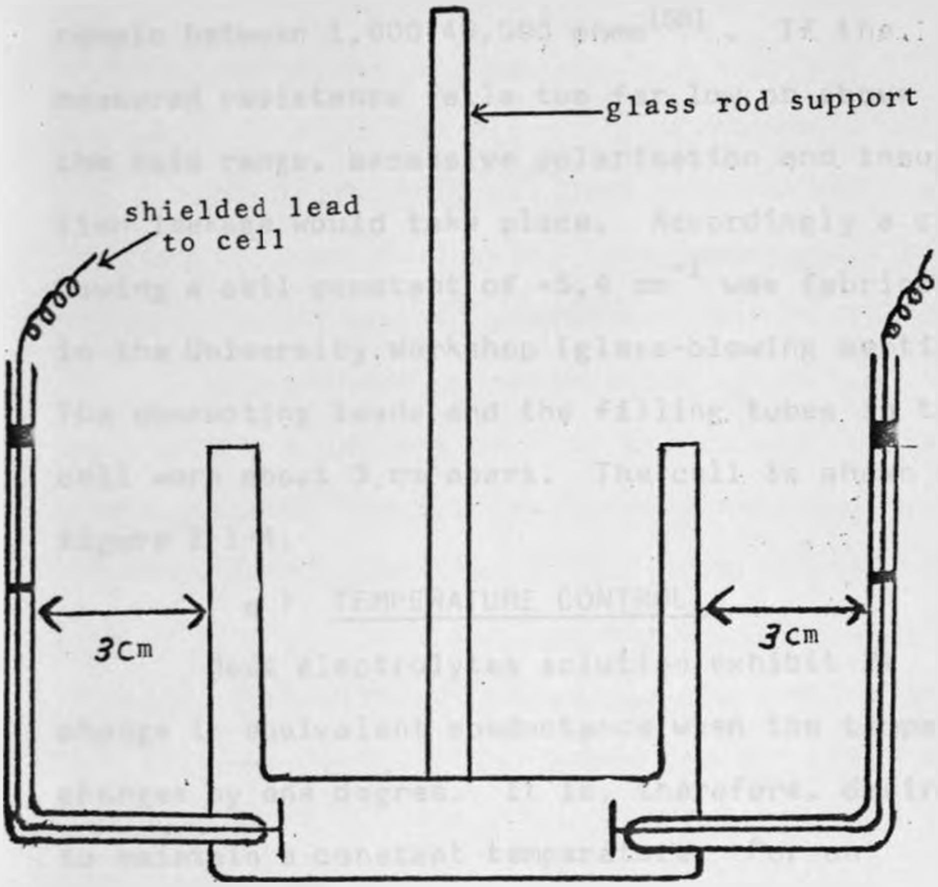


FIGURE (2-1-4): CONDUCTANCE CELL

Selection of a cell with proper cell constant J is another important aspect which demands attention. The chosen cell should have such a cell constant that the measured resistance remain between 1,000-40,000 ohms(68). If the measured resistance falls too far low or above the said range, excessive polarisation and insulation leakage would take place. Accordingly a cell having a cell constant of ≈5.4 cm^{-1} was fabricated in the University Workshop (glass-blowing section). The connecting leads and the filling tubes in this cell were about 3 cm apart. The cell is shown in figure 2-1-4.

(c) TEMPERATURE CONTROL.

Most electrolytes solution exhibit 2% change in equivalent conductance when the temperature changes by one degree. It is, therefore, desirable to maintain a constant temperature. For an accuracy(69) of 0.01% the temperature should be controlled to $\pm 0.005^{\circ}C$. In present experimental set-up, for the conductance measurements, temperature was controlled using THERMIX 1420 from B.BRAUN CO. Ltd.

(d) COPPER CONTAINER.

A copper container in form of an open box of 16 cm long, 8 cm wide and 9 cm high, was fitted at one corner of the waterbath in such a way that it was dipping into water and was exchanging heat from the water. This was filled with non-conducting transformer oil and an additional stirring motor was mounted on to a separate steel structure to stir the oil. The conductance cell was placed inside this oil bath and the temperature fluctuation were monitored. The temperature of this oil tank remained constant within ±0.02°C.

Since the room temperature was below 25°C most of the time, the part of the copper container above the water level, was loosing heat to the surroundings faster than it was absorbing it from the waterbath. This was overcomed by fixing a 40 watts bulb directly above the oil-bath at a convenient height. This warmed the air above the oil bath and facilitated easy observation of pyknometer and viscometer as mentioned earlier.

(e) CONDUCTANCE BRIDGE.

In the present work the conductivity bridge, which was used to measure the resistances of solutions at 25°C was made at the University of Nairobi Science Workshop. The bridge had the following specifications.

Measuring Circuit: A.C. Wheatstone bridge, with Wagner ground and capacitive balance controls.

Range : 0-999,999 ohms measured resistance.

Resistance : Resistance was measured using Decade Resistance Heathkit Model IN-11.

Condenser : Decade condenser Heathkit model IN-21.

Amplifier : The amplifier which was used was made at the University of Nairobi Science Workshop and had a voltage of 9v.

Generator : The type used was an A.F. signal generator Type HTD with a voltage of 4V. and a frequency range of 1000 H_Z to 3000 H_Z.

Detector : General purpose Oscilloscope Heathkit model 10-21.

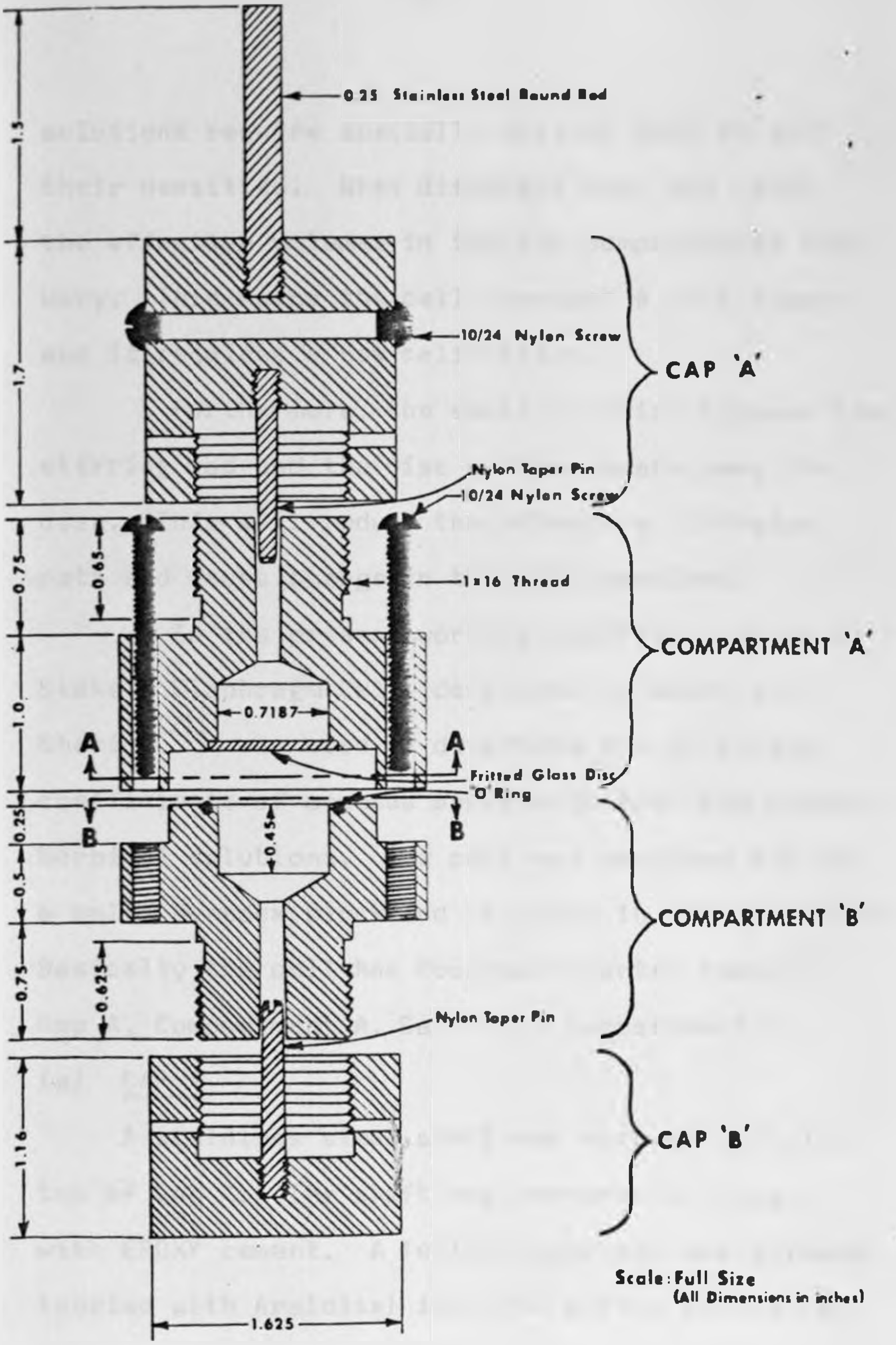
2-1-5 ROTATING DIAPHRAGM CELL (DIFFUSION CELL).

The various boundary conditions described in section (1-5-1) are satisfied by the Stoke's Diaphragm Cell.

In order to ensure that there is no bulk flow in the diffusion cell, the porous disc has to be kept in a horizontal position. Stokes(57) has shown that with the denser solution in the bottom compartment, the amount of bulk flow increases,as an approximately quadratic function of the angle by which the diaphragm departs from the horizontal.

The composition of the solution in each compartment is constantly changing because of the diffusion process and uniformity of concentration in each compartment is achieved by various forms of mechanical stirring. In Stoke's Diaphragm Cell(70) , an external magnet,which induces motion of the glass-encased iron rods, resting lightly on the top and bottom surfaces of the diaphram. The iron rods are slightly shorter than the diameter of the surface which they sweep. The stirring induced also prevent the formation of stagnant layer on the diaphragm disc.

The disadvantage in the use of this original Stoke's Diaphragm Cell is the need of stirring rods. The stirring rods have to be adjusted to a suitable density so that the rod in the bottom compartment floats lightly against the bottom of the disc. The rod in the top compartment sinks lightly on the top of the disc. Therefore experiments with different



Rotating Diffusion Cell
(Vertical Cross Section)

FIGURE (2-1-5)

solutions require specially weighed rods to suit their densities. When different rods are used, the effective volumes in the two compartments also vary. This means the cell constant β will change and it requires a new calibration.

Furthermore, the small friction between the stirring rod and the disc surface wears away the disc. This will reduce the effective diffusion path and cause change in the cell constant.

In the present work, a modified version of Stoke's Diaphragm Cell, developed by Wendt and Shamim,[71] was used to determine the diffusion coefficients of aqueous Barbituric Acid and Sodium Barbital solutions. The cell was machined out of a solid perspex block and is shown in figure (2-1-5). Basically the cell has four main parts, namely Cap A, Compartment A, Cap B and Compartment B.

(a) <u>CAP A</u>

A stainless steel shaft was screwed into the top of Cap A. The shaft was permanently fixed with EPOXY cement. A Teflon taper-pin was screwed (sealed with Araldite) into the bottom of the cap.

(b) <u>COMPARTMENT A</u>

A tapered Teflon pin was machined to fit nicely into a tapered hole of the top of Compartment A to form an air-tight seal between the solution placed in the compartment and water in the thermostatted bath. A G.4 fine porosity (average size = 15μ) fritted glass disc was cemented onto a shoulder in compartment A, with Araldite. A small nylon turbulence-impeller was inserted into the slots. The impeller was placed very close to the surface of the disc.

(c) COMPARTMENT B

An O-ring was placed into the groove made all along the circumference of compartment B. The compartment was fitted with a similar nylon impeller as in compartment A.

The presence of the O-ring immediately around the porous disc separated compartment A from B and sealed off both compartments from the surroundings. The two compartments A and B were clamped together with four brass screws which were never removed once the cell constant β was determined. The impeller in compartment B was almost touching the bottom surface of the disc.

(d) CAP B

A Teflon taper pin in Cap B fitted into the tapered hole in compartment B; and to provide some volume relief, in case of volume changes during diffusion, a small hole was drilled into the end of taper pins.

Each compartment held approximately 2.8 cm^3 of solution. Because of the taper pin arrangements, the closed system was highly reproducible in volume. The cell constant never changed with time. The cell constant should only change with time if the perspex itself changes its dimensions.

The cell was mounted on a motor (voss maldon model, type S30/CB) which rotated it intermittently with varying acceleration in 5 seconds to a sudden stop for the next 5 seconds. The ON-OFF cycles continued throughout the diffusion experiment which lasted for about 4-6 hours. These ON-OFF cycles caused impellers to induce turbulence and consequently stirred very effectively the solutions in the two compartments. Thus the diffusive boundary layers above and below the porous disc were effectively removed.

2-1-6 ON-OFF SWITCH.

A simple electronic device whose electronic circuit is shown in (figure 2-1-6), was used to switch ON or OFF the motor rotating the diffusion cell. The device kept the motor ON for 5 seconds. and OFF for 5 seconds. Consequently, the diffusion cell was also in these intermittent ON-OFF cycles. undergoing 20-25 rotations per second.

TIMER

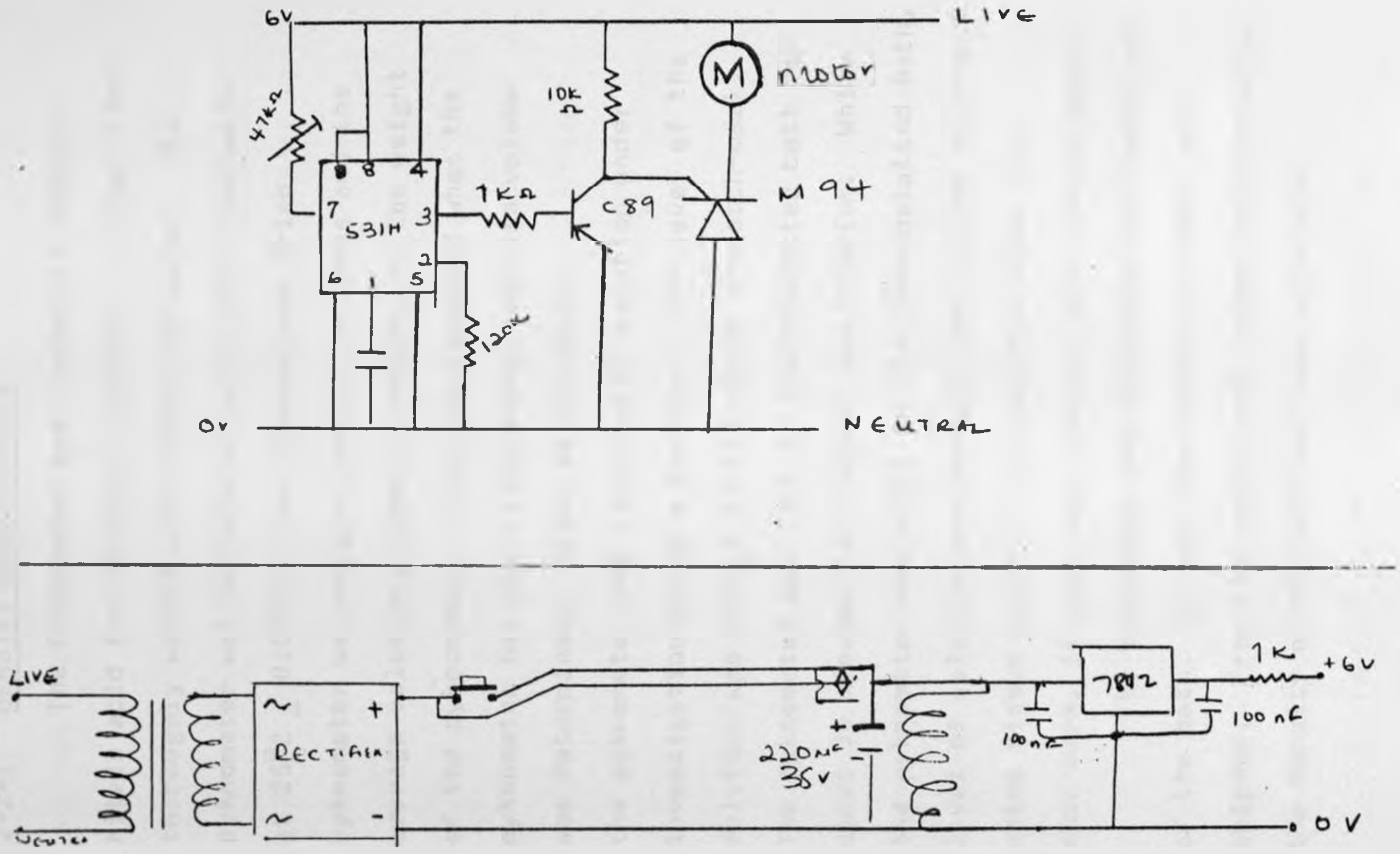


FIGURE (2-1-6)   TIMER

2-2 METHODOLOGY

2-2-1 DENSITY MEASUREMENTS

The Pyknometer was soaked in chromic-Nitric acid for cleaning purposes. It was then thoroughly washed with distilled water. The pyknometer was calibrated using distilled water at $25^{0}C \pm 0.02^{0}C$. The cleaned and dried pyknometer was weighed empty ten times and the average value was taken to represent the weight of the pyknometer. This was repeated when the pyknometer had distilled water, and its volume was determined. After calibration, the pyknometer was filled with solution under investigation using a syringe. The level of the solution was kept a little above the etch-mark. The pyknometer was left in thermostatted bath for about 30 minutes for thermal equilibrium. While the pyknometer was still in the thermostatted bath, level of solution was brought down to the etch-mark using tissue paper. The droplets above the etch-mark, if any, were removed with tissue paper.

The pyknometer was stoppered and taken out of the bath. It was then carefully dried and weighed. From the weight and volume relationship, the density of the solution was calculated.

The above procedure was repeated three times and the weights (pyknometer plus solutions) agreed within ± 0.0005g.

2-2-2 VISCOSITY MEASUREMENTS

The viscometer was soaked in chromic-nitric acid for cleaning purposes. Then it was thoroughly washed with distilled water. For calibration experiments, the viscometer was not dried because distilled water was used as calibrating liquid. For actual test solution, the viscometer was dried by the following procedure.

First, the viscometer was rinsed thoroughly three times with distilled water. Nitrogen gas was then used to dry the viscometer by connecting one of the openings to the Nitrogen gas cylinder for twenty minutes. The viscometer was finally rinsed once with test solution to remove any liquid present on the glass walls.

Certain volume of solution was introduced to the viscometer to bulb K^* through a syringe and was left in thermostatted bath for one hour to attain thermal equilibrium. The solution was then forced above the upper etch-mark with the help of big rubber teat. The solution was then allowed to flow and the flow-time was recorded using an electronic stop-watch capable of reading 1/100th of a second.

Before taking any reading, the liquid was allowed to flow through the capillary twice in order to wet the sides. An average of 10 readings were taken down for each test solution and the extreme variation from the mean was about ± 0.04 seconds.

The viscometer was calibrated using different samples of distilled water and the flow time at $25^{\circ}C \pm 0.02^{\circ}C$ was approximately 454.7 seconds.

Calibration viscosity measurements are shown in Table (2-2-2).

The openings of the viscometer, when not in use, were kept closed with aluminium foil to prevent any dust particles entering the viscometer which adversely affects the flow times.

TABLE (2-2-2): CALIBRATION VISCOSITY MEASUREMENTS WITH DISTILLED WATER AT 25^{o}C.

Water Sample Number	Flow Time t*
1	454.69_8
2	454.68_7
3	454.66_9
4	454.68_2
5	454.67_3
6	454.66_5
7	454.67_7
8	454.66_2

UNITS: t*, Sec.

* an average of 10 readings, last figure resulting from averaging.

Mean = 454.677 sec.

Mean Deviation = 0.009375

Standard Deviation = 0.012964

2-2-3 CONDUCTANCE MEASUREMENTS.

The well washed and well dried cell was rinsed several times with Barbituric Acid or Sodium Barbital solution and was filled with the same. The loaded conductance cell was then placed into the oil bath and was allowed to stand there for half an hour to allow for absorption of acid or salt on the glass and electrode surfaces.

The cell was then taken out and its outer surface washed free of oil using carbon tetrachloride. It was emptied and refilled with fresh solution under test and placed back into the oil bath. Half an hour was allowed for thermal equilibrium before measuring the resistance at a frequence of 3000Hz. The above procedure was repeated to duplicate the experiment and the resistance results agreed within $\pm$ 0.5Ω.

2-2-4 DETERMINATION OF CELL CONSTANT.

The cell constant of a conductance cell was determined by measuring the resistance R of a solution of known specific conductance K. The cell constant J was then calculated from the equation

$$J = \frac{K}{R}$$

Potassium chloride solutions are generally used for this purpose because the specific conductivities of several concentrations of this salt have been very accurately determined(72,73). The Bradshaw demal values(72) at 25°C are most commonly used.

Instead of adopting the tedious method of preparing demal solutions, the author has used an alternative method which allowed the use of KCl solution of any moderate concentration. The method involved analysis(73) of the conductance of an aqueous KCl solution at 25°C by means of the following equation:

$$\Lambda = (\Lambda^{0} + BC + DC \log_{10} C)(1-\nu\sqrt{C}) - 2\sigma\sqrt{C} \qquad (2\text{-}1)$$

where

$\nu = 0.2289$; $\sigma = 30.09$; $\Lambda^{0} = 149.88$;

$B = 153.70$; $D = 32.10$ and C = Molar concentration

To determine the cell constant, the cell was first cleaned with Chromic-Nitric acid mixture followed by several washings with deionized and conductivity water. The cell was then left overnight, in an inverted position for partial drying. The following morning a slow stream of filtered and dried nitrogen gas was passed through the cell to ensure complete dryness. The dried cell was then rinsed several times with KCl solution and filled with the same. The cell was then immersed into the oil-bath, maintained at 25°C ± 0.02°C, and was allowed to equilibrate for half an hour. The measurement was made at a frequency of $3000H_Z$ and the cell was refilled with the same fresh solution, for a duplicate run. The above procedure was repeated for 12-different concentrations.

The measured resistances of various solutions at a frequency of $3000H_Z$ and the resulting cell constants are recorded in Table (2-2-4).

It is evident that the cell showed no trend in the cell constant. The mean value of 5.4144_8 cm^{-1} was adopted for the subsequent calculations.

2-2-5 PLATINIZATION OF ELECTRODES

It has been found that the polarisation effects(74) can be considerably reduced if the platinum electrodes of the conductance cell are given a coating of platinum black. The electrodes of the cell were, therefore, coated.

To platinize the electrodes, the cell was first cleaned with Chromic-Nitric acid mixture, followed by several washing with distilled and

TABLE (2-2-4): CELL CONSTANT OF CONDUCTANCE CELL

C	Λ	Ω* Resistance at 3000 H_Z	J Cell Constant
0.00422_9	144.05_8	8,865.0	5.4007_6
0.00496_5	143.61_2	7,622.0	5.4347_3
0.00593_1	143.08_2	6,411.0	5.4405_1
0.00796_7	142.12_0	4,784.0	5.4167_8
0.00955_9	141.47_2	4,022.0	5.4485_6
0.0150_6	139.68_0	2,587.0	5.4401_4
0.0198_6	138.46_9	1,976.5	5.4340_1
0.0300_9	136.51_9	1,310.5	5.3840_6
0.0400_7	135.12_8	1,000.5	5.4175_4
0.0499_7	134.06_5	806.5	5.4030_4

UNITS: C; mol. l^{-1}, Λ; cm^2 S $equiv^{-1}$

Ω; S, J; cm^{-1}

* an average of 2-readings.

Mean cell constant = 5.4144_8 cm^{-1}

Mean Deviation = 0.021819

Standard Deviation = 0.025500

conductivity water. A solution containing 0.3% chloroplatinic acid and 0.25% lead acetate (75) was placed into the conductance cell and a DC current of ~ 10mA/cm^2 was passed, while reversing the polarity every 30 seconds. After about 15 minutes the electrode surface appeared black and well coated. During the electrodeposition only a moderate stream of gas evolved at the electrodes. Addition of lead acetate improved the adherence of the deposited platinum (76).

After platinization, the cell was thoroughly washed with cleansing mixture, followed by many washings with distilled and conductivity water. The cell, when not in use, was always kept filled with conductivity water and the openings kept covered with tin-foil.

2-2-6 DIFFUSION MEASUREMENTS (71)

First, solutions A (distilled water) and B for diffusion experiment were brought to thermal equilibrium by immersing them into thermostated bath at 25°C ± 0.02°C. Compartment B was then rinsed three times with solution B, the solution was then forced through the porous disc to enter into compartment A with the help of a rubber teat. This process was repeated three times and on the fourth time only half of the solution was forced through. This was done so as to ensure that the disc was free of air and contained only solution B. Finally the compartment B was completely filled with solution B and cap B was slowly screwed into place. The tapered pin in cap B allowed liquid to flow out as the pin advanced to form a tight seal.

Compartment A was rinsed three times with solution A and filled completely with the same solution. Cap A was later screwed into position to isolate solution A from the outside water in the thermostatted bath.

The filled diffusion cell was placed in the water bath. The shaft on Cap A was fastened into the chuck on the stirring motor which had been adjusted previously so that the shaft and the cell were in a vertical position. The porous disc was then assumed to be in a horizontal position. The motor was turned on and intermittent ON-OFF cycles commenced.

After about one hour, the cell was removed from the motor. It was assumed that "pseudo-steady state" had been reached between solution A and B. The porous disc now contained a non-uniform solution instead of uniform solution B initially in the disc.

The cell was wiped;dried and cap B was unscrewed. (Cap A was still in position to ensure that there was no flow of solution from compartment A into B which would destroy concentration gradient in the disc.) solution B was removed with a capillary tube connected to a water-pump.and compartment B was rinsed several times with fresh solution. Finally compartment B was filled with fresh solution B and cap B screwed back slowly in position.

Cap A was then unscrewed and solution withdrawn with a capillary tube connected to a water-pump. This method was found to be more convenient than using a syringe, for withdrawing the solutions from the compartments. Compartment A was rinsed several times with fresh solution A. It was then filled completely with solution A and cap A screwed back in position. The time when the solution A touched the porous disc in the final filling was taken to be t=0, the starting time of diffusion experiment. The cell was then placed back in the thermostatted bath and intermittent ON-OFF cycles commenced.

After about 6 hours for HB and 4 hours for NaB* solutions, the cell was taken out from the thermostatted bath. Cap B was unscrewed and solution B withdrawn using a syringe, and stored in a clean and dried vial. The time when solution B left the porous disc was taken to be t = t, the time at which diffusion ceased. Few drops of solution A were allowed to drain back through the disc, in case any solution in the disc was pulled into compartment A when it was opened. The remaining solution was then withdrawn using a syringe and stored.

Solution from compartment A and B were then analysed. For calibration diffusion experiments, solution A and B of potassium chloride and sodium chloride were analysed by potentiometric method. The same method was used to analyse solution A and B of Barbituric Acid. Analysis of Sodium Barbital was done by measuring the refractive indices of solutions.

For the diffusion experiments, certain experiments were discarded due to formation of air bubbles in either of the two compartments.

2-2-7 DIFFUSION CELL CALIBRATION

Calibration diffusion experiments were done with potassium chloride and sodium chloride solutions. The cell constant β was determined from the known diffusion time t in seconds and the initial and final concentrations of KCl and NaCl solutions in the two compartments.

As mentioned earlier in section (1-3-2) the integral diffusion coefficient $\bar{D}$ is given by the equation

$$\bar{D} = \left[\bar{D}^o(\bar{C}_B) - \frac{\bar{C}_A}{\bar{C}_B} \bar{D}^o(\bar{C}_A) \right] \Bigg/ \left(1 - \frac{\bar{C}_A}{\bar{C}_B} \right) \qquad (2\text{-}2)$$

where

$$\bar{D}^o(C) = \frac{1}{C} \int_o^c D_{dc}$$

$$\bar{C}_B = \frac{C_B^o + C_B^t}{2}$$

$$\bar{C}_A = \frac{C_A^o + C_B^t}{2}$$

The cell constant can be calculated from the diaphragm cell equation

$$\beta = \frac{1}{\bar{D}t} \ln \frac{\Delta C^o}{\Delta C^t} \qquad (2\text{-}3)$$

To calculate the values of $\bar{D}^o(\bar{C}_B)$ and $\bar{D}^o(\bar{C}_A)$, for equation (2-2), of KCl and NaCl solutions, plots of $\bar{D}^o$ against C were made from literature values of D and are shown in figure (2-2-7a) and (2-2-7b) respectively.(77,78) Apart from using the graph directly, in case of KCl one can use the values of $\bar{D}^o_{ci}$ given by Mills and Woolf[79] (table 2-2-7a) which are also obtained from integration of a smooth curve fitted to the values for D. The assumption being made here is that, between two very close concentration values e.g. 0.01M and 0.02M and 0.04M and 0.05M the small portion of the graph is linear. Hence interpolation can be used to get the $\bar{D}^o_{ci}$ values. The author has used this method in case of KCl and used the graph in figure (2-2-7b) for NaCl.

The relevant data and the resulting cell constants are recorded in tables (2-2-7b) and (2-2-7c).

The excellent agreement of β obtained from two different systems indicated the reproducibility of volumes V_A and V_B of the cell, steady-state condition within the disc, alignment, the titration method used for analysing the solutions and the methods used for calculating the $\bar{D}^o_{ci}$ values.
$\beta = 3.66066 \text{ cm}^{-2}$, corresponding to average value of KCl and NaCl experiments, was adopted for subsequent calculations in HB and HB* solutions.

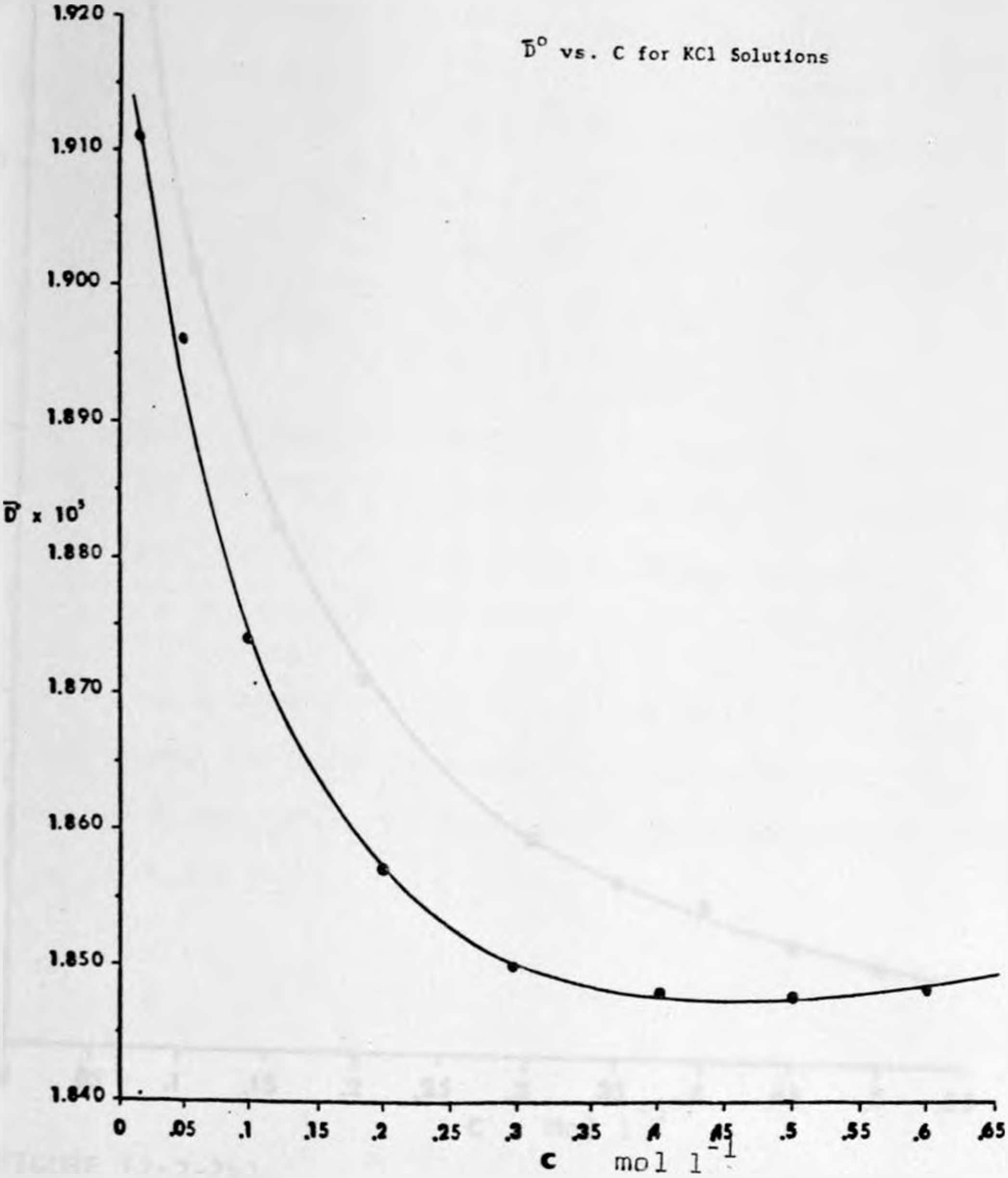

D̄° vs. C for KCl Solutions
D̄° x 10⁵
1.920
1.910
1.900
1.890
1.880
1.870
1.860
1.850
1.840
0
.05
.1
.15
.2
.25
.3
.35
.4
.45
.5
.55
.6
.65
C mol l⁻¹

FIGURE (2-2-7a)

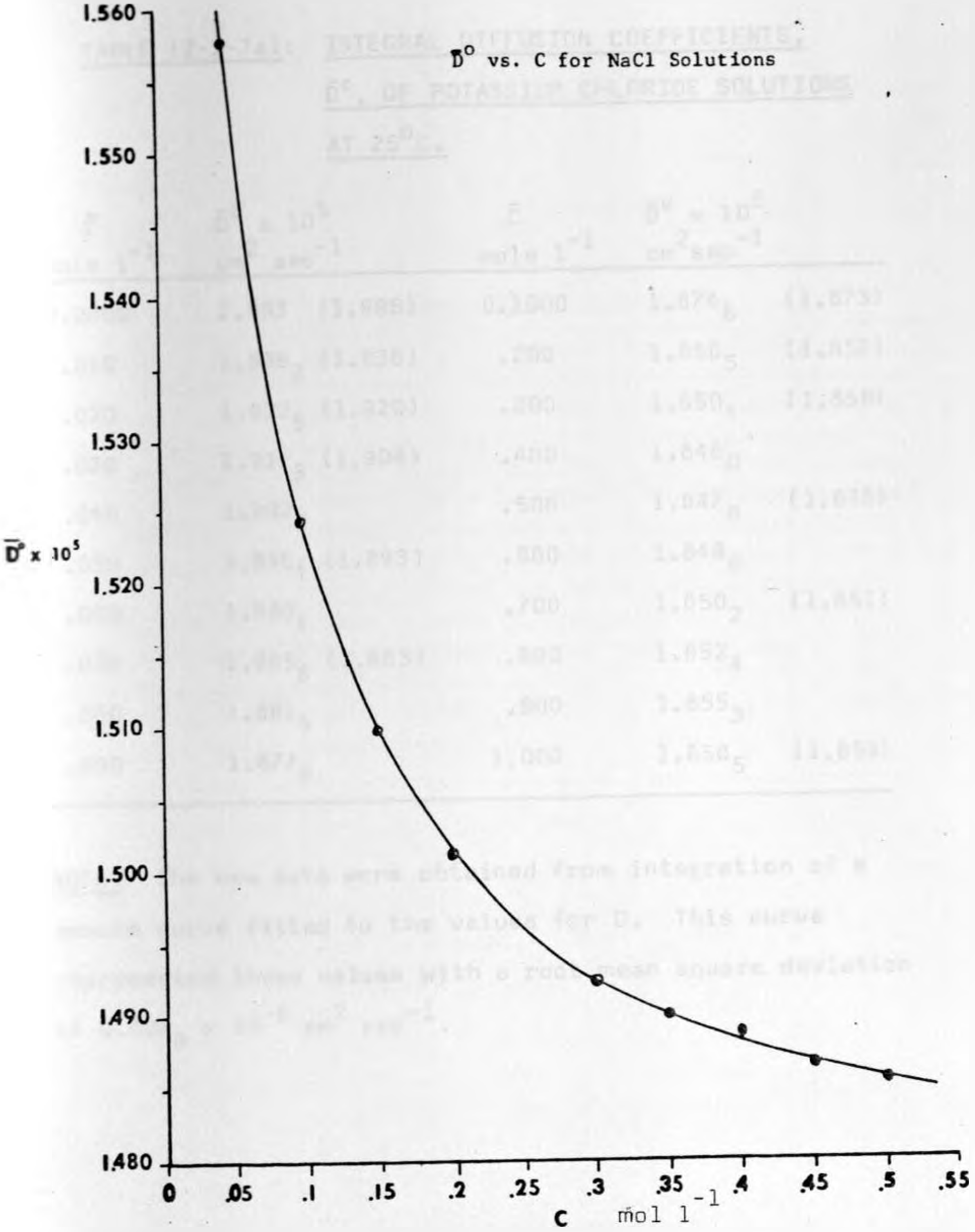

D° vs. C for NaCl Solutions
D° x 10⁵
1.560
1.550
1.540
1.530
1.520
1.510
1.500
1.490
1.480
0
.05
.1
.15
.2
.25
.3
.35
.4
.45
.5
.55
C mol l⁻¹

FIGURE (2-2-7b)

TABLE (2-2-7a): INTEGRAL DIFFUSION COEFFICIENTS, $\bar{D}^o$, OF POTASSIUM CHLORIDE SOLUTIONS AT 25^{o}C.

$\bar{C}$ mole l^{-1}	$\bar{D}^o \times 10^5$ cm^2 sec^{-1}		$\bar{C}$ mole l^{-1}	$\bar{D}^o \times 10^5$ cm^{2}sec^{-1}	
0.0000	1.993	(1.996)	0.1000	1.874_6	(1.873)
.010	1.939_2	(1.938)	.200	1.856_5	(1.857)
.020	1.922_5	(1.920)	.300	1.850_1	(1.850)
.030	1.911_3	(1.908)	.400	1.848_0	
.040	1.902_9		.500	1.847_8	(1.848)
.050	1.896_1	(1.893)	.600	1.848_6	
.060	1.890_4		.700	1.850_2	(1.851)
.070	1.885_6	(1.883)	.800	1.852_4	
.080	1.881_5		.900	1.855_3	
.090	1.877_8		1.000	1.858_5	(1.859)

<u>NOTE:</u> The new data were obtained from integration of a smooth curve fitted to the values for D. This curve represented those values with a root mean square deviation of $0.001_9 \times 10^{-5}$ cm^2 sec^{-1}.

TABLE (2-2-7b): CELL CONSTANT β FROM KCl SOLUTIONS

t	C_B^o	C_A^o	$\bar{C}_B$	$\bar{C}_A$	ΔC^t	$\bar{D}\times10^5$	β
14496	0.0499_6	0.00000	0.04418	0.01003	0.01834	1.8886	3.6604_9
18117	0.0499_6	0.00000	0.04289	0.01078	0.01428	1.8885	3.6603_3
18076	0.0499_6	0.00000	0.04289	0.01075	0.01432	1.8885	3.6604_9
16424	0.0499_6	0.00000	0.04323	0.01025	0.01605	1.8888	3.6603_9
14758	0.0503_7	0.00000	0.04414	0.00988	0.01816	1.8886	3.6602_2
10850	0.0503_7	0.00000	0.04515	0.00808	0.02379	1.8885	3.6609_2
18472	0.0503_7	0.00000	0.04315	0.01095	0.01405	1.8883	3.6604_0
10942	0.0503_7	0.00000	0.04506	0.00804	0.02364	1.8886	3.6605_5
13670	0.0503_7	0.00000	0.04443	0.00948	0.01958	1.8885	3.6601_1
7927	0.0500_8	0.00000	0.04624	0.00671	0.02895	1.8889	3.6602_0
21753	0.0500_8	0.00000	0.04228	0.01167	0.01114	1.8879	3.6600_2
21921	0.0500_8	0.00000	0.04227	0.01172	0.01101	1.8880	3.6601_4

UNITS: t, sec, C_B^o, C_A^o, $\bar{C}_B$, $\bar{C}_A$, ΔC^t, mol. l^{-1},

$\bar{D}$, $cm^2\ sec^{-1}$, β, cm^{-2}

Mean β value = $3.6603_6\ cm^{-2}$

Mean deviation = 0.00000

Standard deviation = 5.48×10^{-4}

TABLE (2-2-7c): CELL CONSTANT β FROM NaCl SOLUTIONS

t	C_B^o	C_A^o	$\bar{C}_B$	$\bar{C}_A$	ΔC^t	$\bar{D} \times 10^5$	β
18051	0.0514_3	0.00000	0.04510	0.01002	0.01880	1.5221	3.6627_8
21747	0.0514_3	0.00000	0.04425	0.01092	0.01533	1.5209	3.6595_9
18094	0.0514_3	0.00000	0.04507	0.00998	0.01875	1.5221	3.6637_5
22682	0.0514_3	0.00000	0.04418	0.01124	0.01454	1.5217	3.6601_8
14640	0.0514_3	0.00000	0.04581	0.00876	0.02274	1.5230	3.6601_6
14690	0.0514_3	0.00000	0.04612	0.00906	0.02269	1.5223	3.6592_2

UNITS: t, sec, C_B^o, C_A^o, $\bar{C}_B$, $\bar{C}_A$, ΔC^t, mol l^{-1}

$\bar{D}$, $cm^2 sec^{-1}$, β, cm^{-2}.

Mean = 3.6609_5 cm^{-2}

Mean deviation = 3.333×10^{-6}

Standard deviation = 1.696×10^{-3}

Accepted cell constant value is the average value of KCl and NaCl. = 3.6607 cm^{-2}.

2-2-8 POTENTIOMETRIC TITRATION

The concentrations of KCl, NaCl and HB solutions at the end of each diffusion experiment from compartment A and B were analysed potentiometrically. For cell calibration diffusion runs with KCl and NaCl solutions, the solutions were titrated against $AgNO_3$ solution using silver as the working and glass as the reference electrode. The two solutions were electrically connected by • potassium nitrate agar salt bridge. The titration cell is shown in figure (2-2-5). The potentiometer used was Radiometer Copenhagen pH-meter 22.

An A-grade milliburette of 5-ml capacity and a 1-ml calibrated pipette were used to read volumes of silver nitrate, KCl and NaCl solutions respectively. For all the solutions, duplicate titrations were carried out to check reproducibility of the titrations. The reproducibility of the titrations was within 0.5%. The end-point was determined by constructing differential plots.

For HB diffusion runs the solutions were titrated against Potassium Hydroxide which was standardized against succinic acid. While carrying out potentiometric titrations a few drops of phenophthalene were added to the solution mixture to act as a guide to the end-point of titration.

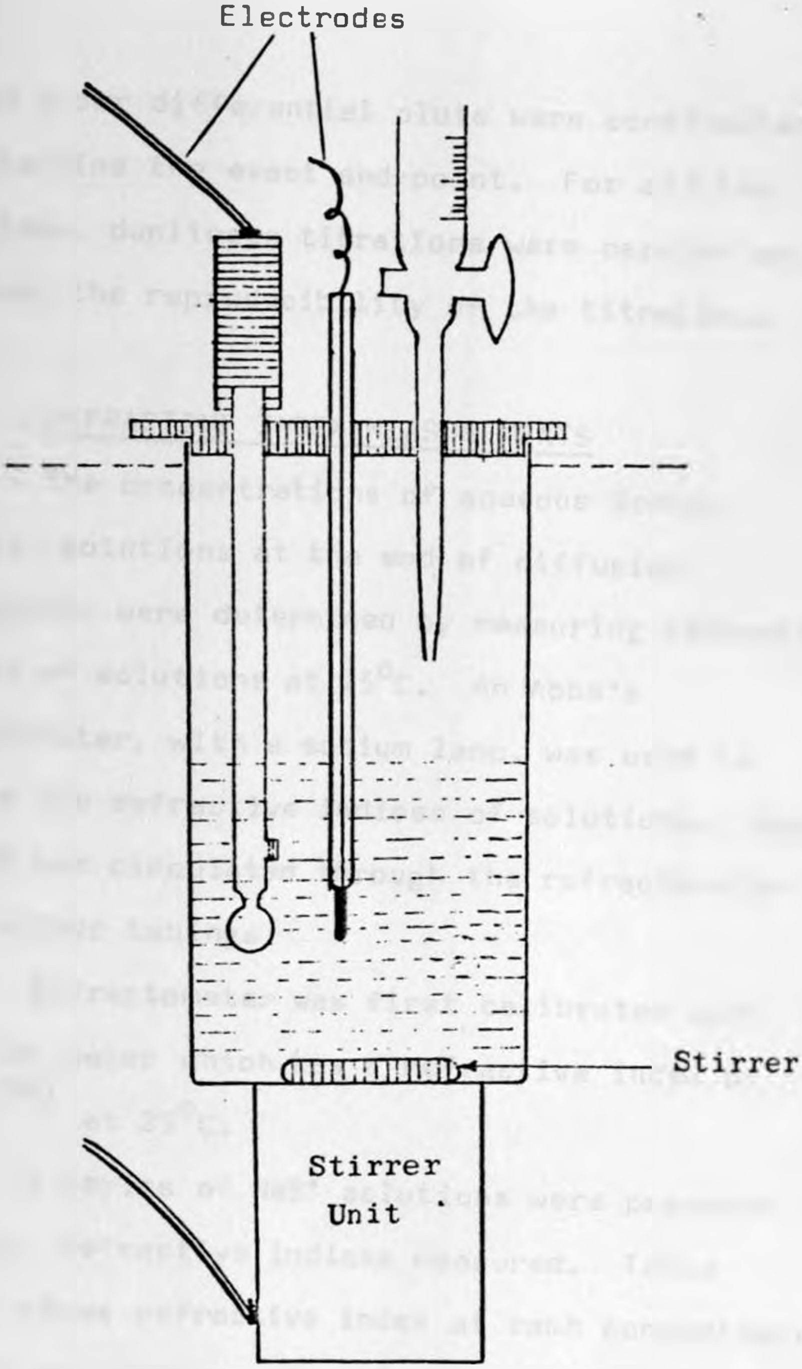


FIGURE (2-2-5) TITRATION CELL

Second order differential plots were constructed to determine the exact end-point. For all the solutions, duplicate titrations were carried out to check the reproducibility of the titrations.

2-2-9 REFRACTIVE INDEX MEASUREMENTS

The concentrations of aqueous Sodium Barbital solutions at the end of diffusion experiments were determined by measuring refractive indices of solutions at 25°C. An Abbe's refractometer, with a sodium lamp, was used to measure the refractive indices of solutions. Water at 25°C was circulated through the refractometer using rubber tubings.

Refractometer was first calibrated with distilled water which has a refractive index of 1.3325 (80) at 25°C.

A series of NaB* solutions were prepared and their refractive indices measured. Table (2-2-9) shows refractive index at each concentration which is an average value of four readings. The refractometer mark was approached from the bottom and from the top, this gave two readings. The process was repeated with a fresh drop of solution. The data was used to construct a plot between

TABLE (2-2-9): CALIBRATION REFRACTIVE INDEX MEASUREMENTS OF AQUEOUS SODIUM BARBITAL SOLUTIONS AT 25°C

C	η_{cal}	η^*_{obs}	$\eta_{cal} - \eta^*_{obs}$
0.000000	1.33245	1.33248	-0.00005
0.049803	1.33430	1.33425	+0.00005
0.052348	1.33439	1.33431	+0.00008
0.100155	1.33616	1.33624	-0.00008
0.103486	1.33628	1.33625	+0.00003
0.200199	1.33986	1.33985	+0.00001
0.201073	1.33989	1.33988	+0.00001
0.399251	1.34722	1.34732	-0.00010
0.400334	1.34726	1.34735	-0.00009
0.600081	1.35466	1.35458	+0.00008
0.603126	1.35477	1.35483	-0.00006
0.799283	1.36203	1.36198	+0.00005
0.800868	1.36208	1.36217	-0.00009

UNITS: C, mol litre

η^*_{obs} is an average of 4 readings.

the last figure resulting from the averaging

THE INTERCEPT = 1.3325

THE GRADIENT = 3.70×10^{-2}

THE CORRELATION COEFFICIENT = 0.99955

$\eta_{cal} = 0.037000C + 1.3325$

refractive indices and concentration, which turned out to be a straight line. The intercept and slope were used to obtain the following analytical expression;

$$\eta = 3.700031 \times 10^{-2}C + 1.332452 \qquad (2\text{-}4)$$

The equation connects observed refractive indices n to the molar concentration C. The expression produced η values which were in excellent agreement with the experimental figures. The last column of table (2-2-9) depicts the difference between the calculated and observed n values. The intercept and slope were obtained using a BBC micro-computer. The programme is attached in the appendix 1.

The refractive indices were measured within an accuracy of $\pm$ 0.0002. The last place in refractive index, i.e. 0.0001 corresponds to 2.7027×10^{-3} mol l^{-1}. The concentration derived from equation (2-4) was within $\pm$ 1.18×10^{-4} mol l^{-1}. When calculating the value of $\bar{D}$ from equation (2-3), refractive indices values were used directly as shown below, instead of calculating the concentrations of NaB* solutions at the end of diffusion experiments.

$$\bar{D} = \frac{1}{\beta t} \ln \frac{\Delta C^{o}}{\Delta C^{t}}$$

$$\Delta C^{t} = \frac{n_D^{C_t^B} - n_D^{C_t^A}}{\theta} \qquad \Delta C^{o} = \frac{n_D^{C^{o}} - C}{\theta}$$

$$\bar{D} = \frac{1}{\beta t} \ln \frac{n_D^{C^{o}} - C}{n_D^{C_t^B} - n_D^{C_t^A}}$$

where

$n_D^{C_t^B}$ = refractive index of solution from compartment B after time t.

$n_D^{C_t^A}$ = refractive index of solution from compartment A after time t.

$n_D^{C^{o}}$ = refractive index of solution initialy.

θ = 3.700031×10^{-2} the gradient from equation (2-4).

For all the diffusion runs the procedure described above were repeated to duplicate the experiments.

2-2-10 STANDARDIZING POTASSIUM HYDROXIDE USING SUCCINIC ACID.

The concentration of KOH used in determining, the final concentrations of HB at the end of each diffusion run was determined potentiometrically. The solution of succinic acid was titrated against KOH solution, using glass electrode as the working electrode and silver-silver chloride electrode as the reference electrode (81). The arrangement of titration was described in section (2-2-8). The end-point was determined by constructing a 2nd order differential plot. An average of four titrations were carried out and the volume of KOH used in titration determined. Having known the volumes of KOH and succinic acid plus the concentration of succinic acid, the concentration of KOH was calculated.

2-3 CHEMICALS: PURIFICATION AND SOLUTION PREPARATION.

2-3-1 DISTILLED WATER.

Distilled water was prepared by distilling tap-water in an all glass apparatus produced commercially for this purpose. Distilled water was stored in two litre volumetric flasks.

2-3-2 POTASSIUM CHLORIDE.

B.D.H. A.R grade potassium chloride was dried for 140 hours at 90°C in a temperature controlled oven. The bottle was removed for shaking at least once a day to remove any trapped water vapours and to powder the KCl lumps.

2-3-3 SODIUM CHLORIDE.

B.D.H A.R grade sodium chloride was dried for 140 hours at 90°C in a temperature controlled oven. The bottle was removed for shaking at least once a day to remove any trapped vapours and to powder the lumps if there were any.

2-3-4 SILVER NITRATE.

B.D.H. A.R grade silver nitrate was used without any purification.

2-3-5 POTASSIUM HYDROXIDE.

B.D.H. A.R grade potassium hydroxide was used without any purification.

2-3-6 SUCCINIC ACID.

B.D.H. A.R grade succinic acid was dried over silica gel in a vacuum desiccator and was used as primary standard.

2-3-7 BARBITURIC ACID.

B.D.H. A.R grade barbituric acid was dried for 30 hours at 90°C in a temperature controlled oven. Shaking of the acid was done from time to time to remove any trapped vapours and to break the lumpy precis of acid if there were any.

2-3-8 SODIUM BARBITAL.

B.D.H. A.R grade sodium barbital was dried for 30 hours at 90^{o}C in a temperature controlled oven.. Shaking of the salt was done occasionally to remove any trapped vapour. The dried salt was powdery and free of lumps.

All the above mentioned chemicals were allowed to cool to room temperature and dried over silica gel in a vacuum desiccator. The chemicals after use were returned to the vaccum desiccator.

2-3-9 ETHANOL.

A.R. grade ethanol was used, without any purification, for cleaning the prism of the refractometer.

2-3-10 PREPARATION OF SOLUTION.

(a) KCl SOLUTION.

Solutions of potassium chloride were prepared by weighing B.D.H. A.R grade potassium chloride and transferring into a calibrated volumetric flask. The solutions were made up at 25^{o}C.

(b) SILVER NITRATE.

Solution of silver nitrate was prepared by weighing dried B.D.H. A.R grade silver nitrate and transferring into a calibrated volumetric flask. The solution were made up at 25°C, and stored in a coloured bottle.

(c) SODIUM CHLORIDE.

Solutions of sodium chloride were prepared by weighing B.D.H. A.R grade sodium chloride and transferring into a calibrated volumetric flask. The solutions were made up at 25°C.

(d) BARBITURIC ACID.

Solutions of barbituric acid were prepared by weighing B.D.H. A.R grade barbituric acid and transferring into a calibrated volumetric flask. The solutions were made up at 25°C.

(e) SODIUM BARBITAL.

Solutions of sodium barbital were prepared by weighing B.D.H. A.R grade sodium barbital and transferring it very carefully into a calibrated volumetric flask. The weighing bottle must be wiped dry by use of tissue paper, and the funnel used to transfer the salt must be big enough so that the salt is poured to the neck of the funnel, so as to prevent any of the salt particles from blowing away. This is because the dry salt itself is so light and fine that it adheres to any vessel used in weighing. This was overcomed as indicated above by wipping the dry vessel with tissue paper, so that the amount sticking is minimal. Since the weights are determined by difference of weights, the amount sticking caused no harm.

The solutions were made up at 25°C.

(f) SUCCINIC ACID.

Solutions of succinic acid were prepared by weighing B.D.H. A.R grade succinic acid and transferring into a calibrated volumetric flask. The solutions were made up at 25°C.

(g) POTASSIUM HYDROXIDE.

A roughly weighed amount of KOH was dissolved in distilled water and was stored in a two litre coloured bottle. Soda-lime guard tube was used to protect the solution from atmospheric carbon dioxide. Concentration of the solution so prepared was determined by potentiometric titration.

Although it was easier to prepare carbonated free NaOH solutions, KOH solutions were prepared because latter gave less electrode error (82) during potentiometric titrations.

2-3-11 CALIBRATION OF MEASURING FLASKS.

The commercially available measuring flasks of high grade are sufficiently accurate, for precise work, however, calibration of flasks is still required. When working at a temperature higher than that at which the flask had been calibrated by the makers the necessity of calibration becomes even more important.

Three measuring flasks of 250 ml each were calibrated, for the purpose of identification different marks were etched on different flasks. To calibrate a flask, it was thoroughly cleaned using chromic-nitric acid cleansing mixture followed by several rinsings with distilled water. The flask was then filled with air-free distilled water and was equilibrated in a constant temperature bath, for an hour. After the flask had attained the temperature of the bath the meniscus was brought upto the calibration mark with the help of a 1 ml pipette. Any drop of water sticking to the neck above the calibration mark was removed by rapping a tissue paper on a glass rod and inserting it into the neck so as to absorb the sticking droplet.

The flask was then weighed and the exact volume calculated by dividing the weight of water in the flask by the density of water at 25.00°C. The density of water[83] at 25.00°C was taken as 0.99707 g ml^{-1}. The weight of water, in the flask, was determined by first weighing a dried empty flask, which was cooled to room temperature while in a desiccator containing silica gel. The flask was then weighed with distilled water. The difference of the two gave the weight of water.

CHAPTER III

3-1 RESULTS AND DISCUSSION

3-2 DENSITY RESULTS.

The density results of aqueous Barbituric acid and Sodium Barbital solutions are shown in table (3-2-1) and table (3-2-2) respectively and the concentration dependence of densities in figures (3-2-1) and (3-2-2) respectively. The densities of the HB solutions in the concentration range 0.0060-0.08M are given by the empirical equation.

$$\rho = 0.007242 + 0.055032C \qquad (3\text{-}1)$$

with an average deviation of $\pm 3 \times 10^{-5}$ g cm^{-3}, and in case of NaB* solutions [0.01-050M] by

$$\rho = 0.997044 + 0.078342C \qquad (3\text{-}2)$$

the average deviation in case being $\pm 2 \times 10^{-5}$ g^{-} cm^{-3}. where C stands for concentration in mole l^{-1} in both equations (3-1) and (3-2).

TABLE (3-2-1): APPARENT AND PARTIAL MOLAL VOLUME OF BARBITURIC ACID FROM DENSITY MEASUREMENTS.

C	m	ρ	V	ϕ	$\bar{V}$
0.00640	0.00642	0.99754	1003.29	54.52	64.01
0.01284	0.01288	0.99795	1003.71	59.90	66.38
0.02560	0.02568	0.99867	1004.62	65.60	69.70
0.03501	0.03511	0.99920	1005.31	67.40	71.63
0.04994	0.05009	1.00000	1006.41	69.29	74.22
0.0511	0.05134	1.00011	1006.47	68.76	74.42
0.05802	0.05819	1.00045	1007.00	69.78	75.46
0.06304	0.06322	1.00069	1007.40	70.54	76.18
0.07998	0.08021	1.00159	1008.67	71.39	78.44

UNITS: C, mol l^{-1}, m, mol kg^{-1}, ρ, gcm^{-3}, V, cm^3, ϕ, $cm^3\ mol^{-1}$, $\bar{V}$, $cm^3\ mol^{-1}$

TABLE (3-2-2): APPARENT AND PARTIAL MOLAL VOLUME OF SODIUM BARBITAL FROM DENSITY MEASUREMENTS.

C	m	ρ	V	ϕ	$\bar{V}$
0.01003	0.01006	0.99784	1004.25	129.84	129.32
0.01993	0.01999	0.99860	1005.53	129.58	128.67
0.02977	0.02985	0.99936	1006.80	129.30	128.18
0.03994	0.04006	1.00016	1008.09	128.57	127.75
0.05002	0.05017	1.00094	1009.39	128.65	127.38
0.07014	0.07035	1.00253	1011.95	128.06	126.73
0.09988	0.10018	1.00491	1015.67	127.08	125.93
0.13991	0.14032	1.00797	1020.79	127.21	125.02
0.20016	0.20075	1.01274	1028.29	126.28	123.87
0.29435	0.29522	1.02023	1039.84	124.99	122.38
0.40176	0.40294	1.02846	1053.11	124.50	120.94
0.50005	0.50152	1.03620	1064.86	123.47	119.79

UNITS: C, $\mathrm{mol\ l^{-1}}$; m, $\mathrm{mol\ kg^{-1}}$; ρ, $\mathrm{g\ cm^{-3}}$;
V, $\mathrm{cm^3}$; ϕ, $\mathrm{cm^3\ mol^{-1}}$, $\bar{V}$, $\mathrm{cm^3\ mol^{-1}}$

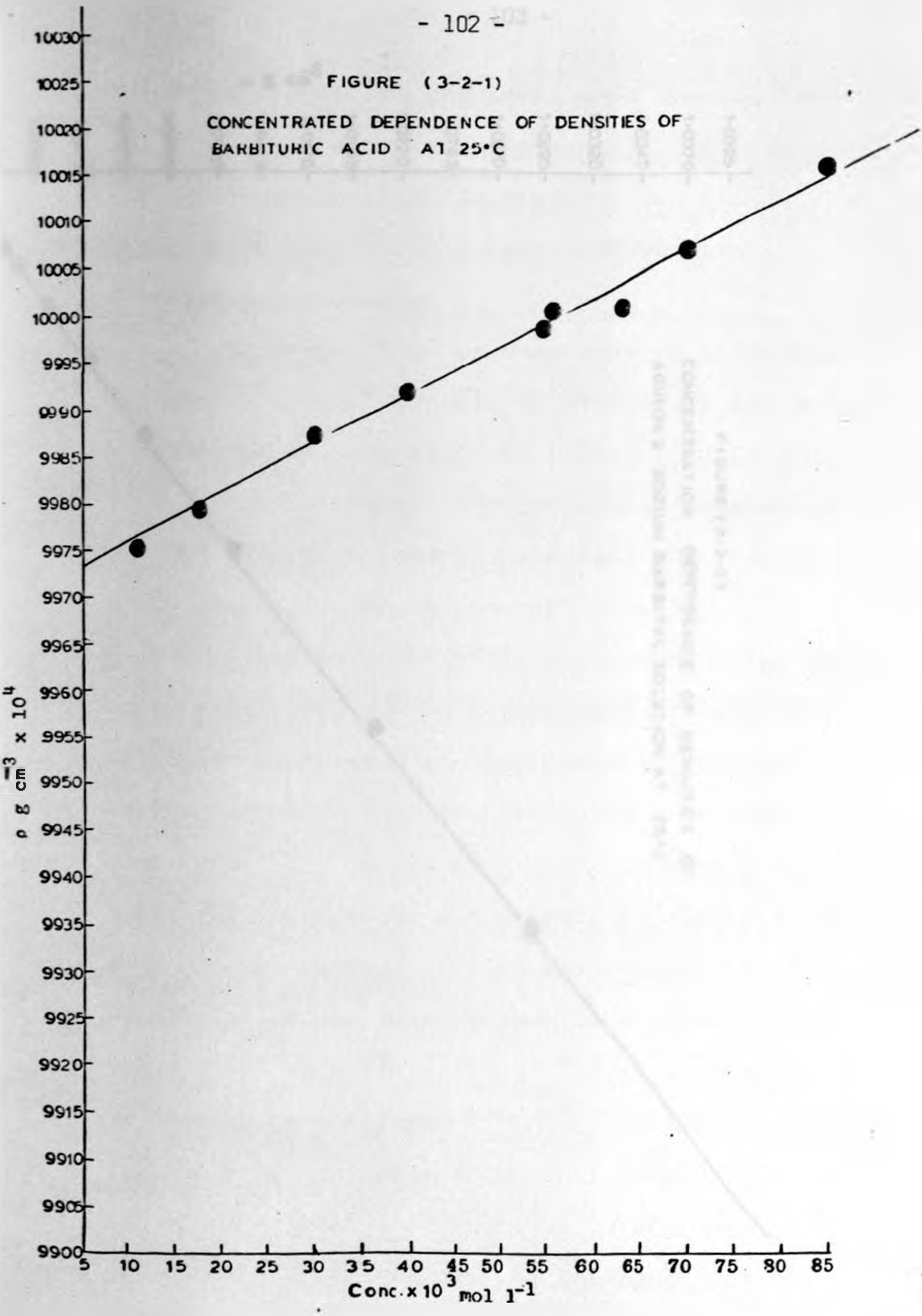


FIGURE (3-2-1)

CONCENTRATED DEPENDENCE OF DENSITIES OF BARBITURIC ACID AT 25°C

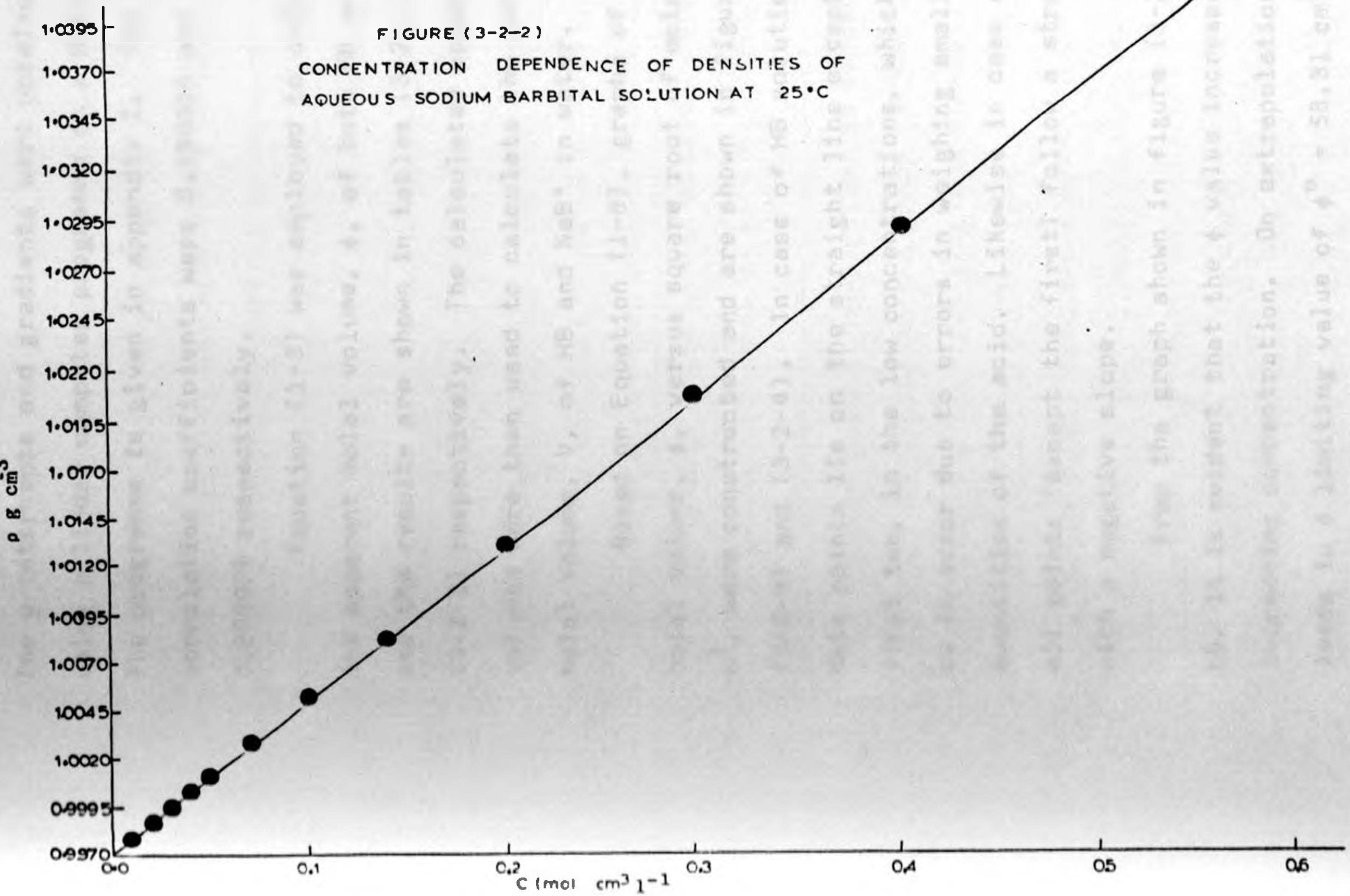


FIGURE (3-2-2)

CONCENTRATION DEPENDENCE OF DENSITIES OF AQUEOUS SODIUM BARBITAL SOLUTION AT 25°C

The y-intercepts and gradients were obtained by using a linear computer programme on a BBC-computer. The programme is given in appendix I. The correlation coefficients were 0.999964 and 0.999926 respectively.

Equation (1-3) was employed to calculate the apparent molal volume, ϕ, of both HB and NaB* and the results are shown in tables (3-2-1) and (3-2-2) respectively. The calculated apparent molal volumes were then used to calculate the partial molal volume, V, of HB and NaB* in water.

Based on Equation (1-8), graphs of apparent molal volume, ϕ, versus square root of molality, $m^{\frac{1}{2}}$, were constructed and are shown in figures (3-2-3) and (3-2-4). In case of HB solutions all data points lie on the straight line except the first two, in the low concentrations, which seem to be in error due to errors in weighing small quantities of the acid. Likewise in case of NaB* all points (except the first) follow a straight line with a negative slope.

From the graph shown in figure (3-2-3) for HB, it is evident that the ϕ value increases with increasing concentration. On extrapolation it leads to a limiting value of $\phi^{o} = 58.31\ cm^{3}\ mol^{-1}$

and yields a slope of 47.45- the constant 'a' for Masson's equation (1-8). Using ϕ^{o} and 'a' values as obtained in equation (1-8) we get

$$\phi = 58.312 + 47.45\ m^{\frac{1}{2}} \qquad (3-3)$$

Incorparating ϕ values from (3-3) in equation (1-9) we obtain, for partial molal volume

$$\bar{V} = 58.312 + 71.178\ m^{\frac{1}{2}} \qquad (3-4)$$

From equation (3-3) and (3-4) the calculated values of ϕ and $\bar{V}$, d picted in table (3-2-1), it is apparent that ϕ and $\bar{V}$ increases with increasing molality. The magnitude of ϕ^{o} value and the positive slope of 47.45 indicates ion-ion and ion-solvent interactions usually found in all the weak acids so far studied. Thus it can be safely said that HB behaves normally in aqueous solutions.

The case of Na-Barbital is somewhat unusual. Referring to the graph (3-2-4) it is worth pointing out that ϕ values decrease with increasing molal concentrations. The extrapolation gives ϕ^{o} = 130.89 and yields a negative slope of -10.46 units. Substituting these values, the corresponding equations for ϕ and $\bar{V}$ are

$$\phi = 130.39 - 10.459\ m^{\frac{1}{2}} \qquad (3-5)$$

$$\bar{V} = 130.39 - 15.688\ m^{\frac{1}{2}} \qquad (3-6)$$

A glance at equation (3-5), (3-6) and table

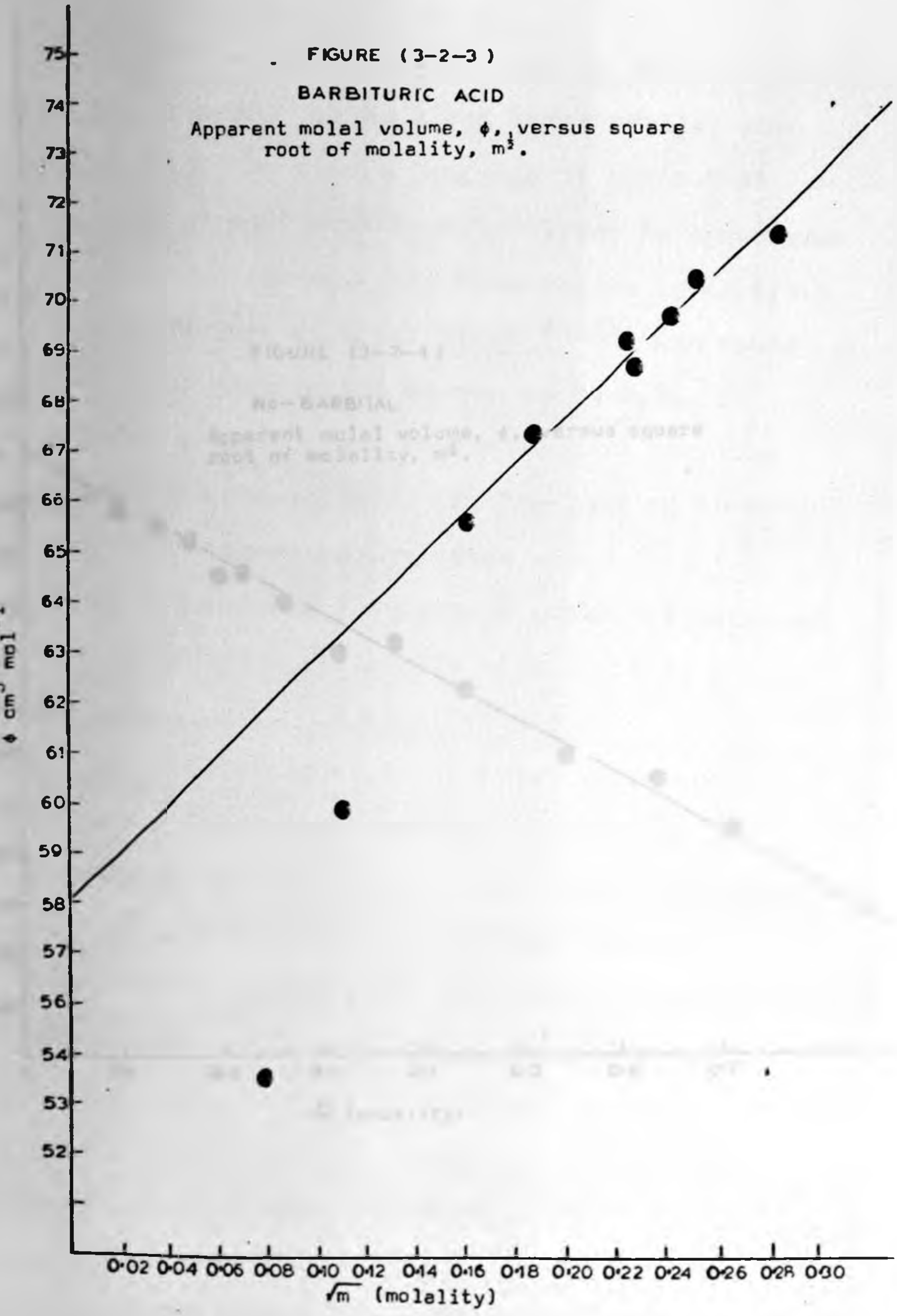


FIGURE (3-2-3)

BARBITURIC ACID

Apparent molal volume, ϕ, versus square root of molality, $m^{\frac{1}{2}}$.

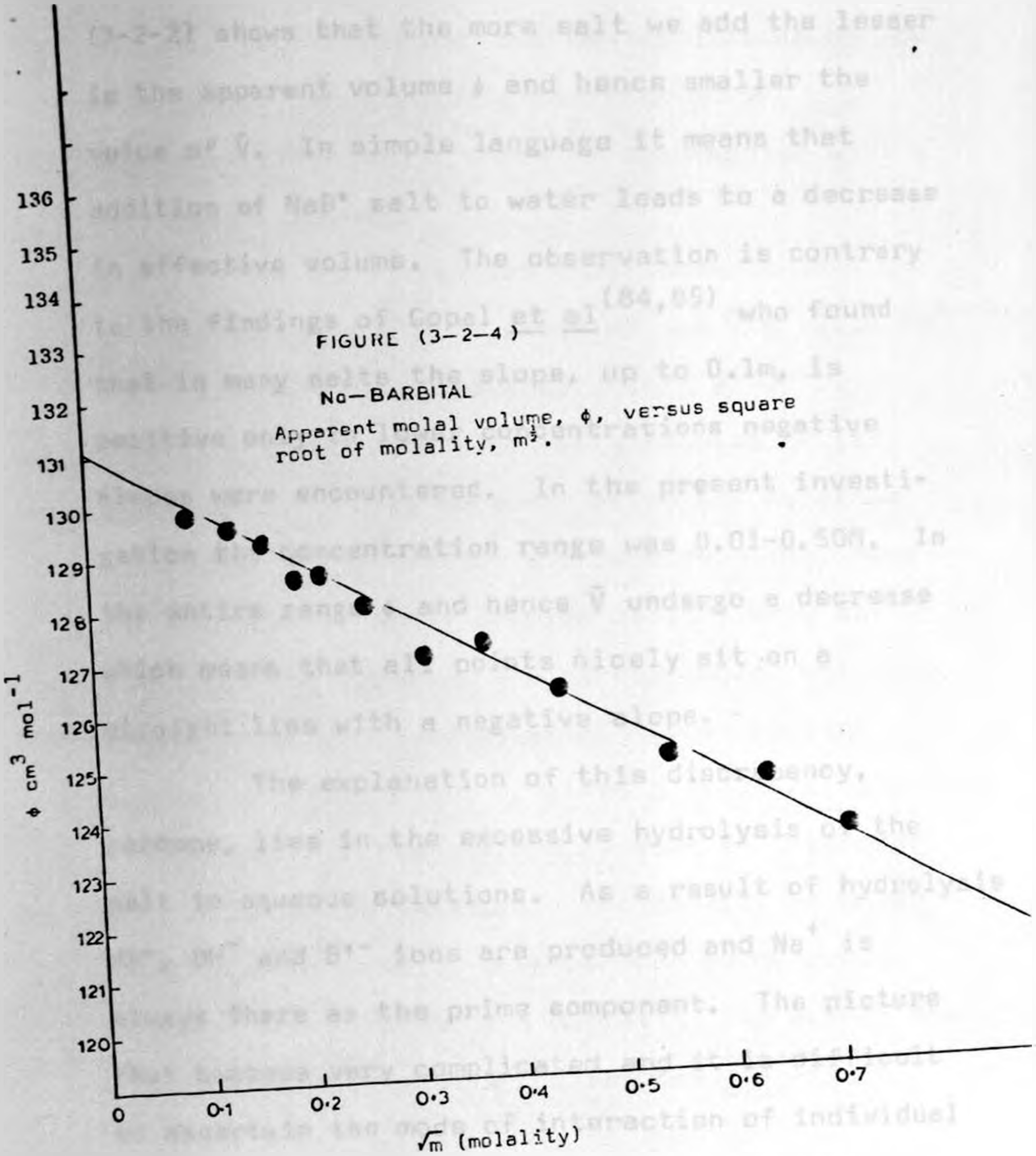


FIGURE (3-2-4)

Na-BARBITAL

Apparent molal volume, φ, versus square root of molality, $m^{\frac{1}{2}}$.

(3-2-2) shows that the more salt we add the lesser is the apparent volume ϕ and hence smaller the value of $\bar{V}$. In simple language it means that addition of NaB* salt to water leads to a decrease in effective volume. The observation is contrary to the findings of Gopal et al(84,85) who found that in many salts the slope, up to 0.1m, is positive only in lower concentrations negative slopes were encountered. In the present investigation the concentration range was 0.01-0.50M. In the entire range ϕ and hence $\bar{V}$ undergo a decrease which means that all points nicely sit on a straight line with a negative slope.

The explanation of this discrepancy, perhaps, lies in the excessive hydrolysis of the salt in aqueous solutions. As a result of hydrolysis HB*, OH^- and B^{*-} ions are produced and Na^+ is always there as the prime component. The picture thus becomes very complicated and it is difficult to ascertain the mode of interaction of individual species with solvent - nevertheless the high magnitude of ϕ^0 clearly suggests an unusually high degree of ion-solvent interactions. In terms of Debye-Huckel model, the solvent molecules surround the ions in such a way that the normal structure of water gets destroyed and the conditions of low free energy for stability dictates such a structure of solution which is accompanied with a decrease in volume.

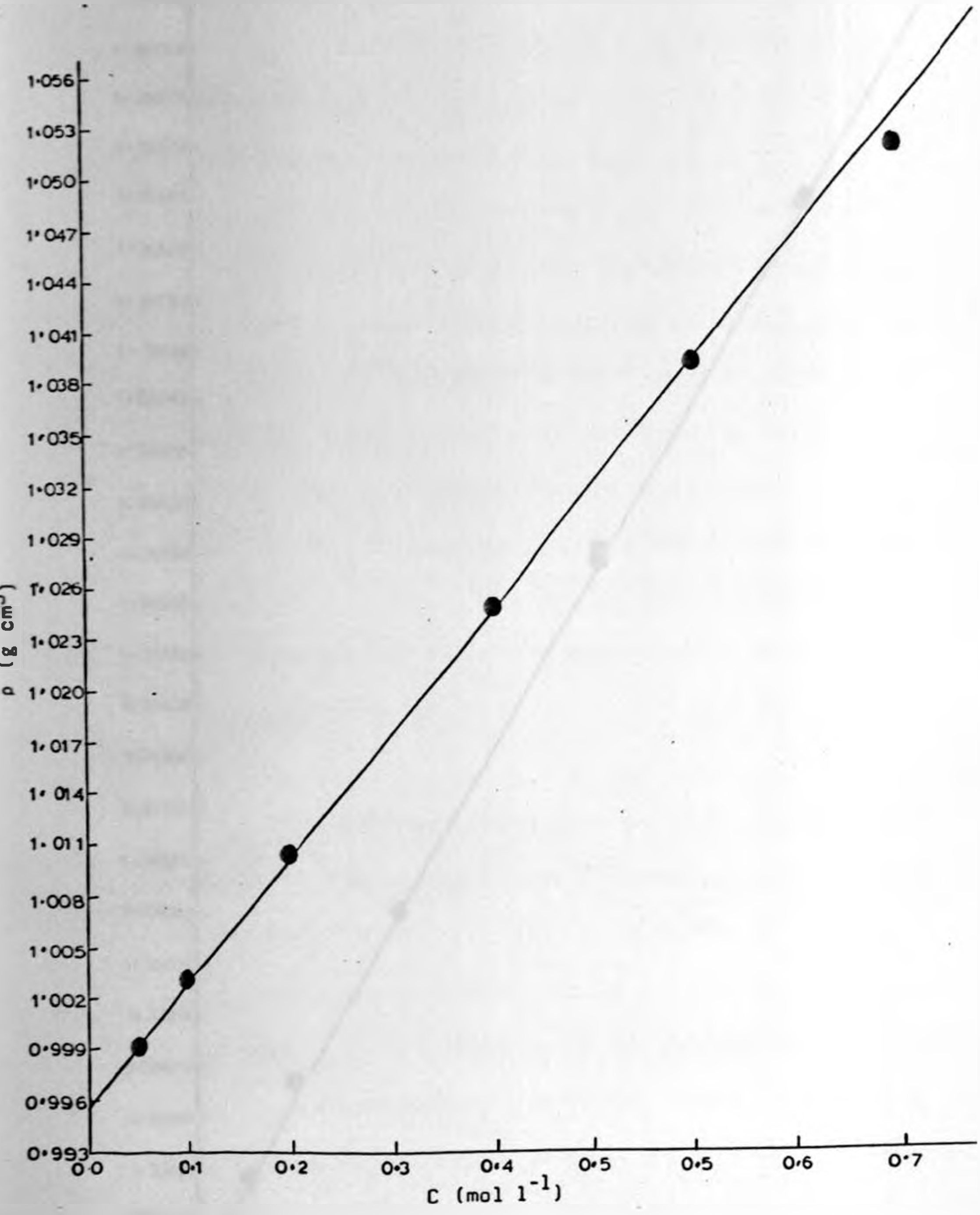
The investigation thus leads to an average value of $\bar{V}$ = 74.3 for HB and $\bar{V}$ = 125.2 cm^3 mol^{-1} for NaB* in aqueous solutions at 25°C.

Looking at the density results of Taft and Helen (1), they have not given any equation connecting concentration and density. They have not made use of their precise density data to calculate the apparent and partial molal volumes. Their density, ρ, values at 30°C when plotted against concentration, C, gives a beautiful straight line which on extrapolation, yields an intercept of 0.99568 which is exactly the density of water at 30°C. The density work is thus commendable. Out of shear interest and curiosity the author has constructed this plot which is shown in figure (3-2-5).

3-3 REFRACTIVE INDEX RESULTS

The refractive index results of aqueous Sodium Barbital are shown in table (3-3-1) and the concentration dependence of refractive index in figure (3-3-1). The refractive index of the NaB*

FIGURE (3-2-5)
Density vs Conc FOR SODIUM BARBITAL AT 30°C



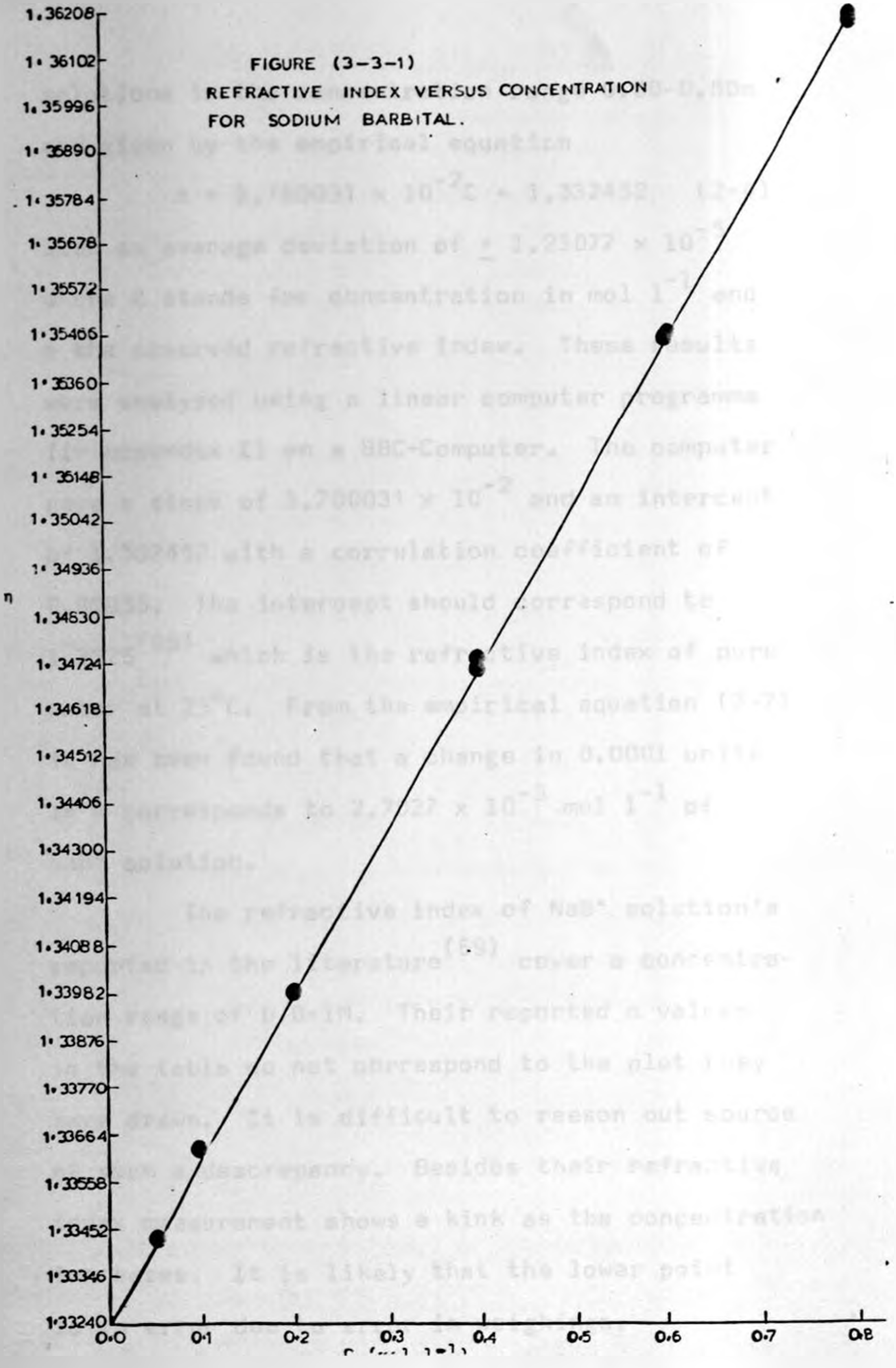


FIGURE (3-3-1)
REFRACTIVE INDEX VERSUS CONCENTRATION FOR SODIUM BARBITAL.

solutions in the concentration range 0.00-0.80m are given by the empirical equation

$$n = 3.700031 \times 10^{-2}C + 1.332452 \quad (2\text{-}4)$$

with an average deviation of $\pm$ 1.23077 x 10^{-5} where C stands for concentration in mol l^{-1} and n the observed refractive index. These results were analysed using a linear computer programme (in appendix I) on a BBC-Computer. The computer gave a slope of 3.700031 x 10^{-2} and an intercept of 1.332452 with a correlation coefficient of 0.99955. The intercept should correspond to 1.3325(65) which is the refractive index of pure water at 25°C. From the empirical equation (3-7) it has been found that a change in 0.0001 units in n corresponds to 2.7027 x 10^{-3} mol l^{-1} of NaB* solution.

The refractive index of NaB* solution's reported in the literature(69) cover a concentration range of 0.0-1M. Their reported n values in the table do not correspond to the plot they have drawn. It is difficult to reason out source of such a descrepancy. Besides their refractive index measurement shows a kink as the concentration increases. It is likely that the lower point is in error due to error in weighings.

TABLE (3-3-1): REFRACTIVE INDEX MEASUREMENTS OF AQUEOUS SODIUM BARBITAL SOLUTIONS AT 25^{o}C.

C	n*
0.00000	1.3324_5
0.04980_3	1.3343_0
0.05234_8	1.3343_9
0.10015_5	1.3361_6
0.10348_6	1.3362_8
0.20019_9	1.3398_6
0.20107_3	1.3398_9
0.39925_1	1.3472_2
0.40033_4	1.3472_6
0.60008_1	1.3546_6
0.60312_6	1.3547_7
0.79928_3	1.3620_3
0.80086_8	1.3620_8

UNITS: C, mol. l^{-1}

* is an average of four readings the last figure resulting from the averaging.

THE INTERCEPT = 1.3325
THE GRADIENT = 3.7000×10^{-2}
THE CORRELATION COEFFICIENT = 0.99955.

A copy of the computer print-out of these results is attached in the appendix II.

In the present investigation the author has not encountered such a break (kink) and the data show a linear concentration dependence.

3-4 VISCOSITY RESULTS

The results of viscosity measurements are shown in Table (3-4-1) and Table (3-4-2) for Barbituric acid and Sodium Barbital respectively and the concentration dependence of the observed relative viscosities, η/η^o, in Figures (3-4-1) and (3-4-2). The relative viscosities, η/η^o, for HB (0.05-0.08M) and NaB* (0.01-0.5M) have been fitted to the extended forms of Jones-Dole Equation; namely

$$\eta/\eta^o = 1 + 0.003\,C^{\frac{1}{2}} + 0.220C - 2.65C^2 \quad (3\text{-}7)$$

$$\eta/\eta^o = 1 + 0.009(\alpha C)^{\frac{1}{2}} + 1.16(\alpha C) \quad (3\text{-}8)$$

(α being the degree of dissociation of Barbituric acid).

and

$$\eta/\eta^o = 1 + 0.008\,C^{\frac{1}{2}} + 0.656C \quad (3\text{-}9)$$

respectively. The graphs of the above equations are shown in Figures (3-4-3) and (3-4-4) for Barbituric acid and Figure (3-4-5) for Sodium Barbital. Figure (3-4-4) and its empirical equation

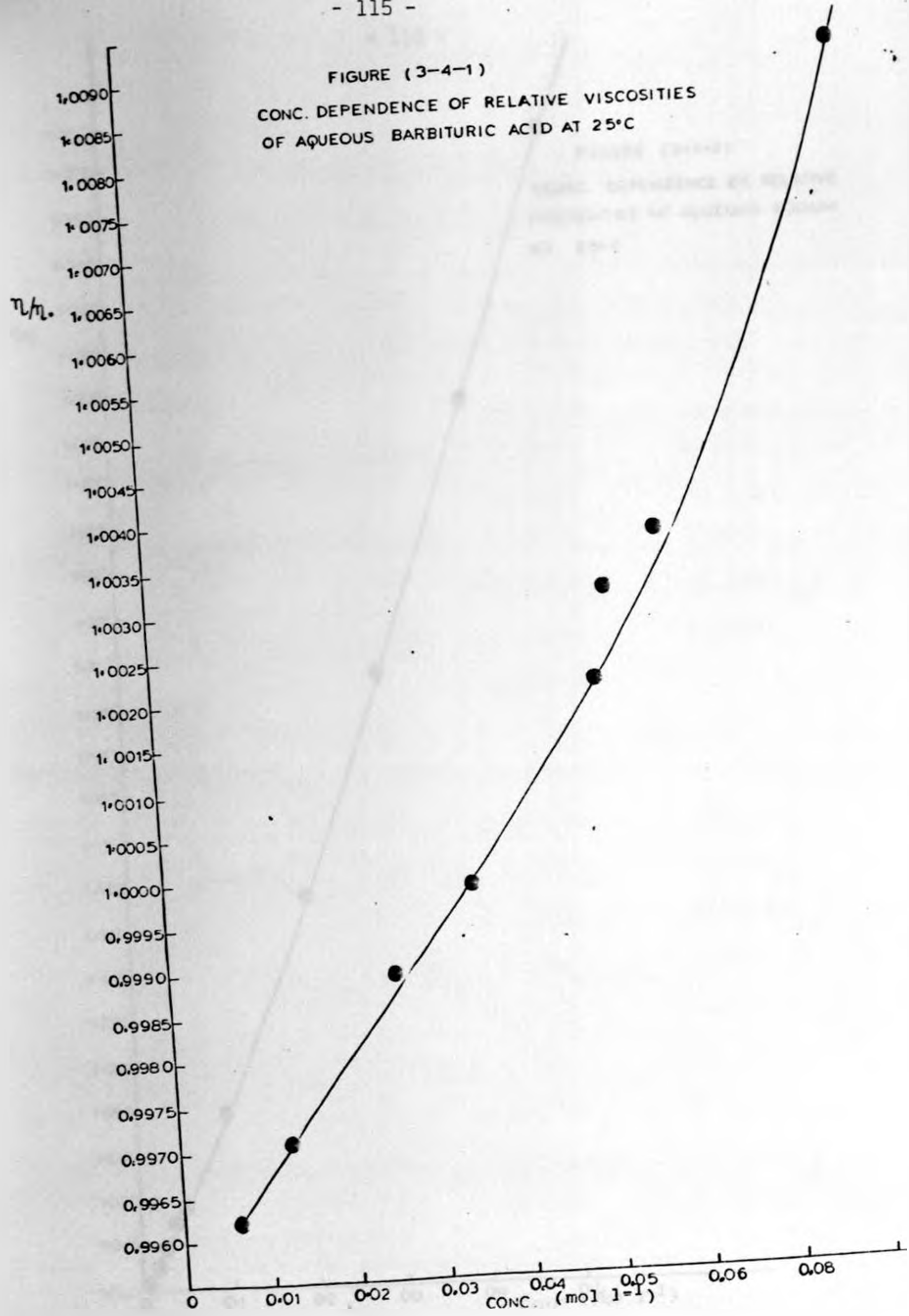


FIGURE (3-4-1)
CONC. DEPENDENCE OF RELATIVE VISCOSITIES
OF AQUEOUS BARBITURIC ACID AT 25°C
η/η.
1,0090
1·0085
1·0080
1·0075
1·0070
1·0065
1·0060
1·0055
1·0050
1·0045
1·0040
1·0035
1·0030
1·0025
1·0020
1·0015
1·0010
1·0005
1·0000
0,9995
0,9990
0,9985
0,9980
0,9975
0,9970
0,9965
0,9960
0
0·01
0·02
0,03
0,04
0,05
0,06
0,08
CONC. (mol l⁻¹)

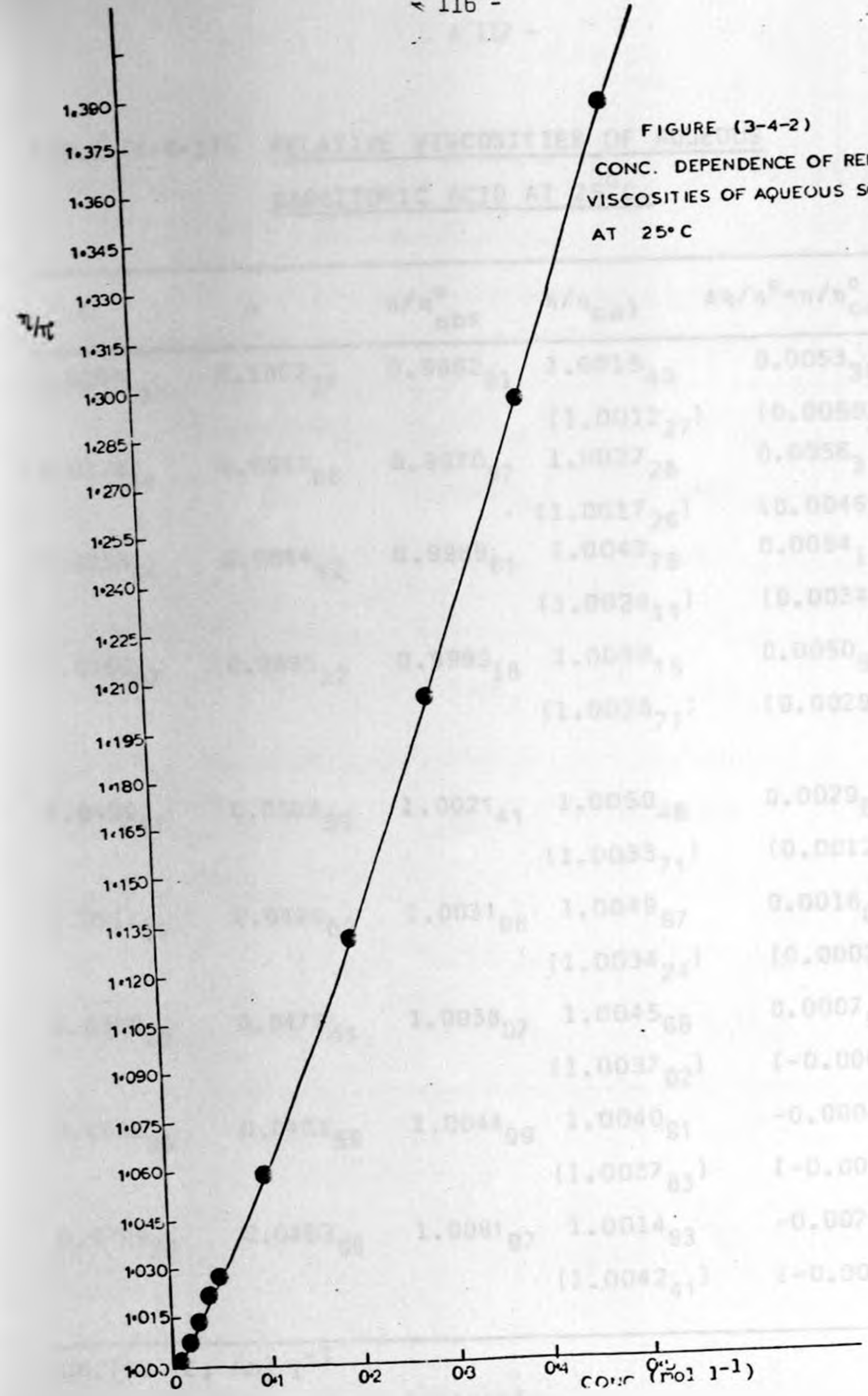


FIGURE (3-4-2)
CONC. DEPENDENCE OF RELATIVE
VISCOSITIES OF AQUEOUS SODIUM
AT 25°C

TABLE (3-4-1): RELATIVE VISCOSITIES OF AQUEOUS BARBITURIC ACID AT 25°C.

C	α	η/η^{o}_{obs}	η/η_{cal}	$\Delta\eta/\eta^{o}=\eta/\eta^{o}_{cal}-\eta/\eta^{o}_{obs}$
0.0064_{01}	0.1302_{27}	0.9962_{01}	1.0015_{40}	0.0053_{39}
			(1.0012_{27})	(0.0050_{26})
0.0128_{44}	0.0947_{66}	0.9970_{97}	1.0027_{28}	0.0056_{31}
			(1.0017_{26})	(0.0046_{29})
0.0256_{04}	0.0684_{92}	0.9989_{61}	1.0043_{76}	0.0054_{15}
			(1.0024_{11})	(0.0034_{50})
0.0350_{07}	0.0605_{12}	0.9999_{18}	1.0050_{15}	0.0050_{97}
			(1.0028_{71})	(0.0029_{53})
0.0499_{41}	0.0503_{99}	1.0021_{41}	1.0050_{48}	0.0029_{07}
			(1.0033_{71})	(0.0012_{30})
0.0511_{85}	0.0499_{89}	1.0031_{96}	1.0049_{97}	0.0018_{00}
			(1.0034_{24})	(0.0002_{28})
0.0580_{20}	0.0479_{41}	1.0038_{07}	1.0045_{66}	0.0007_{59}
			(1.0037_{02})	(-0.0001_{05})
0.0630_{39}	0.0451_{59}	1.0044_{99}	1.0040_{91}	-0.0004_{08}
			(1.0037_{83})	(-0.0007_{16})
0.0799_{75}	0.0402_{09}	1.0091_{97}	1.0014_{93}	-0.0077_{04}
			(1.0042_{41})	(-0.0049_{56})

UNITS: C, mol l^{-1}

α = Degree of ionization.

The values in the brackets are those calculated involving the degree of ionization.

TABLE (3-4-2): RELATIVE VISCOSITIES OF AQUEOUS SODIUM BARBITAL AT 25°C.

C	η/η_{obs}	η/η^{o}_{cal}	$\Delta\eta/\eta^{o}=\eta/\eta_{cal} - \eta/\eta_{obs}$
0.0100_{28}	1.0012_{45}	1.0073_{79}	0.0061_{34}
0.0199_{32}	1.0075_{12}	1.0142_{05}	0.0066_{93}
0.0297_{65}	1.0137_{26}	1.0209_{06}	0.0071_{80}
0.0399_{39}	1.0218_{97}	1.0277_{99}	0.0059_{02}
0.0500_{24}	1.0279_{53}	1.0346_{05}	0.0066_{52}
0.0998_{82}	1.0593_{09}	1.0680_{51}	0.0087_{42}
0.2001_{61}	1.1307_{07}	1.1348_{85}	0.0041_{78}
0.2943_{54}	1.2044_{87}	1.1974_{37}	-0.0070_{50}
0.4017_{62}	1.2948_{56}	1.2686_{27}	-0.0262_{29}
0.5000_{47}	1.3855_{20}	1.3336_{88}	-0.0518_{32}

UNITS: C; mol l^{-1}

FIGURE (3-4-3)

PLOT OF($\eta/\eta^{\circ}-1)/\sqrt{C}$ AGAINST $\sqrt{C}$ FOR BARBITURIC ACID

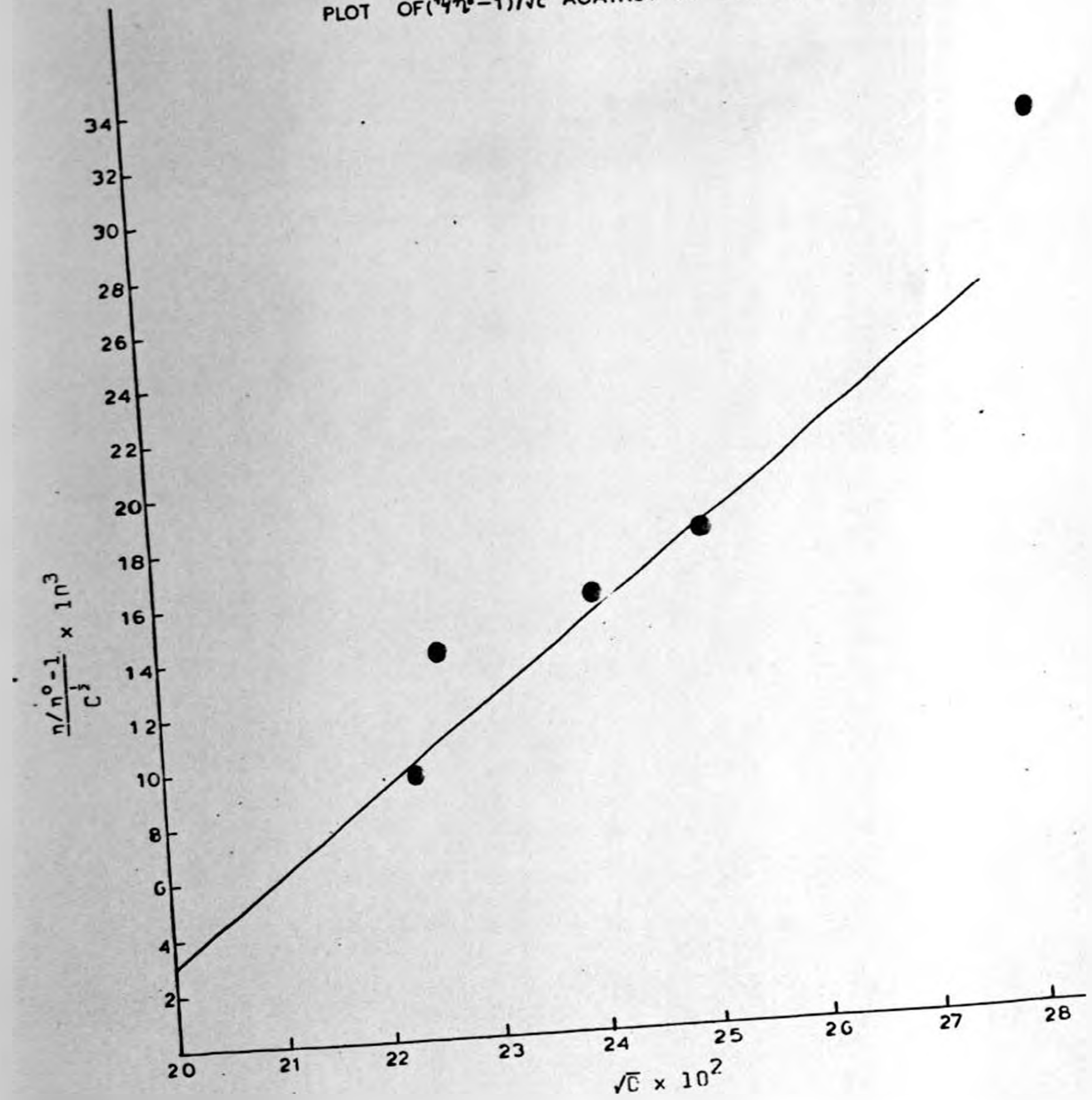
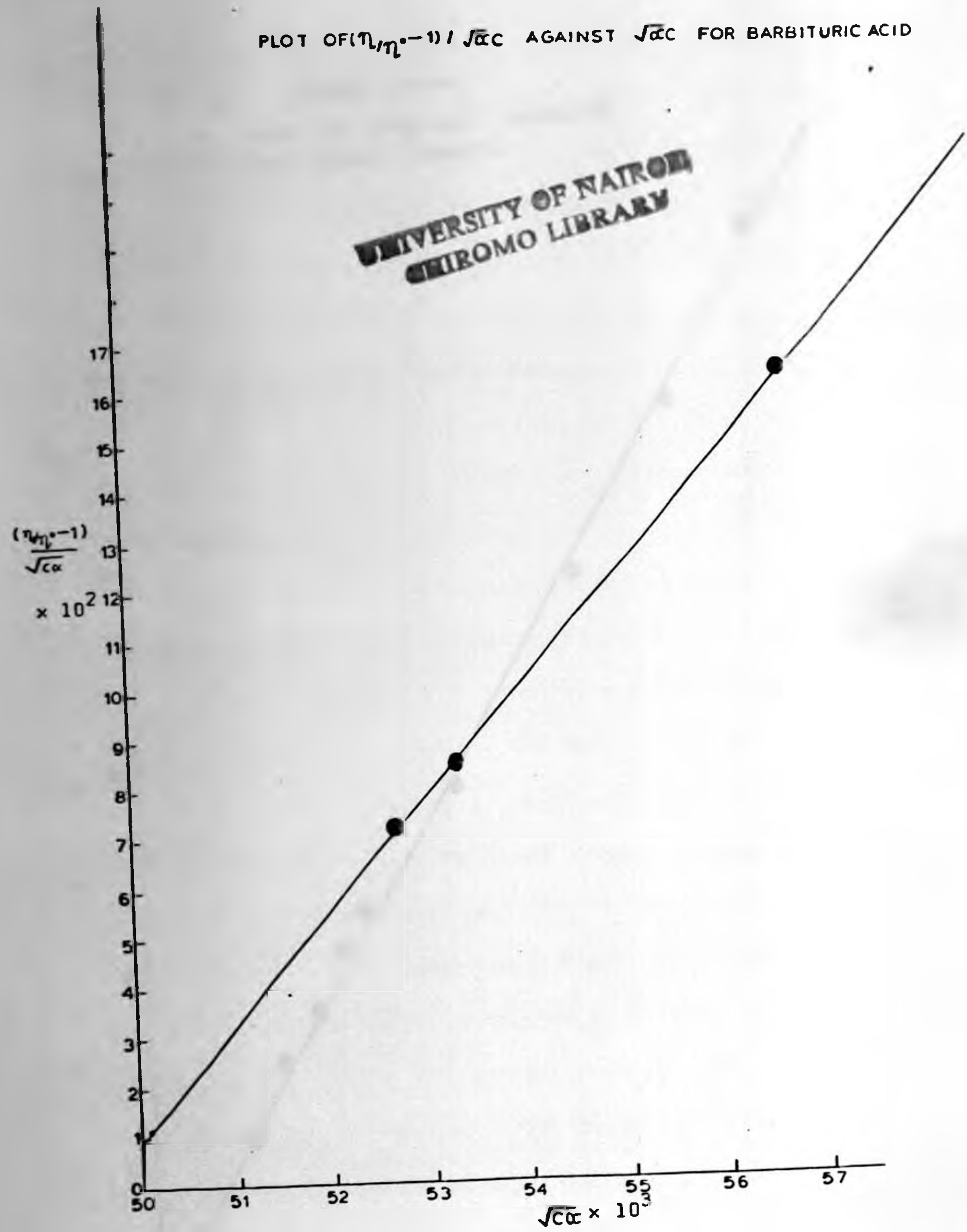


FIGURE (3-4-4)

PLOT OF$(\eta/\eta^{\circ}-1)/\sqrt{\alpha C}$ AGAINST $\sqrt{\alpha C}$ FOR BARBITURIC ACID



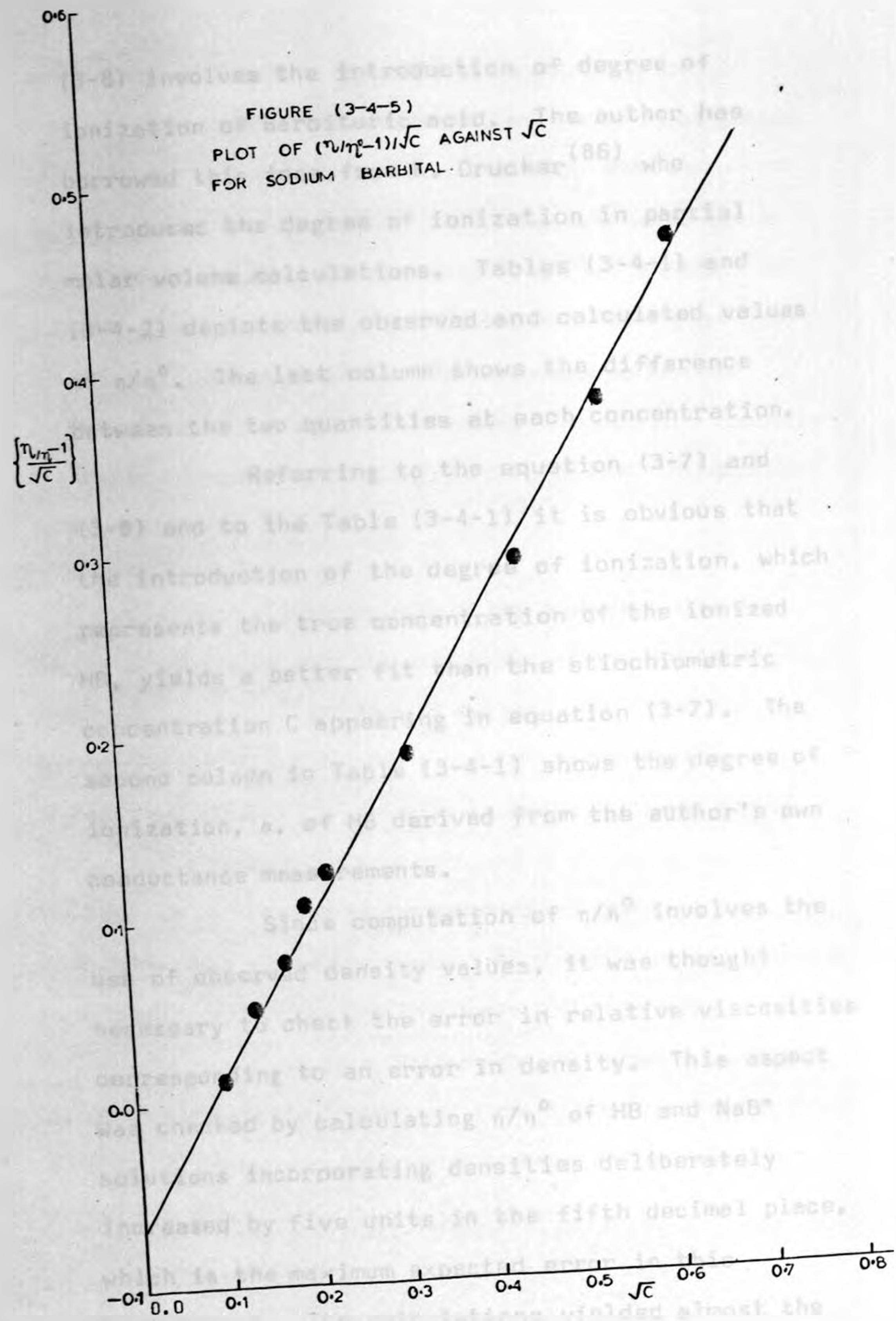


FIGURE (3-4-5)
PLOT OF $(\eta/\eta^{0}-1)/\sqrt{C}$ AGAINST $\sqrt{C}$
FOR SODIUM BARBITAL.

(3-8) involves the introduction of degree of ionization of Barbituric acid. The author has borrowed this idea from K. Drucker(86) who introduced the degree of ionization in partial molar volume calculations. Tables (3-4-1) and (3-4-2) depicts the observed and calculated values of η/η^o. The last column shows the difference between the two quantities at each concentration.

Referring to the equation (3-7) and (3-8) and to the Table (3-4-1) it is obvious that the introduction of the degree of ionization, which represents the true concentration of the ionized HB, yields a better fit than the stiochiometric concentration C appearing in equation (3-7). The second column in Table (3-4-1) shows the degree of ionization, α, of HB derived from the author's own conductance measurements.

Since computation of η/η^o involves the use of observed density values, it was thought necessary to check the error in relative viscosities corresponding to an error in density. This aspect was checked by calculating η/η^o of HB and NaB* solutions incorporating densities deliberately increased by five units in the fifth decimal place, which is the maximum expected error in this measurement. The calculations yielded almost the same values showing that the error in densities do not cast any pronounced effect on viscosities. As an illustration, η/η^{o} of 0.05802_{0}M solution of HB is 1.00380_{7}. When the density is increased by 0.00005 g cm^{-3}, new η/η^{o} works out to be 1.00385_{7}. In case of Sodium Barbital η/η^{o} of 0.09988_{2}M is 1.059309. When the density is increased by 0.00005 g cm^{-3}, the new η/η^{o} becomes 1.05936_{2}. The percentage error thus introduced is only 0.005% in both cases. The relative viscosity results are therefore good enough to subject them to theoretical interpretations.

The value of A coeffiecients of the Jones-Dole Equations have been determined from the y-intercept of the plot of $(\eta/\eta^{o}-1)/C^{\frac{1}{2}}$ versus $C^{\frac{1}{2}}$ for both HB and HaB*. It turned out to positive for HB but for NaB*, contrary to the theory, it has a -ve value which indicates excessive hyrolysis of the salt. A -Coefficient has been interpreted theoretically on the basis of deformation of the Debye-Huckel spherical ion-atmosphere under a shearing stress. It accounts for the increase in viscosity produced by the long range Coulombic forces between the ions(87). Using Falkenhagen and Vernon's Equation(24) |Equation (1-18)|, the theoretical A-coefficient obtained is +0.00355 for Barbituric acid, which is based on the following conductance data:

$$\lambda^{o}_{H^+} = 349.8_{1}^{(88)} \quad \text{and} \quad \lambda^{o}_{B^-} = 22.50$$

S cm^{2} $equiv.^{-1}$ at 25^{o}C.

For NaB* A=0.00840 which has been calculated using $\lambda^{o}_{Na^{+}}$ = 50.10(88) and $\lambda_{B}^{\overset{*}{=}}$ = 39.80 S cm^{2} equiv.$^{-1}$ at 25°C. The experimental A-coefficient were found to be +0.003 for Barbituric acid which is in excellent agreement with the theoretical A-Coefficients.

For NaB* the A-value shows a complete deviation. Experimental value works out to be -0.04 whereas the theory predicts +0.0084. As mentioned earlier A-coefficient should always have a +ve value, the -ve sign clearly shows that the salt undergoes hydrolysis. Unfortunately there is no theoretical model available to account for the hydrolysis effect quantitatively.

The vescosity B-coefficients obtained are +0.220 and +0.656 for HB and NaB* respectively when the degree of ionization of the acid is not considered. If it is taken into account, then the value of B-coefficients becomes 1.160 for Barbituric acid. In both treatments the values of B-coefficient has a positive value. A positive quantity indicates(89) that there are strong interactions of the solvent molecules with the ions. The prevailing conditions would definitely promote rearrangement of the solvent molecules in the immediate vicinity of the ions. The ions present in aqueous Barbituric acid and Sodium Barbital solutions are thus "structure-makers" or "hydrophobic ions"(90). The "hydrophobic ions" give rise to "hydrophobic hydration" of the water molecules by strengthening their hydrogen bonds and thus increasing the viscosity of water.

The viscosity B-coefficient consists of the contribution from the ion-solvent interaction plus the contribution from the size of the ion i.e. Einsten's effect(91). The Einstein's effect is always positive and normally increases with increasing ion-size.

Various workers(28,92) have attempted to split B-coefficient into individual ionic values in aqueous solutions. In aqueous Sodium Barbital solutions, B-coefficient gets contribution from B_{Na^+} and other sources. Since $B_{Na^+} = 0.0863$(93) and B-coefficient, as given by equation (3-9), is equal to 0.656 the contribution of B_{Na^+} to the total B-coefficient values is only ca. 13%. It can be seen that Na^+ plays a less important role in contributing to B-coefficient in the aqueous Sodium Barbital solutions studied.

The D-coefficient(94) is supposed to include all other modes of solute-solvent and solute-solute interactions that were not accounted for by the A- and B-coefficients. These coulombic interactions may include ++ and -- ion pairs, triplets and higher multiplets which exist at higher concentrations. The D-coefficient, the authors believes, also takes into account higher terms of the hydrodynamic effect and the hydrolysis which NaB* undergoes. There is no other way out except to utilize

Jones-Dole equation coefficients to accommodate otherwise unaccountable processes.

It can, therefore, be concluded from density and viscosity measurements that there are strong ion-ion and ion-solvent interactions in aqueous Barbituric acid and Sodium Barbital solutions. In case of Barbituric acid, which is a weak acid, dissociation is incomplete and consequently solutions contain molecular species as well which contribute substantially to the Einstein's effect.

The B-coefficient of Jone-Dole Equation thus provides a quantitative estimate of the over-all interactions. The coefficients envelope the contributions of all ionic species and it is, therefore, difficult to split the B-coefficient into individual species quantitatively.

The literature(1) viscosity work, at 30°C, had been carried out using Ostwald viscometer which requires surface tension corrections which have neither been calculated nor mentioned. This renders the η/η^{o} figures of semi-quantitative value. The situation becomes more serious when one looks at the reported concentration figures. For unknown reasons the concentrations are expressed upto one decimal place only. Furthermore a careful look into their plot of η/η^{o} versus concentration, it is obvious that their concentration axis has an error which makes their plot questionable for interpolation.

Besides, the authors have not tried to explain their results on the standard model and have taken no consideration of the fact that varying degree of hydrolysis would affect the viscosities adversely.

3-5 CONDUCTANCE RESULTS

RAW DATA AND CALCULATION OF Λ^o AND K_a

Upto-date literature survey shows that no conductance work has been done so far on Barbituric acid, HB, which is a weak 1:1 electrolyte with a reported dissociation constant(95) K_a, of 9.8×10^{-5} mol l^{-1}. The following lines describe the results of the authors conductance work on HB aqueous solutions.

3-5-1 BARBITURIC ACID RESULTS:

From the measured resistance R, equivalent conductance Λ(Expt) was calculated from the definition of the quantity using 5.4145 cm^{-1} as the value of the cell constant. The Λ(Exptl) so obtained at various concentrations are collected in Table (3-5-1) and the plot of Λ(Exptl) against $C^{\frac{1}{2}}$ is shown in Figure (3-5-1).

To calculate the equivalent conductance at infinite dilution, Λ^o and the dissociation constant K_a, Shedlovsky(96) method was employed which has already been described in section (1-3-5). The important steps of the calculations would be described in the following lines.

(a) Basically, the method involves getting Λ^o value from graphical approximations which needs

TABLE (3-5-1): EQUIVALENT CONDUCTANCE OF AQUEOUS BARBITURIC ACID AT 25°C.

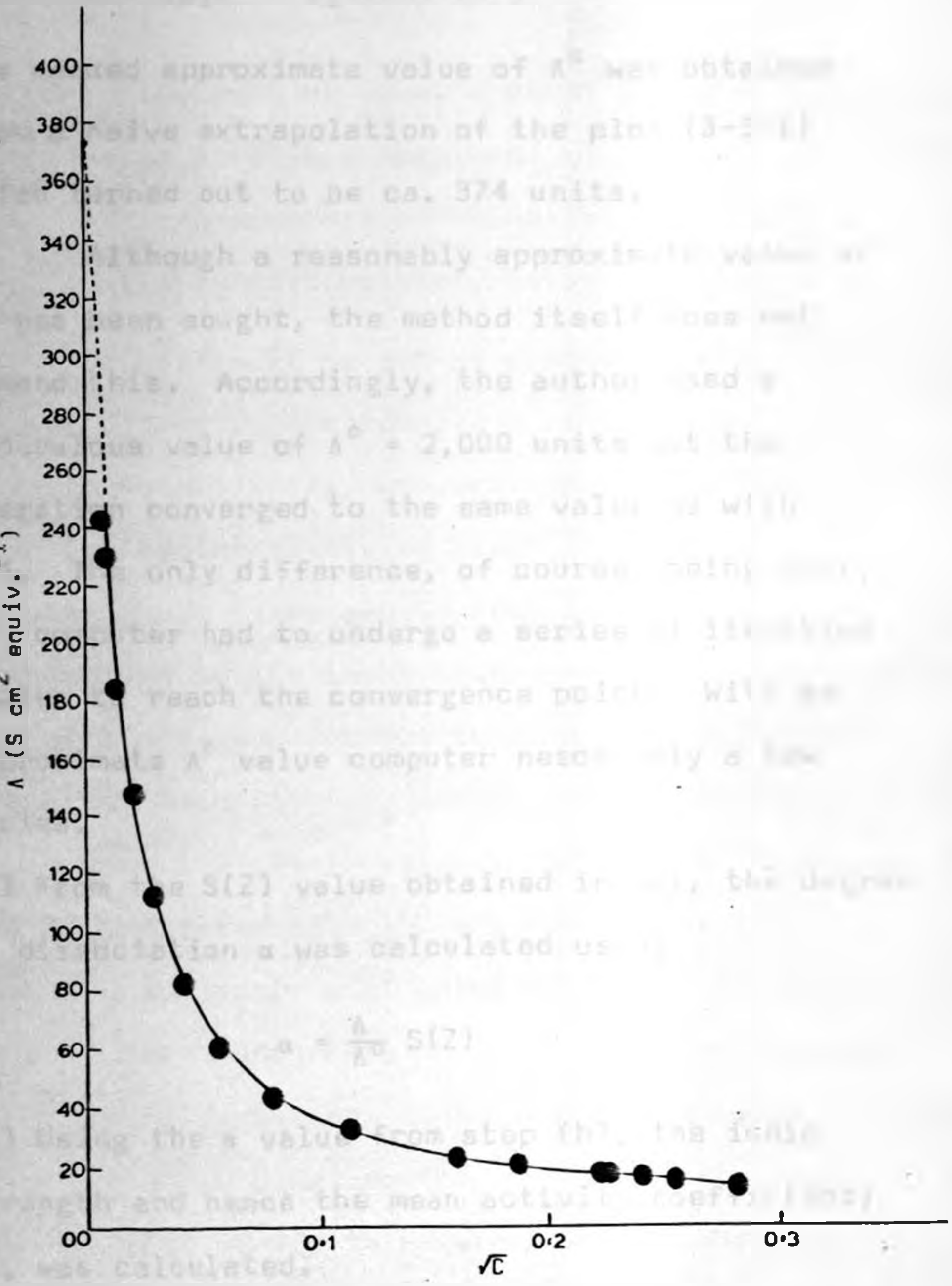
C	Resistance*	Λ(Exptl)
0.000047	476,000.00	242.55
0.000106	221,000.00	230.27
0.000200	145,600.00	185.85
0.000391	93,800.00	147.69
0.000797	60,340.00	112.64
0.001623	39,990.00	83.43
0.003202	27,717.00	61.00
0.006401	19,016.00	44.48
0.012844	13,055.25	32.29
0.025604	9,086.25	23.27
0.035007	7,534.50	20.53
0.049941	6,351.75	17.07
0.051185	6,249.25	16.93
0.058020	5,753.50	16.22
0.065006	5,585.75	14.91
0.079975	4,984.50	13.58

UNITS: C, mol l^{-1}, R, S; Λ, S cm^2 $equiv.^{-1}$

*an average of 4 readings.

FIGURE (3—5—1)

EQUIVALENT CONDUCTANCE AGAINST CONCENTRATION OF BARBITURIC ACID AT 25°C.



an approximate value of Λ^o to initiate the calculation of the function

$$S(Z) = 1 + Z + \frac{Z^2}{2} + \text{-----}$$

where

$$Z = \{B_1\Lambda^o + B_2\}(C\Lambda)^{\frac{1}{2}}(\Lambda^o)^{-1.5}$$

The needed approximate value of Λ^o was obtained from a naive extrapolation of the plot (3-5-1) which turned out to be ca. 374 units.

Although a reasonably approximate value of Λ^o has been sought, the method itself does not demand this. Accordingly, the author used a radiculous value of Λ^o = 2,000 units but the iteration converged to the same value as with 374. The only difference, of course, being that, the computer had to undergo a series of iteration cycles to reach the convergence point. With an approximate Λ^o value computer needs only a few cycles.

(b) From the S(Z) value obtained in (a), the degree of dissociation α was calculated using

$$\alpha = \frac{\Lambda}{\Lambda^o} S(Z)$$

(c) Using the α value from step (b), the ionic strength and hence the mean activity coefficient, $f_\pm$, was calculated.

(d) Finally the quantities $\frac{1}{\Lambda S(Z)}$ and $C\Lambda f_{\pm}^{2}S(Z)$ were calculated for the equation

$$\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda^{o}} + \frac{C\Lambda f_{\pm}^{2}S(Z)}{K_{a}(\Lambda^{o})^{2}}$$

(e) From the plot of $\frac{1}{\Lambda S(Z)}$ against $C\Lambda f_{\pm}^{2}S(Z)$ a second value of Λ^{o} was obtained.

Since the numerical values of the quantity $\frac{1}{\Lambda S(Z)}$, for weak electrolytes, is very small, it is extremely difficult to get an accurate value from the plot itself. Accordingly a computer programme, given in Appendix III, was written to continue the iteration cycles involving steps (a), (b), (c), (d) and (e) 20 times and to read the intercept, and the gradient by the least square method. The programme included instructions to calculate the dissociation constant K_a and pK_a values as well.

When all the 16 values, recorded in Table (3-5-1), were fed into the programme, the computer print out indicated a Λ^{o} value of 345.56 S cm^{2} equiv.$^{-1}$ for Λ^{o} HB. This value is even smaller than the limiting equivalent conductance of H^{+} i.e. $\lambda^{o}_{H^{+}}$ = 349.8[97] S cm^{2} equiv.$^{-1}$. It was therefore, inferred that some data points were not falling on

TABLE (3-5-2): CALCULATIONS OF VARIOUS QUANTITIES FOR THE SHEDLOVSKY CONDUCTANCE EQUATION WITH INITIAL VALUE OF Λ^{o}=370.

C	Λ	S(Z)	α	$f_{\pm}^{2}$	$1/\Lambda S(Z)$	$C\Lambda f_{\pm}^{2}S(Z)$
0.000047	242.55	1.0023	0.7035	0.9866	0.00411	0.01127
0.000106	230.27	1.0034	0.6686	0.9804	0.00433	0.02401
0.000200	185.85	1.0042	0.5401	0.9759	0.00536	0.03643
0.000391	147.69	1.0053	0.4296	0.9700	0.00674	0.05631
0.000797	112.64	1.0066	0.3281	0.9627	0.00882	0.08700
0.001623	83.43	1.0081	0.2434	0.9544	0.01189	0.13028
0.003202	61.00	1.0097	0.1782	0.9455	0.01624	0.18646
0.006401	44.48	1.0117	0.1302	0.9345	0.02222	0.26918
0.051185	16.93	1.0205	0.0500	0.8880	0.05789	0.78519
0.012844	32.29	1.0141	0.0948	0.9214	0.03054	0.38753
0.025604	23.27	1.0170	0.0685	0.9064	0.04225	0.54927
0.079975	13.58	1.0230	0.0402	0.8753	0.07197	0.97273
0.065006	14.91	1.0217	0.0441	0.8819	0.06564	0.87341
0.058020	16.22	1.0214	0.0479	0.8835	0.06036	0.84925
0.035007	20.53	1.0187	0.0605	0.8976	0.04782	0.65705
0.049941	17.07	1.0203	0.0504	0.8889	0.05742	0.77314
0.079974	13.58	1.0230	0.0402	0.8753	0.07197	0.97272

UNITS: C, mol l^{-1}, Λ, S cm^{2} $equiv.^{-1}$

INTERCEPT = 2.8938×10^{-3}

GRADIENT = 7.0377×10^{-2}

CORRELATION COEFFICIENT = 0.9995

Λ^{o} = 345.56

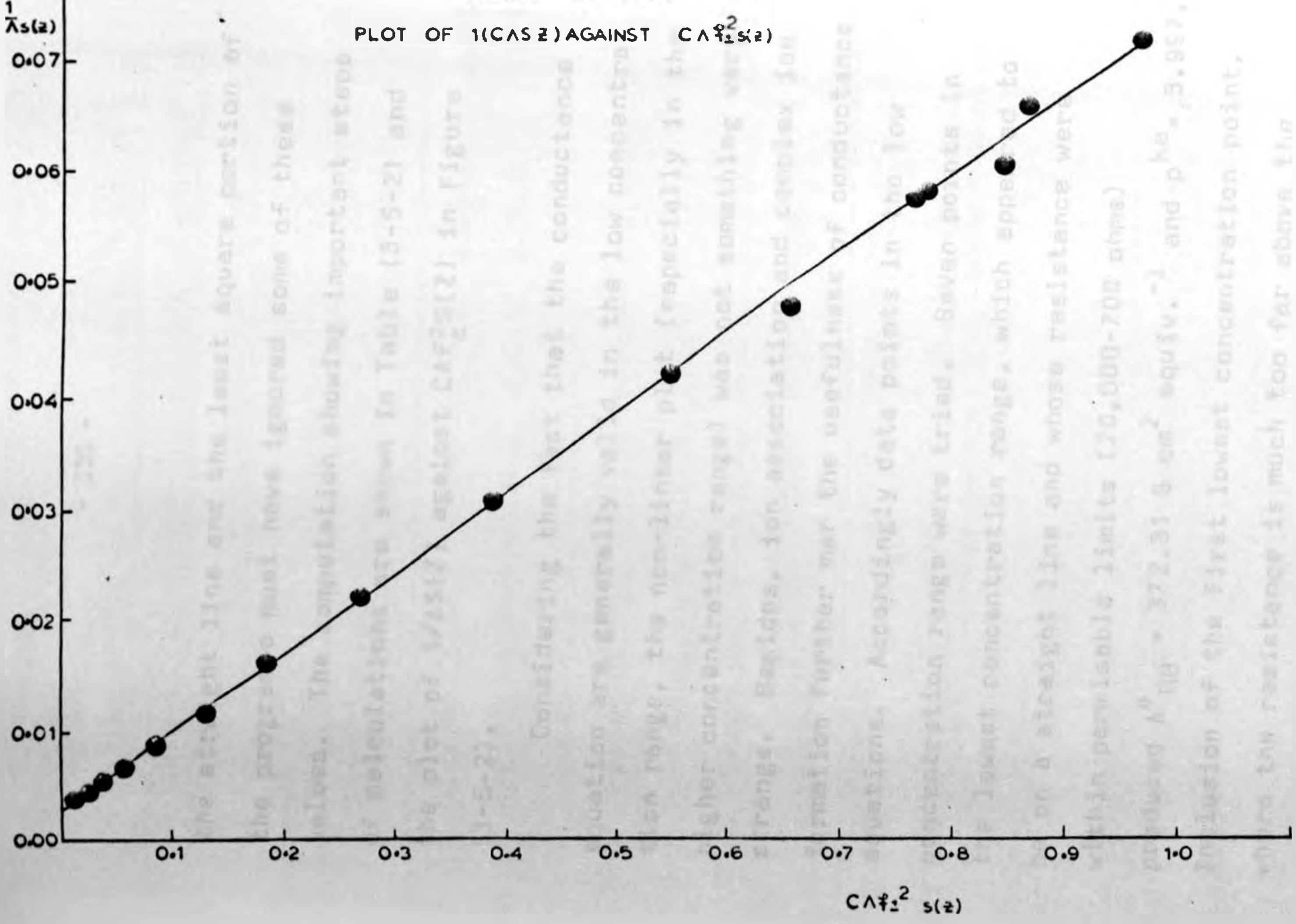
IONISATION CONSTANT = 1.190×10^{-4}

$-\log k_a$ = 3.924

A copy of the original computer print-out is in appendix IV.

FIGURE (3-5-2)

PLOT OF 1(CAS z) AGAINST $CA f_{\pm}^2 s(z)$



the straight line and the least square portion of the programme must have ignored some of these values. The computation showing important steps of calculations are shown in Table (3-5-2) and the plot of $1/\Lambda S(Z)$ against $C\Lambda f_{\pm}^{2}S(Z)$ in Figure (3-5-2).

Considering the fact that the conductance equation are generally valid in the low concentration range, the non-linear plot (especially in the higher concentration range) was not something very strange. Besides, ion association and complex ion formation further mar the usefulness of conductance equations. Accordingly data points in the low concentration range were tried. Seven points in the lowest concentration range, which appeared to be on a straight line and whose resistance were within permisable limits (70,000-700 ohms) produced Λ^{o}_{HB} = 372.31 S cm^{2} equiv.$^{-1}$ and p^{ka}= 3.997. Inclusion of the first lowest concentration point, where the resistance is much too far above the recommended limits,[75] decreased both the value of Λ^{o}_{HB} and p^{ka}.

For the set of these seven points various initial value of Λ^{o} i.e 300, 380 and 2000 S cm^{2} equiv.$^{-1}$ were tried. Each value, however, converged to 372.31 S cm^{2} equiv.$^{-1}$. Important steps of

A COMBINATION OF TABLES (3-5-3), (3-5-4) AND (3-5-5) CALCULATION OF VARIOUS QUANTITIES FOR THE SHEDLOVSKY CONDUCTANCE EQUATION

C	Λ	S(Z)	α	$f_\pm^2$	$1/\Lambda S(Z)$	$C\Lambda f_\pm^2 S(Z)$
0.000391	147.69	1.0049	0.3986	0.9717	0.00674	0.05639
0.000797	112.64	1.0061	0.3044	0.9650	0.00882	0.08716
0.001623	83.43	1.0075	0.2258	0.9574	0.01190	0.13061
0.003202	61.00	1.0090	0.1653	0.9493	0.01625	0.18709
0.006401	44.48	1.0109	0.1208	0.9395	0.02224	0.27042
0.012844	32.29	1.0132	0.0879	0.9280	0.03057	0.38996
0.025604	23.27	1.0158	0.0635	0.9151	0.04230	0.55391

UNITS: C, mol l^{-1}, Λ, S cm^2 $equiv.^{-1}$

NOTE: The difference in the three tables is the initial value of Λ^o. The three values i.e. 300, 380 and 2000 used yielded the same results as above.

INTERCEPT = 2.6859×10^{-3}

GRADIENT = 7.1621×10^{-2}

CORRELATION COEFFICIENT = 0.99995

Λ^o = 372.31

IONIZATION CONSTANT 1.0073×10^{-4}

$-\log k_a = 3.9969$

The copies of the original computer print-out are in appendices V, VI and VII respectively.

calculations for these seven points are depicted in Tables (3-5-3), (3-5-4) and (3-5-5).

An inspection of Tables (3-5-3, 3-5-4 & 3-5-5) shows that $\frac{1}{\Lambda S(Z)}$ is a very small quantity and the other i.e $C\Lambda f_{\pm}^{2}S(Z)$ is not very big either. Thus a small error in $\frac{1}{\Lambda S(Z)}$ would result in a big change of Λ^{o} and hence in k_a value (98).

The analysis of the experimental conductance data thus leads to $\Lambda^{o} = 372.31$ S cm^2 equiv.$^{-1}$ and $k_a = 1.0073\times10^{-4}$. The dissociation constant agrees very well with $k_a = 9.8\times10^{-5}$ reported in the literature (95).

Since $\lambda^{o}_{H^+} = 349.8$, the limiting conductance of the Barbiturate ion $\lambda^{o}_{B^-} = 372.31-349.8=22.51$ S cm^2 equiv.$^{-1}$.

3-5-2 SODIUM BARBITAL

3-5-2a INTRODUCTION

The literature conductance work (1) on Sodium Barbital at 30°C covers a concentration range of 0.05-0.80M. Even the lowest concentration is far too above the concentration limit where theoretical equations find any meaningful application. All conductance equations have been derived for low concentrations where a solution can be expected to experience lesser degree of ionic interactions etc. Under these conditions only the approximations incorporated in theoretical equations stand valid. Coming to the point, the literature on conductance data is not suited to test its validity on any standard equation.

The authors have not taken into account the fact that hydrolysis produces a highly mobile and conductive hydroxyl ion which contributes substantially to the observed conductance. The hydrolysis is much pronounced in the low concentrations which the workers have not studied. Accordingly their data have mislead them and they find their conductance values varying linearly with $C^{\frac{1}{2}}$.

The calculated values of Λ themselves cannot be accurate as they have used a dip-type cell where current leakage gives erroneous resistance readings. Besides, the employed frequency of 1000HZ is not good enough to eliminate the effect of polarization. Thus their experimental method introduces elements of uncertainities.

3-5-2b SODIUM BARBITAL RESULTS

As described earlier about HB solutions, the equivalent conductances, Λ, in NaB* solutions were calculated from the measured resistance R and the cell constant J= 5.4145 cm^{-1}. The Λ(Expt) so obtained at various concentrations are collected in Table (3-5-6) and the plot of Λ(Expt) against $C^{\frac{1}{2}}$ in Figure (3-5-3). Since for accurate data, the measured resistance of solutions should be between 70,000 and 700 Ohms, only those points were used in the plot which fall in this range.

From the plot it can be seen that the line has a kink. The two sections of the lines have been named A and B. On extrapolation to infinite dilution the line A gives Λ^o= 89.90 S cm^2 $equiv.^{-1}$ and line B gives Λ^o=83.15 S cm^2 $equiv.^{-1}$. These values were obtained by feeding these points into a computer programme. The programme was written so as to read the intercept, the slope and the correlation coefficient by the least square method. The computer print-out of the programme used and the results are included in appendix VIII and IX respectively. The reason for the line to have a kink, is mainly due to the hydrolysis which is very much pronounced in the low concentration region. The theoretical Λ values obtained using Robinson-

TABLE (3-5-6): EQUIVALENT CONDUCTANCE OF AQUEOUS SODIUM BARBITAL AT 25^{o}C.

C	Resistance*	Λ(Expt)
0.000063	729,000.00	116.981510
0.000189	292,000.00	98.314493
0.000127	444,000.00	95.949148
0.000392	150,800.00	91.497629
0.000789	74,980.00	91.474584
0.001562	38,805.00	89.331772
0.003165	19,991.00	85.561796
0.005008	12,781.75	84.584293
0.010028	6,551.00	82.421048
0.019932	3,460.00	78.510523
0.029765	2,390.50	76.094814
0.039939	1,818.00	74.570307
0.050024	1,483.25	72.973986
0.070140	1,091.00	76.756306
0.099882	796.00	68.101514
0.139912	594.00	65.150318
0.200161	439.00	61.618820
0.294354	321.00	57.303608
0.401762	258.00	52.235817
0.500047	220.00	49.217862

UNITS: C, mol l^{-1}; R, S; Λ S cm^{2} $equiv.^{-1}$

*an average of 4 readings.

Stokes equation are plotted against $C^{\frac{1}{2}}$ and is shown by the line marked (b) in Figure (3-5-3). The Λ(expt) are thus much lower than the theoretical Λ and differs completely in the slope.

To explain the variation of Λ(expt) with concentration, the hydrolysis process was taken into account and Robinson-Stokes equation was modified to suit the real situation as described in section (1-3-6). The hydrolysis constant, k_h, was calculated using equation (1-49) and a computer programme, given in appendix X, was used to calculate the degree of hydrolysis at each concentration. The programme read the intercept, the slope and the correlation coefficient by the least square method. The result of these calculations are shown in Table (3-5-7) and (3-5-8). The copies of the computer print-out are attached in the appendices XI and XII.

The important steps of calculation would be described in the following lines, even though a detailed description of the method has already been given in section (1-3-6).

(a) The method involves getting an approximate value of k_h so as to calculate α^* from the equation

FIGURE (3-5-3)

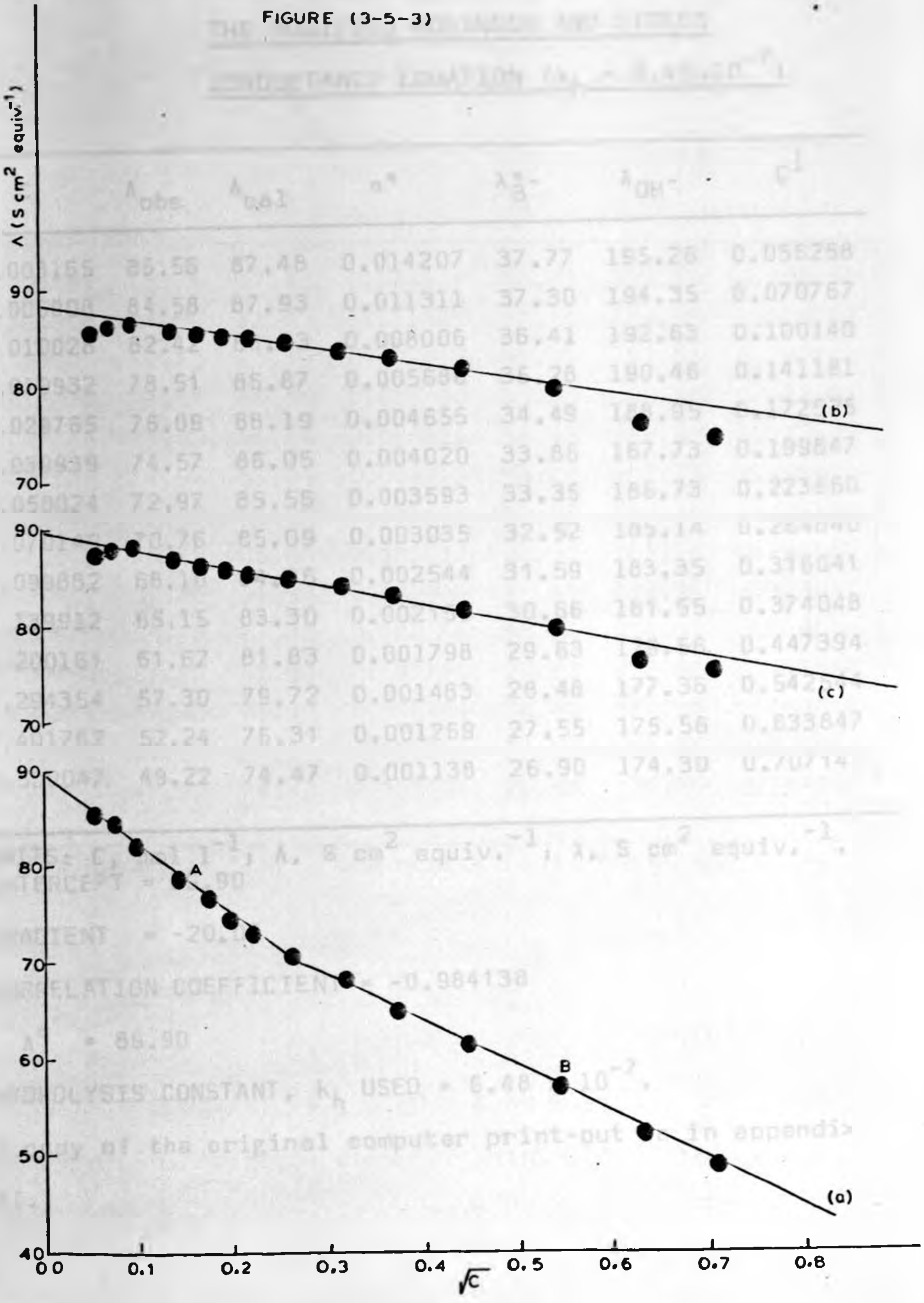

Λ (S cm^2 equiv^{-1})
90
80
70
90
80
70
90
80
70
60
50
40
(b)
(c)
(a)
A
B
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
√C

TABLE (3-5-7): CALCULATION FOR VARIOUS QUANTITIES FOR THE MODIFIED ROBINSON AND STOKES CONDUCTANCE EQUATION (k_h = 6.48×10^{-7})

C	Λ_{obs}	Λ_{cal}	α^*	$\lambda^*_{B^-}$	λ_{OH^-}	$C^{\frac{1}{2}}$
0.003165	85.56	87.48	0.014207	37.77	195.26	0.056258
0.005008	84.58	87.93	0.011311	37.30	194.35	0.070767
0.010028	82.42	88.13	0.008006	36.41	192.63	0.100140
0.019932	78.51	86.87	0.005686	35.28	190.46	0.141181
0.029765	76.09	86.19	0.004655	34.49	188.95	0.172525
0.039939	74.57	86.05	0.004020	33.86	187.73	0.199847
0.050024	72.97	85.56	0.003593	33.35	186.73	0.223660
0.070140	70.76	85.09	0.003035	32.52	185.14	0.264840
0.099882	68.10	84.36	0.002544	31.59	183.35	0.316041
0.139912	65.15	83.30	0.002150	30.66	181.55	0.374048
0.200161	61.62	81.83	0.001798	29.63	179.56	0.447394
0.294354	57.30	79.72	0.001483	28.48	177.36	0.542544
0.401762	52.24	76.31	0.001269	27.55	175.56	0.633847
0.500047	49.22	74.47	0.001138	26.90	174.30	0.707140

UNITS: C, mol l^{-1}, Λ, S cm^2 equiv.$^{-1}$, λ, S cm^2 equiv.$^{-1}$.

INTERCEPT = 89.90

GRADIENT = -20.06

CORRELATION COEFFICIENT = -0.984138

Λ^o = 89.90

HYDROLYSIS CONSTANT, k_h USED = 6.48×10^{-7}.

A copy of the original computer print-out is in appendix XI.

TABLE (3-5-8): CALCULATION FOR VARIOUS QUANTITIES FOR THE MODIFIED ROBINSON AND STOKES CONDUCTANCE EQUATION (k_h=6.49x10^{-7}).

C	Λ_{obs}	Λ_{cal}	α^*	$\lambda^*_{B^-}$	λ_{OH^-}	$C^{\frac{1}{2}}$
0.003165	85.56	87.48	0.014218	37.77	195.26	0.056258
0.005008	84.58	87.93	0.011319	37.30	194.35	0.070767
0.010028	82.42	88.13	0.008013	36.41	192.63	0.100140
0.019932	78.51	86.86	0.005690	35.28	190.46	0.141181
0.029765	76.09	86.19	0.004659	34.49	188.95	0.172525
0.039939	74.57	86.05	0.004023	33.86	187.73	0.199847
0.050024	72.97	85.56	0.003595	33.35	186.73	0.223660
0.070140	70.76	85.09	0.003037	32.52	185.14	0.264840
0.099882	68.10	84.36	0.002546	31.59	183.35	0.316041
0.139912	65.15	83.30	0.002151	30.66	181.55	0.374048
0.200161	61.62	81.83	0.001799	29.63	179.56	0.447394
0.294354	57.30	79.72	0.001484	28.48	177.36	0.542544
0.401762	52.24	76.31	0.001270	27.55	175.56	0.633847
0.500047	49.22	74.47	0.001139	26.90	174.30	0.707140

UNITS: C, mol l^{-1}, Λ, S cm^2 equiv.$^{-1}$; λ, S cm^2 equiv.$^{-1}$;

INTERCEPT = 89.90

GRADIENT = -20.06

CORRELATION COEFFICIENT = -0.984126

Λ^o = 89.90

HYDROLYSIS CONSTANT, k_h, USED = 6.49 x 10^{-7}

A copy of the original computer print-out is in appendix XIII.

$$\alpha^* = \frac{-k_h + (k_h^2 + 4Ck_h)^{\frac{1}{2}}}{2C}$$

$$k_h = \frac{k_w}{k_a}$$

(b) The λ_{OH^-} and $\lambda^*_{B^-}$ values at particular concentration were calculated from the equations

$$\lambda_{OH^-} = \lambda^o_{OH^-} - \frac{(B_1\lambda^o_{OH^-} + \frac{1}{2}B_2)\sqrt{C}}{1 + B_3a^o\sqrt{C}}$$

$$\lambda^*_{B^-} = \lambda^{o*}_{B^-} - \frac{(B_1\lambda^{o*}_{B^-} + \frac{1}{2}B_2)\sqrt{C}}{1 + B_3a^o\sqrt{C}}$$

(c) Finally the values calculated in (a) and (b) were substituted into the modified Robinson Stokes conductance equation

$$\Lambda = \Lambda^o - \frac{(B_1\Lambda^o + B_2)\sqrt{C}}{(1 + B_3a^o\sqrt{C})} + \alpha^*(\lambda_{OH^-} - \lambda^*_{B^-})$$

Various values of k_h were used in each computer run, until an intercept of 89.90, which is Λ^o value for NaB*, was attained and the correlation coefficient reached a value of ±1.

When a value of $k_h = 6.48 \times 10^{-7}$ was used with all the 14 conductance points, the programme yielded an intercept of 89.89774, and with $k_h = 6.49 \times 10^{-7}$ the intercept was 89.89663. The correlation coefficients in both cases were

-0.984138 and -0.984126 respectively. This shows that all the data points are lying on a straight line. The limiting equivalent conductivities of the ions involved in the modified equation, at 25^{o}C in water, were calculated using

$$\lambda^{o}_{OH^-} = 199.18^{(88)} \text{ S cm}^2 \text{ equiv.}^{-1}$$

$$\lambda^{o}_{Na^+} = 50.10^{(88)} \text{ S cm}^2 \text{ equiv.}^{-1}$$

Since limiting conductance for Sodium Barbital Λ^{o}_{NaB*} was found to be 89.90 S cm^{2} equiv.$^{-1}$, it followed that

$$\lambda^{o}_{B^{*-}} = 39.80 \text{ S cm}^2 \text{ equiv.}^{-1}$$

The value for $\lambda^{o}_{B^{*-}}$ obtained above is of the expected magnitude since it compares well with picrate and citrate ions (λ^{o} = 39.4) which are of somewhat comparable size to diethyl-barbiturate ion $(C_2H_5)_2C_4HN_2O_3^-$. The hydrolysis constant of 6.48×10^{-7} is of expected magnitude too.

The meaningfulness and correctness of including hydrolysis process into the conductance equation became obvious when one glances at plot (c) of Figure (3-5-3). The inclusion of hydrolysis not only removes the kink of the graph (a) but pushes the values up by such an amount that the Λ values agrees beautifully with the theoretically predicted value (plot b). Thus the present conductance work gives

$$\Lambda^{o}_{NaB^{*}} = 89.90 \text{ S cm}^{2}\text{equiv.}^{-1}$$

$$\lambda^{o*}_{B^{-}} = 39.80 \text{ S cm}^{2}\text{equiv.}^{-1}$$

and

$$k_{h} = 6.48 \times 10^{-7}$$

3-6 DIFFUSION RESULTS:

3-6-1 INTRODUCTION:

In aqueous electrolyte solutions, the ions can be caused to move from one position to another under two different kinds of forces. Under the effect of electrical gradient the ions migrate towards their respective electrodes with different speeds dictated by the "mobility" of the individual ions. During this migration,ions carry along with them the hydration shell.

The other force - the concentration gradient or gradient of chemical potential - which causes ions to diffuse from higher concentration to lower concentration differs from the electrical migration in the respect that during diffusion process all ions, positive or negative, move in the same direction and with a compromized same speed. This unidirectional and same speed brings about a unique set of conditions which make 'diffusion' a phenomena entirely different from other processes of mass transfer.

In an aqueous dilute NaCl solution, where ionization is 100%, the Na^+ and Cl^- ions possessing widely differing mobilities, diffuse with the same speed and in the same direction. Likewise, in the case of Barbituric acid, HB, the hydrogen and barbiturate ions would move undirectionally with equal velocity. Since, however, HB, is a weak electrolyte the extent of ionization decreases with increasing concentration, the compromized speed will differ considerably in different concentration ranges. This will happen simply because the mobilities of ions are concentration dependent.

In case of Sodium Barbital, NaB*, the state will be different from HB. If the salt produces Na^+ and $\overset{*}{B}{}^-$ ions only, the two ions would move with a certain velocity; however, in presence of hydrolysis, the additional OH^- ions produced will result in a new rate of movement. Thus diffusion in the low concentration rangs will take place under different conditions than in the higher concentration range, where hydrolysis is not that much pronounced.

The sections that follow would describe the results of diffusion in HB and NaB* aqueous solutions.

3-6-2 BARBITURIC ACID RESULTS:

As described earlier in section (1-5-1), a rotating diaphragm cell was used to determine the diffusion coefficients of aqueous acid solutions. From the known duration of the experiment, t; and the initial and final concentrations, the integral diffusion coefficients $\bar{D}$ were calculated using equation

$$\bar{D} = \frac{1}{\beta_t} \ln \frac{\Delta C^t}{\Delta C^o}$$

The integral diffusion coefficients were later converted into differential diffusion coefficients D by the method explained in section (1-5-2).

The relevant experimental data and the measured diffusion coefficients of HB are collected in Table (3-6-1).

The plct, employed to read $\bar{D}^o(\bar{C}_A)$ and to calculate $\bar{D}^o(\bar{C}_B)$ values for HB and to carry out successive approximations using equation (1-82), is shown in Figure (3-6-1). The difference of values in the first and second cycle of successive approximations was so small that the curves remained the same. Figure (3-6-2) dipicts the plot of final values of $\bar{D}^o(\bar{C}_B)$ against $(C_B^o)^{\frac{1}{2}}$ used to determine the slopes for equation

$$D = \bar{D}^o(\bar{C}_B) + \frac{(C_B^o)^{\frac{1}{2}}}{2} \cdot \frac{d(\bar{D}^o)}{d(C_B^o)^{\frac{1}{2}}}$$

and hence to calculate the differential diffusion coefficient D at each concentration.

The last two columns of Table (3-6-1) give the final values of $\bar{D}^o(\bar{C}_B)$ and differential diffusion coefficient D.

TABLE (3-6-1): DIAPHRAGM CELL DATA FOR AQUEOUS BARBITURIC ACID SOLUTIONS AT 25^{o}C.

C_B^o	$\bar{D}\times10^5$	$\bar{C}_B$	$\bar{C}_A$	$\bar{D}^o(\bar{C}_B)$	$D\times10^5$
0.0000	-	-	-	-	1.126*
0.0350_1	1.1649_3	0.0315_8	0.0060_4	1.163_5	1.074_4
0.0350_1	1.1492_4	0.0315_6	0.0059_7	1.150_8	1.061_7
0.0499_4	1.1121_2	0.0449_4	0.0097_2	1.110_6	0.927_3
0.0499_4	1.1082_4	0.0449_8	0.0097_3	1.107_5	0.924_2
0.0580_2	1.0748_6	0.0517_7	0.0106_8	1.074_9	0.814_8
0.0630_9	1.0198_6	0.0578_6	0.0110_0	1.023_7	0.713_8
0.0630_9	1.0506_5	0.0576_5	0.0111_7	1.048_6	0.738_7
0.0799_8	0.9572_6	0.0723_6	0.0137_4	0.958_7	0.481_5
0.0799_8	0.9731_2	0.0720_4	0.0137_7	0.971_6	0.494_3

UNITS: C_B^o, mol. $1.^{-1}$, $\bar{D}$, cm^2 sec.$^{-1}$, $\bar{C}_B$, mol.1.$^{-1}$
$\bar{C}_A$, mol.1.$^{-1}$, $\bar{D}^o(\bar{C}_B)$, cm.^{2}sec.$^{-1}$

Nernet limiting value $D^o = \dfrac{\nu_+ + \nu_-}{\nu_+|Z_+|} \dfrac{\lambda_+^o\lambda_-^o}{\lambda_+^o + \lambda_-^o} \cdot \dfrac{RT}{F^2}$

FIGURE (3-6-1)

INTEGRAL DIFFUSION COEFFICIENTS $\bar{D}$ Vs CONCENTRATION FOR BARBITURIC ACID

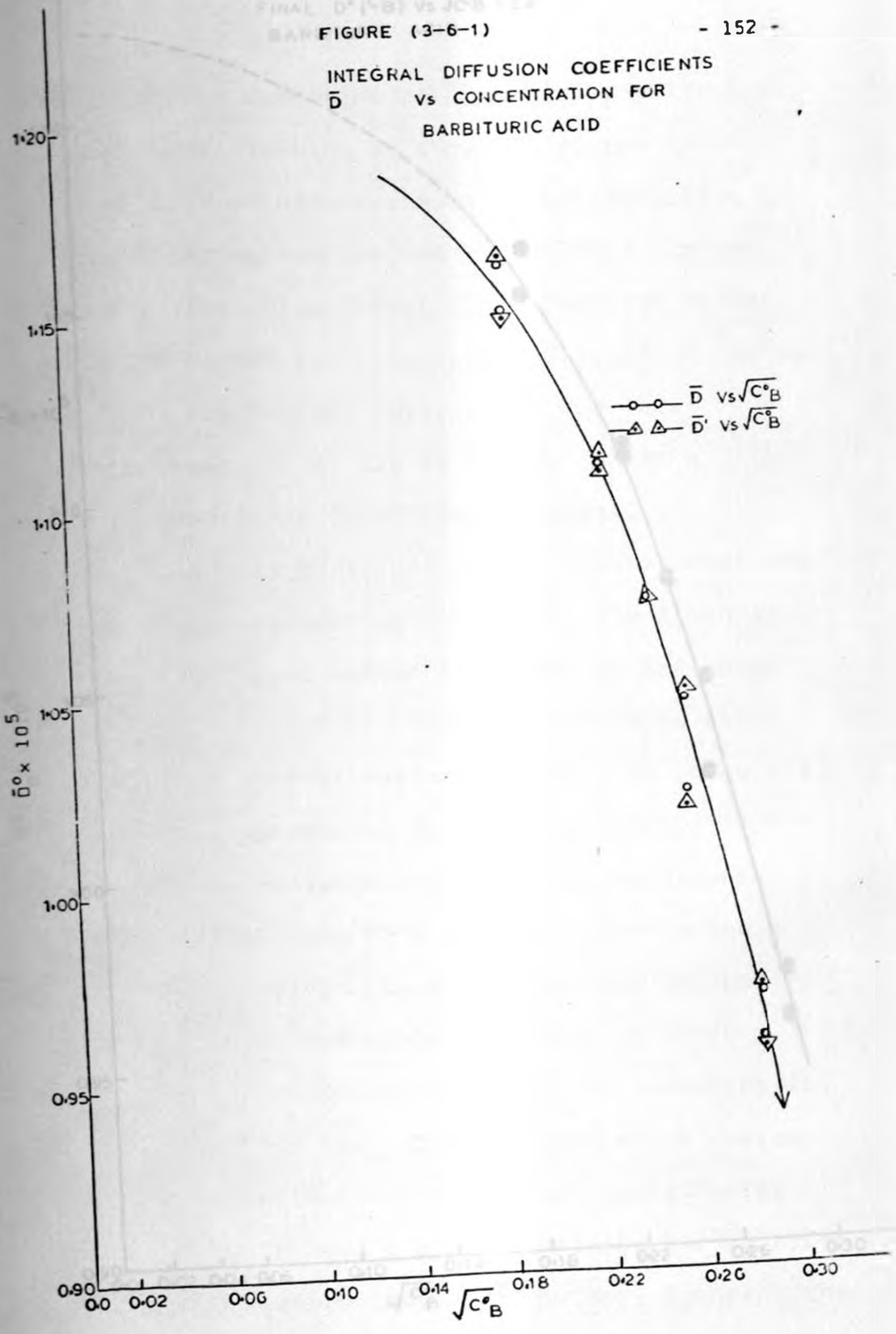
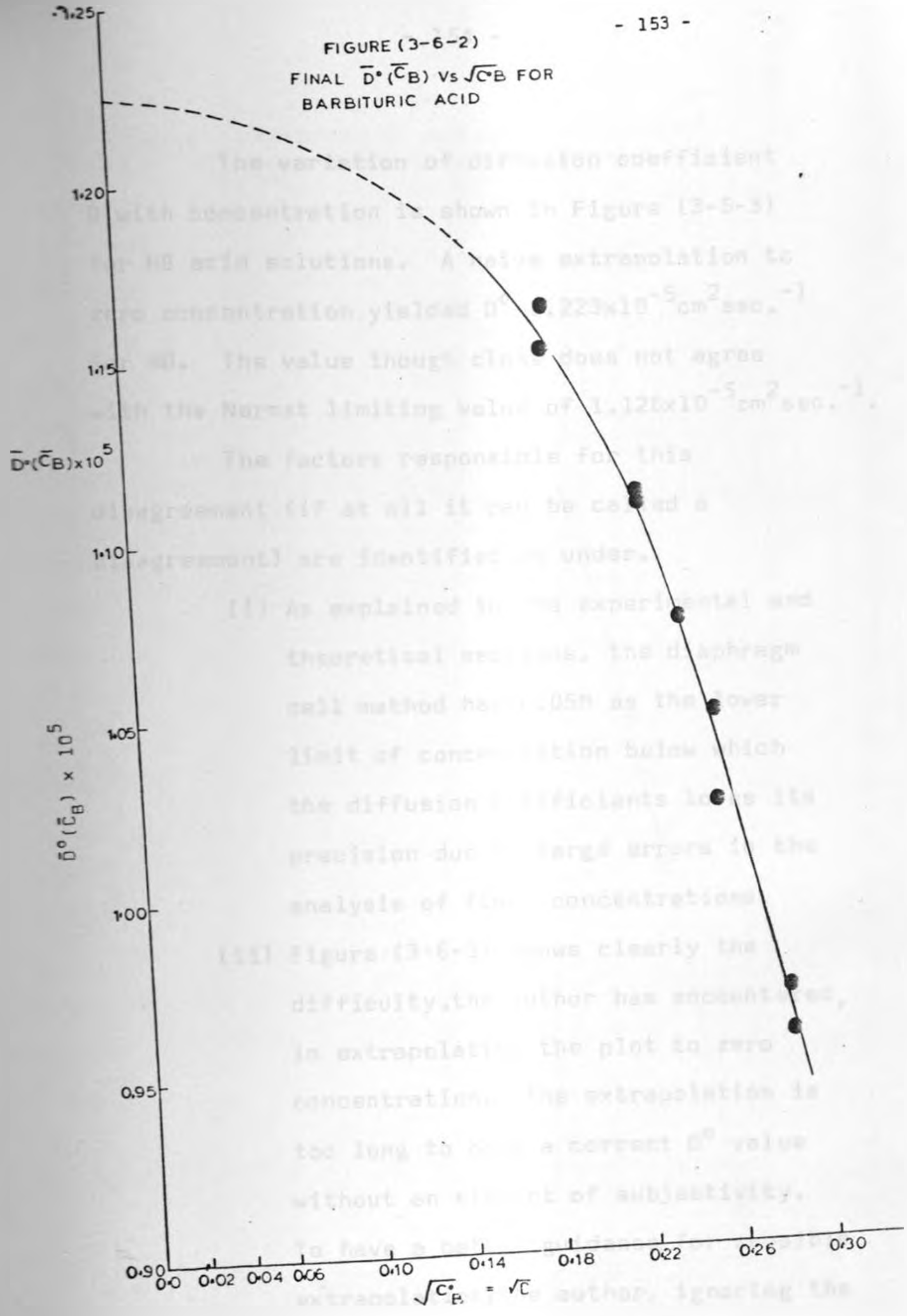


FIGURE (3-6-2)

FINAL $\bar{D}^\circ(\bar{C}_B)$ Vs $\sqrt{C^\circ_B}$ FOR BARBITURIC ACID



The variation of diffusion coefficient D with concentration is shown in Figure (3-6-3) for HB acid solutions. A naive extrapolation to zero concentration yielded $D^{o}=1.223\times10^{-5}cm^{2}sec.^{-1}$ for HB. The value though close does not agree with the Nernst limiting value of $1.126\times10^{-5}cm^{2}sec.^{-1}$.

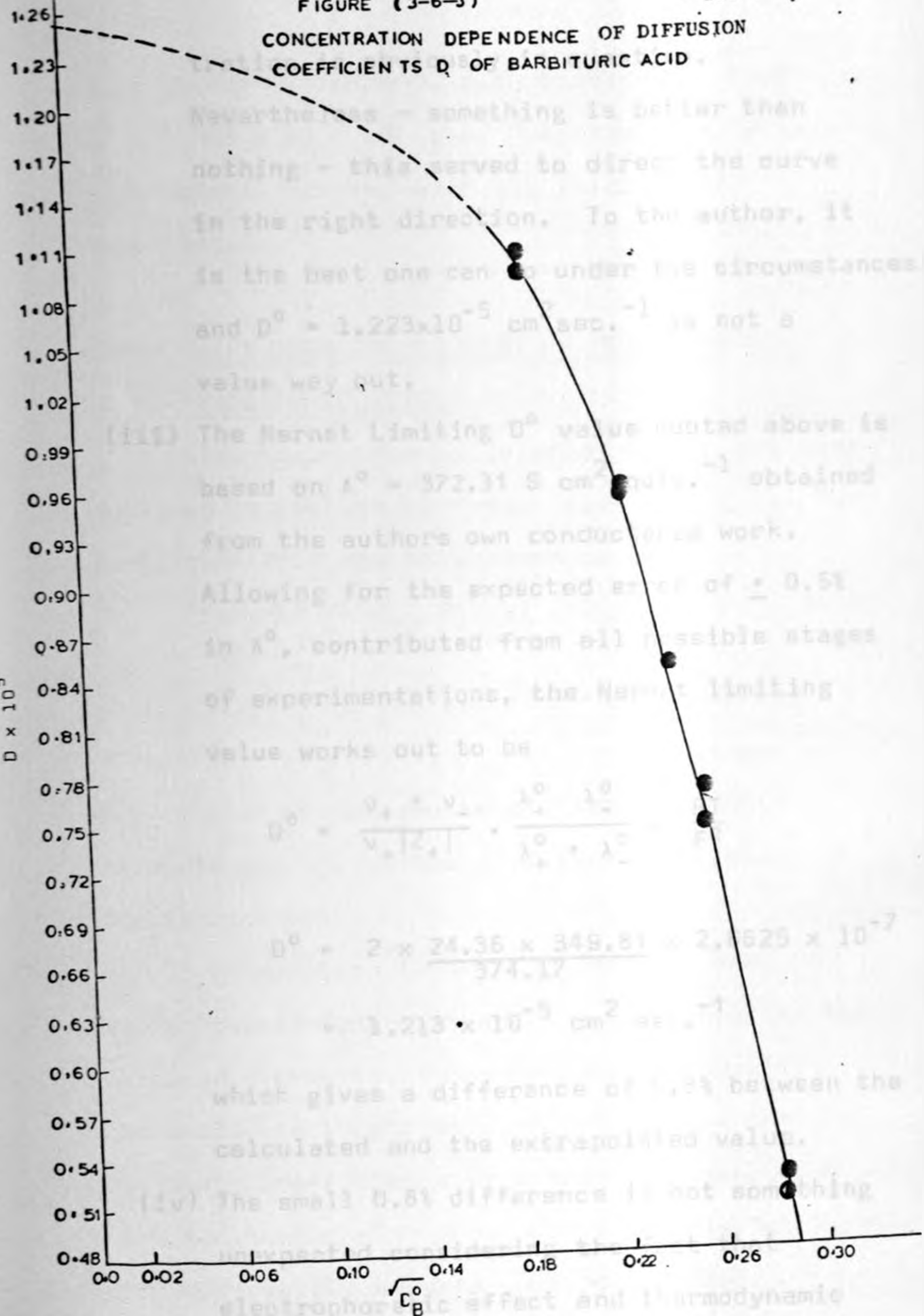
The factors responsible for this disagreement (if at all it can be called a disagreement) are identified as under.

(i) As explained in the experimental and theoretical sections, the diaphragm cell method has 0.05M as the lower limit of concentration below which the diffusion coefficients loses its precision due to large errors in the analysis of final concentrations.

(ii) Figure (3-6-3) shows clearly the difficulty,the author has encountered, in extrapolating the plot to zero concentration. The extrapolation is too long to have a correct D^{o} value without an element of subjectivity. To have a better guidance for sensible extrapolation,the author ignoring the limits of diaphragm cell method, did an experiment at 0.035M. The accuracy of this D value at such a low concen-

FIGURE (3-6-3)

CONCENTRATION DEPENDENCE OF DIFFUSION COEFFICIENTS D OF BARBITURIC ACID



tration is obviously in question. Nevertheless - something is better than nothing - this served to direct the curve in the right direction. To the author, it is the best one can do under the circumstances; and $D^o = 1.223 \times 10^{-5}$ cm^2 sec.$^{-1}$ is not a value way out.

(iii) The Nernst Limiting D^o value quoted above is based on $\Lambda^o = 372.31$ S cm^{2}equiv.$^{-1}$ obtained from the authors own conductance work. Allowing for the expected error of ± 0.5% in Λ^o, contributed from all possible stages of experimentations, the Nernst limiting value works out to be

$$D^o = \frac{\nu_+ + \nu_-}{\nu_+|Z_+|} \cdot \frac{\lambda^o_+ \ \lambda^o_-}{\lambda^o_+ + \lambda^o_-} \cdot \frac{RT}{F^2}$$

$$D^o = 2 \times \frac{24.36 \times 349.81}{374.17} \times 2.6625 \times 10^{-7}$$

$$= 1.213 \times 10^{-5} \text{ cm}^2 \text{ sec.}^{-1}$$

which gives a difference of 0.8% between the calculated and the extrapolated value.

(iv) The small 0.8% difference is not something unexpected considering the fact that electrophoretic effect and thermodynamic non-ideality have not been incorporated due to the non-availability of the needed data in the literature.

Thus it can be deduced, with confidence, that $D^{o} = 1.223 \times 10^{-5}$ cm^{2} sec.$^{-1}$ agrees well, within experimental errors, with the theoretical expectations.

3-6-3 DIFFUSION COEFFICIENT OF MOLECULAR BARBITURIC ACID.

The theory for calculation of D^{o}_{HB} has been outlined in section (1-4-4). Equation (1-72) for Barbituric acid may be written as

$$D(\text{Exptl}) = D_{HB} \cdot \frac{2(1-\alpha)}{(2-\alpha)} + D_{B^-} \cdot \frac{\alpha}{2-\alpha} \qquad (3\text{-}10)$$

Where D(Exptl) is the experimentally observed diffusion coefficient, D_{HB} is the diffusion coefficient of undissociated Barbituric acid molecule and D_{B^-} is the diffusion coefficient of barbiturate ion.

In equation (3-10), D_{HB} and D_{B^-} are concentration dependent and are influenced by the solution viscosity, thermodynamic non-ideality and small electrophoretic effect. Since the diffusion coefficients of barbiturate ion, D_{B^-}, were not needed with great accuracy, electrophoretic and non-ideality effects could be ignored. However, because barbiturate ion and the molecule both are large, the effect of solution viscosity was accommodated by writing in equation (3-10)

$$D_{HB} = D^{o}_{HB} \cdot \eta^{o}/\eta$$

and

$$D_{B^-} = D^{o}_{B^-} \cdot \eta^{o}/\eta \qquad (3\text{-}11)$$

Here D^{o} represents the diffusion coefficient at zero concentration and η/η^{o} is the relative viscosity of the solutions.

Equations (3-11) and (3-10) give the following extrapolation function(32) to obtain D^{o}_{HB}.

$$D'_{HB} = \{(1-\alpha/2)\ D(\mathrm{Exptl})\ \eta/\eta^{o} - (\alpha/2)\ D^{o}_{B^-_i}\}/(1-\alpha) \qquad (3\text{-}12)$$

Thus a plot of D'_{HB} against C gave D^{o}_{HB}, on extrapolation to zero concentration.

The viscosity data needed for equation (3-12) were obtained from the authors' own viscosity measurements, given in Table (3-4-1). $D^{o}_{B^-_i}$ was calculated from the Nernst equation

$$D^{o}_{B^-_i} = \frac{2RT}{F^2} \cdot \frac{\lambda^{o}_{H^+} \cdot \lambda^{o}_{B^-}}{\lambda^{o}_{H^+} + \lambda^{o}_{B^-}} \qquad (3\text{-}13)$$

$$D^{o}_{B^-} = \frac{RT\lambda^{o}_{B^-}}{F^2} = 0.599 \times 10^{-5}\,\mathrm{cm}^{2}\,\mathrm{sec.}^{-1}$$

Relevant data for the calculation of D'_{HB} values at various concentration are recorded in Table (3-6-2). The α values were obtained from the conductance work.

A plot of D'_{HB} against C is depicted in Figure (3-6-4) which lead to a value of 1.96 × 10^{-5} cm^2 $sec.^{-1}$ on extrapolation to zero concentration.

Further refinements in D'_{HB} could have been made using the equation

$$D''_{HB} = D'_{HB}\left(1 + C\,\frac{d\ln f_{HB}}{dc}\right) \qquad (3\text{-}14)$$

if f_{HB}, the activity coefficients of the undissociated Barbituric acid, were available.

The results obtained above, thus show that the diffusion coefficient of an isolated barbiturate ion is 0.599 × 10^{-5} cm^2 $sec.^{-1}$ and that of the molecular form is 1.196 × 10^{-5} cm^2 $sec.^{-1}$. The diffusion coefficient of Barbiturate ion is much lower than the molecular form. This indicates that the Barbiturate ion interacts fairly strongly with water molecules.

TABLE (3-6-2): DIFFUSION COEFFICIENTS OF BARBITURIC ACID MOLECULES AT 25°C.

C_B^o	$D\times10^5$	α	η/η^o	$D'_{HB}\times10^5$
0.0350_1	1.074_4	0.060_5	1.000_0	1.071_5
0.0350_1	1.061_7	0.060_5	1.000_0	1.058_4
0.0499_4	0.927_3	0.050_4	1.002_1	0.923_0
0.0499_4	0.924_2	0.050_4	1.002_1	0.919_8
0.0580_2	0.814_8	0.047_9	1.003_8	0.819_2
0.0630_9	0.713_8	0.045_2	1.004_5	0.706_4
0.0630_9	0.738_7	0.045_2	1.004_5	0.732_0
0.0799_8	0.481_5	0.040_2	1.009_2	0.471_7
0.0799_8	0.494_3	0.040_2	1.009_2	0.484_9

UNITS: C_B^o, mol.l^{-1}, D, $cm^2 sec.^{-1}$, D'_{HB}, $cm^2 sec.^{-1}$

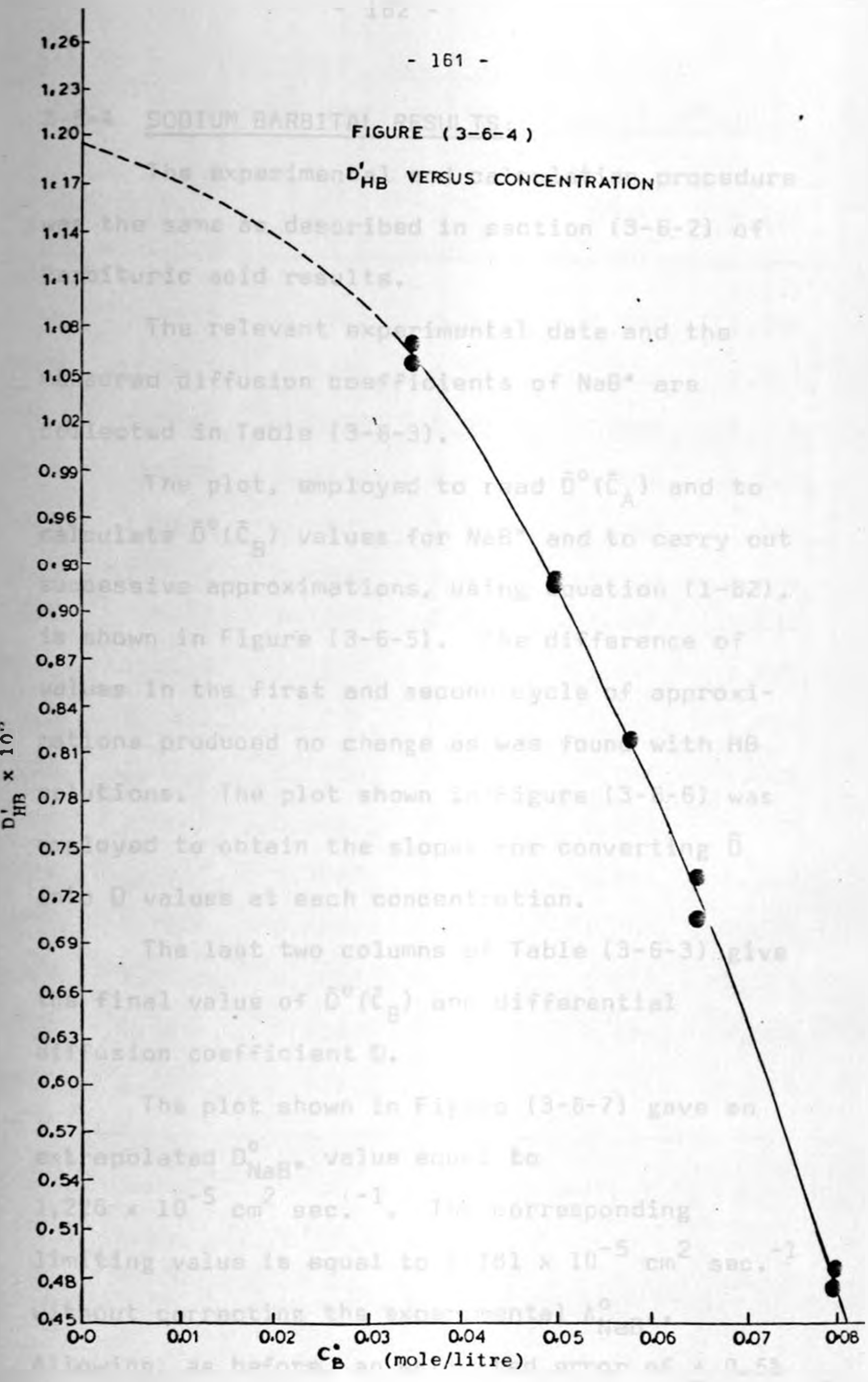


FIGURE (3-6-4)

D'_{HB} VERSUS CONCENTRATION

3-6-4 SODIUM BARBITAL RESULTS:

The experimental and calculation procedure was the same as described in section (3-6-2) of Barbituric acid results.

The relevant experimental data and the measured diffusion coefficients of NaB* are collected in Table (3-6-3).

The plot, employed to read $\bar{D}^o(\bar{C}_A)$ and to calculate $\bar{D}^o(\bar{C}_B)$ values for NaB* and to carry out successive approximations, using equation (1-82), is shown in Figure (3-6-5). The difference of values in the first and second cycle of approximations produced no change as was found with HB solutions. The plot shown in Figure (3-6-6) was employed to obtain the slopes for converting $\bar{D}$ into D values at each concentration.

The last two columns of Table (3-6-3) give the final value of $\bar{D}^o(\bar{C}_B)$ and differential diffusion coefficient D.

The plot shown in Figure (3-6-7) gave an extrapolated D^o_{NaB*} value equal to $1{,}228 \times 10^{-5}$ cm^2 sec.$^{-1}$. The corresponding limiting value is equal to 1.181×10^{-5} cm^2 sec.$^{-1}$ without correcting the experimental Λ^o_{NaB*}. Allowing, as before, an estimated error of $\pm$ 0.5% in Λ^o_{NaB*}, gives:

TABLE (3-6-3): DIAPHRAGM CELL DATA FOR AQUEOUS SODIUM BARBITAL SOLUTIONS AT 25°C.

C^o_B	$\bar{D}\times10^5$	$\bar{C}_B$	$\bar{C}_A$	$\bar{D}^o(\bar{C}_B)$	$D\times10^5$
0.000000	-	-	-	-	1.181*
0.0486_5	1.1002_3	0.0432_4	0.0054_1	1.100_7	1.054_9
0.0513_5	1.0997_7	0.0459_5	0.0067_6	1.099_8	1.054_4
0.0702_7	1.0803_3	0.0635_1	0.0086_5	1.080_2	1.046_3
0.0851_4	1.0667_5	0.0770_3	0.0100_0	1.066_8	1.042_6
0.1000_0	1.0602_6	0.0905_4	0.0121_6	1.060_2	1.038_9
0.1000_0	1.0601_9	0.0905_4	0.0121_6	1.060_2	1.038_9
0.1391_9	1.0483_2	0.1271_6	0.0174_3	1.048_5	1.032_1
0.2027_0	1.0414_1	0.1837_8	0.0243_2	1.041_9	1.023_1
0.2027_0	1.0412_7	0.1837_8	0.0243_2	1.041_3	1.022_5
0.2135_1	1.0408_5	0.1959_5	0.0279_7	1.040_8	1.022_1
0.2944_8	1.0343_0	0.2688_6	0.0364_9	1.034_3	1.017_3
0.3297_3	1.0317_6	0.3067_6	0.0468_9	1.031_9	1.014_0
0.4081_1	1.0320_6	0.3729_7	0.0513_5	1.031_6	1.011_6
0.4027_0	1.0288_9	0.3689_2	0.0513_5	1.028_9	1.010_6
0.5000_0	1.0244_4	0.4554_1	0.0608_1	1.024_4	1.006_8
0.5000_0	1.0242_9	0.4554_1	0.0608_1	1.024_5	1.006_8

UNITS: C^o_B, mol.l^{-1}. $\bar{D}$, cm^2 sec.$^{-1}$, $\bar{C}_B$, mol. l^{-1}.
$\bar{C}_A$, mol. l^{-1}, $\bar{D}^o(\bar{C}_B)$, cm^2 sec^{-1}.

*Extrapolation to zero concentration (Nernst Limiting Value).

*Nernst Limiting Value $D^o = \dfrac{\nu_+ + \nu_-}{\nu_+|Z_+|} \cdot \dfrac{\lambda^o_+ \lambda^o_-}{\lambda^o_+ + \lambda^o_-} \cdot \dfrac{RT}{F^2}$

FIGURE (3-6-5)

INTEGRAL DIFFUSION COEFFICIENTS D Vs CONCENTRATION FOR SODIUM BARBITAL

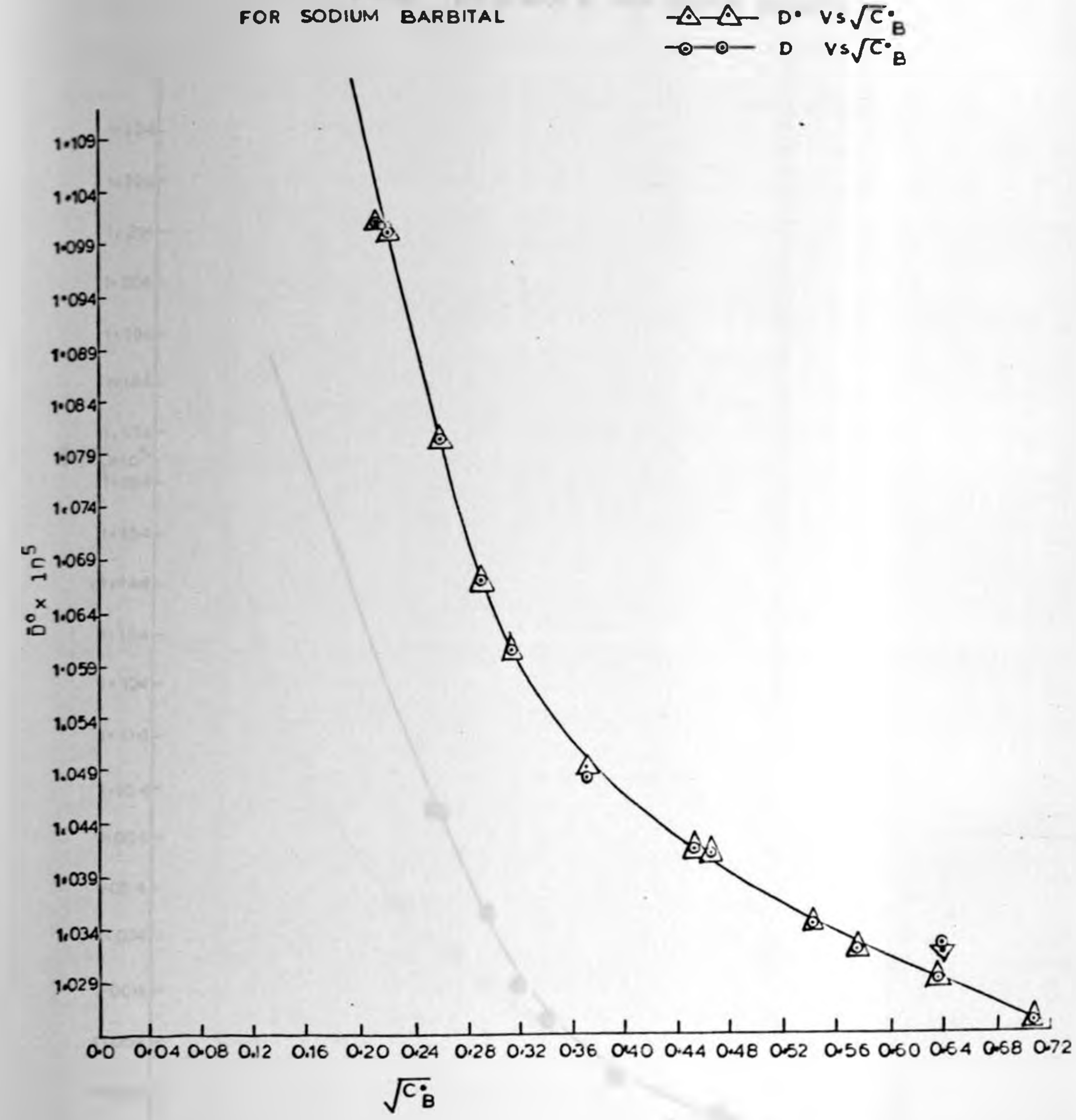


FIGURE (3-6-6)

FINAL $\bar{D}(\bar{C}_B)$ Vs $\sqrt{C^\circ_B}$ FOR SODIUM BARBITAL.

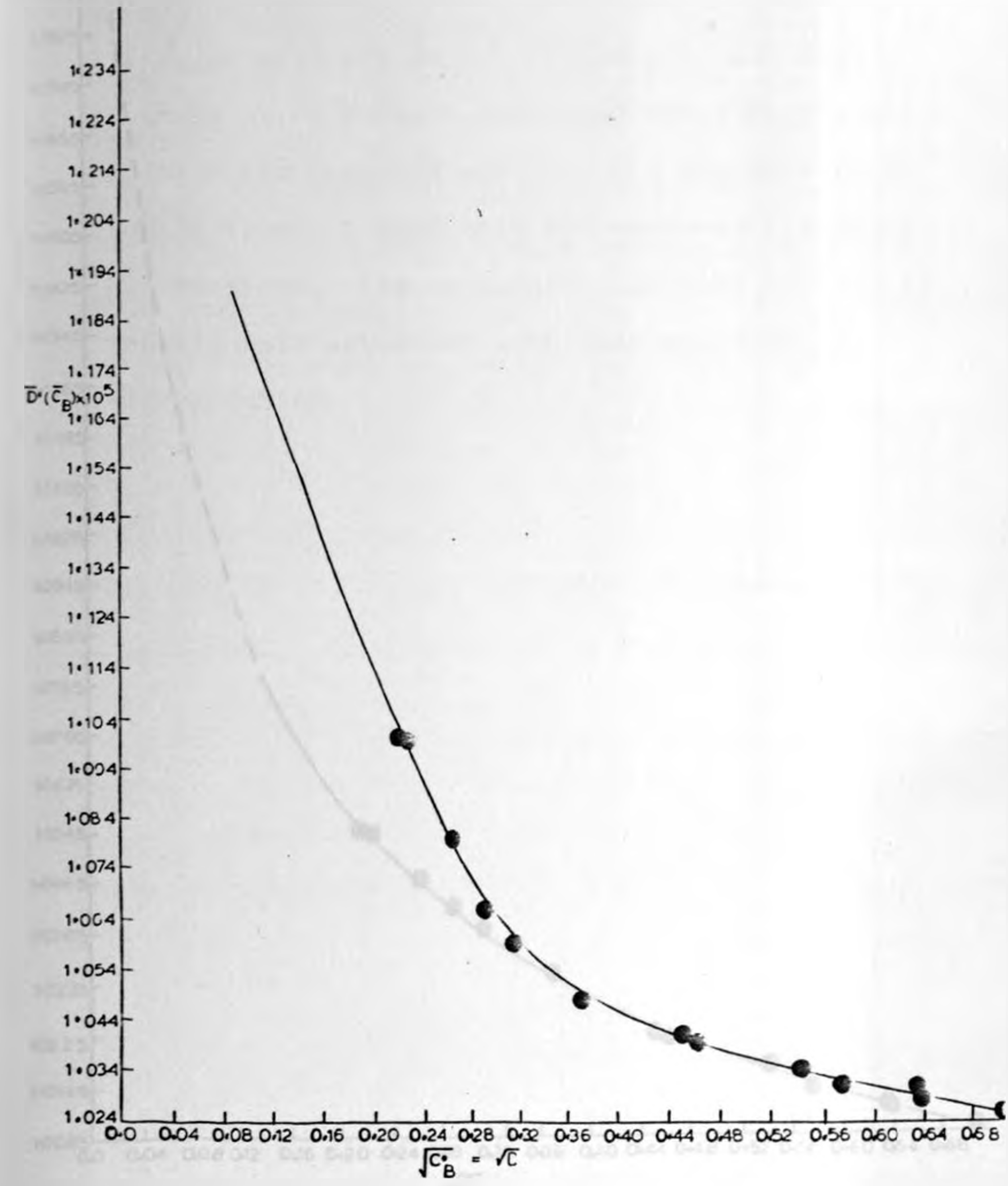
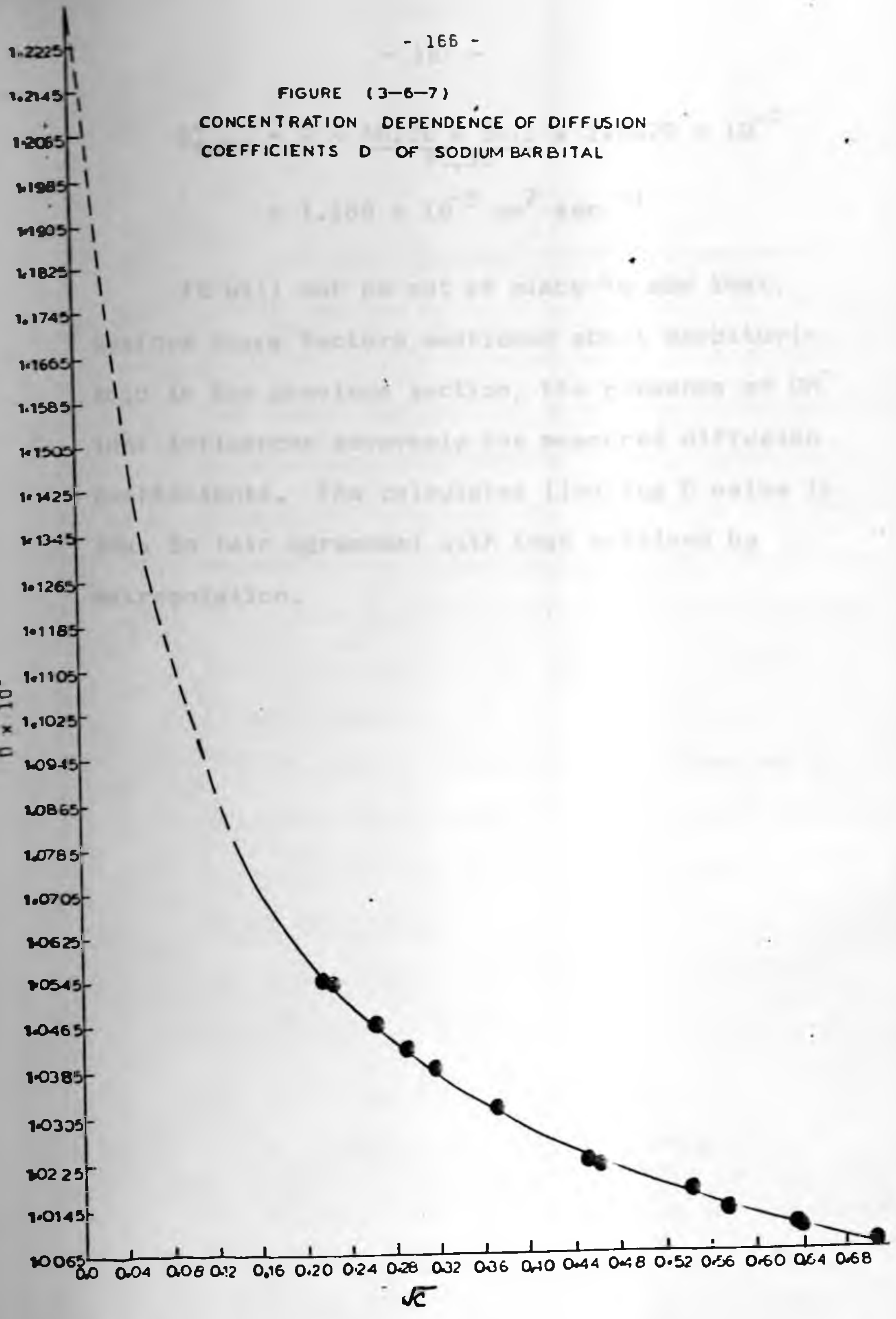


FIGURE (3—6—7)
CONCENTRATION DEPENDENCE OF DIFFUSION COEFFICIENTS D OF SODIUM BARBITAL



$$D^{o}_{NaB^{\bullet}} = 2 \times \frac{40.26 \times 50.1}{90.36} \times 2.6625 \times 10^{-7}$$

$$= 1.189 \times 10^{-5}\ cm^{2}\ sec.^{-1}$$

It will not be out of place to add that, besides those factors mentioned about Barbituric acid in the previous section, the presence of OH^{-} ions influences adversely the measured diffusion coefficients. The calculated limiting D value is thus in fair agreement with that obtained by extrapolation.

CONCLUSION

The five independent measurements carried out in aqueous Barbituric acid and Sodium Barbital solution at 25^{o}C have revealed that anions of both compounds undergo a strong interaction with water molecules. Partial molal volume ($\bar{V}$) studies with Na-Barbital show that the compound decreases the effective volume of the system. This gives a physical explanation of the fact that this compound can cause a decrease in blood pressure.

The study undertaken by the author has produced the following new and important physico-chemical data on the two substances at 25^{o}C.

BARTITURIC ACID

a) Equation for densities in the range (0.006 - 0.08M)

$$\rho = 0.997242 + 0.055032C$$

(confidence limit ± 0.00003)

b) Equation for relative viscosity in the range (0.05-0.08M)

$$\eta/\eta o = 1 + 0.003C^{\frac{1}{2}} + 0.220C - 2.65C^{2}$$

(confindence limit ± 0.002)

$$\frac{\eta}{\eta^o} = 1 + 0.009\ (\alpha C)^{\frac{1}{2}} + 1.16\ (\alpha C)$$

(confindence limit ± 0.001)

c) Average Partial Molal Volume $\bar{V} = 74.3\ cm^3\ mol^{-1}$

d) Limiting Equivalent Conductance $\Lambda^o = 372.31$ $Scm^2\ equiv.^{-1}$ (Confidence limit ±0.50)

e) Dissociation Constant $K_a = 1.01 \times 10^{-4}\ mol\ 1^{-1}$ (confidence limit $\pm 0.01 \times 10^{-4}$).

f) Diffusion Coefficients in the range(0.05 - 0.08M) (Confidence limit ± 0.02)and $D^o = 1.223 \times 10^5$ $cm^2 sec.^{-1}$ (Confidence limit $\pm\ 0.02 \times 10^{-5}$).

SODIUM BARBITAL

a) Equation for densities in the range (0.01- 0.50M)

$$\rho = 0.997044 + 0.078342C$$

(Confidence limit ± 0.00002).

b) Equation for relative viscosity in the range (0.01 - 0.5M)

$$\eta/\eta^o = 1 + 0.008C^{\frac{1}{2}} + 0.659C$$

(Confidence limit ± 0.004).

c) Equation for refractive index in the range (0.00 - 0.80M)

$$\eta = 3.700031 \times 10^{-2}C + 1.332452$$

(Confidence limit ± 0.00001)

d) Average partial molal volume $\bar{V} = 125.2\ cm^3\ mol^{-1}$

e) Limiting Equivalent Conductance

$\Lambda^o = 89.90\ Scm^2\ equiv^{-1}$

(Confidence limit ± 0.50)

f) Hydrolysis Constant $K_h = 6.48 \times 10^{-7}$

(Confidence limit $\pm 0.01 \times 10^{-7}$)

g) Diffusion Coefficients in the range

(0.05 - 0.50M)

(Confidence limit ±0.02)and $D^o = 1.228 \times 10^{-5} cm^2 sec.^{-1}$.

(Confidence limit $\pm 0.02 \times 10^{-5}$)

REFERENCES

1. Robert Taft and Helen M. Patton, University of Kansas Lawrence (Conductance and related properties of aqueous solutions of Sodium Diethylbarbiturate). Transactions of the Kansas Academy of Science, Vol. 53, No.4, 1950.

2. Prickner and Hilport, Jour. Amer. Med. Assoc., Vol. 52, p.311- (1909).

3. CRC - Handbook of Chemistry and Physics. 55th Edition (1974-1975), D-129.

4. E. Grimaux, Bull. Soc. Chim. Fr., 1879, (ii) 31, 146.

5. E.H. Rodd, Chemistry of Carbon Compounds A modern comprehensive treatise. Vol. IV Part B Heterocyclic Compound. Elsevier Publishing Compound, 1959 p.1276.

6. A.O. Filton and R.K. Smalley - Practical Heterocyclic Chemistry. Academic Press p.105.

7. J. Schmidt., A text-book of organic chemistry 7th Edition - Oliver and Boyd London, 1955 p.1872.

8. I.L. Finar, Organic Chemistry. 4th Edition Longman p.544.

9. H. Biltz and H. Wittek, Ber., 1921, 54, 1035.

10. H. Michael, J. Pr. Chem., 1887, (ii), 35, 456.

11. Org. Synth., Coll. Vol. 2, 1943, p.60.

12. F. Arndt, Rev. Fac. Sci. Istanbul, 1944, 9, 19.

13. E.R. Nightingale Jr., J. Phys. Chem., 63,
1277, (1959).

14. R.H. Stokes & R. Mills, Viscosity of Electrolytes
and Related Properties, Pergamon Press,
Oxford, (1965), p.585.

15. A.I. Vogel, Practical Org. Chem. Longman Green
and Co. Ltd. 3rd Edition 1956 p.1002.

16. D.A. MacInnes, The Principles of Electrochemistry,
Dover Publication Inc., New York, (1961)
p.82.

17. Ibid., 82-83.

18. D.O. Masson, Phil. Mag., 8, 218, (1929).

19. R.H. Stokes & R.Mills, Viscosity of Electrolytes
and Related Properties, Pergamon Press,
Oxford, (1965), p.7.

20. R.A. Robinson & R.H. Stokes, Electrolyte
Solution', 2nd ed., Butterworth, London,
(1959), p.304.

21. G. Jones & M. Dole, J. Am. Chem. Soc., 51,
295 , (1929).

22. S. Phang, Sains Malaysiana, 5, 103, (1976).

23. R.H. Stokes & R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon Press, Oxford, (1965), p.22.

24. H. Falkenhgen & E.L. Vernon, Philos. Mag., 14, 537, (1932).

25. R.H. Stokes & R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon Press, Oxford, (1965), p.23-30.

26. R.T.M. Bicknell, K.G. Lawrence & D. Feakins, J. Chem. Soc., Faraday Trans. I, 76, 637, (1980).

27. R.H. Stokes & R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon Press, Oxford, (1965), p.36.

28. Gurney, Ionic Processes in Solutions, McGraw Hill, (1953), p.168.

29. Kaminsky, Disc. Faraday Soc., 24, 171, (1957).

30. S.K. Mandal & S.K. Sangal, J. Indian Chem. Soc., 58, 1051, (1981).

31. E.R. Nightingale Jr., J. Phys. Chem., 63, 1381, (1959).

32. H.S. Harned & B.B. Owen, The Physical Chemistry of Electrolyte Solutions, 3rd. ed., Reinhold, New York, 1958, p.58-66.

33. R.A. Robinson & R.H. Stokes, Electrolyte Solutions, 2nd ed., Butterworth, London, (1959), p.74-86.

34. D.A. MacInnes, The Principles of Electrochemistry, Dover Publication Inc., New York, (1961), P.332.

35. C.W. Davies, Ion Association, Butterworth, London (1962) p.9.

36. R.A. Robinson & R.H. Stokes, Electrolyte Solutions, 2nd ed., Butterworth, London (1959), p.457.

37. R.A. Robinson & R.H. Stokes, Electrolyte Solutions, 2nd ed., Butterworth, London p.11.

38. T. Shedlovsky, J.Am. Chem. Soc. 54, 1405, (1932). T. Shedlovsky and A.S. Brown, Ibid., 56, 1066 (1934).

39. R.A. Robinson and R.H. Stokes, J.Am. Chem. Soc., 76, 1991 (1954).

40. J.E. Prue and P.J. Sherrington, Trans. Faraday Soc., 57, 1795 (1961).

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

42. H.S. Harned & B.B. Owen, The Physical Chemistry of Electrolyte Solutions, 3rd. ed., Reinhold, New York, 1958, p.287-298.

43. B.J. Levien, J. Phys. Chem., 59, 640 (1955).

44. Samuel Glasstone, Textbook of Physical Chemistry. D.Van Nostrand Company, Inc. July 1947. p.984.

45. R.A. Robinson & R.H. Stokes, Electrolyte Solutions, 2nd ed., Butterworth, London, (1959), p.285.

46. Ibid, p.287

47. G.T.A. Muller and R.H. Stokes, Trans. Faraday Soc., 53, 642 (1957).

48. R.A. Robinson & R.H. Stokes, Electrolyte Solutions, 2nd ed., Butterworth, London, (1959), p.304.

49. Ibid, p.256.

50. J.D.F. Christopher and H.P. Hutchinson, I.E.C. Fundamentals, 10, 303 (1971).

51. R.A. Robinson & R.H. Stokes, Electrolyte Solutions, 2nd ed., Butterworth, London, (1959), p.284.

52. J.H. Northrup and M.L. Anson, J. Gen. Physiol., 12, 543 (1929).

53. G.S. Hartley and D.F. Runnicles, Proc. R. Soc. A168, 401 (1938).

54. J.W. McBains and C.R. Dawson, Proc. R. Soc. A148 32, (1935).

55. H. Mougiun and W.H. Cathcart, J. Am. Chem. Soc., 57, 1971 (1935).

56. A.R. Gordon, Ann. N.Y. Acad. Sci., 46, 285. (1945).

57. R.H. Stokes, J. Am. Soc., 72, 763 (1950).

58. R.H. Stokes, Ibid., 72, 2243 (1950).

59. R.A. Robinson & R.H. Stokes, Electrolyte Solution', 2nd ed., Butterworth, London, (1959), p.254-256.

60. Ibid., p. 257

61. H. Mougiun and W.H. Catecart, J. Am. Chem Soc., 57, 1971 (1935).

62. R.H. Stokes, J. Am. Chem. Soc., 72, 763 (1950).

63. R.H. Stokes & R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon Press, Oxford, (1965), p.20.

64. N. Bauer and S.Z. Lewin, 'Determination of Density', Physical Methods of Chemistry Vol,m A. Weissberger and B.W. Rossiter, Eds., Wiley Interscience, New York, 1971, Chapter 2.

65. R.H. Stokes & R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon Press, Oxford, (1965), p.35.

66. W.A. Caw and R.G. Wylie, Br. J. Appl. Phys., 12, 94 (1961).

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

68. T. Shedlovsky and L. Shedlovsky, 'Conductometry' in Physical Methods of Chemistry, A. Weissberger and B.W. Rossiter, Eds., Part IV, Interscience, New York, 1971.

69. R.A. Robinson & R.H. Stokes, Electrolyte Solutions, 2nd ed., Butterworth, London, (1959), p.87.

70. Ibid, p.255.

71. R.P. Wendt and M. Shamim, J. Phys. Chem., 74 2770 (1970).

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

73. Arthur M. James, Practical Pysical Chemistry, J. and A. Churchill Ltd., London, 1961, p.45-47.

74. F. Kohlrausch, Weien Wien. Ann., 60, 315 (1897).

75. G. Jones and G.M. Bollinger, J. Am. Soc., 57, 280 (1935).

76. F. Kurlbaum and O. Lummer, Verh. Phy. Ges. Berlin., 14, 56 (1895).

77. R.H. Stokes, J. Am. Chem. Soc., 72, 2245 (1950).

78. R.P. Wendt, M. Shamim, Diffusion in Ternary Aqueous Saline Solutions. Loyola University, New Orleans, Louisiana. Research and Development progress Report No.504. Dec. 1969. p.39.

79. R. Mills and L.A. Woolf. The diaphragm cell. The Australian National University October 1968. p.47 (Table 5.1).

80. Operating Instructions Abbe-Refractometer Carl Zeiss. 7082 Oberkochen West Germany p.16.

81. Alexander Findlay. Practical Physical Chemistry. Longmans 8th Edition. p.286 -287.

82. Adrien Albert and E.P. Serjeant; The Determination Ionization Constants' Chapman and Hall Ltd., London, 1971, p.13.

83. R.A. Robinson & R.H. Stokes, Electrolyte Solutions, 2nd ed., Butterworth, London, (1959), p.457.

84. R. Gopal, D.K. Anggrawal & R. Kumar, Z. Phys. Chem., 84, 141, 1973.

85. R. Gopal, D.K. Anggrawal & R. Kumar, Bull. Chem., Soc. Japan, 46, 1973.

86. K. Drucker, Arkiv Kemi, Mineral Geology A22 171 (1946).

87. R.H. Stokes & R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon Press, Oxford, (1965), p.22.

88. R.A. Robinson & R.H. Stokes, Electrolyte Solutions, 2nd ed., Butterworth, London, (1959), p.463.

89. R.H. Stokes & R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon Press, Oxford, (1965), p.36.

90. R.L. Kay, T. Vituccio, C. Zawoyski & D.F. Evans, J. Phys. Chem., 70, 2336, 1966.

91. R.H. Stokes & R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon Press, Oxford, (1965), p.39.

92. Kaminsky, Disc. Faraday Soc., 24, 171, 1957.

93. R.H. Stokes & R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon Press, Oxford, (1965), p.37.

94. S. Phang. The treatment of viscosity data from solutions of electrolytes and non-electrolyte University Sains Malaysia. Sains Malaysiana 5(2), 103-111 (1976).

95. CRC-Handbook of Chemistry and Physics. 55th Edition (1974-1975), p.D-129.

96. H.S. Harned & B.B. Owen, The Physical Chemistry of Electrolyte Solutions, 3rd. ed., Reinhold, New York, 1958, p.287-298.

97. R.A. Robinson & R.H. Stokes, Electrolyte Solutions, 2nd ed., Butterworth, London, (1959), p.465.

98. D.A. MacInnes, The Principles of Electrochemistry, Dover Publication Inc., New York, (1961) p.336.

APPENDIX I

```
   1 CLS
  10DIM X(50), Y(50)
  20SX = 0
  30SX2 = 0
  40SY = 0
  50SY2 = 0
  60SXY = 0
  70PRINT TAB(0,4);"INPUT YOUR NUMBER       OF X,Y PAIRS"
  80INPUT N
  90PRINT TAB(0,4);"INPUT THE X AND Y       PAIRS BELOW"
 100PRINT TAB(0,5);"SEPARATE                INDIVIDUAL VALUES"
 110PRINT TAB(0,6);"EACH PAIR BY A          COMMA"
 120FOR I=1 TO N
 130INPUT X(I),Y(I)
 140NEXT I
 150FOR I=1 TO N
 160SX = SX + X(I)
 170SX2 = SX2 + X(I)^2
 180SY = SY + Y(I)
 190SY2 = SY2 + Y(I)^2
 200SXY = SXY + X(I)*Y(I)
 210NEXT I
 220INP = (SY*SX2-SX*SXY)/(N*SX2-(SX^2      ))
 230GRAD = (N*SXY-SX*SY)/(N*SX2-(SX^2)      )
 240SR=SQR(((N*SX2-(SX^2))*(N*SY2-(SY^      2))))
 250COEFF = (N*SXY-SX*SY)/SR
 270CLS
 280PRINT
 500 PRINT TAB(0,8);"THE INTERCEPT=";       INP
 510 PRINT TAB(0,10);"THE GRADIENT=";        GRAD
 520 PRINT TAB(0,12);"THE CORRELATION       COEFF =";COEFF
>RUN

INPUT YOUR NUMBER       OF X,Y PAIRS
```

APPENDIX II

```
INPUT YOUR NUMBER OF X,Y PAIRS
?28
INPUT THE X AND Y PAIRS BELOW
SEPARATE INDIVIDUAL VALUES
IN EACH PAIR BY A COMMA
?0.01.,1.33240
?0.0523484,1.33425
?0.1001548,1.33615
?0.2010727,1.33925
?0.3992507,1.34735
?0.6031261,1.35495
?0.7992834,1.36250
?0.0,1.332525
?0.0523484,1.3344
?0.10001548,1.33625
?0.2010727,1.3400
?0.3992507,1.34715
?0.6031261,1.35355
?0.79992834,1.361925
?0.0,1.33245
?0.0523484,1.334275
?0.1001548,1.336325
?0.2010727,1.3404
?0.3992507,1.34745
?0.6031261,1.35505
?0.7992834,1.362075
?0.0,1.33255
?0.049803,1.33425
?0.1034862,1.33625
?0.2001986,1.33985
?0.4003341,1.34725
?0.6000811,1.354825
?0.8008675,1.361975


THE INTERCEPT = 1.33245231
THE GRADIENT = 3.70003093E-2
THE CORRELATION COEFF = 0.999550495
```

APPENDIX III

```
 20S=0
 30REM INTIALIZING VALUES
 40DIM L(100),C(100),Z(100),X(100),Y(100),SZ(100),A(100),F2(100)
 50B1=0.23:B2=60.65:B3=0.3291E8
 60A0=5E-8:POWER=-1.5
 70REM DATA ENTRY
 80INPUT"ENTER THE VALUE OF LAMBDA-0";LO
 90PRINT
100PRINT"ENTER THE EXPERIMENTAL VALUES OF"
110PRINT"LAMBDA AND CONCENTRATION IN PAIRS"
120PRINT
130PRINT"SEPARATE EACH PAIR WITH A COMMA"
140 PRINT"YOUR TERMINATOR SHOULD BE 0.025604,23.273383"
150PRINT
160N=0
170INPUT C(N+1),L(N+1)
180N=N+1
190IF C(N) <>0.025604 THEN 170
200IF L(N) <>23.273383 THEN 170
210REM PROCESSING STAGE
220FOR H=1 TO 20
230FOR I=1 TO N
240Z(I)=((B1*LO)+B2)*SQR(C(I)*L(I))*(LO^POWER)
250SZ(I)=1+Z(I)+(Z(I)^2)/2
260A(I)=(L(I)*SZ(I))/LO
270F1=-1.0196*SQR(C(I)*A(I))
280F3=1+B3*A0*SQR(C(I)*A(I))
290F4=(F1/F3)
300F2(I)=10^F4
310NEXT I
320REM LEAST SQUARES
330SX=0:SY=0
340SX2=0:SY2=0:SXY=0
350FOR J=1 TO N
360Y(J)=1/(L(J)*SZ(J))
370X(J)=C(J)*L(J)*F2(J)*SZ(J)
380SX=SX+X(J)
390SX2=SX2+X(J)^2
400SY=SY+Y(J)
410SY2=SY2+Y(J)^2
420SXY=SXY+X(J)*Y(J)
430NEXT J
440S=S+1
450REM PRINT S
460INPT=(SY*SX2-SX*SXY)/(N*SX2-(SX^2))
470LO=1/INPT
480NEXT H
490REM RESULTS
500GRAD=(N*SXY-SX*SY)/(N*SX2-(SX^2))
510SR=SQR(((N*SX2-(SX^2))*(N*SY2-(SY^2))))
520COEFF=(N*SXY-SX*SY)/SR
530PRINT
540 FOR I=1 TO N
550 PRINT C(I);" ";L(I);" ";SZ(I);" ";A(I);" ";F2(I);" ";Y(I);" ";X(I
560 NEXT I
570K=1/((LO^2)*GRAD)
575K1=-LOGK
580PRINT"INTERCEPT";INPT
590PRINT"GRADIENT";GRAD
```

APPENDIX IV

```
ENTER THE VALUE OF LAMBDA-0370

ENTER THE EXPERIMENTAL VALUES OF
LAMBDA AND CONCENTRATION IN PAIRS

SEPARATE EACH PAIR WITH A COMMA
YOUR TERMINATOR SHOULD BE 0.0799746,13.582600

? 0.000047,242.553378
?0.0000106,230.273256
?0.000200,185.850589
?0.000391,147.686559
?0.000797,112.641641
?0.001623,83.432460
?0.003202,61.000302
?0.006401,44.480989
?0.0511845,16.927339
?0.012844,32.290891
?0.025604,23,.273383
?0.079975,13.582600
?0.065006,14.911488'
?0.058020,16.2197558
?0.035007,20.527798
?0.049941,17.068913
?0.0799746,13.582600
     C         Λ          S(z)        α           f±²         1/ΛS(z)        CΛf±²S(z)
   4.7E-5 242.553378 1.00233182 0.703540787 0.986590553 4.11321259E-3 1.12733672E-2
 2E-2
  1.06E-4 230.273256 1.0034139 0.668642613 0.980429107 4.32709171E-3 2.40129588
E-2
     2E-4 185.850589 1.0042145 0.540083445 0.975895212 5.35808466E-3 3.64270173
E-2
  3.91E-4 147.686559 1.00525572 0.429623433 0.970029968 6.73569596E-3 5.6309209
9E-2
  7.97E-4 112.641641 1.00655741 0.328101302 0.962747036 8.81987606E-3 8.6997751
8E-2
 1.623E-3 83.43246 1.0080594 0.243383768 0.954411243 1.18899171E-2 0.130279247
 3.202E-3 61.000302 1.00968727 0.178233487 0.945458267 1.62360781E-2 0.18645866
 6.401E-3 44.480989 1.0117076 0.130226655 0.934463436 2.22213558E-2 0.269178016
5.1185E-2 16.927339 1.02051111 4.99892781E-2 0.888024515 5.788867E-2 0.78518879
2
1.2844E-2 32.290891 1.01414707 9.47657505E-2 0.92135758 3.0536484E-2 0.38753370
5
2.5604E-2 23.273383 1.01698093 6.84924596E-2 0.906363145 4.22500935E-2 0.549265
576
7.9975E-2 13.5826 1.02299398 4.02092921E-2 0.875348627 7.19687583E-2 0.97272772
4
6.5006E-2 14.911488 1.02170764 4.40877626E-2 0.881893156 6.56375523E-2 0.873407
745
 5.802E-2 16.219756 1.02138546 4.79407058E-2 0.883539924 6.03623324E-2 0.849254
566
3.5007E-2 20.527798 1.01866303 6.05122564E-2 0.89757828 4.78219289E-2 0.6570526
03
4.9941E-2 17.068913 1.02034322 5.0399077E-2 0.888888243 5.74179726E-2 0.7731371
51
7.99746E-2 13.5826 1.02299392 4.02092898E-2 0.875348922 7.19687624E-2 0.97272313
1
INTERCEPT=2.89381286E-3
GRADIENT=7.03770971E-2
CORRELATION COEFF=0.999510568
LAMDA-0 =345.564847
IONISATION CONSTANT =1.18989745E-4  - !
-LOG K =3.92449046
```

APPENDIX V

```
ENTER THE VALUE OF LAMBDA-0 300

ENTER THE EXPERIMENTAL VALUES OF
LAMBDA AND CONCENTRATION IN PAIRS

SEPARATE EACH PAIR WITH A COMMA
YOUR TERMINATOR SHOULD BE 0.025604,23.273383

?0.000391,147.686559
?0.000797,112.641641
?0.001623, 83.432460
?0.003202, 61.000302
?0.006401, 44.480989
?0.012844, 32.290891
?0.025604, 23.273383
```

$C \quad \Lambda \quad S(z) \quad \alpha \quad f_{\pm}^{2} \quad \frac{1}{\Lambda S(z)} \quad C\Lambda f_{\pm}^{2} S(z)$

```
   3.91E-4 147.686559 1.00490514 0.398621762 0.97168859 6.73804582E-3 5.638582E-
2
   7.97E-4 112.641641 1.00611974 0.304399267 0.964974315 8.82371275E-3 8.7161102
2E-2
  1.623E-3 83.43246 1.00752112 0.225779325 0.957366457 1.18962695E-2 0.130612858
  3.202E-3 61.000302 1.00903978 0.165323746 0.949285446 1.62464967E-2 0.18709338
1
  6.401E-3 44.480989 1.01092435 0.120778062 0.939486769 2.22385726E-2 0.27041550
4
 1.2844E-2 32.290891 1.01319957 8.78759415E-2 0.927983282 3.05650403E-2 0.389955
883
 2.5604E-2 23.273383 1.01584218 6.35010233E-2 0.915051576 4.22974553E-2 0.553909
931
INTERCEPT2.68593168E-3
GRADIENT7.16213678E-2
CORRELATION COEFF0.999950596
LAMBA-0372.31029
1ONISATION CONSTANT1.00727327E-4
-LOG K3.99685269
```

APPENDIX VI

```
ENTER THE VALUE OF LAMBDA-0 380

ENTER THE EXPERIMENTAL VALUES OF
LAMBDA AND CONCENTRATION IN PAIRS

SEPARATE EACH PAIR WITH A COMMA
YOUR TERMINATOR SHOULD BE 0.025604,23.273383

?0.000391,147.686559
?0.000797,112.641641
?0.001623, 83.432460
?0.003202, 61.000302
?0.006401, 44.480989
?0.012844,32. 32.290891
?0.025604, 23.273383
                                                           1
                                                          ----
    C       Λ        S(z)        α            f±²         ΛS(z)         CΛf±²S(z)
  3.91E-4 147.686559 1.00490514 0.398621765 0.971688589 6.73804502E-3 5.638582
-2
  7.97E-4 112.641641 1.00611974 0.30439927 0.964974315 8.82371275E-3 8.71611023
E-2
 1.623E-3 83.43246 1.00752112 0.225779327 0.957366457 1.18962695E-2 0.130612858
 3.202E-3 61.000302 1.00903978 0.165323747 0.949285446 1.62464967E-2 0.18709338
1
 6.401E-3 44.480989 1.01092435 0.120778063 0.939486769 2.22385726E-2 0.27041550
4
 1.2844E-2 32.290891 1.01319957 8.78759422E-2 0.927983282 3.05650403E-2 0.389955
893
 2.5604E-2 23.273383 1.01584218 6.35010238E-2 0.915051576 4.22974553E-2 0.553909
931
INTERCEPT2.68593166E-3
GRADIENT7.16213679E-2
CORRELATION COEFF0.999950596
LAMBA-0372.310291
IONISATION CONSTANT1.00727326E-4
-LOG K3.9968527
```

APPENDIX VII

```
ENTER THE VALUE OF LAMBDA-0 2000

ENTER THE EXPERIMENTAL VALUES OF
LAMBDA AND CONCENTRATION IN PAIRS

SEPARATE EACH PAIR WITH A COMMA
YOUR TERMINATOR SHOULD BE 0.025604,23.273383

?0.000391,147.686559
?0.000797,112.641641
?0.001623, 83.432466
?0.003202, 61.000302
?0.006401, 44.480989
?0.012844, 32.290891
?0.025604, 23.273383
                           S(z)         α            f±²            1/ΛS(z)        CΛf±²S(z)
     C         Λ
   3.91E-4 147.686559 1.00490514 0.398621762 0.97168859 6.73804582E-3 5.638582E-
2
   7.97E-4 112.641641 1.00611974 0.304399267 0.964574315 8.82371275E-3 8.716110
2E-2
   1.623E-3 83.43246 1.00752112 0.225779325 0.957366457 1.18962695E-2 0.130612858
   3.202E-3 61.000302 1.00903978 0.165323746 0.949285446 1.62464967E-2 0.18709338
 1
   6.401E-3 44.480989 1.01092435 0.120778062 0.939486769 2.22385726E-2 0.27041559
 4
  1.2844E-2 32.290891 1.01319957 8.78759415E-2 0.927983282 3.05650403E-2 0.389955
883
  2.5604E-2 23.273383 1.01584218 6.35010233E-2 0.915051576 4.22974553E-2 0.553909
931
INTERCEPT2.68593168E-3
GRADIENT7.16213678E-2
CORRELATION COEFF0.999950596
LAMBA-0372.31029
IONISATION CONSTANT1.00727327E-4
-LOG K3.99685269
```

APPENDIX VIII

```
  1 CLS
 10DIM X(50), Y(50)
 20SX = 0
 30SX2 = 0
 40SY = 0
 50SY2 = 0
 60SXY = 0
 70PRINT TAB(0,4);"INPUT YOUR NUMBER        OF X,Y PAIRS"
 80INPUT N
 90PRINT TAB(0,4);"INPUT THE X AND Y        PAIRS BELOW"
100PRINT TAB(0,5);"SEPARATE                 INDIVIDUAL VALUES"
110PRINT TAB(0,6);"EACH PAIR BY A           COMMA"
120FOR I=1 TO N
130INPUT X(I),Y(I)
140NEXT I
150FOR I=1 TO N
160SX = SX + X(I)
170SX2 = SX2 + X(I)^2
180SY = SY + Y(I)
190SY2 = SY2 + Y(I)^2
200SXY = SXY + X(I)*Y(I)
210NEXT I
220INP = (SY*SX2-SX*SXY)/(N*SX2-(SX^2       ))
230GRAD = (N*SXY-SX*SY)/(N*SX2-(SX^2)       )
240SR=SQR(((N*SX2-(SX^2))*(N*SY2-(SY^       2))))
250COEFF = (N*SXY-SX*SY)/SR
270CLS
280PRINT
300 PRINT TAB(0,8);"THE INTERCEPT=";        INP
310 PRINT TAB(0,12);"THE CORRELATION        COEFF =";COEFF
320 PRINT TAB(0,12);"THE CORRELATION        COEFF =";COEFF
>RUN

  ?7
  INPUT THE X AND Y        PAIRS BELOW
  SEPARATE                 INDIVIDUAL VALUES
  EACH PAIR BY A           COMMA
  ?0.0562627,85.561796
  ?0.0707682,84.584293
  ?0.1001395,82.421048
  ?0.141181,78.510523
  ?0.172526731,76.09481353
  ?0.199847349,74.57030685
  ?0.223659363,72.9739855


     THE INTERCEPT = 89.8975926


     THE GRADIENT = -77.3201526


     THE CORRELATINON COEFF = -0.997717166
```

APPENDIX IX

```
RUN
INPUT THE X AND Y        PAIRS BELOW
SEPARATE                 INDIVIDUAL VALUES
EACH PAIR BY A           COMMA
?0.246839857,70.75630617
?0.316040964,68.10151442
?0.3874047542,65.15031758
?0.447393168,61.61881996
?0.54254379,57.30360802
?0.633846722,52.23581668
?0.7071402937,49.2178619


 THE INTERCEPT=83.1499795


 THE GRADIENT=-48.0510643


 THE CORRELATION COEFF =-0.998793937
```

APPENDIX X

```
  1CLS
 10REM INITIALIZING VALUES
 20DIM L(100),L1(100),C(100),X(100),Y(100),A(100),LB(100),LH(100)
 30B1=0.23:B2=60.65:B3=0.3291E8:A0=5E-8:LB0=39.80:LH0=199.18
 40REM DATA ENTRY
 50INPUT TAB(0,2);"ENTER THE VALUE OF CONST"KH
 60PRINT TAB(0,4)"PLEASE ENTER THE CONCENTRATION AND LAMDA"
 70PRINT"IN PAIRS SEPARETED WITH A COMMA"
 80PRINT
 90PRINT"REMEMBER TO ENTER 0.500047,49.217862"
100PRINT"AS THE LAST VALUE"
110PRINT
120PRINT
130N=0
140INPUT C(N+1),L(N+1)
150N=N+1
160IF C(N)<>0.500047 THEN 140
170IF L(N)<>49.217862 THEN 140
180REM PROCESSING STAGE
190FOR I=1 TO N
200A(I)=(-KH+SQR((KH^2)+4*C(I)*KH))/(2*C(I))
210M1 =1+B3*A0*SQR(C(I))
220M2 =(B1*LH0+(B2/2))*SQR(C(I))
230LH(I)=LH0-(M2/M1)
240M3 =(B1*LB0+(B2/2))*SQR(C(I))
250LB(I)=LB0-(M3/M1)
260F =A(I)*(LH(I)-LB(I))
270L1(I)=(M1*(L(I)-F)+B2*SQR(C(I)))/(M1-B1*SQR(C(I)))
280X(I)=SQR(C(I))
290Y(I)=L1(I)
300NEXT I
310REM
320REM LEAST SQUARES
330SX=0:SY=0
340SX2=0:SY2=0:SXY=0
350FOR I =1 TO N
360SX =SX+X(I)
370SX2=SX2+X(I)^2
380SY=SY+Y(I)
390SY2=SY2+Y(I)^2
400SXY=SXY+X(I)*Y(I)
410NEXT I
420REM RESULTS
430INPT=(SY*SX2-SX*SXY)/(N*SX2-(SX^2))
440GRAD=(N*SXY-SX*SY)/(N*SX2-(SX^2))
450SR=SQR(((N*SX2-(SX^2))*(N*SY2-(SY^2))))
460COEFF=(N*SXY-SX*SY)/SR
470L0=INPT
480PRINT
490FOR I = 1 TO N
495MODE0
500PRINT C(I);"";L(I);"";L1(I);"";A(I);"";LB(I);"";LH(I);"";X(I);
510NEXT I
520PRINT"INTERCEPT=";INPT
530PRINT"GRADIENT=";GRAD
540PRINT"CORRELATION COEFF=";COEFF
550PRINT"LAMDA-0";L0
560END
```

APPENDIX XI

```
ENTER THE VALUE OF CONST  6.48E-7
PLEASE ENTER THE CONCENTRATION AND LAMDA
IN PAIRS SEPARETED WITH A COMMA

REMEMBER TO ENTER 0.500047,49.217862
AS THE LAST VALUE


?0.003165,85.561796
?0.005008,84.584293
?0.010028,82.421048
?0.019932,78.510523
?0.029765,76.094814
?0.039939,74.570307
?0.050024,72.973986
?0.070140,70.756306
?0.099882,68.101514
?0.139912,65.15031780.
?0.200161,61.618820
?0.294354,57.303608
?0.401762,52.2358170.5
?0.500047,49.217862
     c      Λobs      Λcal        α*             λB-*        λOH-       √c
  3.165E-3 85.561796 87.483383 1.42067119E-2 37.7671632 195.259615 5.62583327E-2

  5.008E-3 84.584293 87.9342329 1.13105906E-2 37.2975811 194.354012 7.0767224E-2

 1.0028E-2 82.421048 88.1271149 8.00635395E-3 36.4058633 192.634309 0.100139902

 1.9932E-2 78.510523 86.8655578 5.68556901E-3 35.2770625 190.457383 0.141180735

 2.9765E-2 76.094814 86.189631 4.65501811E-3 34.4949301 188.949018 0.17252536

/3.9939E-2 74.570307 86.0494688 4.01989068E-3 33.8626983 187.729741 0.199847442

 5.0024E-2 72.973986 85.5557551 3.59266525E-3 33.3455582 186.732421 0.223660457

  7.014E-2 70.756306 85.0902603 3.0349015E-3 32.5178933 185.136245 0.264839574

 9.9882E-2 68.101514 84.3596704 2.54384588E-3 31.591702 183.350058 0.316041137

  0.139912 65.150318 83.3049839 2.14977348E-3 30.6591267 181.55156 0.374048125

  0.200161 61.61882 81.8278236 1.79765797E-3 29.6267528 179.560597 0.447393563

  0.294354 57.303608 79.7237488 1.48262168E-3 28.4836481 177.356086 0.542544008

  0.401762 52.235817 76.3102333 1.26919192E-3 27.5514911 175.558394 0.633846985

  0.500047 49.217862 74.4708377 1.1377187E-3 26.8968779 174.295954 0.707140014

INTERCEPT=89.89774
GRADIENT=-20.0637615
CORRELATION COEFF=-0.98413753
LAMDA-089.89774
```

APPENDIX XII

```
ENTER THE VALUE OF CONST  6.49E-7
PLEASE ENTER THE CONCENTRATION AND LAMDA
IN PAIRS SEPARETED WITH A COMMA

REMEMBER TO ENTER 0.500047,49.217862
AS THE LAST VALUE

?0.003165,85.561796
?0.005008,84.584293
?0.010028,82.421048
?0.019932,78.51.0523
?0.029765,76.094814
?0.039939,74.570307
?0.0500234,72.973986
?0.070140,70.756306
?0.099882,68.101514
?0.139912,65.150318
?0.200161,61.618820
?0.294354,57.303608
?0.401762,52.235817
?0.500047,49.217862
    C         Λobs         Λcal            α*                λB-*          λOH-        √C
  3.165E-3 85.561796 87.4816491 1.42175912E-2 37.7671632 195.259615 5.62583327E-
2
  5.008E-3 84.584293 87.9328504 1.13192649E-2 37.2975811 194.354012 7.0767224E

 1.0028E-2 82.421048 88.1261346 8.01250447E-3 36.4058633 192.634309 0.100139902

 1.9932E-2 78.510523 86.8648609 5.68994182E-3 35.2770625 190.457383 0.141180735

 2.9765E-2 76.094814 86.1890601 4.65860018E-3 34.4949301 188.949018 0.17252536

 3.9939E-2 74.570307 86.0489757 4.022985E-3 33.8626983 187.729741 0.199847442

 5.0024E-2 72.973986 85.5553142 3.59543131E-3 33.3455582 186.732421 0.223660457

  7.014E-2 70.756306 85.0898878 3.03723878E-3 32.5178933 185.136245 0.264839574

 9.9882E-2 68.101514 84.359358 2.54580546E-3 31.591702 183.350058 0.316041137

  0.139912 65.150318 83.3047199 2.15142983E-3 30.6591267 181.55156 0.374048125

  0.200161 61.61882 81.8276028 1.79904327E-3 29.6267528 179.560597 0.447393563

  0.294354 57.303608 79.7235667 1.48376439E-3 28.4836481 177.356086 0.54254400

  0.401762 52.235817 76.3100774 1,27017023E-3 27.5514911 175.558394 0.63384698

  0.500047 49.217862 74.4706979 1.13859573E-3 26.8968779 174.295954 0.70714001

INTERCEPT=89.8966259
GRADIENT=-20.0619613
CORRELATION COEFF=-0.98412594
LAMDA-089.8966259
```