A PHYSICOCHEMICAL AND ELECTROCHEMICAL STUDY OF AQUEOUS THIAMINIUM DICHLORIDE AT 25°C

By

ASA OKOTH OOKO
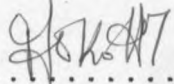
This thesis has been submitted to the college of Biological and Physical Sciences, University of Nairobi in partial fulfillment of the requirements for the degree of Master of Science.

July, 1990.

DECLARATION

I, Asa Okoth Ooko, hereby declare that the work described here-in was carried out by me at the Physical Chemistry Research laboratory of the Chemistry Department, University of Nairobi. I further declare that this work has neither been accepted nor being concurrently submitted in candidature for any other degree in another university.
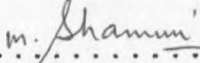
Signed: ....

ASA OKOTH OOKO

Date: ..01-07-1991...

This work has been presented for examination with the knowledge of:

The Project Supervisor,

Signed: ....

DR. MOHAMMED SHAMIM

Date: 17-07-1991...

ii

DEDICATION

To the family of Ooko Angwang'a - especially his sons.

ACKNOWLEDGEMENTS

ABSTRACT

Investigation of density, viscosity, refractive index, conductivity and diffusivity of aqueous Thiaminium dichloride solutions at 25°C have been carried out over the concentration range 0 - 1M. The concentration dependence of density and related quantities - apparent and partial molal volumes- have been obtained and the latter agrees with Masson's theory. The values of the latter quantities at infinite dilution have been obtained as $\phi^0 = V^0 = 157 \pm 2$ cm³ mol⁻¹ and the ionic contribution have been discussed. The variation of viscosity, refractive index and molal refractivity with concentration have also been shown. The viscosity results support the Jones-Dole and Einstein's theories, with the A and B coefficients having magnitudes that confirm strong interactions between the solute and solvent particles. B_{ion} values have been discussed. The value of molal refractivity at infinite dilution, $[R_{app}]^0_D = 70.0 \pm 1.4$ cm³ mol⁻¹, suggests the presence of loosely bound or delocalised electrons and therefore high polarisability of some solution constituents. The concentration variation of conductivity can be explained by proposing higher valency ionic species resulting from a two step ion association scheme with association constants being $K_1 = 1/K_{a1}$ and $K_2 = 1/K_{a2}$

1 mol^{-1}. K_{a1} and K_{a2} values are calculated from literature[18] pK_{a1} and pK_{a2} values respectively. The mixture rule is more appropriate to this situation as opposed to Kohlrausch's isoionic rule. The limiting ionic equivalent conductivity of the ions involved have been found to be; $\lambda^{\circ}_{ThI^{+}} = 29.3 \pm 0.3$, $\lambda^{\circ}_{ThIH^{2+}} = 35.8 \pm 0.3$ and $\lambda^{\circ}_{ThIH^{3+}} = 41.3.0 \pm 0.3$ S cm^2 (g equiv.)$^{-1}$. The electrolyte's infinite dilution equivalent conductivity was 532.7 ± 0.5 S cm^2 (g equiv.)$^{-1}$. The variation of the differential diffusion coefficient, determined within an accuracy of 0.5 % using a modified diaphragm cell, with concentration has been established and the electrolyte's infinite dilution value, D^0, was $1.27_5 \times 10^{-5}$ cm^2 s^{-1}.

These results indicate strong ion-ion, ion-solvent and solvent-solvent interactions.

CONTENTS

LIST OF PRINCIPAL SYMBOLS

A   Area, coefficient in Jones-Dole equation

a^0 Distance of closest approach in Angstrom

a   Coefficient in Masson's equation, ionic radii including water of hydration

a_1 Coefficient in Einstein's equation

B   Coefficient in Jones-Dole equation

b   Coefficient in the extended Onsager equation

B_1, B_2 and B_3 parameters of conductivity equations

C   Concentration in $mol.l^{-1}$ or gram equivalent

C_A, C_B Concentrations in chambers A and B of the diffusion cell

C^0_A, C^0_B Initial concentrations in the specified chambers

C^t_A, C^t_B Final concentrations in the specified chambers

$\bar{C}_A$, $\bar{C}_B$ $(C^0_A + C^t_A)/2, (C^0_B + C^t_B)/2$

ΔC^0, ΔC^t $(C^0_B - C^0_A), (C^t_B - C^t_A)$

D   Coefficient in Jones-Dole equation and the differential diffusion coefficient

D^0 Differential diffusion coefficient at infinite dilution

$\bar{D}_{exp}$ Experimental diaphragm cell integral diffusion coefficient

$\bar{D}(C_i)$ Integral diffusion coefficient at concentation C_i

$\bar{D}_0(C_1)$ Hypothetical integral diffusion coefficient defined by equation (2-87)

E   Electric field strength

e   Electronic charge

F   Faraday constant = 96487 C equiv.$^{-1}$

F   Force per unit area in equation (2-16)

f_i Activity coefficient of species i

$f_{\pm}$ Mean activity coefficient

H   Matrix in the Onsager-Fuoss conductivity equation

h   Coefficient in Redlich-Meyers equation

I, I   Ionic strength and identity matrix respectively

J   Flux of matter

K   Coefficient in Redlich - Meyers and Kohlrausch's equations respectively

K_n Conductivity cell constants and association constants

L   Effective length of diffusion path in the porous disc and distance between electrodes in the conductivity cell

M   Molarity

m   Molality

n, N   Refractive indices in equation (2-35)

n   Hydration number

P   Pressure

p   Pressure gradient

q   Velocity vector in equation (2-16)

R   Resistance, Molar gas constant and radius in equation (2-20)

Re   Reynold's number

T   Absolute temperature

t   Time in seconds

u   Mobility

V_A, V_B Volumes of chambers A and B

V_i, V_e, V_{oi}, V_o, V Partial Molal volume of component i, electrostriction volume, partial molal volume of component i at infinite dilution, volume of solvent and volume of solution respectively

W   Molecular weight

X   Modification factor in the Onsager equation (2-61)

$y_\pm$ Mean activity coefficient divided by mean ionic molar concentration

α First degree of association, coefficient in equation (4-8)

β Diffusion cell constant, second association constant or coefficient in equation (4-8)

ε Dielectric constant

η, η, η_{rel} Absolute viscosities of solvent, solution and relative viscosities of solutions respectively

κ Specific conductance or conductivity

Λ, Λ^o Electrolytic equivalent conductivity at finite concentration and infinite dilution respectively

λ_i, λ^o_i Ionic equivalent conductivity of ion i at finite concentration and infinite dilution respectively

$\nu+$, $\nu-$ and ν Number of positive, negative ions, coefficient in equation and Kinematic viscosity respectively

π Coefficient in equations (2-20) and (2-21)

ρ Specific resistivity, density or coefficient of ionic friction in equation (2-26)

σ Coefficient in equation (3-6)

τ Force per unit area

ϕ, ϕ_0, ϕ_f Apparent Molal volumes at finite concentration, infinite dilution and fluidity respectively

LIST OF APPENDICES

LIST OF TABLES

TABLE OF FIGURES

CHAPTER 1

INTRODUCTION, OBJECTIVE AND
CHEMISTRY OF THE COMPOUND

1-1   INTRODUCTION

The experiments - refractive index, density, viscosity, conductivity and diffusion measurements - described in this work were undertaken with an intention of gaining a new insight and to produce some physicochemical data on aqueous Thiamine chloride hydrochloride (Vitamin B1) solution. The behaviour and properties of ions in solutions, with special reference to ionic association-dissociation processes, have been looked into critically to explain the observed behaviour in the light of available theories of electrolyte solutions.

The development of electrolytic theory[1] began ealier than 1800. In 1805 T. Von Grotthuss made the first attempt to explain electrolytic conductivity on the basis of molecule chains. R. Clausius (1857) objected to the theory on the basis of relatively little energy expended in the processes of electrolysis. Arrhenius put forward the theory of electrolytic dissociation in 1883 and modified it in 1887 to accommodate Vant Hoff's discovery of large deviations of osmotic pressure shown by electrolytes in solution. Finally this became the basis of the modern treatment of electrolytes.

The mathematical formulations on the dynamic theory[2] of interionic attraction were developed by Sutherland and Milner. Debye and Huckel, Onsager and Fuoss[3] worked on the thermodynamics of ionic solutions and concentration dependence of equivalent conductivity. Later, statistical mechanics[4,5] was used to include the finer details of theoretical models. Falkenhagen[6], Onsager and Fuoss[7] also developed a theory of viscosity of electrolyte solutions.

These theories, in most cases, support experimental findings in strong low-valent electrolytes and predictions have been found to be remarkably exact, especially by the Debye-Huckel(1923) formulation.

More detailed knowledge of the behaviour of electrolyte solutions arose complimentarily as much from studies of the dynamics as from the thermodynamic properties of ions in solutions e.g conductance and diffusion measurements.

Certain properties do not just depend on the total ionic strength of the solution but on the individual ions actually involved, especially at high ionic concentrations where such effects must be attributed to ionic solvation - characteristic of the ionic radius, charge and structure of the ions. Thus Bronsted[8] recognised the necessity of considering specific ionic interactions with Oxyanions and Alkylammonium cations. He also recommended the disordered solution lattice theory instead of the

Debye-Huckel theory at concentrations above 0.1M where the latter is expected to fail. The work of Guggenheim and Turgeon[9] also emphasised this fact. These effects are largely attributed to ion-solvent interactions except in the case of weak electrolytes and complex ions.

There exists enough individual behaviour to warrant specific study on any one chosen electrolyte. Specific effects exhibited by electrolytes at high concentrations require that more precise knowledge of individual thermodynamic properties and certain scales of ionic properties be set up. Such attempts have been previously reported by Mukerjee[10], Couture and Laidler[11], Conway, Desnoyers and Verrall[12], Halliwell and Nyburg[13].

If the bases of these individual ionic properties are accepted, more theoretical work[7] is necessary such as using dielectric and electrostatic theory coupled with the methods of statistical mechanics, where the Debye-Huckel theory fails, so as to find adequate interpretations of any specificities in the ionic thermodynamic properties.

Such specificities in ionic behaviour are undoubtedly of importance in the areas of Biophysics e.g the mechanism of transport of ions through the cell wall, the generation of action potential across the neuron, and specific ion association effects in proteins and polynucleotides. This will be important in

the dynamics of folding, unfolding, extension and contraction of certain proteins and also in the mechanism of scission of DNA.

This study is uniquely placed since for many electrolyte solutions very precise information is obtained from e.m.f and isopiestic measurements on the deviations from ideality which such solutions exhibit and which arise from long-range interaction effects between particles of the solute already at high dilutions. These measurements have been and still are carried out with relatively simple and cheaper instruments.

The experiments carried out to test some of the consequences of the modern existing theory of electrolytes are described and discussed in chapter 3.

1-2   OBJECTIVE

Thiaminium dichloride (Vitamin B1) functions in enzyme systems as Thiamine pyrophosphate, a coenzyme known as co-carboxylase. It is only required by animals in small amounts and an adult human requirement is about 5 mg per day. Thiamine deficiency is symptomised by poor growth since muscles and nerve tissues are affected. People with Beriberi may suffer from partial paralysis of the motor nerves of the eyes.

The above information[14] is just a glimpse of the extensive biological work on Vitamin B1 that has been done. The literature surveyed between 1917 and 1987 indicates that work concerning physicochemical and electrochemical properties of this Vitamin has been mainly ignored. It is now understood that enzyme systems mainly ˍoperate through specific folding, unfolding, extension, contraction and adsorption etc. These manifestations, in turn, are dependent on the physicochemical and electrochemical properties of the constituents of the enzyme system.

As mentioned earlier, specific ionic behaviour are important for the function of nerves; in areas of Biophysics, ion transportation across membranes and cell wall, generation of action-potentials and ion association at protein sites are very significant. It follows that if the ionic

5

constituents of biological systems were known, the overall behaviour of the system could be predicted from individual ionic properties.

Schneeberger, Stahl and Loncin[15] have reported diffusion measurements, using the Diaphragm cell method, of Thiaminium dichloride solution, at 0.1 mol dm^{-3} over a temperature range 25-50°C; and at 25°C they have studied concentration dependence in the range 0.01 - 0.1 mol dm^{-3}. Shamim and Baki[16] in their work have pointed out that the result of the former group were contrary to expectation.

Yao et al[17] have reported Ka_1 value for Thiaminiun dichloride using quininium selective electrodes. Other values[18] of dissociation constant are pKa_1 = 4.8 and $pKa_2 + pKa_3$ = 9.2. William and Ruehle[19] also reported an estimated values of pK_b (stronger base) = 5.0 and pk_b (weaker base) = 9.5.

The objective of the present work is to study Viscosity, Density, Refractive index, Conductivity and Diffusivity of Thiamine in aqueous solutions over a concentration range 0 - 1M in the light of the present theories. Hopefully this work will avail part of the physicochemical and electrochemical data so far not available in the literature.

<u>THE CHEMISTRY OF THIAMINE CHLORIDE HYDROCHLORIDE</u>

IUPAC'S commission for the reform of nomenclature in Biological Chemistry adopted the name 'Thiamine' for the substance curing beriberi. Other names are Vitamin B1 and Aneurine.

R. R. Williams et al[20a,b] followed the attempts of workers[21] to isolate and concentrate sufficient Thiamine to enable its constitution to be worked out. Williams[14] has described his own studies and of others, which finally led to the elucidation of the structure of Vitamin B1.

Neutral Sodium Sulphite solution at room temperature[22] cleaved the Thiaminium dichloride molecule into two halves:

$$C_{12}H_{18}N_4SOCl_2 + Na_2SO_3 \longrightarrow C_6H_9N_3SO_3 + C_6H_9NSO + 2NaCl$$

The primary cleavage product, $C_6H_9N_3SO_3$, on hydrolysis with acid[23], yielded ammonia and another substance $C_6H_8N_2SO_4$. Both $C_6H_9N_3SO_3$ and $C_6H_8N_2SO_4$, on treatment with water at 200°C, yielded sulphuric acid, and with alkali sulphurous acid. This proved the presence of a sulphonic acid group in both. Ultra-violet absorption spectra characteristic of a pyrimidine nucleus was also given by both compounds. This was confirmed by conversion[24] of the former compound into 4-amino-2,5-dimethyl-pyrimidine (I), by action of sodium in liquid ammonia.
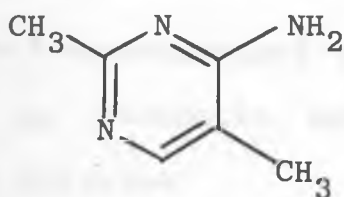
(I)

The constitution of the pyrimidine ring was established by sythesis[25]. 5-ethoxymethyl-4-hydroxy-2-methyl-pyrimidine[26] was similary prepared, which on treatment with sodium sulphite, yielded 4-hydroxy-2-methylpryrimidyl-5-methane-sulphonic acid; identical to the compound $C_6H_8N_2SO_4$. The primary cleavage product, $C_6H_9N_3SO_3$, was thus presumed to be 4-amino-2-methyl-pyrimidyl-5-methane-sulphonic acid (II).
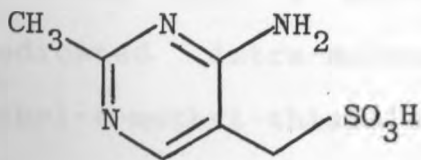
(II)

The other primary cleavage product, C_5H_9NSO, was oxidized with nitric acid[27] giving 4-methyl-thiazole-5-carboxylic acid, identical with a compound previously prepared by M. Wohmann[28]. This substance had also been obtained by A. Windaus et al[29] during oxidation of thiamine with nitric acid, but they did not detect the presence of the thiazole nucleus.

8

H. T. Clarke and S. Gurin[30] synthesised and established the correctness of the assumption that this compound was 6-β-hydroxyethyl-4-methyl-thiazole (III), it contained an alcoholic hydroxy groups readily replaceable by chlorine.
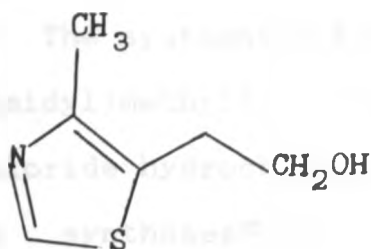
(III)

The point of attachment to the pyrimidine ring was settled by the position of the sulphonic group in the sulphite cleavage product (II) whilst the point of attachment to the thiazole ring was established by titration experiments[19] where one mole of the Thiamine dichloride reacted with 3 moles of alkali. This behaviour indicated intra-molecular rearrangement. 5-β-hydroxyethyl-4-methyl-thiazole methiodide[27] behaved similarly, towards the last two moles of alkali, on titration. Thus it was concluded that Thiamine chloride hydrochloride was also a quartenary ammonium salt. The titration result after consumption of the first mole of the alkali was explained[18] by the opening of the thiazole ring forming mercapto and aldehydic groups. The first mole of alkali liberated the weakly basic amine group on the pyrimidine ring. The third mole neutralised the mecarpto group.

The formula known to be correct,

(IV)
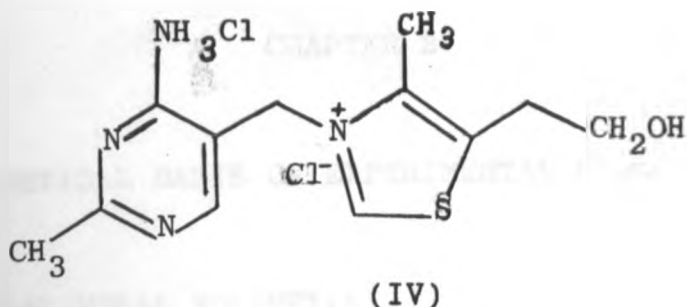
was proposed by R. R. Williams and confirmed as explained earlier. The systematic name is 3-[(4'-amino -2'-methyl-5'-pyrimidyl)methyl]-5- β-hydroxyethyl-4-me- thyl-thiazolium chloride hydrochloride.

Complete syntheses[20 a, b] of Thiaminium dichloride are due to R. R. William et al, A. R. Todd et al, A. Windaus et al, K. Makino and T. Imai and H. Andersag and K. Westphal. Methods involving Biosythesis also exist. These are reviewed in standard texts of heterocyclic organic compounds.

The chemical reactions of this compound are also summarised in most standard organic texts[21]. It is perhaps important to mention certain reactions.

Thiaminium dichloride is a stable[18] salt of Thiamine, m.p. 247-80 C with decomposition, molecular weight 337.3 (unhydrous), 355.3 (hydrated). Thiamine is heat-labile and acts like a weak base but can be adsorbed on basic ion-exchangers such as Decalso and Fuller's earth. It is relatively stable in acid solutions (pH 3 - 6) but in alkaline solutions it is rapidly destroyed. Nitric acid oxidizes the Vitamin to destruction. Concentrated HCl acid converts it to a chloro-oxy Vitamin. Many reactions are characteristic of the thiazolium structure.

THEORETICAL BASIS OF EXPERIMENTAL PROCEDURES

2-1 PARTIAL MOLAL VOLUME[31a]

The density of any substance, ρ, is defined as mass per unit volume, i.e,

$$\rho = M / V \qquad\qquad 2\text{-}1$$

where, ρ can be expressed in g cm^{-3}, if the mass, M, is in g, and its volume, V, in cm^3.

The partial molal volume[31b], $\bar{V}_i$ of a solute i in solution, is a quantity derived from the density of the solution and may be defined as

$$\bar{V}_i = \left[\frac{\partial V}{\partial m_i} \right]_{T, m_j, m_k - - - -} \qquad\qquad 2\text{-}2$$

where, V is the volume of the solution, m_i is the concentration of solute i on the molality scale, the concentration of the other components of the solution, j, k, - - - - and temperature T, being kept constant.

More explicitly, $\bar{V}_i$ may be regarded as the increase or decrease of volume due to the addition of a mole of component i to an infinite amount of solution at constant temperature.

The value of $\bar{V}_i$ (here-after $\bar{V}$) is obtained as follows:

The apparent molal volume of the solute, $\emptyset$, is defined by the equation

$$\emptyset = (V - V_0) / m \qquad\qquad 2-3$$

in which V is the volume of an m molal solution of component i and V_0 is the corresponding volume of the solvent.

Differentiating equation (2-3) with respect to m one obtains

$$\frac{d\emptyset}{dm} = \frac{1}{m}\left(\frac{\partial V}{\partial m} - \frac{V}{m} + \frac{V_0}{m}\right)$$

$$= \frac{1}{m}\left(\frac{\partial V}{\partial m} - \emptyset\right) \qquad\qquad 2-4$$

It follows that

$$\bar{V} = \partial V/\partial m = (m\, \partial\emptyset/\partial m) + \emptyset \qquad\qquad 2-5$$

Values of $\emptyset$ may be computed from equation (2-3) using V and V_0 defined by the equations

$$V = \frac{1000 + Wm}{\rho} \quad \text{and} \quad V_0 = \frac{1000}{\rho 0} \qquad\qquad 2-6$$

i.e. $$\phi = \frac{W}{\rho} - \frac{1000}{m}\left(\frac{(\rho - \rho^0)}{\rho\rho^0}\right)$$

$$= \frac{W}{\rho} - \left(\frac{1000\Delta\rho}{m\rho\rho^0}\right) \qquad 2\text{-}7$$

Where, W is the molecular weight of the solute ρ, ρ^0, and $\Delta\rho$ are the densities of solution, solvent and their difference respectively.

In the low cencentration range, the following limiting equation is provided by the theory of electrolyte solution.

$$\phi = \phi^0 + am^{1/2} \qquad 2\text{-}8$$

Where, ϕ and 'a' are constants which are determinable graphically by constructing a plot of ϕ against $m^{1/2}$. Equation (2-8), known as Masson's[32] equation, together with equation (2-5), yields

$$\bar{V} = \partial V / \partial m = \phi^0 + (3/2)am^{1/2} \qquad 2\text{-}9$$

The author has used his density measurements in the above equations to calculate the partial molal volumes of Vitamin B1 in aqueous solutions.

13

2-2   <u>VISCOSITY</u>[33a]

Earlier workers, among them, Daniell, Bernoulli, d'Alembert, Euler and Langrange dealt with perfect fluids. These fluids were showing no internal friction or viscosity. The stress across any element of surface in such fluids is wholly normal to that surface. There is no tangential component of stress. A shearing motion is involved in which one portion of fluid moves tangentially with respect to an adjacent portion without opposition.

Newton in his second book of the Principia, considered problems of motion in a resisting medium. In Newtonian liquids, as known today, the frictional resistance is directly proportional to the velocity of the shearing motion.

Navier and Stokes[34] have made major developments in the modern theory of viscous fluids. When tangential stresses across every element of surface is introduced in perfect fluids then viscosity is considered. The component stresses are proportional to the corresponding velocity-gradients in Newtonian fluids and the constant of proportionality is called the viscosity or viscosity coefficient of the fluid. The following, more specific terms, have been defined in connection with viscosity.

Absolute Viscosity. For laminar flow in a Newtonian fluid, the absolute viscosity is the force per unit area required to maintain unit difference in velocity between two parallel layers of the fluid which are unit distance apart.

$$\eta = \tau /(du/dy) \qquad \qquad 2\text{-}10$$

Where η is the absolute viscosity, τ is the force per unit area or shear stress and du/dy is the velocity gradient normal to the plane of flow.

The units of η are $g\ cm^{-1}\ s^{-1}$ or Poise. Centipoise, cP, is the unit commonly used.

Kinematic viscosity. This is the ratio of absolute viscosity to density.

$$\nu = \eta / \rho \qquad \qquad 2\text{-}11$$

in $cm^2\ s^{-1}$ or Stokes.

Relative Viscosity. This is defined as the ratio of the viscosity of a solution to that of the pure solvent under the same conditions.

$$\eta\,rel = \eta / \eta^{o} \qquad \qquad 2\text{-}12$$

Specific Viscosity. The ratio of difference between the solution and solvent viscosities to the solvent

15

viscosity is known as specific viscosity.

$$\eta_{sp} = (\eta - \eta^0)/\eta^0$$

$$= \eta_{rel} - 1 \qquad \qquad 2\text{-}13$$

Instrinsic viscosity. This is defined as

$$\eta_{int} = \lim_{c \to 0} (\eta - \eta^0)/ C \eta^0 \qquad \text{or}$$

$$\eta_{int} = \lim_{c \to 0} (1/C) \ln (\eta/\eta^0) \qquad 2\text{-}14$$

for a solution of concentration C.

Fluidity. This is the reciprocal of absolute viscosity.

$$\emptyset_t = 1/\eta \qquad \qquad 2\text{-}15$$

From fundamental equations[34] of the hydrodynamics of viscous fluids, the results which are of importance in the theory of electrolyte solutions are stated briefly.

The differential equation of motion of a viscous liquid is of the form

$$\rho((\partial q/\partial t) + q \cdot \nabla q) = \rho F - \nabla p + \eta \nabla^2 q \qquad 2\text{-}16$$

where $q \cdot \nabla q$ and $\nabla^2 q$ are dyadic products, ∇p denotes the pressure gradient, ρ is the density of the incompressible fluid, q is the velocity vector, with such components as u, v and w, while F is the external

force per unit mass, with components X, Y and Z. η is the viscosity which is independent of direction and rate of shear.

When equation (2-16) is expressed in terms of cartesian components, terms arise that are non-linear in the velocities and so have no exact solutions. For low velocities, quadratic terms are ignored provided the Reynold number (Re) associated with the solution do not exceed 1000 (For most ions Re $\simeq 10^{-9}$). Reynold numbers are expresses as

$$Re = ua\ \rho/\eta \qquad 2\text{-}17$$

where u is velocity of the order occuring in the problem, a is a quantity of the relevant linear dimension, such as diameter of the tube through which the fluid is flowing, ρ is density of solution and η its viscosity.

For steady-state conditions, $\partial q/\partial t = 0$ and so at small Reynolds number the general equation in the X-direction becomes

$$\rho X = \partial p/\partial x - \eta \nabla^2 u \qquad 2\text{-}18$$

and in the absence of an external force

$$\partial p/\partial x = \eta \nabla^2 u \qquad 2\text{-}19$$

Such a differential equation, when supplemented with the boundary conditions[33a,b]

17

applicable to viscous flow, yields solutions specific to the shape of the instrument intended for measurement of viscosity.

One case of such a solution, important for the theory of electrolyte solutions and the method of measurement used here-in, is the Poiseuille's formula and concerns laminar flow through a cylindrical tube under pressure.

$$V/t = \pi (P_0 - P_1) R^4 / 8 \eta L \qquad 2\text{-}20$$

Where P_0, P_1 are the pressures at the two ends of the tube, L is the length of the tube having radius R, V is the volume flowing through the tube in time t and η is the viscosity.

This formula arose from the work of Poiseuille[35] and Hagenbach[36] and is known as Poiseuille's Law. This law applies under the following assumptions:

(a). The flow is parallel to the axis of the tube throughout

(b). The flow is steady, initial disturbance due to accelerations from rest having been dumped out

(c). There is no slip at the walls of the tube

(d). The fluid is incompressible

(e). The fluid will flow when subjected to the smallest shearing force, the viscous resistance being proportional to the velocity gradient

These assumptions dictate the design of appropriate instrument, otherwise corrective[33a] measures must be taken where the instrument departs from these assumptions.

In this work the author has employed Poiseuille's Law in measuring relative viscosities of aqueous solutions. A capillary viscometer of the Kinematic type is employed where the head of the liquid itself furnishes the pressure differential across the capillary. Hence for liquids of densities ρ_1 and ρ_2, the average pressure differences are $h\rho_1 g$ and $h\rho_2 g$, h being the average difference of the liquid level during the flow period.

If the times of flow are taken for the two liquids, then

$$V = \pi h\rho_1 gR^4 t_1 / 8\eta_1 L$$
$$= \pi h\rho_2 gR^4 t_2 / 8\eta_2 L. \qquad\qquad 2\text{-}21$$

Thus

$$\eta_2 / \eta_1 = \rho_2 t_2 / \rho_1 t_1 \qquad\qquad 2\text{-}22$$

If the subscript (1) refers to the solvent or a primary standard (e.g water) then η_{rel} or η_2 can be easily determined with accuracy. This was the method used by the author. For pure water[37] at 25°C, $\eta_1 = 0.008937$ Poise and $\rho_1 = 0.99707$ g cm^{-3}.

2-2-1   Concentration dependence of relative viscosity

Gruneisen[38] measured and found out that in the dilute range, the viscosities of solutions show characteristic negative curvations with increase in concentration - meaning an increase in viscosity - regardless of what happens at higher concentration.

Jones and Dole[39] gave a semi-empirical equation that described this effect qualitatively. Namely,

$$\eta / \eta^{\circ} = 1 + AC^{1/2} + BC \qquad 2\text{-}23$$

Desnoyers[40] and others extended equation to the form

$$\eta / \eta^{0} = 1 + AC^{1/2} + BC + DC^{2} \qquad 2\text{-}24$$

where A, B, D, are coefficients with both quantitative and qualitative properties and C is the concentration.

Once the Debye-Huckel interionic theory was accepted, Jones and Dole correctly surmised the dependence of η / η^{0} on $C^{1/2}$ and Falkenhagen[6] (cf. reference 7) used the equilibrium theory to calculate the A coefficient. Later work by Onsager and Fuoss[7] on irreversible processes in electrolytes led to the more general case of multicomponent systems.

2-2-2   A coefficient

The A coefficient possesses a non-zero value only for electrolytes where it is always positive. It accounts for the increase in viscosity produced by the

long range coulombic forces between the ions.

It has been interpreted on the basis of deformation of the Debye-Huckel spherical ion atmosphere under a shearing stress.

Falkenhagen and Vernon[41], Harned and Owen[42] have shown that the A coefficient can be calculated from limiting molar conductivities. For a strong uni-univalent electrolyte at 25^{0}C the equation is

$$ A = \frac{0.2577\lambda^0}{\eta(\varepsilon T)^{1/2}\lambda_+^\circ \lambda_-^\circ} \left[1 - 0.6863 \left(\frac{\lambda_+^\circ - \lambda_-^\circ}{\Lambda^0} \right)^2 \right] $$

...........2-25

where λ_+°, λ_-° and Λ^0 represent the limiting conductivities of the substripted ions and salt; and η , ε and T are viscosity, dielectic constant and absolute temperature respectively.

A general expression given for the electrostatic contribution to the viscosity, η^*, by Onsager and Fuoss[7] for electrolyte solutions is

$$ \eta^* = \frac{0.362}{(\varepsilon T)^{1/2}} \left(\sum_i \frac{\mu_i Z_i}{\lambda_i} - 4r \sum_{n=0}^{\infty} C_n s(n) \right) I^{1/2} $$

...........2-26

where r and s are vectors with elements, $I - \rho_i / \bar{\rho}$ and $((Z_i/\lambda_i) - ((Z/\Lambda)^2/(Z/\Lambda)))$ respectively. $s(n) = 2(H - I)S(n-1)$ and Z is the total sum of valencies. ρ_i and $\bar{\rho}$ are the ionic and the average frictional coefficients respectively. The other quantities are as defined later in section (2-4-5).

Since $\eta^* = \eta^0 A I^{1/2}$, when I, the ionic

21

strength, is taken as a measure of concentration, it follows that

$$A = \frac{0.362}{\eta^{o}(\epsilon T)^{1/2}} \left(\sum_i \frac{\mu_i z_i}{\lambda_i} - 4r \sum_{n=o}^{\infty} C_n s(n) \right)$$

..........2-27

Falkenhagen and Kelbg[43] and also Pitts[44] attempted to calculate the A coefficient by including the parameter 'a' the distance of closest approach. But Stokes and Mills[45] have indicated that the concentration range of validity extends negligibly and in some cases even wrong results are obtained.

Evidently A is a function of solvent properties, ionic mobilities and temperature.

Generally, beyond 0.002M the absolute magnitude of the electrostatic increment to the viscosity is small while the contribution from ion-solvent interaction represented by the BC term is large and swamps the small changes due to the $AC^{1/2}$ term.

The constant A may also be evaluated from experimental data by plotting a suitable form of equation (2-23).

2-2-3 B coefficient

Various correlations[46] concerning viscosity B coefficents are only qualitative in nature as a quantitative theory for the B Coefficient is yet to be developed.

22

Stokes and Mills[45] have given a representative selection of B coefficients for various salts and made the following two deductions:

(a). Negative B coefficients are confined to highly associated solvents, such as water, at fairly low temperatures. B values vary widely for different solvents and accordingly S. Phang[46] indicates that in aqueous solutions the B coefficients are positive for non-electrolyte and can be positive or negative for electrolytes. For electrolytes, negative values become less negative or change to positive as the temperature is raised. In non-aqueous solutions the B coefficients of electrolytes are mostly positive although negative values have been reported[47].

(b). Ions present in highly associated solvents at low temperatures exert a "structure breaking" effect. At higher temperatures the solvent structure is already affected by thermal agitation, thus ions exert little effect. Negative B coefficient hardly decrease the viscosity by 10%. Positive B coefficients signify "Structure making" effects.

The B coefficient is an additive property[48] of the constituent ions. B values for pairs of salts with the same anion but different cations have constant differences. Additivity is thus adduced to the separate ions and most correlations with other solution

23

properties are made in terms of ionic B coefficients. Interpretations are more significant if given for individual B_{ion} values and such facts and regulations have been discussed by Stokes and Mills[45] showing, like Kaminsky[47], that the observed viscosity changes result from competition between various effects occuring in the ionic neighbourhood, that is,

$$= \eta_0 + \eta^* + \eta_E + \eta_A + \eta_D$$

$$= \eta_0 + \eta_0 (AC^{1/2} + BC) \qquad 2\text{-}28$$

where $\eta^* = \eta_0 AC^{1/2}$ is the ionic interaction contribution and is positive and $\eta_E + \eta_A + \eta_D = \eta_0 BC$. The terms on the L.H.S. of the latter expression are more specialized viscosity effects defined as:

η_E - the increment arising from size and shape of an ion which is closely related to the Einstein effect.

η_A - the increment due to the orientation of polar molecules by the ionic field with subsequent restriction of motion.

η_D - change associated with distortion of the solvent structure leading to greater fluidity.

2-2-4   D coefficient[40]

This includes all those solute-solvent, solute-solute interaction not accounted for by A and B coefficients. These interactions may include ion-pair, triple ions or even higher ionic complexes and higher terms of hydrodynamic effects.

2-2-5   The Einstein effect

For particles relatively larger than the solvent molecule the B coefficient values are mainly due to the effect of large solute size and shape. In electrolytes containing such ions - either due to strong hydration or the intrinsic size - the hydrodynamic theories applicable to particles in a fluid continuum states that the increase in viscosity is due to the particles lying across the fluid streamlines. These particles are subjected to torsional forces, they tend to rotate and absorb energy which results in an increased viscosity of the solution.

The first quantitative treatment was given by Einstein[48] who dealt with the case of rigid spheres suspended in a continuum. The results were restricted to cases of small volume fractions of spherical particle and is given by the equation

$$\eta/\eta^0 = 1 + 2.5 \; \emptyset \qquad\qquad 2\text{-}29$$

Generally, for non-spherical particles the equation becomes

$$\eta/\eta^0 = 1 + a_1 \emptyset \qquad\qquad 2\text{-}30$$

where η/η^0 has its usual meaning, a_1 takes values greater than 2.5 and $\emptyset$ is the volume fraction occupied by particles so that

$$\emptyset = C\overline{V} \qquad\qquad 2\text{-}31$$

where C is the concentration in mol l^{-1} and $\overline{V}$ is the molar volume of the solute in $l\ mol^{-1}$. Holtzer and Emerson[50] have shown that $\overline{V}$ includes the hydration shell as part of the ion dimension.

An extended form of equation (2-29), for concentrated suspensions, has been employed by Eirich and Ford[51].

$$\eta/\eta^0 = (1 + 2.5\emptyset + k_1\emptyset^2 + k_2\emptyset^3 \qquad 2\text{-}32$$

Where k_n are the interaction constants.
Vand[52] had proposed the equation

$$\ln(\eta/\eta^0) = a_1\emptyset/(1 - k\emptyset) \qquad\qquad 2\text{-}33$$

Thomas[53] has shown that for $\emptyset < 0.25$, the equation becomes

$$\eta/\eta^0 = (1 + 2.5\emptyset + 10.05\emptyset^2) \qquad 2\text{-}34$$

Investigations[48] on large ions in solution and the calculated B coefficients agree satisfactorily with literature B coefficients which were obtained at low concentrations. For spherical and relatively large ions, compared to the solvent molecules, Einstein effect may be observed.

2-3   REFRACTIVE INDEX[54a, b]

When a ray of monochromic light passes from
an optically lighter medium to a denser one, it gets
bent or refracted towards the normal. If i is the
angle of incidence in the less dense medium and r the
angle of refraction in the second medium, then
according to the law of refraction

$$Sin\ i/Sin\ r = N/n \qquad\qquad 2\text{-}35$$

where n, N are the refractive indices of the lighter
and denser media respectively.
When i = 90°; r has a maximum value and when i > 90°
then the ray undergoes total internal reflection.
Since Sin 90° = 1, then;

$$Sin\ r = n/N \qquad\qquad 2\text{-}36$$

and n = N sin r, where r is measurable and N is the
known absolute refractive index of the denser medium,
e.g prism material in the refractometer. Thus n can be
measured.

Refraction arises[55] from the fact that
extra-nuclear electrons of atoms tend to follow the
oscillations of the electromagnetic field associated
with light. The extent and nature of binding of
electrons - polarizability - in atoms, molecules, etc.

27

governs the extent of refraction in a medium containing these particles.

Refraction changes with temperature, pressure and wavelength. Due to this latter phenomenon, known as dispersion, the wavelength must be specified when refractive indices are stated.

2-3-1 Specific and molar refractivity

From the electromagnetic theory of light, Lorentz and Lorenz have deduced an equation

$$r_D = \frac{n^2-1}{n^2+2} \cdot \frac{1}{\rho}$$

2-37

where r_D is the specific refraction which is independent of temperature and pressure and ρ is the density of the medium.

Molar refraction, $[R]_D$, is the product of specific refraction and the molecular weight, i.e

$$[R]_D = r_D = \frac{n^2-1}{n^2+2} \cdot \frac{W}{\rho}$$

2-38

The Clausius-Mosotti equation also gives a quantitative relationship between molar refraction and polarizability, thus

$$[R]_D = 4 \pi N_A \alpha / 3 \qquad\qquad 2\text{-}39$$

where N_A and α are the Avogadro number and electronic polarizability respectively.

2-3-2 The Molal Refractive Index in Solution

The apparent molal refractive index, R_{app}, of a solute of molecular weight W_1, is defined by the condition that the total molal refraction of the solution, R, containing one mole of solute, is the sum of R_{app} and the refraction which the amount, W_0 (gram), of solvent present in the solution would have in pure state.

For the solvent

$$r_0 = \frac{n^2_0 - 1}{n^2_0 + 2} \cdot \frac{1}{\rho_0} \qquad\qquad 2\text{-}40$$

Thus $R_0 = r_0 W_0$ and $R = R_{app} + R_0$.

It follows, therefore, that

$$R_{app} = \left(\frac{n^2 - 1}{n^2 + 2} \cdot \frac{W_1 + W_0}{\rho} \right) - \left(\frac{n^2_0 - 1}{n^2_0 + 2} \cdot \frac{W_0}{\rho_0} \right) \qquad 2\text{-}41$$

R_{app} is not equal to the molal refraction of the pure solute, R_1. The difference, $R_{app} - R_1$, indicates the deviation from exact additivity in the mixture due to all possible causes. It includes any refractometric effects due to a change in the state of

29

the solute and the solvent which might arise as a result of mixing. $R_{app} - R_1$ will be small for solutions in which components have similar physical properties or do not exert strong forces on each other. On the molality scale

$$R_{app} = \left(\frac{n^2 - 1}{n^2 + 2} \cdot \frac{V}{m} \right) - \left(\frac{n^2_0 - 1}{n^2_0 + 2} \cdot \frac{V_0}{m} \right) \qquad 2\text{-}42$$

Electronic interactions between the components may also be analysed through the difference between R_{exp} ($= R_{app}$) and R_{add}. On the mole fraction scale the value of R_{add} is given by the equation

$$R_{add} = X_1 \left(\frac{n^2_1 - 1}{n^2_1 + 2} \cdot \frac{W_1}{\rho_1} \right) + X_0 \left(\frac{n^2_0 - 1}{n^2_0 + 2} \cdot \frac{W_0}{\rho_0} \right) \qquad 2\text{-}43$$

where in all cases quantities with subscripts 0, 1 denote a solvent, solute and those without subscripts denote a solution respectively.

Pure solids, liquids and solutions obey Ohm's Law, i.e

$$I = V/R \qquad\qquad 2\text{-}44$$

where V (in volts) is the potential difference across the conductor carrying a current I (in amperes) and having resistance R (in ohms).

The resistance of an electrical conductor is directly proportional to its length L, and inversely proportional to its cross-sectional area, A, thus

$$R \propto L/A \quad \Rightarrow \quad R = \rho L/A \qquad\qquad 2\text{-}45$$

where ρ is the proportionality constant known as the specific resistance or resistivity of the conductor.

Conductivity or specific conductance, κ, which is a more important quantity in electrolyte solutions is defined as the reciprocal of resistivity.

$$\kappa = 1/\rho \qquad\qquad 2\text{-}46$$

From equations (2-45) and (2-46) it follows that

$$\kappa = L/R.A \qquad\qquad 2\text{-}47$$

In the measurement of conductivities of electrolyte solutions, L is a fixed distance between the two electrodes each having an effective area A. The quantity L/A is constant for a particular cell and is called the Cell Constant, K, of the conductivity cell.

Consequently equation (2-47) becomes

$$\kappa = K/R \qquad\qquad 2-48$$

2-4-1 Measurement of conductivity

The resistance of a KCl solution of precisely known concentration and conductivity, is measured using a conductance cell and the Cell Constant is calculated using equation (2-48). The units of the cell constant are obviously cm^{-1}.

Once K is known, the resistance of the solutions under investigation can be measured and κ calculated at each concentration using equation (2-48).

To compare the specific conductivities of solutions containing different amounts of the same electrolytes or of solutions having different electrolytes, the quantities, equivalent or molar conductivity have been defined as

$$\Lambda = 1000 \ \kappa/C \qquad\qquad 2-49$$

where C is the concentration of electrolytes under study in gram equivalent or gram mole per litre.

2-4-2 Kohlrausch's equations

Kohlrausch[57] proposed the following two relationships as a result of his studies on equivalent

conductivities of various electrolyte solutions:

The law of independent migration of ions. This states
that the limiting equivalent conductivity of an
electrolyte AB, Λ^0_{AB}, is equal to the sum of the
individual ionic equivalent conductivities λ^0_{A+} and
λ^0_{B-}, at infinite dilution.

$$\Lambda^0_{AB} = \lambda^0_{A+} + \lambda^0_{B-} \qquad\qquad 2\text{-}50$$

The empirical conductivity equation. An empirical
equation relating observed equivalent conductivity to
the corresponding concentration was put forward in the
form

$$\Lambda = \Lambda^0 - KC^{1/2} \qquad\qquad 2\text{-}51$$

where K is a constant and C the concentration in units
specified earlier.

Kohlrausch could not assign any specific
physical meaning to the constant, K, but the equation
did explain the concentration dependence of equivalent
conductivities of most dilute aqueous solutions of
strong 1:1 electrolytes. The observed Λ decreases
with increase in concentration.

Arrhenius[58] was first person who attempted to
explain this phenomenon using the theory of
electrolytic dissociation as outlined in the following
lines.

When an acid, base or salt is dissolved in

33

water, a considerable portion becomes spontaneously dissociated into positive and negative ions. These ions are free to move independently and are simply guided to the electrodes of opposite sign by the applied electric field. The proportion of molecules which dissociate into ions were believed to vary with concentration, such that the degree of ionization approached unity at infinite dilution. Arrhenius explained that the change in the degree of ionization caused the variation of conductivity with concentration.

The assumption that the conductivity of solutions only depended on the total number of ions is approximately true for weak electrolytes only, where the degree of dissociation, α, as defined by Arrhenius, is

$$\alpha = \Lambda / \Lambda^0 \qquad\qquad 2\text{-}52$$

This calculated proportion of ions explained the concentration dependence of equivalent conductivity in weak electrolytes. The data for strong electrolytes, however, could not find any explanation since these electrolytes were known to undergo complete dissociation at all concentrations.

A theory was, therefore, needed which could explain the concentration dependence of conductivity in both types of solutions.

2-4-3   The interionic theory

The conductivity of a solution is known to depend on

(i)   the total number of the ions,

(ii)   the charge on the ions, and

(iii) the speed of the ions.

The present view is that strong electrolytes are completely ionized in the pure solid, pure liquid and solution states. The decrease in equivalent conductivity with increasing concentration must, therefore, be attributed to the diminution in the ionic velocity.

A simple picture of the theory is that with an increase in concentration the coulombic interactions between ions of opposite charge and hydrodynamic effects result in the decrease of the speed of ions and hence in the equivalent conductivity of the solutions.

The quantitative treatment of the theory of interionic attraction is due to the efforts of many workers, the main ones being P. Debye, E. Huckel and L. Onsager[3].

The fundamental idea underlying the deductions is that due to the electrical attraction superimposed over thermal motion, 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 as long as the system is not exposed to an applied electric field or shearing force which causes a disturbance.

When a current is passed the central ions are continuously caused to move off center. In the new position, the spherical ionic atmosphere begins to form while it dies out at the previous centre. The restoration of the ionic atmosphere and its decay - infront and behind the ion respectively - to an equilibrium value, involves a molecular concept of relaxation of the ionic atmosphere with a definite relaxation time. Since there will be an excess of ions of opposite sign behind the central ion, its motion will be retarded. The average restoring force experienced by the central ion is called the Relaxation Effect or Asymmetry Effect.

Another effect results from the movement of the ionic atmosphere, in the opposite direction to that of central ion with its associated solvent molecules. The ion has thus to moves in a direction opposite to that of solvent molecules and thus experiences a dragging force causing further retardation. This additional retardation effect is known as the Electrophoretic Effect.

Finally, the normal frictional resistance of the medium - determined by Stokes Law and dependent on

the speed of the ion, its radius and the viscosity of the medium - also adversely affects the migrating ions.

On the basis of the above argument Debye and Huckel derived an expression relating observed equivalent conductivity at a particular concentration to that at infinite dilution in terms of the physical properties of the ions and the solvent. This expression was subsequently improved by L. Onsager to the form

$$\lambda_i = \lambda^o_i - \left[\frac{2.801 \times 10^6 \ Z_i Z_j \ q \ \lambda^o_i}{(\epsilon T)^{3/2}(1 + q^{1/2})} + \frac{41.25 \ Z_i}{\eta(\epsilon T)^{1/2}} \right] I^{1/2}$$

................2-53

where

$$q = \frac{Z_i Z_j (\lambda^o_i + \lambda^o_j)}{(Z_i + Z_j)(Z_i \lambda^o_j + Z_j \lambda^o_i)} \qquad 2-54$$

and the ionic strength

$$I = 1/2 \sum_{K=1}^{j} C_k Z^2_k \qquad 2-55$$

Z_i, Z_j, are the valencies and λ^o_i, λ^o_j are the limiting equivalent conductivities of ions i and j respectively. ϵ and η are the respective dielectric constant and viscosity of the solvent at temperature T.

The first term in the brackets in equation (2-53) accounts for the Relaxation Effect and the second, the Electrophoretic Effect.

For a strong uni-univalent electrolyte, the equation becomes

37

$$\lambda_i = \lambda_i^o - (B_1 \lambda_i^o + (1/2) B_2)C^{1/2} \qquad \text{2-56}$$

where I and C have the same value.

By adding two such equations - one for anion, i, and another for cation j - we get an equation for the equivalent conductivity of the electrolyte.

$$\Lambda = \Lambda^o - (B_1 \Lambda^o + B_2)C^{1/2} \qquad \text{2-57}$$

This is the Debye-Huckel-Onsager equation. A comparison of equation (2-51) and (2-57) shows that K in Kohlrausch's equation is equivalent to $(B_1 \Lambda^o + B_2)$.

If water is the solvent at 25°C then $B_1 = 0.2300$ $l^{1/2}(g \text{ equiv.})^{-1/2}$ and $B_2 = 60.65$ S cm^2 $l^{1/2}$ $(g \text{ equiv.})^{-3/2}$ These values[37] are based on $\eta = 0.008937$ Poise and $\varepsilon = 78.35$. According to equation (2-57) a plot of Λ against $C^{1/2}$ should give a straight line curve of slope $(B_1 \Lambda^o + B_2)$. This is the case with most dilute solutions of strong uni-univalent electrolytes ~in the concentration range below 0.002M.

In concentrated solutions, however, deviation from the equation occur because in the derivation of equation (2-57) simplifying assumptions and subsequent mathematical approximations, true only in dilute solutions, are used. Shedlovsky et al[59] found that calculated Λ values using equation (2-57) are within experimental expections in the concentration range below 0.001M.

Accurate experimental data fits upto 0.003M for 1:1 electrolytes and also for 1:2 and 1:3

electrolytes at lower concentrations.

More exact equations[60] exist. Falkenhagen and others extended the theory by including finite size of the ions, a different distribution law and a more complete definition of the potential without Onsager's approximation. Pitts also employed a more complete solution of Poisson-Boltzmann equation due to Gronwall, LaMer, and Sandred. This treatment differed from Falkenhagen's in the choice of expression for the potential resulting from a different distribution function.

2-4-4 Extension of the Onsager equation for high concentrations

Various empirical extension[60] of the limiting Onsager equation have been proposed to account for the deviations at higher concentrations. Shedlovsky[59] proposed the equation given below which fitted very well for many electrolytes at relatively higher concentrations but there is no simple meaning associated with constant b in the equation:

$$\Lambda = \Lambda^{0} - (B_1 \Lambda^{0} + B_2)C^{1/2} + bC(1 - B_1 C^{1/2}) \qquad 2-58$$

Robinson and Stokes[60] have once more proposed the inclusion of the factor, $(1 + \kappa a)$ in the denominator of $I^{1/2}$ as implied earlier by Onsager and

suggested by Lattey, Kaneko and later implemented by Ritson and Hasted. The use of a reasonable value of 'a' extends the validity of the Onsager equation above 0.001M. In this case neglecting the cross-product of the relaxation and electrophoretic terms, equation (2-53) becomes:

$$\lambda_i = \lambda^0{}_i - \left(\frac{2.801 \times 10^6 \; Z_i Z_j \; q \lambda^0{}_i}{(\varepsilon T)^{3/2}(1 + q^{1/2})} + \frac{41.25 Z_i}{\eta(\varepsilon T)^{1/2}} \right) \frac{I^{1/2}}{(1+\kappa a)}$$

$$\dots\dots\dots\dots\dots\dots 2\text{-}59$$

For 1:1 electrolytes this may be expressed as

$$\Lambda = \Lambda^0 - \frac{(B_1 \Lambda^0 + B_2) \; I^{1/2}}{1 + B_3 a^0 I^{1/2}} \qquad\qquad 2\text{-}60$$

where 'a' is the ionic radius and a^0 is the distance of closest approach.

Or

$$\Lambda^0 = \Lambda + \frac{(B_1 \Lambda + B_2) \; I^{1/2}}{1 + (B_3 a^0 - B_1) I^{1/2}} \qquad\qquad 2\text{-}61$$

where B_3 is a constant with a value[37] of 0.3291×10^{-8} and a^0 is the distance of closest approach of the ions in Angstroms(Å). This equation gives a fairly good account of the conductivities of aqueous solutions of strong 1:1 electrolytes up to 0.1M and yields reasonable values of a^0 parameter. However the equation fails to account for the concentration dependence in non-aqueous systems[61]. In the present work, equations (2-60) and (2-61) have been further modified and used to analyse the conductivity data of aqueous Thiaminium dichloride solutions.

Ionic conductivity in electrolyte mixtures

The general limiting law of conductivity in mixtures were derived by Onsager and Fuoss[7]. The ionic equivalent conductivity at finite concentrations is given by the equation

$$\lambda_i = \lambda^0_i - \left[\frac{1.971 \times 10^6}{(\epsilon T)^{3/2}} \, Z_i \lambda^0_i \, \sum C_n r_i^{(n)} + \frac{28.98 \, Z_i}{\eta(\epsilon T)^{1/2}} \right] I^{1/2}$$

............2-62

where λ^0_i is the Kohlrausch's value of limiting ionic equivalent conductivity, C_n are the coefficients of the series expansion of $(I - H^{1/2})$, $r_i(n)$ are vectors defined as $r_i(n) = (2H - I)_i \, r_i(n-1)$; $r_i(0) = r_i$, n is the ionic concentrations (or number), I is the total 'ionic strength', $I = n_r z_r^2$, H is a matrix with elements $h_{ji} = \mu_\gamma \omega_\gamma j \, \delta_{ij} + \mu_i \omega_{ij}$ (subscripted greek letters indicate summations), μ_i is the ratio of concentration of i ions to the total ionic concentration, ω_i is the mobility of the ith species of ions, $\omega_{ij} = \omega_i / \omega_j + \omega_j$ and δ_{ij} is the Kronecker symbol.

This formula gives the limiting law for the conductivity of the ith species of ions in a mixture of different kinds. It is evident that of the two effects that tend to diminish the velocity of an ion in solution, only the relaxation effect has a different value in a mixture of salts than it would have in a pure salt solution. The electrophoretic term depends only on $I^{1/2}$ but the relaxation effect depends on the

41

ratios of mobility, ω, and those of the ionic concentrations, μ. This change in the expected value of the relaxation term is known as the mixture effect.

The consequences of the above effect are that Kohlrausch's rule of the independent migration of ions, valid as a limiting law for simple binary electrolytes, neither apply to mixtures nor to the conductivities summed together. The Lee-Wheaton and QuintViallard equations also exist for such systems.

2-4-6 The modified conductivity equation

Conductivity in a number of solutions show concentration dependence contrary to theoretical expectations. Selvaratnam and Spiro[62a] and Pethybridge and Prue[62b] have respectively explained such an anomolous concentration dependence by postulating complex ion formations on H_3PO_4 and HIO_3 solutions. Similar explainations were used by Shamim and Spiro[62c], Shamim and Seng[62d] for tartaric, picric and citric acids solutions.

Several values of pK_a and pK_b values have been reported in the literature (see section 1-2). These values refer either to the Vitamin itself or its moieties[63], Thiazole (pK_a (proton gain)) = 2.53 and Pyrimidine (pK_a (proton gain)) = 1.30.

Generally, these values indicated the presence of two or three organic basic groups and for this reason a three step mechanism has been proposed

42

for Vitamin B1 solutions.

1. $ThiCl.HCl \longrightarrow Thi^+ + H^+ + 2\ Cl^-$

2. $H^+ + Thi^+ \xrightarrow{\ \alpha,\ K_1\ } ThiH^{2+}$

3. $H^+ + ThiH^{2+} \xrightarrow{\ \beta,\ K_2\ } ThiH_2^{3+}$
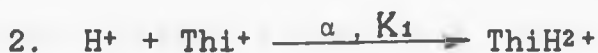
Where Thi refers to the Thiamine moiety , α and β are the degrees of complexation associated with the equilibrium constants K_1 and K_2 respectively.

The concentrations of these ionic species are

$[Cl^-] = 2C$; $[Thi^+] = (1 - \alpha)C$; $[H^+] = (1 - \alpha - \beta)C$; $[ThiH^{2+}] = (\alpha - \beta)C$; $[ThiH_2^{3+}] = \beta C$.

where C is the concentration of the electrolyte in mol 1^{-1}.

From equation (2-55),

$$J = C\ [2(1 + \beta) + \alpha] \qquad\qquad 2\text{-}63$$

The observed equivalent conductivity, Λ_{obs}, should be the sum of the equivalent conductivities of all the ionic species suggested, thus from equation (2-49)

$$1000\ \kappa = C\ \Lambda_{obs} = C\{2\ \lambda_{Cl^-} + (1 - \alpha)\lambda_{Thi^+} + (1 - \alpha - \beta)\lambda_{H^+}$$
$$+\ 2(\alpha - \beta)\ \lambda_{ThiH^{2+}} + 3\beta\lambda_{ThiH_2^{3+}}\ \} \qquad\qquad 2\text{-}64$$

It follows that a fitted value, Λ_{fit} should be

43

$$\Lambda_{fit} = 2\ \lambda_{Cl^-} + (1-\alpha)\lambda_{Thi^+} + (1-\alpha-\beta)\lambda_{H^+} + 2(\alpha-\beta)\lambda_{ThiH^{2+}} + 3\beta\lambda_{ThiH_2^{3+}}$$

$$= (2\lambda_{Cl^-} + \lambda_{Thi^+} + \lambda_{H^+}) - [\ \alpha\lambda_{Thi^+} + (\alpha+\beta)\lambda_{H^+} + (\beta-\alpha)2\lambda_{ThiH^{2+}} - 3\beta\lambda_{ThiH_2^{3+}}] \qquad 2\text{-}65$$

For a normal 1:1 electrolyte,

$$\Lambda_{salt} = (2\lambda_{Cl^-} + \lambda_{Thi^+} + \lambda_{H^+})$$

$$= \Lambda^0_{salt} - \frac{(B_1\ \Lambda^0_{salt} + B_2)}{1 + B_3 a^0 I^{1/2}}\ I^{1/2} \qquad 2\text{-}66$$

Therefore,

$$\Lambda_{fit} = \Lambda_{salt} - X \qquad 2\text{-}67$$

where

$$X = \alpha\lambda_{Thi^+} + (\alpha+\beta)\lambda_{H^+} + (\beta-\alpha)2\lambda_{ThiH^{2+}} - 3\beta\lambda_{ThiH_2^{3+}}$$

Similarly X can be added to equation (2-61) to calculate conductivity at infinite dilution , Λ^0_{cal} . Λ_{fit} should be equal to Λ_{obs} if the proposed mechanism is correct.

2-4-7 Calculations of α and β

From the proposed mechanism above, step 2 yields the equilibrium constant

$$K_1 = \frac{[ThiH^{2+}]}{[H^+][Thi^+]}$$

$$= \frac{(\alpha-\beta)C.f_{ThiH^{2+}}}{(1-\alpha)C.(1-\alpha-\beta)C.f_{Thi^+}f_{H^+}}$$

44

where
$$\log f_i = \frac{-A Z^2_i I^{1/2}}{1 + B_3 a^0 I^{1/2}}$$

and A has a value[37] of 0.5115 at 25°C.

Rearranging this equation into a quadratic form

$$K_1 C^2 f_{Thi^+} f_{H^+} \alpha^2 + [(\beta-2)K_1 C^2 f_{Thi^+} f_{H^+} - C f_{ThiH^{2+}}]\alpha + (1-\beta)K_1 C^2 f_{Thi^+} f_{H^+} + \beta C f_{ThiH^{2+}} = 0 \qquad \ldots\ldots\ldots\ldots 2\text{-}68$$

If
$$a = K_1 C^2 f_{Thi^+} f_{H^+}$$

$$b = (\beta-2)K_1 C^2 f_{Thi^+} f_{H^+} - C f_{ThiH^{2+}}$$

$$c = (1-\beta)K_1 C^2 f_{Thi^+} f_{H^+} + \beta C f_{ThiH^{2+}}$$

then
$$\alpha_{1,2} = \frac{b \pm (b^2 - 4ac)^{1/2}}{2a} \qquad\qquad 2\text{-}69$$

For step 3

$$K_2 = \frac{[ThiH_2^{3+}]}{[ThiH^{2+}][H^+]}$$

Similar treatment, as above, yields;

$$K_2 C^2 f_{H^+} f_{ThiH^{2+}} \beta^2 - (C f_{ThiH_2^{3+}} + K_2 C^2 f_{H^+} f_{ThiH^{2+}})\beta - K_2 C^2 f_{H^+} f_{ThiH^{2+}}(\alpha^2 - \alpha) = 0 \qquad \ldots\ldots\ldots\ldots 2\text{-}70$$

In this case
$$a = K_2 C^2 f_{H^+} f_{ThiH^{2+}}$$

$$b = -(C f_{ThiH_2^{3+}} + K_2 C^2 f_{H^+} f_{ThiH^{2+}})$$

$$c = -K_2 C^2 f_{H^+} f_{ThiH^{2+}}(\alpha^2 - \alpha)$$

Thus β can be calculated using equation (2-69).

45

Diffusion is one of the most fundamental irreversible process. If a difference of concentration of a solute exists in different regions of a solution, this process automatically set in and the solute spontaneously diffuses from higher to lower concentration until the concentration difference ceases to exist. The solvent, likewise, flows in the direction opposite to that of the solute.

The process of diffusion and conductance both involve migration of ions. In the latter, the positive and negative ions move in opposite direction while in diffusion the movement is in the same direction. At infinite dilution the ionic movement is independent of the other ions while conducting current. However, in case of diffusion all ions must move in the same direction and with the same speed otherwise electrical charge separation would result. The forces that make the ions move with the same speed are:

(i). The concentration gradient, dc/dx, defined as the rate of change in concentration with distance in the direction of flow. This is also taken as the positive direction of distance x. This force is more accurately refered to as the gradient of chemical potential, $d\mu/dx$, for the diffusing ionic species.

(ii). The electrical force, $Z_i eE$, which results from the tendency of the more mobile ions to move

faster than the less mobile ones, creating a charge separation - on a microscopic scale - or a gradient of electrical force which then causes a faster motion of slower ions and slows down the faster ions. The result is an identical speed for all ions. This phenomenon eliminates the relaxation effect which is associated with the conducting ions.

2-5-1   The Nernst-Hartley relationship in strong electrolytes

The forces on single ions due to the gradients of chemical potential and electrical field when expressed in terms of measurable physical quantities yield the following relationship - known as the Nernst-Hartley relationship[65].

$$D = \frac{v_+ + v_-}{v_+ |Z_+|} \; \frac{\lambda^0_+ + \lambda^0_-}{\lambda^0_+ + \lambda^0_-} \; \frac{RT}{F^2} \left(1 + \frac{d\ln y_{\pm}}{d\ln C} \right) \qquad 2\text{-}71$$

Where v_+, v_- are the number of subscripted ions of valencies Z_+, Z_- and conductivities λ^0_+, λ^0_-, R, T and F are the molar gas constant, temperature and Faraday constant respectively. $y_{\pm}$ represents the mean activity coefficient divided by the mean ionic molar concentration, at molar concentration C of the salt, as defined earlier. The limiting value of diffusion coefficient D^0, when ($d\ln y_{\pm}/d\ln C$) tends to zero, is given by

47

$$D^0 = \frac{v_+ + v_-}{v_+\,|Z_+|} \cdot \frac{\lambda^0_+ + \lambda^0_-}{\lambda^0_+ + \lambda^0_-} \cdot \frac{RT}{F^2} \qquad 2\text{-}72$$

It follows that

$$D = D^0 \left(1 + \frac{d\ln y_\pm}{d\ln C} \right) \qquad 2\text{-}73$$

For single electrolytes yielding two ionic species, equation (2-71) is composed of two parts; the mobility factor,

$$\frac{v_+ + v_-}{v_+\,|Z_+|} \cdot \frac{\lambda^0_+ + \lambda^0_-}{\lambda^0_+ + \lambda^0_-} \cdot \frac{RT}{F^2}$$

This factor solely determines the diffusion coefficient at infinite dilution. The activity factor,

$$1 + \frac{d\ln y_\pm}{d\ln C}$$

is a seperately available experimental quantity; thus interest centres on the contribution of the mobility factor at finite concentrations in the dilute range.

When the observed D values are divided by the activity factor, a quantity proportional to the actual mobility of the diffusing solute is obtained and can be compared with the limiting value D^0. Robinson and Stokes[84] have shown that the variation of diffusion coefficient with concentration is many times greater than that of the quantity $D/f(y)$ where $f(y)$ represents the activity factor. Thus a greater part of change in D is attributed to non-ideality in thermodynamic behaviour. The residual variation in $D/f(y)$ with concentration indicates that the actual mobility of ions vary slightly with concentration.

48

Their re-examination of Nernst-Hartley equation shows that actual ionic conductivities at finite concentrations cannot be used since experiments indicate that ionic mobilities during electrolytic conduction have a much greater variation and always decrease. However, in diffusion, these may decrease, increase or remain constant with concentration changes.

The relaxation effect is absent in diffusion, but a small electrophoretic effect is thought to be responsible for the slight variation of mobility with concentration and is included in the Nernst-Hartley equation in the forms

$$D = (D^0 + \triangle_1)\left(1 + \frac{d\ln y_\pm}{d\ln C}\right) \qquad 2\text{-}74$$

for asymmetric electrolytes, and

$$D = (D^0 + \triangle_1 + \triangle_2)\left(1 + \frac{d\ln y_\pm}{d\ln C}\right) \qquad 2\text{-}75$$

for symmetric electrolytes.

Where $\triangle_1$ and $\triangle_2$ are quantities reflecting electrophoretic effect in diffusion as given by Robinson and Stokes. These authors have shown that, generally, the above theory holds up to 0.01M for 1:1 electrolytes.

Where more than two ionic species are present, the situation becomes more complex since there is an infinite number of ways of satisfying the electrical neutrality condition (cf. reference 7). Generally, equations can be derived, but not necessarily solved for such cases.

2-5-2   **Diffusion coefficient in concentrated electrolyte solutions**

Effects, negligible for dilute solution below 0.02M, that become important in concentrated solution are as follows:

(i) the solvent molecules will in general move in the opposite direction to the solute molecules.

(ii) ions may carry with them a permanent hydration layer which acts as part of the diffusing solute entity and

(iii) the viscous forces may be considerably modified by the presence of large numbers of ions.

The above situation is complex and involves difficult concepts, Robinson and Stokes have given a theoretical treatment based on the work of Hartley and Crank. The equation applicable in this case is

$$D = (D^0 + \Delta_1 + \Delta_2)\left(1 + \frac{m\ d\ln y_\pm}{dm}\right)\left[1 + 0.036m\left(\frac{D^*_{H_2O}}{D^0} - n\right)\right]\frac{\eta^0}{\eta}$$

$$\dots\dots\dots 2\text{-}76$$

where m, n, η^0, η and $D^*_{H_2O}$ are molality, moles of bound water, viscosities of solvent, solution and self-diffusion coefficient of water respectively.

2-5-3 Fick's Laws

The flux of matter, J. This is defined as the amount of material, in grams or moles, crossing a unit area of a plane perpendicular to the direction of flow in unit time. J has the units of mole cm^{-2} s^{-1} and is given by the equation:

$$J = -D \, \partial c / \partial x \qquad \qquad 2\text{-}77$$

The diffusion coefficient, D. Essentially diffusion coefficient, D, is defined by equation (2-77). J is expressed as a partial differential of concentration, C, with respect to distance, x, because C is dependent both on time, t, and distance. The negative sign means that the direction of flow of matter is opposite to that of the concentration gradient as per the definition of distance x and D is a positive quantity. If x is expressed in cm, C in mol cm^{-3} and J in mol cm^{-2} s^{-1}, D would have units of cm^2 s^{-1}.

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

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \, \frac{\partial C}{\partial x} \right) \qquad \qquad 2\text{-}78$$

Equations (2-77) and (2-78) are known as Fick's first and second laws of diffusion respectively. The two Laws, thus summarise D as a constant for a given system; the constancy is, however, not followed

and D varies with concentration. The main interest of diffusion studies lies in the variation of D with C.

2-5-4   Methods of determining diffusion coefficient

Various methods for the determination of diffusion coefficients have been described in the literature[84]. They are classified into absolute and relative methods. Gouy interference and conductometric methods are examples of the former. Stokes porous diaphragm cell facilitates a relative method. The latter method has been universally accepted for measuring diffusion coefficients above 0.05M[64].

The diaphragm cell is a relative method because it requires calibration with a known solute. It has great advantage over absolute methods for being inexpensive and easy to install and calibrate; and can be successfully employed to determine diffusion coefficient at elevated temperatures[66] and is considered to be capable of yielding diffusion coefficients with a relative precision of 0.3%. This method was employed to study diffusion coefficients of aqueous Vitamin B1 solutions and a detailed discussion of its theory is as follows.

CHAMBER A

POROUS
DIAPHRAGM

V_A

$x = L$

V_D

$x = 0$

V_B

CHAMBER B
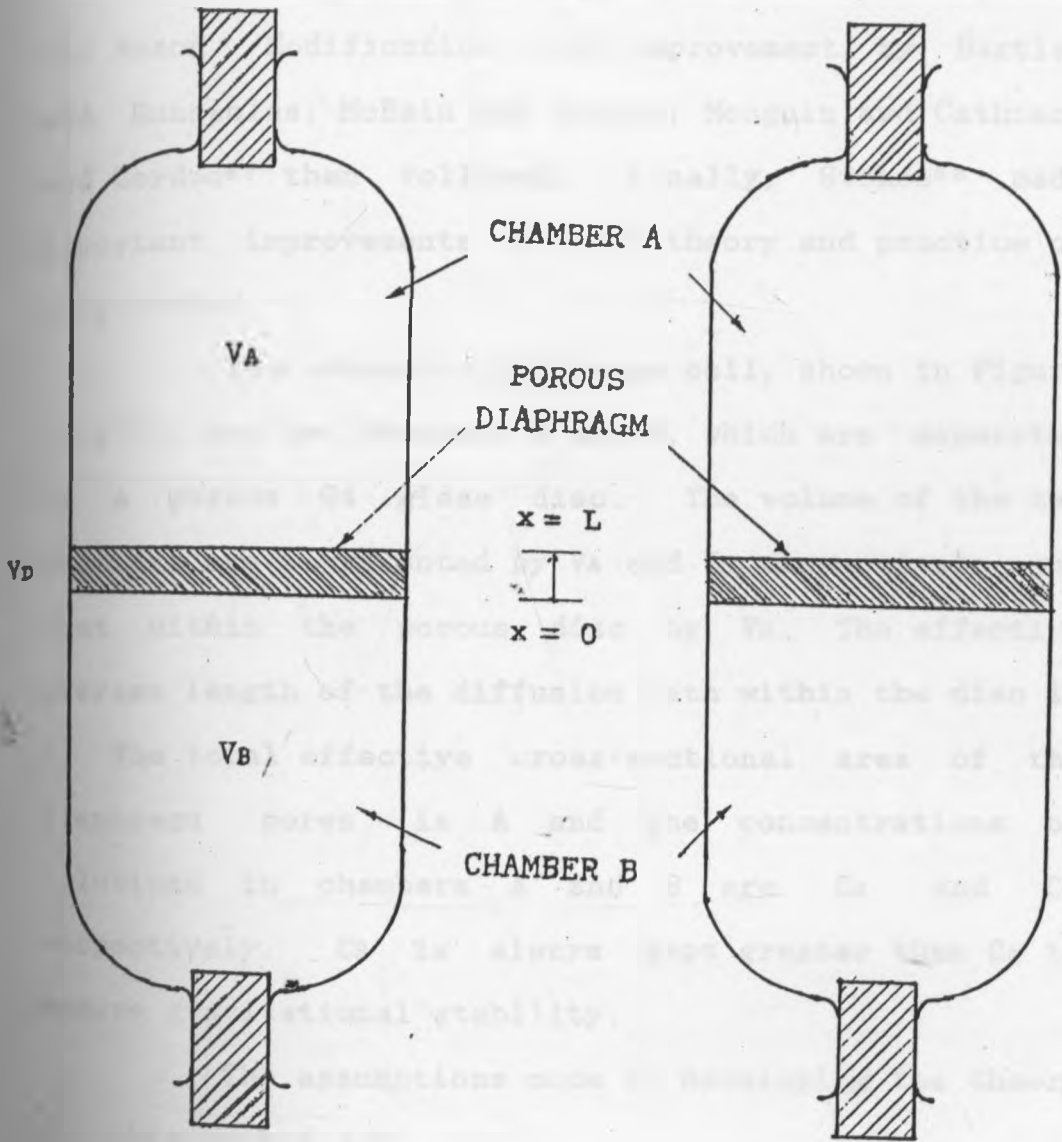
INITIAL	CONDITIONS	FINAL
$t = 0$		$t = t$
$C_A = C^o_A$		$C_A = C^t_A$
$C_B = C^o_B$		$C_B = C^t_B$

FIGURE 2-5-5. DIFFUSION CELL (SCHEMATIC DIAGRAM)[64]

Theory of the porous diaphragm cell method

This method was first introduced by Northrup and Anson. Modification, with improvement, by Hartley and Runnicles; McBain and Dawson; Monguin and Cathcart and Gordon[67] then followed. Finally, Stokes[68] made important improvements in the theory and practice of this method.

The schematic diaphragm cell, shown in Figure (2-5-5), has two chambers A and B, which are separated by a porous G4 glass disc. The volume of the two chambers are represented by V_A and V_B respectively and that within the porous disc by V_D. The effective average length of the diffusion path within the disc is L. The total effective cross-sectional area of the diaphragm pores is A and the concentrations of solutions in chambers A and B are C_A and C_B respectively. C_B is always kept greater than C_A to ensure gravitational stability.

The assumptions made in developing the theory for this method are:

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

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

(iii)   the flux, J, at any time, t, is independent

of the distance x, but only depends on time. To stress this fact J is represented as J(t),

(iv) 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 being called the 'pseudo-steady state' and

(v) there is no material accumulation within the diaphragm during the time when transport by diffusion is proceeding.

The rate of change of solute concentrations in the top and bottom chambers are related to the flux, J(t), by the following equations.

$$dC_A/dt = J(t)A/V_A; \quad dC_B/dt = - J(t)A/V_B$$

Hence

$$\frac{d(C_B - C_A)}{dt} = - J(t) \cdot \left(\frac{1}{V_B} + \frac{1}{V_A} \right) \cdot A \qquad \text{2-79}$$

The average value of the diffusion coefficient $\bar{D}$, with respect to concentration, over the concentration C_B to C_A prevailing at the time considered (this quantity is also time dependent) is denoted by $\bar{D}(t)$ and is given by the equation

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

$$= - \frac{1}{C_B - C_A} \int_{x=0}^{L} D \, \frac{\partial c}{\partial x} \, dx$$

$$= \frac{LJ(t)}{C_B - C_A} \qquad\qquad 2\text{-}80$$

Since $J(t) = -D(\partial c/\partial x)$ is constant for all points within the diaphragm at time t. x is the distance of the plane considered from the lower surface of the diaphragm (in the opposite direction of concentration gradient). Combining equations (2-79) and (2-80) one gets

$$- \frac{d \ln (C_B - C_A)}{dt} = \frac{A}{L} \left(\frac{1}{V_B} + \frac{1}{V_A} \right) \bar{D}(t) \qquad 2\text{-}81$$

Hence integrating between initial and final conditions as shown in Figure (2-5-5) one obtains

$$\ln \frac{C^0_B - C^0_A}{C^t_B - C^t_A} = \frac{A}{L} \left(\frac{1}{V_B} + \frac{1}{V_A} \right) \int_{t=o}^{t=t} \bar{D}(t) \, dt \qquad 2\text{-}82$$

$\bar{D}(t)$ is a concentration average, its time average is denoted by $\bar{D}$ such that

$$\bar{D} = \frac{1}{t} \int_o^t \bar{D}(t) \, dt \qquad\qquad 2\text{-}83$$

Let the cell constant, $\dfrac{A}{L} \left(\dfrac{1}{V_B} + \dfrac{1}{V_A} \right)$, be denoted by β. Equation (2-82) then becomes

$$\bar{D} = \frac{1}{\beta t} \ln \left(\frac{\Delta C^0}{\Delta C^t} \right) \qquad\qquad 2\text{-}84$$

where $\Delta C^0 = C^0_B - C^0_A$ and $\Delta C^t = C^t_B - C^t_A$.

Concentrations of Vitamin B1 solutions were determined, in this experiment, by refractive index

measurements, such that,

$$\overline{D} = \frac{1}{\beta t} \ln \left(\frac{\Delta n^0}{\Delta n^t} \right) \qquad 2\text{-}85$$

where $\Delta n^0 = n^0_B - n^0_A$, $\Delta n^t = n^t_B - n^t_A$ and n^0_B, n^0_A, n^t_B, and n^t_A are the initial and final refractive indices of the solutions in the subscripted chambers.

The average diffusion coefficient $\overline{D}$ which is calculated directly from the initial and final solute concentrations in the top and bottom cell chambers, the duration of the run and cell constant using equation (2-84) or (2-85), is a rather complicated double average of both concentration and time, and is called the Diaphragm cell integral diffusion coefficient. The integral diffusion coefficient, $\overline{D}$, so obtained can be converted into the real or differential diffusion coefficient, D, by the method described below.

2-5-6   Calculation of differential diffusion coefficient, D, from the integral diffusion coefficient, $\overline{D}$

Gordon[67] has shown that the integral diffusion coefficient, $\overline{D}$, is related to the true or differential diffusion coefficient, D, within an error of 0.02%, by the equation

$$\overline{D} = \frac{1}{\overline{C}_B - \overline{C}_A} \int_{\overline{C}_A}^{\overline{C}_B} D \, dc \qquad 2\text{-}86$$

where $\bar{C}_B = (C^0_B + C^t_B)/2$ and $\bar{C}_A = (C^0_A + C^t_A)/2$

To compute the differential diffusion coefficient at particular concentrations from the $\bar{D}$ values, an analytical expression[68] with arbitrary coefficients is usually assumed for $\bar{D}$.

A hypothetical integral diffusion coefficient, $\bar{D}^0(C)$, is defined such that it would be obtained in an experiment of vanishingly short duration with initial concentrations C and 0 in the lower and upper sides of diaphragm respectively. From equation (2-86) one obtains

$$\bar{D}^0(c) = \frac{1}{C} \int_0^C D \, dc \qquad 2\text{-}87$$

In such hypothetical experiments with initial concentrations in the lower chamber being $\bar{C}_B$ and $\bar{C}_A$, the corresponding integral diffusion coefficients would be $\bar{D}^0(\bar{C}_B)$ and $\bar{D}^0(\bar{C}_A)$. The experimental diffusion coefficient, $\bar{D}$, is incorporated in this hypothetical situation by the equation

$$\bar{D}^0(\bar{C}_B) = \bar{D} - (\bar{C}_A/\bar{C}_B)(\bar{D} - \bar{D}^0(\bar{C}_A) \qquad 2\text{-}88$$

$\bar{D}^0$ can be calculated for the higher concentration, $\bar{C}_B$, from experimental $\bar{D}$ value provided we know it for the lower concentration, $\bar{C}_A$.

A solution to this equation is possible since plots of $\bar{D}^0(\bar{C}_B)$ against $(\bar{C}_B)$ and $\bar{D}$ against (C^0_B) lie within 1%. In this connection, a graphical method

based on Stokes method[68] of successive approximations which converge rapidly to give excellent results for the differential diffusion coefficients was employed. This was as follows:

(i) Experimental $\bar{D}$ values were fitted against $(C^0_B)^{1/2}$ using a BBC Basic Computer programme, based on the weighted least squares polynomial calculation by Forsythe's method, given in appendix II. From the best polynomial equation covering the concentration range down to infinite dilution, $\bar{D}^0(\bar{C}_A)$ was calculated, as a first approximation, by substituting $\bar{C}_A$ values for each run into the polynomial equation. The resulting $\bar{D}^0(\bar{C}_A)$ values were substituted in equation (2-88) for calculations of $\bar{D}^0(\bar{C}_B)$ values.

(ii) The above $\bar{D}^0(\bar{C}_B)$ values were also fitted against $(\bar{C}_B)^{1/2}$ from which, as a second approximation, $\bar{D}^0(\bar{C}_A)$ values were again calculated and substituted in equation (2-88) to calculate new values of $\bar{D}^0(\bar{C}_B)$ for each run.

(iii) Step (ii) was repeated with new $\bar{D}^0(\bar{C}_B)$ values until their subsequent values did not vary.

(iv) The $\bar{D}^0(\bar{C}_B)$ values finally obtained in (iii) were fitted against $(C^0_B)^{1/2}$. The slopes, at each $(C^0_B)^{1/2}$ point obtained from the concentrations of experimental solutions, were calculated using a BBC Basic Computer program given in appendix IV. This program differentiated the polynomial equation of the best fitting curves. On

59

differentiating equation (2-87), with $(C^0_B)^{1/2}$ substituted for C one obtains the equation:

$$D = \bar{D}^0(\bar{C}_B) + \frac{(C^0_B)^{1/2}}{2} \cdot \frac{d\ \bar{D}^0(\bar{C}_B)}{d(C^0_B)^{1/2}}$$

..........2-89

The slope, $d\ \bar{D}^0(\bar{C}_B)/d(C^0_B)^{1/2}$, together with values of $(C^0_B)^{1/2}/2$ are substituted in the above equation to calculate the Differential Diffusion Coefficient, D.

This method overcame the problem of drawing tangents to the curve of the graph of $\bar{D}^0(\bar{C}_B)$ against $(C^0_B)^{1/2}$ in order to get slopes at each concentration, a method that was quite subjective although the second factor in equation (2-89) is the product of two small factors and subjectivity in the reading of slope may not produce a pronounced error in the final D value.

The author has obtained the Differential Diffusion Coefficients of Thiaminium dichloride in aqueous solution at 25°C using this method.

CHAPTER 3

EXPERIMENTAL

3-1   APPARATUS AND EQUIPMENT

3-1-1   The Tanks

Two tanks were fabricated using 1.5 inches angle-iron framework and glass plates; one was filled with non-conducting oil and the other with water.

The Oil Tank. The dimensions of the tank were 29.5 X 29.5 X 50.0 cm. Five sides were made of 3 mm glass plates. The tank was placed on a working bench of convenient height. It was filled with a non-conducting and adequately transparent Shell Diala BX oil.

The constant temperature was maintained using a GALLENKAMP adjustable contact thermometer[68] Model JUMO D.B.P 2.67 connected through an NGN - Relais LR VI relay[69] and employing a 40 Watts bulb as a heater. The stirring motors were fixed on to separate steel stands to minimise vibrations. These GALLENKAMP a.c. induction motors were connected to BERCO rotary regulators Type 72A capable of varying the output voltage from 0 to 110 %. Several paddles were welded onto each stirring steel rod.

A B. BRAUN thermoregulator model Thermix 1420 Type 850 022 also circulated water through a hollow copper coil immersed in the oil bath when room

temperatures were far below or above 25⁰C.

Conductance measurements were carried out in this tank, with temperature variations being monitored using a Beckmann thermometer. This arrangement kept the temperature constant at $25^{0}C \pm 0.01^{0}C$.

The Water Tank. This tank had dimensions of 71 X 40 X 35 cm. The walls and the base were made of 3 mm glass plates and all, except the walls facing the experimeter were painted white to enable easy inspection of immersed apparatus.

It was placed on a working bench of convenient height and filled with distilled water. The same type of a thermoregulator as for the oil tank maintained the temperature at $25^{0}C \pm 0.01^{0}C$. A water circulator - HETO Type FX23 - attached to a BERCO rotary regulator type LSOLAB was also used. The bath's temperature was then monitored using a Beckmann's thermometer. Water was added occasionally to replace losses due to evaporation.

This tank was set next to a large window providing enough daylight. The use of a magnifying glass greatly facilitated the inspection and use of apparatus.

3-1-2   Temperature Control

Density,   Viscosity,   Refractive   index,
Conductance   and   Diffusion   coefficient,   like   most
properties,   are   both   concentration   and   temperature
dependent.   The   intention   of   this   study   was   to
investigate   the   concentration   dependence   of   these
properties in aqueous Thiaminium   dichloride   solution.
The   measurements were therefore carried out at 25.00 $\pm$
0.01°C.

The facts that follow will   help   the   reader
realise the need for precise temperature control.

A change of 0.01°C causes approximately 0.02%
change   in   the   viscosity of water[70a].   The density[70b]
decreases by 0.03% $^{\circ}$C^{-1} rise in temperature for aqueous
solutions or   water.   Refractive   indices   of   aqueous
solutions   and   water   also   show   a   temperature
dependence[54a] of 0.0001 $^{\circ}$C^{-1}.   The Abbe's refractometer
may require a control to   within   0.5°C   for   liquids.
The   calibration   changes[54b]   by 0.0001 units for every
15°C.   Diffusion[71] coefficients and conductivity[72] both
change by about 2% per every degree change.

The   Beckmann   and   the   adjustable   contact
thermometers used were capable of detecting temperature
variations within $\pm$ 0.005°C.   The recorded fluctuations
were within 25.00 $\pm$ 0.01°C.

STOPPER

ETCH-MARK

3mm

25ml
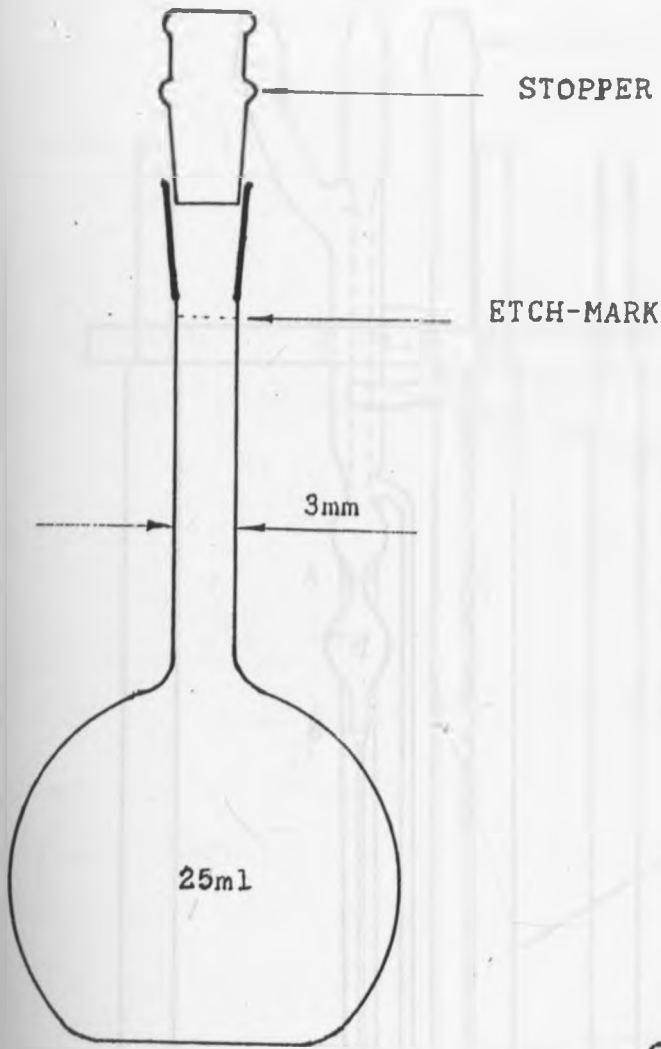
FIGURE 3-1-3(a)
FLASK-TYPE PYKNOMETER
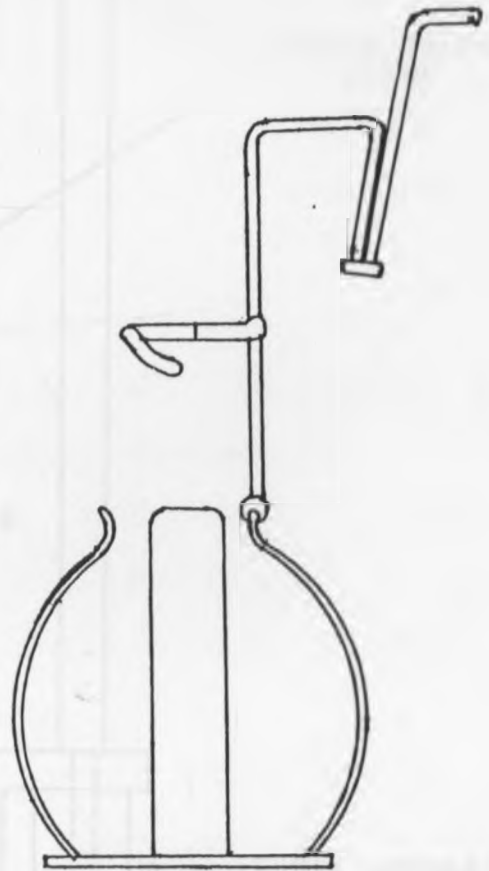
FIGURE 3-1-3(b)
HOLDER
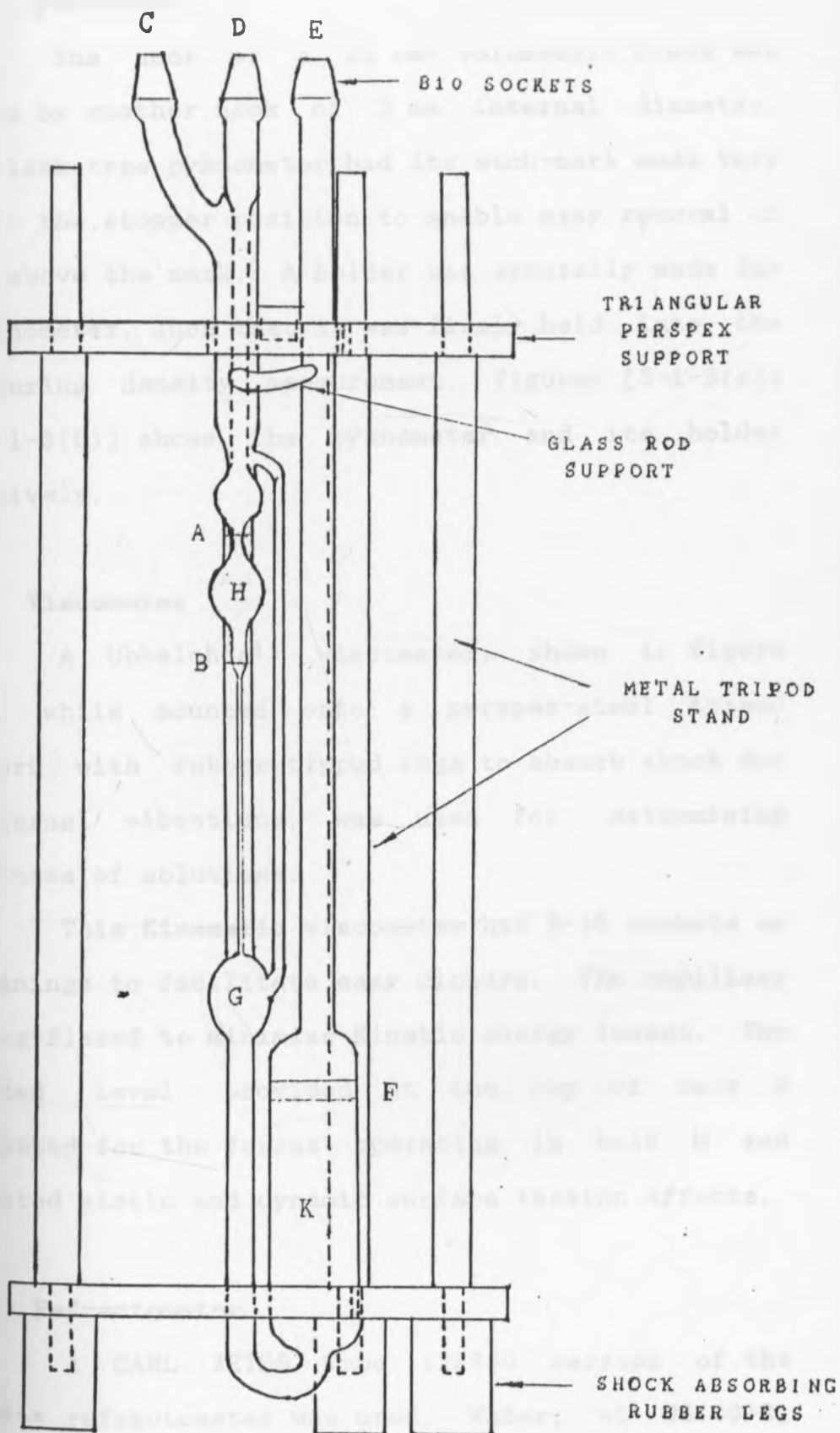
FIGURE 3-1-4 UBBELOHDE-TYPE VISCOMETER

(ON PERSPEX-IRON FRAMEWORK)

(NOT TO SCALE)

3-1-3   Pyknometer

The   neck   of   a   25 cm^3 volumetric flask was replaced by another neck of 3 mm internal diameter. This flask-type pyknometer had its etch-mark made very close to the stopper position to enable easy removal of liquid above the mark. A holder was specially made for the pyknometer, such that it was firmly held into the tank during density measurement. Figures [3-1-3(a)] and [3-1-3(b)] shows the pyknometer and its holder respectively.

3-1-4   Viscometer

A Ubbelohde[33] viscometer, shown in Figure (3-1-4) while mounted onto a perspex-steel tripod framework with rubber-tipped legs to absorb shock due to external vibrations, was used for determining viscosities of solutions.

This Kinematic viscometer had B-10 sockets on all openings to facilitate easy closure. The capillary was long-flared to minimise Kinetic energy losses. The suspended level provided at the top of bulb G compensated for the forces operating in bulb H and eliminated static and dynamic surface tension effects.

3-1-5   Refractometer

A CARL ZEISS Type 120650 version of the Abbe's[54a] refractometer was used. Water, at 25.00^{0}C, from the thermostatted bath was connected to the device through a circulator such that it maintained the

solutions and the prism-box at the desired temperature. The instrument required only a few drops of liquid and the refractive index could be read very quickly. The refractometer covered a range from 1.3000 to 1.7000 with an accuracy of $\pm$ 0.0002 when using light from a GRIFFIN & GEORGE sodium lamp connected through a 500 Watts control transformer. Thus the refractive index was measured with respect to the sodium D-line[54a] although white or day light could also be used with elimination of coloured bands in the telescope. The Thiaminium dichloride solution from compartment A and B before and after diffusion runs were analysed by refractometry.

3-1-6   **Conductivity Cell and Bridge**
Conductivity Cell. Figure [3-1-6(a)] shows a conductivity cell that was fabricated in the science workshop of the University of Nairobi.

This cell was designed with a cell constant such that the measured resistance remained between 1000 - 30,000 ohms[73] for the concentration range 0 - 0.2M. The measured resistance was not to fall too far above or below this range because excessive polarization or insulation leakage would respectively occur. The filling tubes and the connecting leads were relatively far apart to avoid parasitic current[74] flow through capacity resistance paths causing an apparent variation in the cell constant.
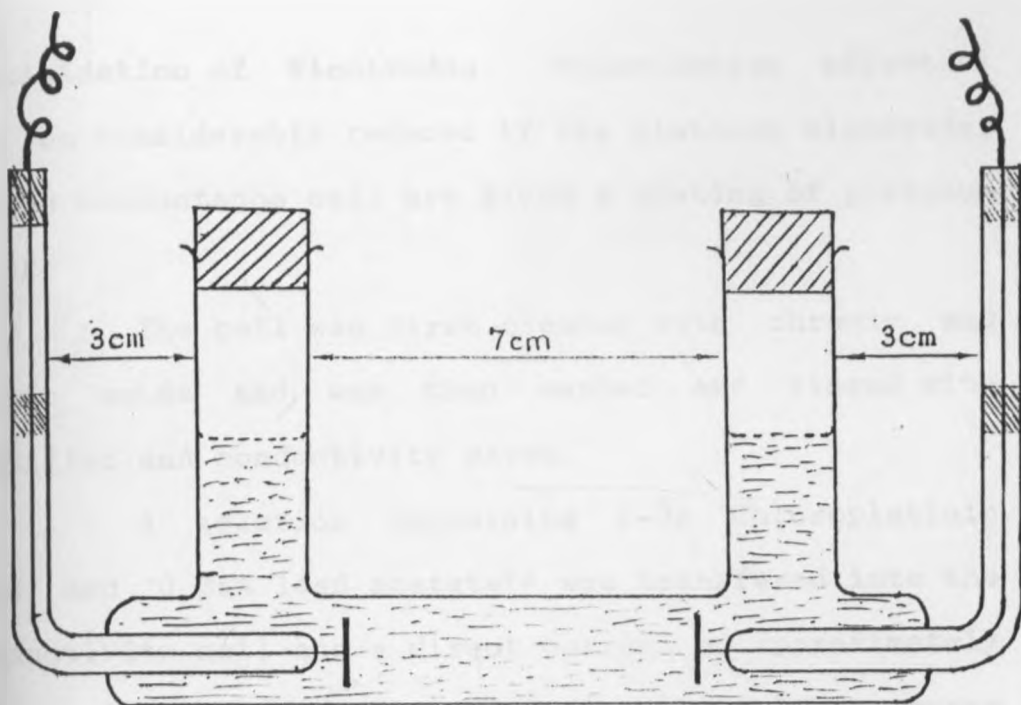
FIGURE 3-1-6(a) CONDUCTIVITY CELL
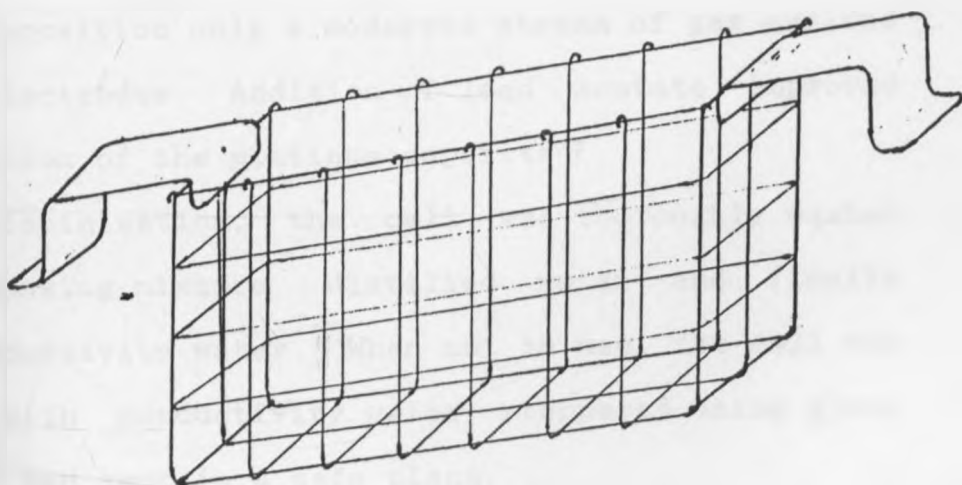
FIGURE 3-1-6(b) CELL HOLDER

Platinization of Electrodes. Polarization effects[75] can be considerably reduced if the platinum electrodes of the conductance cell are given a coating of platinum black.

The cell was first cleaned with chromic and nitric acids and was then washed and rinsed with distilled and conductivity water.

A solution containing 0.3% Chloroplatinic acid and 0.25% lead acetate[76] was transfered into the conductivity cell and a direct current of approximately 10mA cm^{-2} was passed while reversing the polarity every 30 seconds. After about 15 minutes, the electrode surfaces appeared black and well coated. During electrodeposition only a moderate stream of gas evolved at the electrodes. Addition of lead acetate improved the adhesion of the platinum deposits[77].

After platinization, the cell was thoroughly washed with cleansing mixture, distilled water and finally with conductivity water. When not in use, the cell was filled with conductivity water, stoppered using glass stoppers and kept in a safe place.

Conductivity Bridge. For the purpose of conductance determination, resistance measurement are almost always measured by means of an a.c. wheatstone bridge circuit (Kohlrauch's method) shown in Figure [3-1-6(d)].
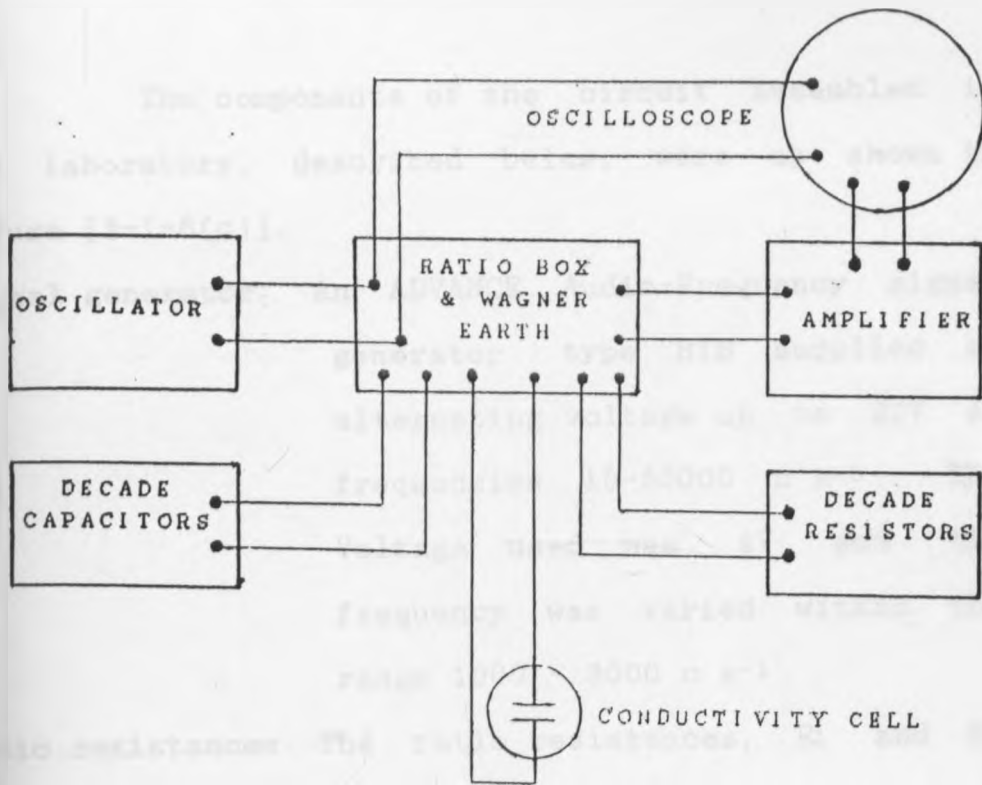
FIGURE 3-1-6(c) COMPONENTS OF THE CIRCUIT
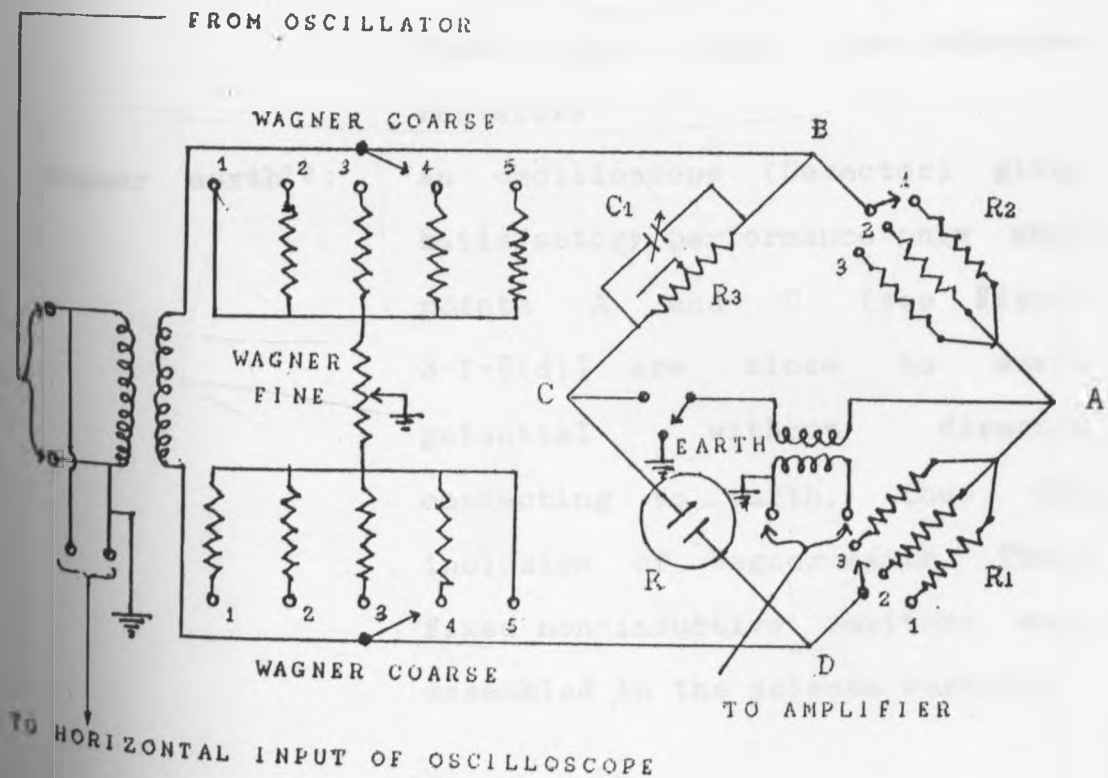
FIGURE 3-1-6(d) COMPLETE CIRCUIT DIAGRAM

The components of the circuit assembled in
the laboratory, described below, were as shown in
Figure [3-1-6(c)].

Signal generator: An ADVANCE Audio-Frequency signal
                generator type HIB supplied an
                alternating voltage up to 22V at
                frequencies 15-50000 c s^{-1}. The
                Voltage used was 4V and the
                frequency was varied within the
                range 1000 - 3000 c s^{-1}.

Ratio resistances: The ratio resistances, R_1 and R_2
                were assembled in the University's
                science workshop and had provisions
                for varying the ratio resistances
                on the ratio arms of the bridge.
                These were fixed non-inductive
                resistors.

Wagner earth[72]: An oscilloscope (Detector) gives
                satisfactory performance only when
                points A and C [see Figure
                3-1-6(d)] are close to earth
                potential without directly
                connecting to earth, thus the
                inclusion of Wagner earth. These
                fixed non-inductive resitors were
                assembled in the science workshop.
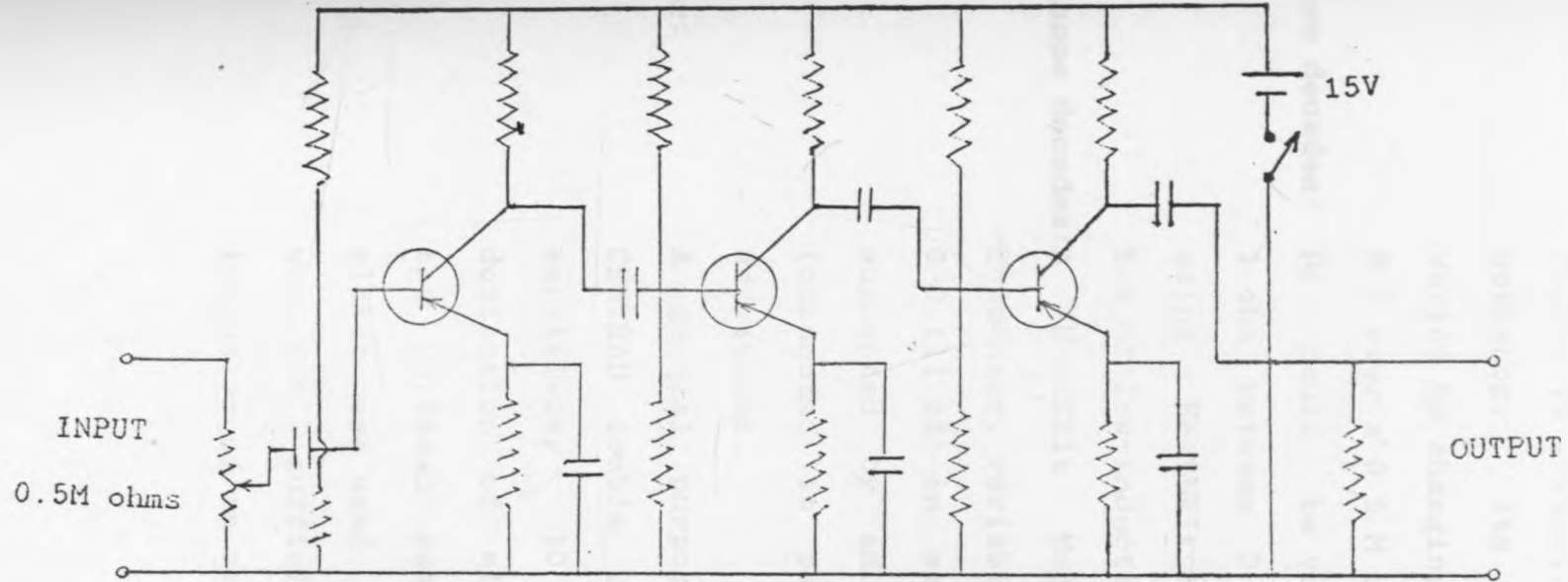
FIGURE 3-1-6(e) AMPLIFIER CIRCUIT

Amplifier[72] :   This was assembled as shown on Figure [3-1-6(e)], in the science workshop. Its sensitivity was varied by changing the voltage upto 9 V over a 0.5 M ohms resistor.

Resitance decades: R_3 could be varied in steps of 1 ohm between 0 - 999,999 ohms using a Heathkit model IN-11 Decade box of low-inductive resistors.

Capacitance decades: A Heathkit Model IN-21 decade condenser, variable over the range $0-0.111$ µf in steps of 10^{-4} µf and augmented by an air capacitor (connected in parallel) for finer adjustment.

Detector: A general purpose oscilloscope, CENTRAD double beam Type 273E, of sensitivity 10 mV per 1 mm deflection of electron beam over the vertical set of condenser plates was used. This sensitivity was not sufficient hence the inclusion of an amplifier.
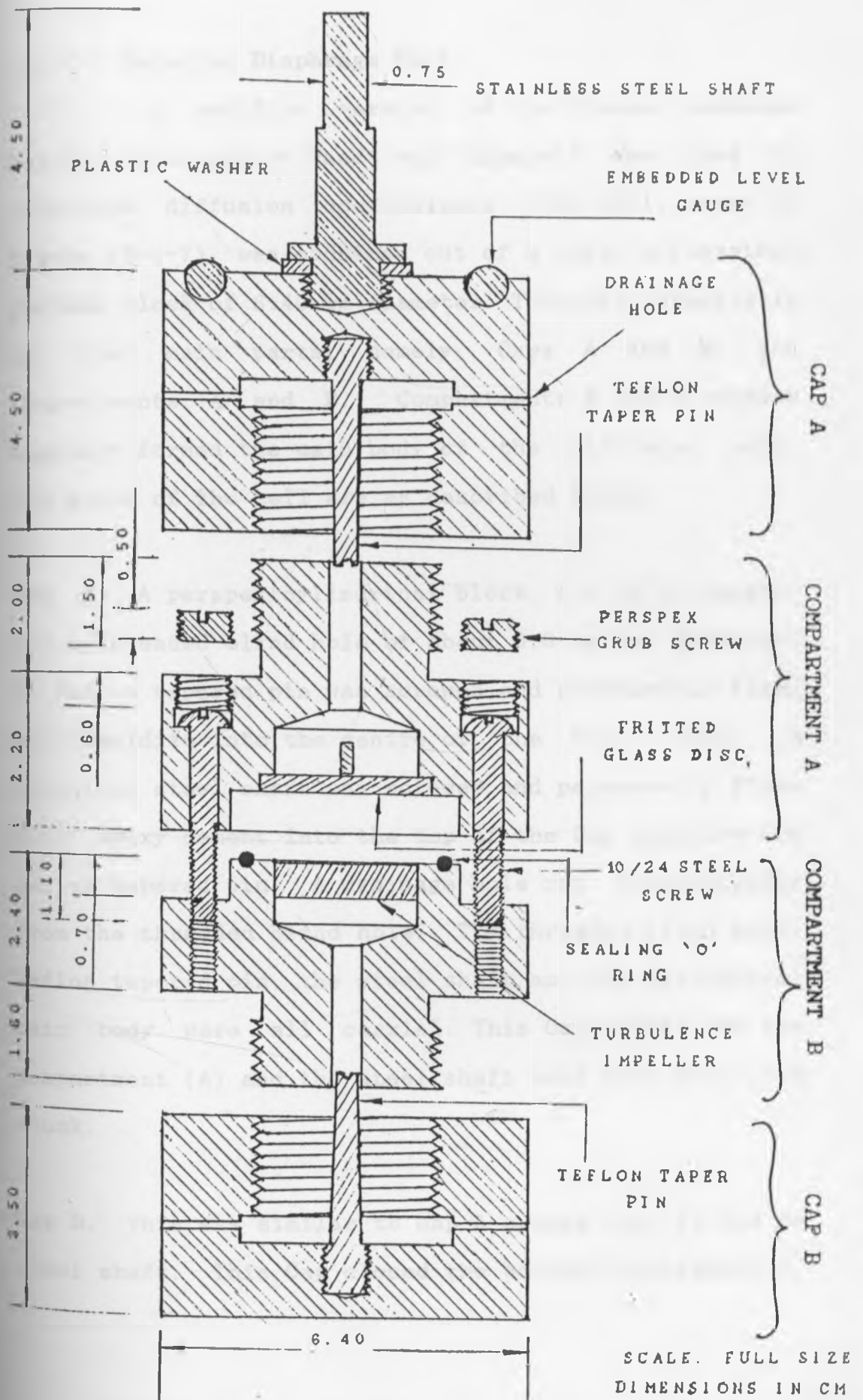
FIGURE   3-1-7   ROTATING DIAPHRAGM CELL
(vertical cross-section)

3-1-7 Rotating Diaphragm Cell

A modified version of the Stokes diaphragm cell[68], developed by Wendt and Shamim[78] was used to determine diffusion coefficients. The cell, shown in Figure (3-1-7), was machined out of a solid cylindrical perspex block of 6.40 cm diameter. The cell essentially has four main parts, namely, Caps A and B and Compartments A and B. Compartments A and B screwed together formed the main body of the diffusion cell. The parts of the cell are as described below:

Cap A. A perspex cylindrical block, 4.5 cm in length, had a threaded blind hole of about 3.0 cm in diameter. A Teflon tapered pin was screwed and permanently fixed with Araldite into the centre of the blind hole. A stainless steel shaft was screwed and permanently fixed with epoxy cement into the top of the Cap opposite the teflon tapered pin. A drainage hole ran diametrically from the threaded blind hole. The threaded blind hole, Teflon tapered pin, the steel shaft and the cylindrical main body were all coaxial. This Cap closed the top compartment (A) and the steel shaft went into motorized chuck.

Cap B. This was similar to cap A except that it had no steel shaft. This Cap closed the bottom compartment B.

Compartment A. This consisted of a threaded section, 2.0 cm long, that fitted into the threaded hole in cap A. Concentric with this section was a hole into which the Teflon tapered pin tightly fitted. This hole ran into a solution chamber. This solution chamber had a concentric shoulder into which fine porosity, G4, fritted glass disc was permanently fixed using Araldite.   The two ends of a small turbulence impeller were fixed into two slots cut into the walls of this chamber before fixing the fitted glass disc.

This compartment had four circumdrilled holes into which 3.5 cm long screws went through into similar but threaded holes in compartment B holding both compartments tightly together.   Another shoulder was machined around the fritted glass disc to accomodate a protruding edge in compartment B.

Compartment B. This was made similar to Compartment A except that it had no fritted glass disc but had a sealing ring seated into a groove concentric with the solution chambers.   Once the two compartments were secured together the sealing ring sat around the porous disc and sealed off the solution chambers from the water bath.   The turbulence impellers in both compartments were placed very close to the surface of the disc.   These compartments were never separated after calibrating the cell.   Compartment B held the denser[71] solutions during diffusion runs.

Compartments A, B and the porous disc held approximately 3.00 cm³, 3.50 cm³ and 0.25 cm³ of solution respectively. The tapered pin design made sure of sealing off solution volumes which were highly reproducible. The cell constant did not change with time.

The assembled cell was mounted into a motorized chuck. The motor, a 30 Watts GRIFFIN & GEORGE, Type LC8 - with variable speed, rotated it intermittently. Accelaration increased to maximum set speed within five seconds, followed by a sudden stop for the next five seconds. During the 4-6 Hours diffusion runs, these intermittent rotations were continously executed since these caused the impellers to induce turbulence and consequently stirred[71] the solutions in the two chambers thereby effectively removing the diffusive boundary or stagnant layers immediately above and below the porous disc.

The above motor was fixed on a separate support such that it hang above the water bath. This avoided vibrations which would otherwise interfere with other measurements.

3-1-8   **ON-OFF Switch[79]**

A simple electronic device whose electronic circuit is shown in Figure (3-1-8) was used to control the motor's intermittent rotation at intervals of 5 seconds. The mounted diffusion cell was therefore similarly controlled.
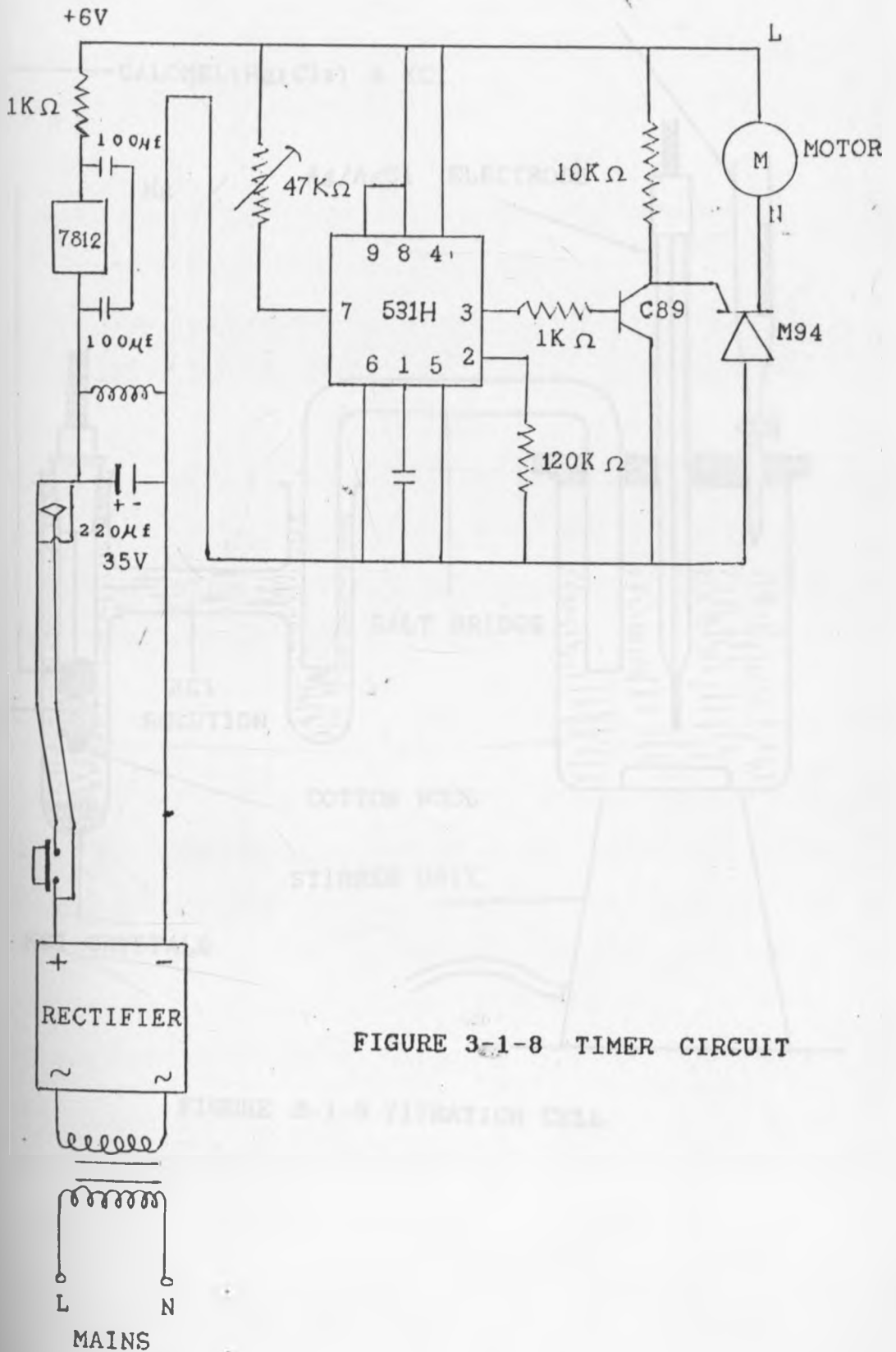
FIGURE 3-1-8 TIMER CIRCUIT

78
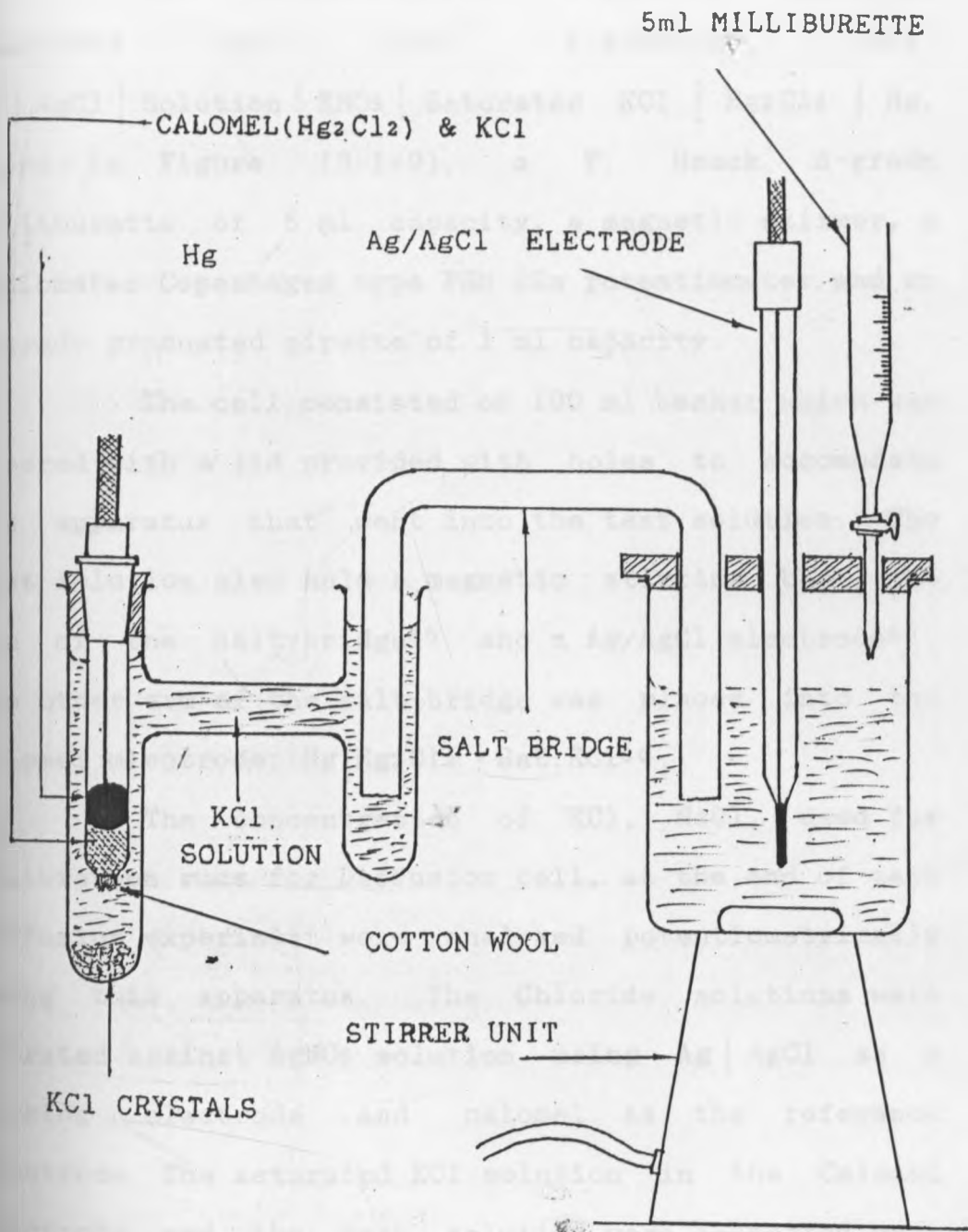
FIGURE 3-1-9 TITRATION CELL

Labels within figure:
- 5ml MILLIBURETTE
- CALOMEL(Hg_2Cl_2) & KCl
- Ag/AgCl ELECTRODE
- Hg
- SALT BRIDGE
- KCl SOLUTION
- COTTON WOOL
- STIRRER UNIT
- KCl CRYSTALS

3-1-9   Potentiometer and Titration Cell

The potentiometric titration apparatus consisted of the titration cell, $Ag \mid AgCl \vdots Solution \vdots KNO_3 \vdots Saturated \; KCl \vdots Hg_2Cl_2 \mid Hg$, shown in Figure (3-1-9), a P. Haack A-grade milliburette of 5 ml capacity, a magnetic stirrer, a Radiometer Copenhagen type PHM 22a potentiometer and an A-grade graduated pipette of 1 ml capacity.

The cell consisted of 100 ml beaker which was covered with a lid provided with holes to accomodate the apparatus that went into the test solution. The test solution also held a magnetic stirring bar, one arm of the salt-bridge[80] and a Ag/AgCl electrode[80]. The other arm of the salt-bridge was placed into the calomel electrode, $Hg \mid Hg_2Cl_2 \vdots Sat.KCl$[80].

The concentration of KCl, NaCl, used for calibration runs for Diffusion cell, at the end of each diffusion experiment were analysed potentiometrically using this apparatus. The Chloride solutions were titrated against $AgNO_3$ solution using $Ag \mid AgCl$ as a working electrode and calomel as the reference electrode. The saturated KCl solution in the Calomel electrode and the test solution were connected by a potassium nitrate, agar-agar salt bridge.

3-2 METHODOLOGY

3-2-1   Density Measurements

The pyknometer was soaked in Chromic acid overnight then in concentrated nitric acid for cleaning purposes. It was then thoroughly washed with distilled water and finally rinsed with double-distilled water. The pyknometer was dried in a vacuum desiccator. The dried pyknometer was stoppered and weighed on a METTLER TYPE H10 balance upto an accuracy of $\pm$ 0.00005gm. This procedure was repeated ten times with weights agreeing within $\pm$ 0.0005g. The average value of the weights was taken as the apparent weight of the empty pyknometer.

The pyknometer was then filled with degassed double-distilled water to a level slightly above the etch-mark using a 30ml syringe with a large bore hypodermic needle fixed to a 15cm long plastic tubing. The stoppered pyknometer was then placed in the water bath for 30 minutes to attain thermal equilibrium. The level of water in the pyknometer was brought to the etch-mark by blotting the water with thinly cut filter paper strips. The area above the mark was dried carefully with the same filter paper strips. The pyknometer was then taken out of the water-bath and its outer surface wiped and dried. It was weighed and the procedure was repeated many times. The weights were corrected for air bouyancy[80] and the volume of the vessel was determined from the corrected weight and density of water at 25.00°C. The volume of the

pyknometer was found to be 25.70278 ± 0.0005 cm^3. The calibration density measurements are shown in Table [3-2-1(a)].

The same procedure was repeated 'for aqueous vitamin B1 solutions. Their densities were determined from the volume and corrected weight relationship given by equation (2-1). The pyknometer was cleaned after each density determination and was occasionally recalibrated.

The density of solid Vitamin B1 was determinated by the liquid displacement method [31b] using acetone and benzene as the non-dissolving solvents.

When correcting the apparent weights of the solutions and the solid, the accurate densities of either is required yet this is the quantity sought. For this reason a simple computer program was developed. It used the apparent densities calculated using apparent weights to iteratively correct themselves until constant density values were obtained (see Appendix I). The density data in the concentration range 0.001 to 1M were related by the analytical equation,

$$\rho = 0.99707 + 0.10684C - 0.00114 \; C^2 \qquad \text{3-1}$$

The standard errors in the y-intercept and in the coefficients of C and C^2 were ± 0.00003, ± 0.0009 and ± 0.007 respectively. The correlation coefficient was 0.9998.

TABLE 3-2-1(a)   VOLUME CALIBRATION OF THE PYKNOMETER AT
25°C

W_F *	W_E *	W_{WA}	W_{WC}	V
42.8738	17.2730	25.6008	25.6279_5	25.7032_6
42.8730	17.2734	25.5996	25.6266_5	25.7020_6
42.8735	17.2727	25.6008	25.6279_5	25.7032_6
42.8736	17.2728	25.6008	25.6279_5	25.7032_6
42.8731	17.2732	25.5999	25.6270_5	25.7023_6
42.8732	17.2726	25.6006	25.6277_5	25.7030_6
42.8730	17.2730	25.6000	25.6271_5	25.7024_6
42.8733	17.2730	25.6003	25.6274_5	25.7027_6
42.8738	17.2730	25.6008	25.6279_5	25.7032_6
42.8729	17.2730	25.5996	25.6266_5	25.7020_6

W_F * = Weight of filled pyknometer.

W_E * = Weight of empty pyknometer.

W_{WA} = Weight of water (apparent).

W_{WC} = Weight of water (corrected).

V = Volume of pyknometer.

UNITS:- Weights, g; V, cm³.

* Averages of ten readings for each water sample.

Mean Volume = 25.7027_8 cm³.

Standard Deviation = ± 0.0005 cm³.

Statistical Analysis done by a BBC INSTAT program.

TABLE 3-2-1(b)   DENSITY MEASUREMENTS OF AQUEOUS THIAMINIUM DICHLORIDE SOLUTIONS AT 25°C

C	ρ_{obs}	$\rho^*cal.$	$\Delta\rho$
0	0.99707	0.99707	- 0.00000
0.00098	0.99726	0.99730	- 0.00004
0.00196	0.99738	0.99740	- 0.00002
0.00300	0.99750	0.99751	- 0.00001
0.00415	0.99764	0.99764	- 0.00000
0.00491	0.99764	0.99772	- 0.00008
0.00598	0.99785	0.99783	0.00002
0.00702	0.99798	0.99794	0.00004
0.00829	0.99807	0.99807	0.00000
0.00906	0.99816	0.99816	0.00000
0.00982	0.99828	0.99824	0.00004
0.01964	0.99933	0.99928	0.00005
0.03000	1.00039	1.00037	0.00002
0.04146	1.00149	1.00158	- 0.00009
0.05894	1.00346	1.00343	0.00003
0.06821	1.00443	1.00440	0.00003
0.07712	1.00542	1.00534	0.00008
0.11342	1.00917	1.00915	0.00002
0.21212	1.01939	1.01942	- 0.00003
0.28981	1.02737	1.02743	- 0.00006
0.50377	1.04919	1.04913	0.00006
0.59802**	1.07052	1.05851	0.01201
0.75388	1.07664	1.07380	0.00284
0.78205	1.07918	1.07653	0.00266
0.99538	1.10110	1.09693	0.00417

UNITS:- C, mol l^{-1}; ρ and ρ^*, g cm^{-3} and $\Delta\rho$= ρ_{obs} - $\rho^*cal.$

* Calculated using equation (3-1).

The equation fits within ± 0.0001 upto 0.5M.

The 5TH decimal place arises from averaging of ten weight readings and titration readings.

** The values below this are not represented by equation (3-1).

84

TABLE 3-2-2   CALIBRATION VISCOSITY MEASUREMENTS AT 25ºC

WATER SAMPLE	TIME*
1	451.816
2	451.831
3	451.851
4	451.835
5	451.807
6	451.826
7	451.870
8	451.821
9	451.839
10	451.801

UNITS:- Time in seconds.

* Results from averaging over ten readings.

Mean time = 451.830 sec.

Standard Deviation = ± 0.02 seconds.

85

This analytical equation best fits the density data in the concentration range 0.001 - 0.500M. Table [3-2-1(a)] gives density values at corresponding concentrations. The density data was used to compute the partial molal volume using equation (2-9).

3-2-2   **Viscosity Measurements**

The earlier stated cleaning procedure was followed for the Ubbelohde-type viscometer. Calibration was done using double-distilled water without drying the apparatus.

The viscometer was dried using a stream of dry Nitrogen then rinsed with the test solution ensuring that the prepared concentration does not suffer a change due to moisture in the viscometer.

The solution was finally introduced into the viscometer bulb, K, to either of the marked levels, F, [see Figure (3-1-4)] using a 30 ml syringe. The loaded instrument was placed at a marked position in the thermostatted bath for one hour to attain thermal equilibrium. The solution was then forced above the upper etch-mark, A, using a spray bellow operating through mouth E, having stoppered mouth C. By opening C and releasing the spray bellow, the solution was allowed to flow. The flow-time between the etch-marks A and B were recorded using an ALBA electronic stop-watch within $\pm$ 0.01 seconds. The actual starting

and ending points on the etch-marks were sighted using a 4 inches magnifying eye-piece.

The liquid was initially allowed to flow through the capillary several times before taking readings which were recorded until ten subsequent recordings agreed within 0.05 seconds.

Calibration was similarly done using several samples of double-distilled water.

The openings of the viscometer when in use were kept covered with aluminium foil to prevent any dust particles from entering the apparatus; and when not in use they were closed with rubber teats over aluminium foil. Relative viscosities were calculated using equation (2-22) using an average flow-time of water as 451.83o $\pm$ 0.02 seconds and density of water as 0.99707 g cm^{-3}. Calibration viscosity measurements are shown in Table [3-2-2]. The Jones-Dole equations were fitted to the graph of relative viscosity versus concentration. The A, B and D coefficients were then derived.

TABLE 3-2-3   CONCENTRATION CALIBRATION REFRACTIVE INDEX MEASUREMENTS OF AQUEOUS THIAMINIUM DICHLORIDE SOLUTIONS AT 25°C

C	nobs	ncal*	Δn
0.0010_3	1.33253_3	1.3325_5	$-\ 0.00002$
0.0019_8	1.3326_0	1.3326_2	$-\ 0.00002$
0.0026_2	1.3326_5	1.3326_7	$-\ 0.00002$
0.0050_4	1.3328_5	1.3328_6	$-\ 0.00001$
0.0300_0	1.3348_0	1.3348_1	$-\ 0.00001$
0.0414_6	1.3357_0	1.3357_0	0.00000
0.0500_6	1.3363_8	1.3363_7	0.00001
0.0589_7	1.3370_8	1.3370_7	0.00001
0.0682_1	1.3378_0	1.3377_9	0.00001
0.0771_2	1.3385_0	1.3384_8	0.00002
0.0936_8	1.3398_0	1.3397_8	0.00002
0.1134_2	1.3413_5	1.3413_1	0.00004
0.2121_2	1.3491_0	1.3490_2	0.00008
0.2898_1	1.3552_0	1.3550_8	0.00011
0.3993_4	1.3638_0	1.3636_7	0.00013
0.5037_7	1.3720_0	1.3718_5	0.00015
0.5980_2	1.3794_0	1.3792_4	0.00016
0.7062_7	1.3879_0	1.3877_4	0.00016
0.7820_5	1.3938_5	1.3937_0	0.00015
0.9953_8	1.4106_0	1.4105_0	0.00010

UNITS:- C, mol l⁻¹ and n is a ratio.

Δn = nobs - ncal*

* Calculated using equation (3-2) which fits nobs values within - 0.00002 and + 0.0002 in the concentration range 0.001 to 1M.

3-2-3   Refractive Index Measurements

A series of Thiaminium dichloride solutions
with concentrations ranging from approximately 0.001 to
1.00M, were prepared at 25.00⁰C. The prism box of the
properly levelled refractometer was then opened and its
surfaces wiped clean using a tissue paper soaked in
absolute ethanol, water and finally with
double-distilled water. A drop of double-distilled
water - previously kept at 25.00⁰C in a flask - was
transfered on to the lower prism. The prism box was
then closed and fastened and the index recorded.

For each sample, the intersection of the
cross-wires was approached from the top and bottom to
eliminate error due to backlash on the meter screw.
Readings were duplicated using another sample of water.
The final refractive index was thus an average of four
readings.

On using double-distilled water, the
refractometer was calibrated by setting it at
1.33255[4a], at 25.00⁰C.

The average refractive index values for a
series of Thiaminium dichloride solutions were used to
obtain a calibration equation by fitting the indices,
n, against concentrations, C as shown in Table [3-2-3].

Thiaminium dichloride is a very fine powder
and is difficult to weigh accurately. The
concentration of solutions prepared for these

measurements were confirmed using potentiometric titrations against 0.05M AgNO₃ solutions.

The slope and intercept calculated using a BBC micro-computer statistical package, are related by the analytical expression

$$n = 1.33247 + 0.07793C + 0.00047 C^2 \qquad 3-2$$

The standard errors in the y-intercept and in the coefficients of C and C^2 were $\pm$ 0.0002, $\pm$ 0.001 and $\pm$ 0.001 respectively. The correlation coefficient was 0.9998. Table [3-2-3] shows experimental and calculated values of Refractive indices and their difference at each concentration. The refractive indices were measured within $\pm$ 0.0002 but averaging over four values increased this accuracy.

3-2-4   Conductivity Measurements

The cell was cleaned with chromic acid, concentrated nitric acid, deionized water and rinsed with conductivity water. The cell was then left overnight in an inverted position for partial drying. The following day, a slow stream of filtered dry nitrogen gas was passed through the cell to ensure complete dryness. The cell was rinsed several times with aqueous Thiaminium Dichloride solution and then filled with the same. The loaded conductivity cell was placed in a wire gauze holder, shown in Figure [3-1-6(b)], then placed in the oil bath to attain the

bath's temperature.   During this period the glass and electrode surfaces adsorbed some Thiaminium dichloride from the solution.

The cell was removed, its outer surface washed free of oil using carbon tetrachloride, emptied, refilled with the same but fresh solution and put back into the oil bath.   Half an hour was allowed for thermal equilibration before measuring[72] the resistance at a frequency within 1000 - 3000 Hz.   Duplicate experiments agreed within 0.1%.

3-2-5   Determination of Cell Constant

The cell constant of a conductivity cell is usually obtained by measuring the resistance, R, of a solution of known specific conductivity, κ .   The cell constant, K, is then calculated from the equation,

$$K = \kappa R = C \Lambda R/1000 \qquad\qquad 3-3$$

Potassium chloride solutions are generally used for this purpose because the specific conductivities of its solutions at various concentrations have been very accurately determined[81]. The Bradshaw demal values[81] at 25.00°C are most commonly used.

In this work the author used an alternative method which allows for the use of KCl solutions of any moderate concentrations.   The method involves analysis[82] of the molar or equivalent conductivity of

91

aqueous KCl solutions at 25.00°C by means of the following equations:

$$\Lambda = 149.82 - 93.85C^{1/2} + 94.9C(1-0.2274C^{1/2}) \qquad 3-4$$

$$\Lambda = 149.93 - 94.65C^{1/2} + 58.74C\log C + 198.4C \qquad 3-5$$

$$\Lambda = \{(\Lambda^0 + BC + D\log C)(1- \nu C^{1/2})\}-2\sigma C^{1/2} \qquad 3-6$$

where $\nu = 0.2289$, $\sigma = 30.09$, $\Lambda^0 = 149.88$, $B = 153.70$, $D = 32.10$ and C is the molar concentration.

The cell constant arising from all these equations were compared and an average value, based on all the equations above, was adopted for calculating related quantity.

To determine the cell constant, the clean and dry cell was then rinsed several times with KCl solution of known molar concentration and filled with the same. The cell was then immersed into the oil bath and the resistance measured.

This was carried out for about ten solutions of KCl at different concentrations. The measured resistances of various solutions and the resulting cell constants are recorded in Table (3-2-5). Every analytical equation produced a matching but different value for the cell constant and revealed no trend with concentration. A mean value of 5.40_8 cm^{-1} was adopted for subsequent calculations.

92

TABLE 3-2-5   CONDUCTIVITY CELL CONSTANT

C	R	K_1	K_2	K_3
0.0053_8	6949.90	5.36_9	5.36_7	5.36_6
0.0066_0	5714.40	5.39_0	5.38_7	5.38_6
0.0083_9	4573.30	5.45_2	5.45_0	5.44_8
0.0097_7	3876.80	5.35_7	5.35_4	5.35_3
0.0101_5	3768.90	5.40_4	5.40_2	5.40_0
0.0104_7	3679.90	5.44_0	5.43_8	5.43_6
0.0153_7	2529.60	5.42_9	5.42_9	5.42_9
0.0294_6	1354.20	5.44_1	5.45_0	5.46_0
0.0399_0	1001.00	5.38_0	5.39_8	5.41_8

UNITS:- C, mol l^{-1}; R, Ohms and K_n, cm^{-1}.

K_1, K_2 and K_3 are based on Λ values from equations (3-4), (3-5) and (3-6) respectively.

Mean cell constant = 5.40_9 cm^{-1}.

Standard Deviation = $\pm$ 0.034 cm^{-1}.

Standard error of mean = $\pm$ 0.007 cm^{-1}.

Coefficient of variation = 0.6 %.

Statistical analysis by BBC INSTAT program.

3-2-6   Diffusion Measurements

Double-distilled water and the solution under study were kept at 25.00 $\pm$ 0.01°C in the water bath and degassed using a water-pump.

Hypodermic needles were cut shorter so as not to damage the porous glass disc when filling and emptying the chambers. The syringes were each marked for each chamber and were used for filling, emptying or collecting sample solutions. Chamber B was rinsed three times with solution B (under study). Each time the solution was forced through the fritted glass disc with the help of a rubber teat. This was repeated four times with chamber B retaining half its contents to ensure that the disc was air-free and contained solution B only. Finally, Chamber B was completely filled with the same solution and Cap B was carefully screwed into place. The tapered pin in the cap allowed liquid to flow out as it advanced to form a tight seal.

Chamber A was also rinsed several times with double-distilled water and eventually filled completely with the same. Cap A was then screwed into position to isolate solution A from the water in the thermostatted bath.

The diffusion cell was inspected for air bubbles and then clamped into the motorized chuck via the steel shaft such that the cell was vertically held in the water bath. The porous disc was then assumed to

94

lie in a horizontal plane[68]. The motor was switched ON and the intermittent ON-OFF rotation commenced. The motor speed was then so adjusted as to have an ON and OFF duration of 5 seconds each.

After about one hour pre-diffusion time[67], the cell was removed from the motor, assuming that the 'pseudo-steady state' had been established between solution A and B and so fritted glass disc contained a non-uniform solution instead of a uniform solution B initially present. The cell was wiped dry using a towel and Cap B unscrewed. Cap A remained in position to ensure that no solution flows through. This would have destroyed the steady-state. Solution B was drained off with the syringes described earlier, rinsed the chamber several times with fresh degassed test solution still kept at 25.00°C, filled with the same and Cap B carefully screwed back in position.

Cap A was then unscrewed, solution A drained out, rinsed several times and filled Chamber A with fresh degassed double-distilled water kept at 25.00°C. The time when water touched the porous disc surface in Chamber A during the final filling was considered as the starting time for the diffusion run, t = 0. An ALBA electronic stop-watch was switched ON at this point. Cap A was then screwed back, the cell put back into the thermostatted bath and the motor switched ON. During the diffusion run, the cell was occasionally inspected for air bubbles in the solution chambers.

Their presence meant a repetition of the diffusion run.

The cell was taken out of the water bath after an interval of 3 - 6 Hours, wiped dry, Cap B unscrewed, solution B withdrawn using a syringe and the solution stored in a clean and dry vial. The moment solution B left the porous disc surface, the stop-watch was stopped marking the time when the diffusion ceased, t = t. Cap A was then unscrewed a few drops of solution A were allowed to drain into Chamber B through the porous disc, in case any solution in the disc was sucked into Chamber A when Cap B was opened. The remaining solution A was drained off using a syringe and stored for analysis.

For calibration diffusion experiments with Potassium Chloride and Sodium Chloride solutions, the concentration changes in chambers A and B were determined by potentiometric titrations. Analysis of Thiaminium dichloride solution was done by refractometry using equation (3-2).

The experiments were discarded in case there were any air bubbles in either of the chambers at the end of a diffusion run.

3-2-7 Diffusion Cell Calibration

Calibration diffusion experiments were done with Potassium and Sodium Chloride solutions. The cell constant was determined from the known diffusion time t in seconds and the initial and final

concentrations of KCl[83] and NaCl solutions in the two chambers.

As mentioned earlier in section (2-5), the integral diffusion coefficient D is given by the equation

$$\bar{D} = (\bar{D}^0(\bar{C}_B) - (\bar{C}_A/\bar{C}_B)\ \bar{D}^0(\bar{C}_A))/(1 - (\bar{C}_A/\bar{C}_B)) \qquad 2\text{-}88$$

where $\bar{D}^0(\bar{C}_1)$, $\bar{C}_B$ and $\bar{C}_A$ are as defined earlier.

The cell constant was then calculated from the diaphragm cell equation

$$\beta = (1/\bar{D}t)\ln(\Delta C^0/\Delta C^t) \qquad 2\text{-}84$$

Values of $\bar{D}^0(\bar{C}_B)$ and $\bar{D}^0(\bar{C}_A)$ in equation (2-88) for KCl solution were obtained by fitting literature[68,84] $\bar{D}^0(C)$ values against C using the BBC Basic computer program given in Appendix II then calculating them using the so obtained equations for the curve.

The following procedure was adopted to test the computer program, when proved satisfactory it was used to process $\bar{D}^0(\bar{C}_B)$ and $\bar{D}^0(\bar{C}_A)$ values from the literature D values[83] for NaCl.

(i)   Literature D values[83] for KCl were obtained and a curve(s) fitted to the D against C graph using the above mentioned method [see Table 3-2-7(a)].

(ii) $\bar{D}^0(\bar{C}_1)$ values were then obtained as per equation (2-87) using a program that integrated and

97

averaged D values over the concentration range from 0 to C (see appendix III).

(iii) The so obtained average integral diffusion coefficients at respective concentrations, $\bar{D}^0(C_1)$, were compared with literature $\bar{D}^0(C_1)$ values for KCl and the agreement was excellent as shown in Table [3-2-7(b)].

(iv) Literature D values for NaCl were then treated as in steps (i), (ii) and (iii) The results are shown in Table [3-2-7(c)].

For each electrolyte, curves were fitted to $\bar{D}^0(C_1)$ against C graphs and extrapolated to infinite dilution. The curve polynomial equations were then used to calculate $\bar{D}^0(\bar{C}_B)$ and $\bar{D}^0(\bar{C}_A)$ in each case.

(v) From the values of $\bar{D}^0(\bar{C}_B)$ and $\bar{D}^0(\bar{C}_A)$, $\bar{D}$ was calculated for each case using equation (2-88). Having known $\bar{D}$, ΔC^0 and ΔC^t values, β was calculated using equation (2-84).

The relevant data and resulting cell constants are recorded in Tables [3-2-7(d)] and [3-2-7(e)]. Solutions of approximately 0.1M were used for calibration in both cases. The agreement between β values obtained from these systems of different electrolytes indicated the reproducibility of volumes V_A and V_B of the cell, steady state condition within the disc, its horizontal alignment, titration method used for analysis and the method used for obtaining $\bar{D}^0(C_1)$ values.

TABLE 3-2-7(a)   COMPARISON OF FITTED AND LITERATURE D VALUES OF KCl AT 25°C

C	D_{lit}	D_{fit}	$\Delta D = D_{lit} - D_{fit}$
0.000	1.996	1.995_8	0.0002
0.001	1.964	1.964_9	− 0.0009
0.002	1.954	1.952_4	0.0016
0.003	1.945	1.946_1	− 0.0011
0.005	1.934	1.933_7	0.0003
0.007	1.925	1.925_1	− 0.0001
0.010	1.917	1.917_0	0.0000
0.050	1.864	1.863_8	0.0002
0.100	1.844	1.844_1	− 0.0001
0.200	1.838	1.838_0	0.0000
0.300	1.838	1.838_0	0.0000
0.500	1.850	1.850_0	0.0000
0.700	1.866	1.865_6	0.0004
1.000	1.892	1.892_1	− 0.0001
1.500	1.943	1.943_1	− 0.0001
2.000	1.999	1.998_9	0.0001
2.500	2.057	2.057_0	0.0000
3.000	2.112	2.112_0	0.0000
3.500	2.160	2.160_0	0.0000
3.900	2.196	2.196_0	0.0000

UNITS:- C, mol l^{-1}; D_{lit} and D_{fit}, cm^2 s^{-1} x 10^{-5}.
D_{fit} values obtained by computer program shown in Appendix II.

TABLE 3-2-7(b)   COMPARISON OF LITERATURE AND CALCULATED
$D^o(C_1)$ VALUES FOR KCl AT 25°C

C	$\bar{D}^o(C_1)_{lit}$		$\bar{D}^o(C_1)_{cal}$		$\Delta \bar{D}^o(C_1)$
0.000	1.996	(1.995_8)	1.995_8	(1.995_8)	0.0002
0.001	1.974	(1.974_4)	1.978_1	(1.978_1)	$- 0.0007$
0.002	1.966	(1.965_4)	1.967_9	(1.967_9)	$- 0.0013$
0.003	1.960	(1.960_5)	1.961_6	(1.961_6)	$- 0.0016$
0.005	1.951	(1.950_9)	1.953_0	(1.953_0)	$- 0.0020$
0.007	1.945	(1.945_0)	1.946_0	(1.946_0)	$- 0.0010$
0.010	1.938	(1.938_0)	1.938_5	(1.938_5)	$- 0.0005$
0.020	1.920	$(-)$	$-$	$(-)$	$-$
0.030	1.908	$(-)$	$-$	$(-)$	$-$
0.050	1.893	(1.892_8)	1.897_0	(1.896_7)	$- 0.0040$
0.070	1.880	$(-)$	$-$	$(-)$	$-$
0.100	1.873	(1.873_1)	1.874_1	(1.874_3)	$- 0.0011$
0.200	1.857	(1.857_0)	1.857_5	(1.857_5)	$- 0.0005$
0.300	1.850	(1.850_0)	1.850_3	(1.850_2)	$- 0.0003$
0.500	1.848	(1.848_0)	1.847_7	(1.847_9)	0.0003
0.700	1.851	(1.850_7)	1.850_6	(1.850_4)	0.0005
1.000	1.859	(1.859_1)	1.859_0	(1.859_0)	0.0000
1.200	1.866	$(-)$	$-$	$(-)$	$-$
1.400	1.874	(1.874_0)	$-$	$(-)$	$-$
1.500	$-$	$(-)$	1.878_4	(1.878_4)	$-$
1.600	1.882	(1.882_0)	$-$	$(-)$	$-$
1.800	1.892	$(-)$	$-$	$(-)$	$-$
2.000	1.901	(1.901_0)	1.901_4	(1.901_4)	$- 0.0004$
2.500	1.927	(1.927_0)	1.926_8	(1.926_8)	0.0002
3.000	1.953	(1.953_0)	1.953_1	(1.953_0)	$- 0.0001$
3.500	1.979	(1.979_0)	1.979_3	(1.979_0)	$- 0.0003$
3.900	2.000	(2.000_0)	1.999_7	(1.999_7)	0.0003

UNITS:- C, mol l^{-1}; $\bar{D}^o(C_1)$, cm^2 s^{-1} x 10^{-5}.

The values in brackets were those fitted using the program
in Appendix II.

$\bar{D}^o(C_1)_{cal}$ values were calculated using the program in
Appendix III.

$\Delta D^o(C_1) = \bar{D}^o(C_1)_{lit} - \bar{D}^o(C_1)_{cal}$.

TABLE 3-2-7(c)   LITERATURE D AND CALCULATED $D^o(C_i)$ VALUES FOR NaCl AT 25ºC

C	D_{lit}		$\bar{D}^o(C_i)_{cal}$	
0	1.612	(1.611_9)	1.611_9	(1.611_9)
0.001	1.585	(1.585_3)	1.596_5	(1.596_5)
0.002	1.576	(1.575_4)	1.588_1	(1.588_1)
0.003	1.570	(1.570_4)	1.583_0	(1.583_0)
0.005	1.560	(1.559_8)	1.575_9	(1.575_9)
0.007	1.555	(1.555_0)	1.570_3	(1.570_3)
0.010	1.545	(1.545_0)	1.565_9	(1.565_9)
0.050	1.506	(1.506_7)	1.533_4	(1.533_3)
0.100	1.484	(1.483_0)	1.513_1	(1.513_1)
0.200	1.478	(1.478_5)	1.495_7	(1.495_7)
0.300	1.477	(1.476_9)	1.490_1	(1.490_1)
0.500	1.474	(1.474_0)	1.483_9	(1.483_9)
0.700	1.475	(1.475_7)	1.481_1	(1.481_2)
1.000	1.483	(1.482_6)	1.480_5	(1.480_5)
1.500	1.495	(1.495_1)	1.483_1	(1.483_1)
2.000	1.514	(1.514_0)	1.488_4	(1.488_4)
2.500	1.529	(1.529_0)	1.495_0	(1.495_0)
3.000	1.544	(1.543_8)	1.502_0	(1.502_0)
3.500	1.559	(1.559_0)	1.509_0	(1.509_0)
4.000	1.584	(1.584_0)	1.516_7	(1.516_7)

UNITS:- C, mol l^{-1}; D_{lit} and $\bar{D}^o(C_i)$, cm^2 s^{-1} x 10^{-5}.
The values in brackets were those fitted using the
Program in Appendix II.
$\bar{D}^o(C_i)_{cal}$ values were calculated using the program in
Appendix III.

TABLE 3-2-7(d)   DIFFUSION CELL CONSTANT FROM 0.09977 M (C^O_B) KCl SOLUTION

t	$\bar{C}_B$	$\bar{C}_A$	ΔC^t	$\bar{D}$	β
10860	0.01307	0.08878	0.05143	1.8679	3.2764
10820	0.01321	0.08893	0.05146	1.8677	3.2864
10810	0.01304	0.08883	0.05159	1.8679	3.2763
10800	0.01307	0.08888	0.05163	1.8678	3.2755
14415	0.01587	0.08655	0.04138	1.8668	3.2783
14420	0.01596	0.08661	0.04133	1.8668	3.2817
14420	0.01599	0.08666	0.04136	1.8668	3.2786
14405	0.01600	0.08670	0.04143	1.8667	3.2763
18000	0.01769	0.08430	0.03323	1.8665	3.2788
18050	0.01786	0.08441	0.03312	1.8664	3.2794
18120	0.01791	0.08439	0.03299	1.8663	3.2793
18090	0.01792	0.08442	0.03302	1.8663	3.2811

UNITS:- t, sec.; $\bar{C}_A$, $\bar{C}_B$, ΔC^t and C^O_B , mol l^{-1}; $\bar{D}$ in cm^2 s^{-1} x 10^{-5} and β, cm^{-2}.

Mean cell constant = 3.2790 cm^{-2}.

Standard deviation = ± 0.0030 cm^{-2}.

Standard error of mean = ± 0.0009 cm^{-2}.

Coefficient of variation = 0.1 %.

All calculations done using the BBC INSTAT statistical program.

TABLE 3-2-7(e)   DIFFUSION CELL CONSTANT FROM 0.09786 M (C^oB) NaCl SOLUTION

t	$\bar{C}_B$	$\bar{C}_A$	ΔC^t	$\bar{D}$	β
11330	0.08991	0.01150	0.05705	1.5089	3.2706
11300	0.08992	0.01142	0.05721	1.5090	3.2627
10970	0.08993	0.01098	0.05811	1.5092	3.2660
11020	0.08978	0.01092	0.05794	1.5093	3.2687
14450	0.08835	0.01397	0.04897	1.5080	3.2669
14470	0.08844	0.01413	0.04883	1.5079	3.2753
14480	0.08837	0.01406	0.04884	1.5079	3.2724
14490	0.08832	0.01396	0.04893	1.5080	3.2611
18075	0.08630	0.01590	0.04101	1.5075	3.2636
18070	0.08640	0.01604	0.04093	1.5074	3.2719
18020	0.08635	0.01595	0.04102	1.5075	3.2727
18000	0.08642	0.01602	0.04103	1.5074	3.2756

UNITS:- t, sec.; $\bar{C}_A$, $\bar{C}_B$, ΔC^t and C^oB , mol l^{-1}; $\bar{D}$ in cm^2 s^{-1} x 10^{-5} and β in cm^{-2}.
Mean cell constant = 3.2690 cm^{-2}.
Standard deviation = ± 0.0046 cm^{-2}.
Standard error of mean = ± 0.0013 cm^{-2}.
Coefficient of variation = 0.1 %.
All calculations done using the BBC INSTAT statistical
Program.

The average value of β over both electrolytes was 3.274_0 cm^{-2} with a standard deviation of $\pm 0.006_5$, standard error of mean being $\pm 0.001_3$ and coefficient of variation being 0.2 %. This value was adopted for subsequent $\bar{D}$ and D calculations in Thiaminium dichloride solutions.

3-2-8   Potentiometric Titrations

The concentrations of KCl, NaCl during each diffusion experiment and Thiaminium dichloride during calibration refractive index measurements were analysed potentiometrically.

0.01M and 0.05M AgNO$_3$ solutions were used for analysing KCl and NaCl, and Thiaminium dichloride solutions respectively. In each case the appropriate AgNO$_3$ solution was loaded into the milliburette. A graduated 1ml pipette was used to pipette out 1ml volume of the inorganic chlorides from each diffusion experiment and lesser volumes of the Vitamin B1 solutions depending on the prepared concentration.

AgNO$_3$ solution was then added in convenient proportions after setting up the titration cell and the potentiometer. The total volume already added and the corresponding potentiometer reading was recorded. As the end-point approached, the change in potential difference increased markedly with every proportion of AgNO$_3$ solution added necessitating the latters reduction so that a sharp end-point was obtained.

The end-points were determined by constructing second order differential plots[85] i.e. d^2E/dV^2 against V. For each sample, titrations were duplicated with reproducibility being within $\pm$ 0.5 %.

3-2-9 Calibration of Volumetric Flasks

When working at temperatures other than those at which commercially available volumetric flasks have been calibrated by the manufacturers, volume recalibration must be done.

Flasks were thoroughly cleaned with chromic and then concentrated nitric acids, followed by rinsing with plenty of distilled water. They were dried in a vacuum desiccator over silica gel. On drying the marked flasks were weighed together with their marked stoppers using a METTLER H1200 top pan balance weighing within $\pm$ 0.005g.

The flasks were then filled to just below the etch-mark with air-free double-distilled water, stoppered and placed in constant temperature water bath. After 30 minutes, the levels of water were carefully brought upto the mark, any water adhering onto the neck above the mark was removed using a fine tissue paper. Calibrations were done as outlined for the pyknometer in section (3-2-1). 250 and 100 cm³ volumetric flasks, six of each type, were calibrated in this manner.

Double-distilled water. This was prepared by distilling twice tap-water in an all glass apparatus commercially available for this purpose. The distilled water was stored in two litres volumetric flasks.

Conductivity Water. The above double-distilled water was passed through an Elgastat deionizer Type C113 packed with Elgalite (Resin) Type c208. The conductivity, measured using a GALLENKAMP Type CM11 conductometer, was 1.45×10^{-7} mho.

Ethanol. The ALPHA AnalaR grade absolute ethanol was used as bought for cleaning purposes.

Potassium Nitrate. ALPHA GPR grade potassium salt, used as it was bought.

Potassium Dichromate. The ALPHA GPR salt was used as obtained.

Concentrated Nitric acid. The ALPHA GPR acid was used as obtained.

Concentrated Sulphuric acid. The ALPHA GPR acid was used as obtained.

Potassium Chloride. The BDH AnalaR grade salt was dried for 140 hours at 98°C in a temperature controlled oven. The bottle was occasionally removed for shaking to allow the escape of trapped water vapour and to break the lumps if any.

Sodium Chloride. The BDH AnalaR grade salt was also treated as above.

Silver Nitrate. The BDH AnalaR grade salt was used as bought without any reprocessing.

Thiamine Chloride Hydrochloride. The SIGMA AnalaR grade salt was dried for 48 hours at 98°C in a temperature controlled oven. The salt was shaken occasionally to crush lumps that formed from fine powder and trapped water vapour. The dried salt was distinctively fine, powdery and lump free.

All the chemicals that were dried in the oven were cooled to room temperature while stored over silica gel in a vacuum desiccator. Vitamin B1 powder was kept in a vacuum desiccator through out the work.

3-4   <u>SOLUTIONS</u>

KCl, NaCl and AgNO₃. Solutions of these salts were prepared by transfering a known weight of the substances. The exact weight transfered was determined by the difference method. The solutions were made up at 25.00°C. Concentration values were based on the

corrected weights of the reagents.

KNO₃. This solution was prepared for the purpose of making the Agar-Agar salt bridge. Approximate amount for making 0.01M KNO₃ solution was weighed out.

Thiaminium Dichloride.   This dry salt was so fine and light that weighing was a difficult task. The weighing bottle (50 ml beaker) and the funnel used for transfer into the volumetric flask were thoroughly cleaned. A little water was put into the weighing bottle and weighed before adding approximate weight of the salt required and recording the actual weight. The contents of the weighing bottle were then washed into the volumetric flask and the solution made up to the mark.
Since the density of Thiaminium Dichloride was not available, its apparent weights could not be corrected for air bouyancy. Attempts to measure the density at 25.00⁰C failed but at 20.00⁰C the density was measured. For this reason the concentration of the Vitamin solutions were verified by refractometry.

Chromic Acid.   This was prepared by adding one volume of concentrated H₂SO₄ to the same volume of saturated K₂Cr₂O₇ solution previously filtered through sintered glass.

CHAPTER 4

RESULTS, DISCUSSIONS AND CONCLUSION

4-1 RESULTS AND DISCUSSIONS

4-1-1 Density

The densities, at various concentrations, of aqueous Thiaminium dichloride are shown in Table [3-2-1(b)]. The concentration dependence of these densities in the concentration range 0 - 0.5M is given by equation (3-1). The expected cumulative[86] standard error in density measurements was $\pm$ 0.00003 g cm^{-3}

Equation (2-7) was employed to calculate the values of apparent molal volumes, $\emptyset$, which have been plotted against $m^{1/2}$. Figure [4-1-1(a)] shows the plot. It is obvious from the plot that the first three points, in the very dilute range, fall way off the expected straight line. The most likely reason for the deviation is the error incurred in weighing small quantities of the sample and hence in calculating the values of $\emptyset$. Error analysis shows that at 0.0009851m the standard error was $\pm$ 15 cm^3 mol^{-1} for $\emptyset$. However, at the remaining concentrations, $\emptyset$ shows a good linear dependence. Linear regression using a BBC INSTAT statistical program yielded a limiting value of $\emptyset^0$ = 157 $\pm$ 2 cm^3 mol^{-1} and 640 $\pm$ 25 cm^3 mol^{-1} Kg$^{1/2}$ as the slope. The correlation coefficient was 0.9894. The slope corresponds to the constant 'a' in the Massons's equation.

Inserting $\emptyset^0$ and 'a' values obtained above, equation (2-8) becomes

$$\emptyset = 157 + 640 \, m^{1/2} \qquad\qquad 4\text{-}1$$

and hence the equation for the partial molal volume, $\overline{V}$, takes the form

$$\overline{V} = 157 + 960 \, m^{1/2} \qquad\qquad 4\text{-}2$$

$\emptyset$ and $\overline{V}$, calculated from equation (4-1) and (4-2) respectively, are shown in Table (4-1-1).

Redlich and Meyer[87] derived the semi-qualitative relationship

$$\emptyset = \emptyset^0 + kw^{3/2}m^{1/2} + hm. \qquad\qquad 4\text{-}3$$

where $k = 1.867$ for 1:1 electrolytes and can be calculated from the gas constant, R, and properties of the solvent, w is similar to the ionic strength with C_k in equation (2-55) equal to the number of species k produced by one molecule of the electrolyte, h is a factor responsible for the interactions not accounted for by k and w. The quantity $kw^{3/2}$ accounts for ion-ion interactions in dilute solutions.

TABLE 4-1-1   APPARENT AND PARTIAL MOLAL VOLUMES OF THIAMINIUM DICHLORIDE IN AQUEOUS SOLUTIONS AT 25°C

C	m	ρ	$\emptyset$	$\overline{V}$
0.0009_8	0.0009_8	0.9972_5	148.0	187.5
0.0010_3	0.0010_3	0.9972_6	150.5	188.2
0.0019_6	0.0019_7	0.9973_8	179.5	200.1
0.0019_8	0.0019_9	0.9973_7	185.0	200.2
0.0026_2	0.0026_3	0.9974_6	190.0	206.6
0.0029_9	0.0030_0	0.9975_0	192.5	210.0
0.0041_5	0.0041_6	0.9976_4	200.4	219.3
0.0050_4	0.0050_6	0.9977_5	202.7	225.7
0.0059_8	0.0060_1	0.9978_5	208.1	231.8
0.0070_2	0.0070_5	0.9979_8	208.9	238.0
0.0082_9	0.0083_3	0.9980_7	216.9	245.0
0.0090_6	0.0091_0	0.9981_6	217.9	249.0
0.0196_4	0.0197_9	0.9993_3	222.7	292.5
0.0350_9	0.0354_8	1.0009_4	227.7	338.3
0.0452_8	0.0458_9	1.0019_8	229.4	363.2
0.0503_8	0.0511_1	1.0025_8	228.5	374.6
0.0589_7	0.0599_6	1.0034_6	229.5	392.6
0.0733_0	0.0747_8	1.0049_6	230.2	420.1
0.0771_2	0.0787_4	1.0054_2	229.7	427.0
0.0975_0	0.1000_4	1.0075_1	230.9	461.2
0.1134_2	0.1168_2	1.0091_7	231.2	485.7
0.1993_9	0.2097_1	1.0180_3	232.8	597.3
0.2898_1	0.3117_5	1.0273_7	233.4	693.8
0.3993_4	0.4414_4	1.0393_0	232.2	795.7
0.4592_0	0.5156_4	1.0454_1	232.7	847.2
0.5037_7	0.5729_4	1.0491_9	234.5	884.6
0.7062_7	0.8477_3	1.0713_4	232.8	1041.9
0.7820_5	0.9590_7	1.0791_9	232.9	1098.2
0.9953_8	1.3004_8	1.1011_0	233.4	1253.0

UNITS:-   C, mol l^{-1}; m, mol Kg^{-1}; ρ, g cm^{-3}; $\emptyset$, cm^3 mol^{-1}; $\overline{V}$, cm^3 mol^{-1}.

FIGURE 4-1-1(a). APPARENT MOLAL VOLUME, ϕ, VERSUS $m^{1/2}$
IN THE CONCENTRATION RANGE 0 - 1.0M
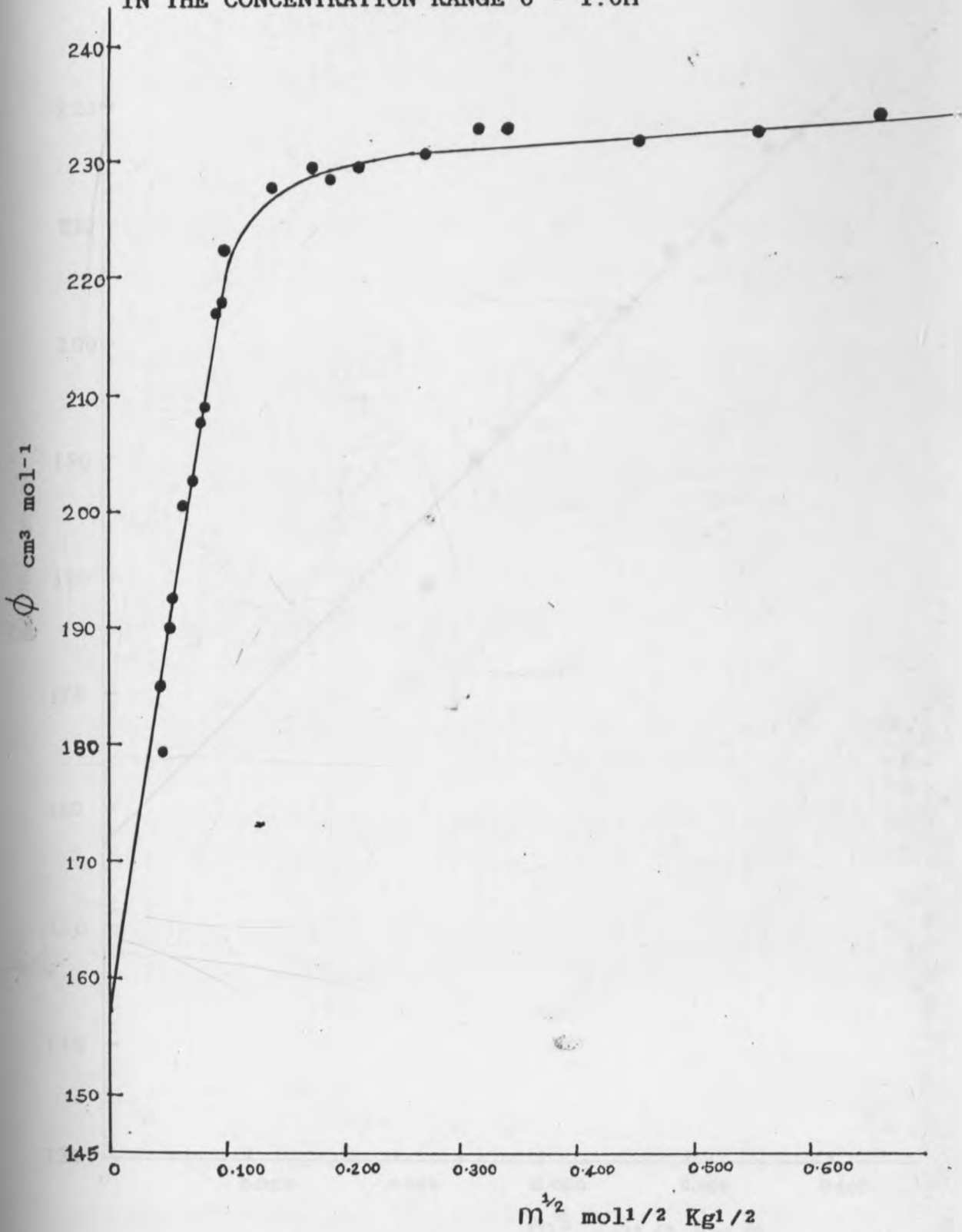
FIGURE 4-1-1(b). APPARENT MOLAL VOLUME, ϕ, VERSUS $m^{1/2}$ IN THE CONCENTRATION RANGE 0 - 0.01M
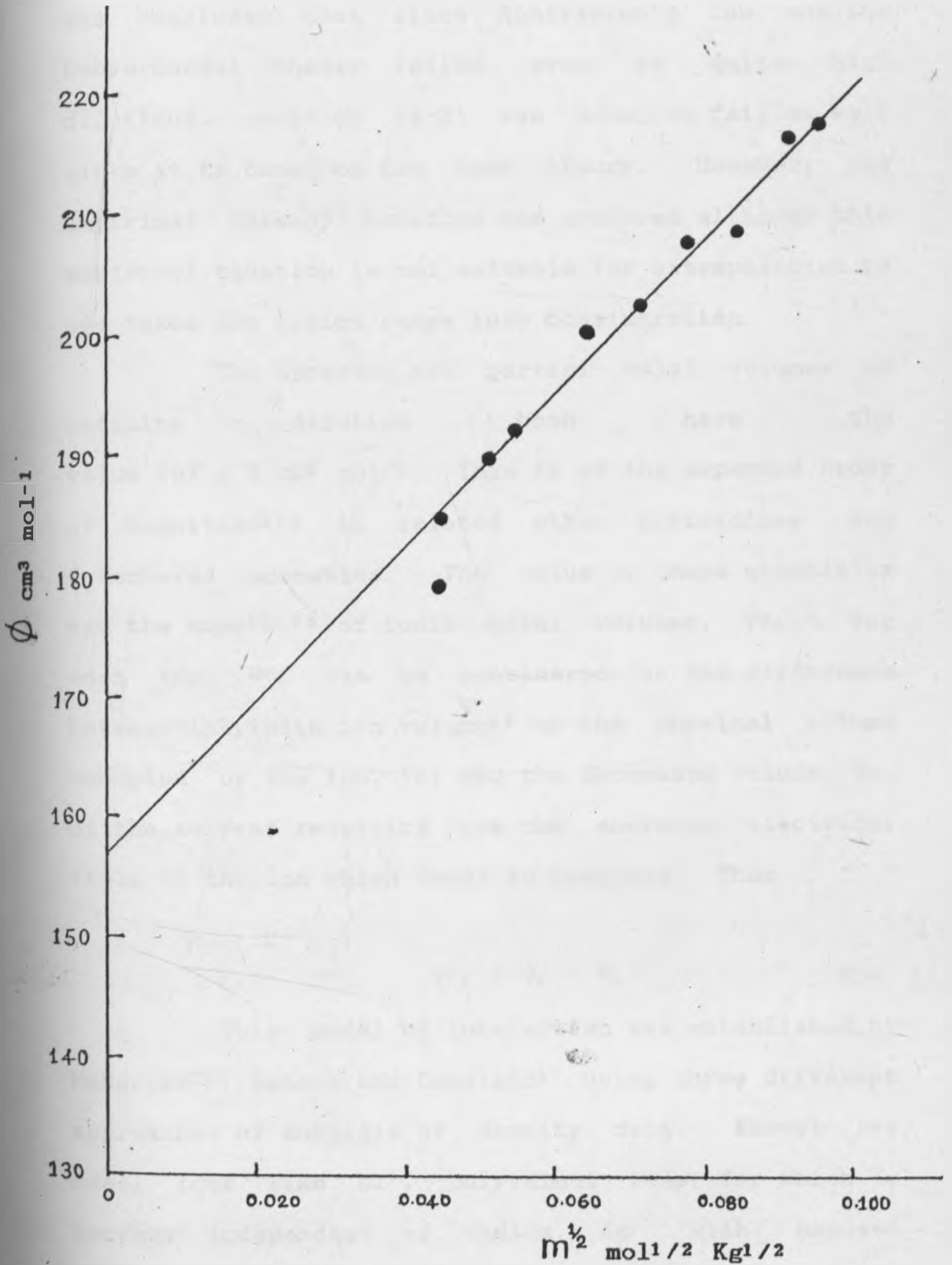
In the light of the conductivity results it was concluded that since Kohlrausch's law and the Debye-Huckel theory failed even at quite high dilutions, equation (4-3) was bound to fail as well since it is based on the same theory. However, the empirical Masson's equation was prefered although this empirical equation is not suitable for extrapolation if one takes the entire range into consideration.

The apparent and partial molal volumes at infinite dilution both have the value 157 ± 2 cm^3 mol^{-1}. This is of the expected order of magnitude[31a] in related other pyrimidines and 6-membered aromatics. The value of these quantities are the sums[10,88] of ionic molal volumes, $V^0{}_i$. For each ion, $V^0{}_i$ can be considered as the difference between intrinsic ion volume[88] or the physical volume occupied by the ion, V_i, and the decreased volume, V_e, of the solvent resulting from the enormous electrical field of the ion which tends to compress. Thus

$$V^0{}_i = V_i - V_e \qquad\qquad 4\text{-}4$$

This model of interaction was established by Mukerjee[10]; Benson and Copeland[87] using three different approaches of analysis of density data. Except for small ions like Li$^+$, polyvalent ions; for which V_e becomes independent of radius, Ag$^+$ with exposed d-electrons for special interactions and unsymmetrical polyatomic ions whose anomalous behaviour could be

explained by taking their detailed charge distribution into account, this model is generally in very good agreement.

According to the results from conductivity measurements the value, 157 cm^3 mol^{-1} is apparently due to Thi$^+$, ThiH^{2+}, ThiH$_2^{3+}$, H$^+$ and Cl$^-$. V^0_i values for H$^+$ and Cl$^-$ were taken[10] as $-$ 4.5 and 22.3 cm^3 mol^{-1} respectively. The other ions are polyatomic so additivity may not be that straight forward.

The partial molal volume shows a marked increase[10] with concentration as expected because of a decrease in V_e caused by increasing ionic interactions. In the expression for $\bar{V}$, the slope at moderate concentrations depends[88] primarily on the charge type of the ions and somewhat on their individual nature.

4-1-2   The Density of solid Thiaminium Dichloride

Attempts were made to obtain the density of Thiaminium dichloride at 25^{0}C by the liquid displacement method but the volatility of the non-dissolving solvents, Benzene and Acetone[88], rendered this measurement impossible at the above temperature. However density was measured using the same method at 20^{0}C. The average density value was 1.4109$_0$ $\pm$ 0.0005 g cm^{-3}.

The apparent density of the solute calculated[90] from the density of solutions at 25^{0}C was 1.1163 g cm^3. The density of salts[88], at temperatures far below their melting points, vary negligibly with temperature. Thus

the difference between the apparent and measured densities is due to the strong interactions between solute and solvent particles.

4-1-3 Viscosity

The results of viscosity measurements are shown in Table [4-1-3(a)]. The absolute and relative viscosity, η and η_{rel}, values were calculated using equation (2-22). The expected cummulative error in η was ± 0.00007 cP.

The relative viscosities, for aqueous Thiaminium dichloride were fitted to two forms of the Jones-Dole equation. The non-extended form was fitted by plotting ($\eta_{rel} - 1)/C^{1/2}$ against $C^{1/2}$ giving a straight line whose slope and intercept gave the respective values of B and A coefficients of the Jones-Dole equation. Regression was done using the BBC INSTAT statistical package and the equation that best fitted the concentration range 0 - 0.1M was

$$\eta_{rel} = 1 + 0.009 \ C^{1/2} + 0.823 \ C \qquad 4-5$$

The standard errors in the coefficients of $C^{1/2}$ and C were ± 0.002 and ± 0.01 respectively. The correlation coefficient was 0.9959. This equation is generally valid[33a] up to a few tenths molar.

TABLE 4-1-3(a)   VISCOSITIES OF AQUEOUS THIAMINIUM DICHLORIDE SOLUTIONS AT 25°C

C	t	ρ	η	η_{rel}
0.00098	452.219	0.99725	0.89462	1.00103
0.00103	452.610	0.99726	0.89540	1.00190
0.00196	452.863	0.99738	0.89600	1.00258
0.00198	452.961	0.99737	0.89619	1.00279
0.00262	453.292	0.99746	0.89692	1.00360
0.00415	453.564	0.99764	0.89762	1.00439
0.00491	453.953	0.99764	0.89840	1.00525
0.00504	454.138	0.99775	0.89886	1.00577
0.00598	454.323	0.99785	0.89931	1.00628
0.00702	454.653	0.99798	0.90008	1.00714
0.00829	454.907	0.99807	0.90067	1.00780
0.00906	455.112	0.99816	0.90115	1.00834
0.00982	455.336	0.99828	0.90171	1.00896
0.01964	459.194	0.99933	0.91031	1.01858
0.03000	462.290	1.00039	0.91741	1.02654
0.03508	463.770	1.00094	0.92086	1.03039
0.05006	467.682	1.00252	0.93010	1.04072
0.05897	471.293	1.00346	0.93815	1.04974
0.06821	474.820	1.00443	0.94608	1.05862
0.07712	477.000	1.00542	0.95137	1.06452
0.09750	484.038	1.00751	0.96741	1.08248
0.11342	489.263	1.00917	0.97947	1.09597
0.17583	510.848	1.01544	1.02903	1.15142
0.19938	520.008	1.01803	1.05016	1.17507
0.28981	554.613	1.02737	1.13031	1.26475
0.45920	638.048	1.04541	1.32318	1.48057
0.50377	663.356	1.04919	1.38064	1.54486
0.56554	697.264	1.05999	1.46464	1.63885
0.70627	803.011	1.07134	1.70660	1.90959
0.75388	840.872	1.07664	1.79403	2.00742
0.78205	864.211	1.07919	1.58011	2.07017

UNITS:- C, mol l^{-1}; t, sec.; ρ, g cm^{-3}; η, cP or g cm^{-1} s^{-1} .

117

TABLE 4-1-3(b)   COMPARISON OF FITTED AND OBSERVED RELATIVE VISCOSITIES OF AQUEOUS THIAMINIUM DICHLORIDE SOLUTIONS AT 25°C

C	η_{rel}	η^*_{rel}	$\Delta\eta_{rel}$
0.00098	1.00103	1.00109	-0.00006
0.00103	1.00190	1.00113	0.00077
0.00196	1.00258	1.00201	0.00057
0.00198	1.00279	1.00203	0.00076
0.00262	1.00360	1.00261	0.00090
0.00415	1.00439	1.00398	0.00041
0.00491	1.00525	1.00466	0.00059
0.00504	1.00577	1.00478	0.00090
0.00598	1.00628	1.00561	0.00067
0.00702	1.00714	1.00652	0.00062
0.00829	1.00780	1.00763	0.00017
0.00906	1.00834	1.00830	0.00004
0.00982	1.00896	1.00896	0.00000
0.03000	1.02654	1.02622	0.00032
0.03509	1.03039	1.03053	-0.00014
0.05006	1.04072	1.04317	-0.00246
0.05897	1.04974	1.05067	-0.00093
0.06821	1.05862	1.05843	0.00019
0.07712	1.06452	1.06591	-0.00139
0.09750	1.08248	1.08298	-0.00050
0.11342	1.09597	1.09629	-0.00032
0.17583	1.15142	1.14836	0.00306
0.19939	1.17507	1.16860	0.00647
0.28981	1.26475	1.25800	0.00675
0.45920	1.48057	1.47398	0.00659
0.50377	1.54486	1.54178	0.00308
0.56554	1.63885	1.64341	-0.00456
0.70627	1.90959	1.90873	0.00086
0.75388	2.00742	2.00916	-0.00174
0.78205	2.07017	2.07117	-0.00100

UNITS:- C, mol l^{-1} and η_{rel}, η^*_{rel}, $\Delta\eta_{rel}$ are all ratios.

* Values calculated using the Jones-Dole equations applicable at that concentration.

FIGURE 4-1-3. THE EXTENDED AND THE NON-EXTENDED JONES-DOLE EQUATIONS FITTED TO η_{rel} DATA

A = EXTENDED

B = NON-EXTENDED

η_{rel}

C mol l^{-1}
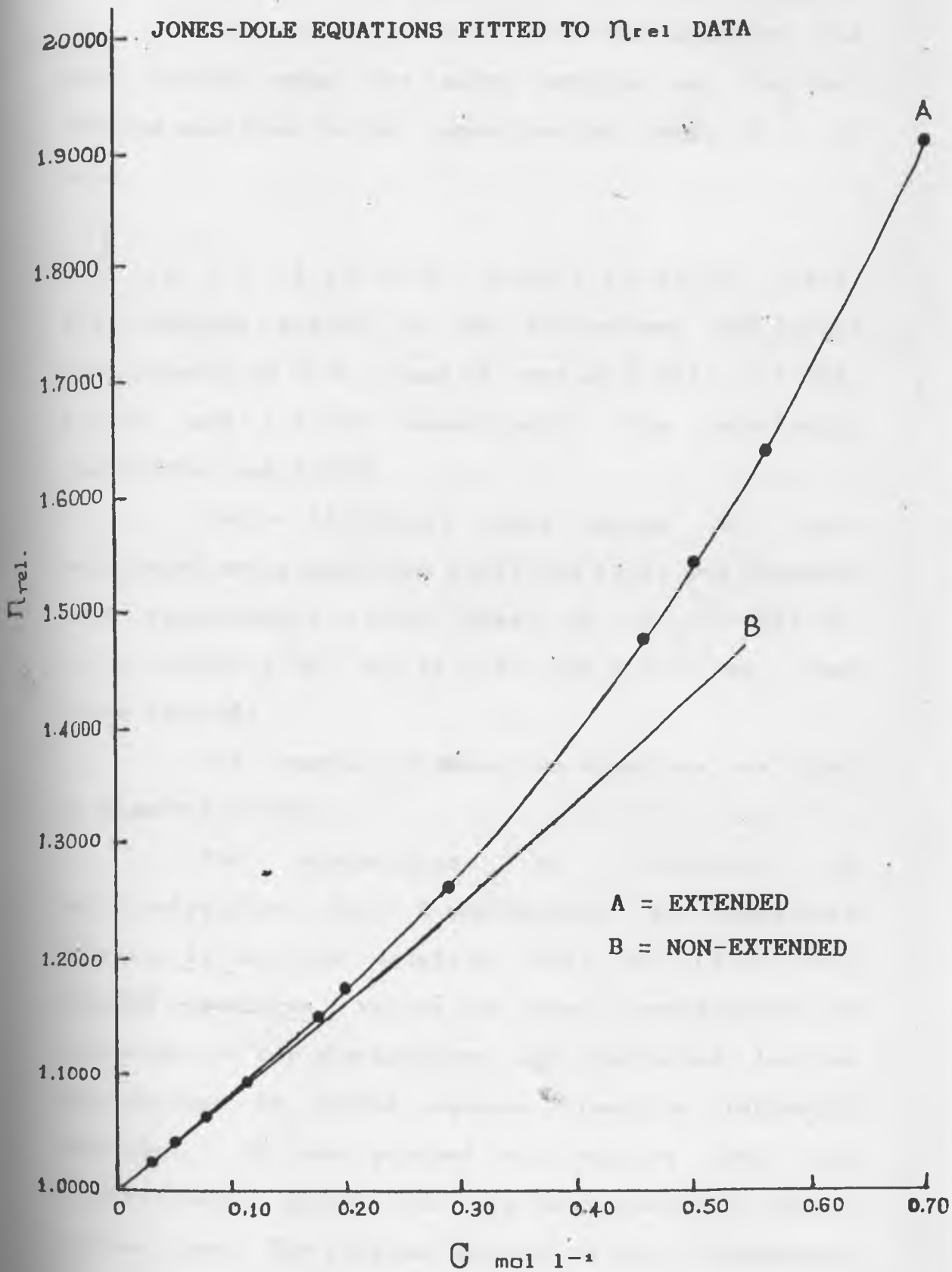
The extended form of Jones-Dole equation was also fitted using the above program and the best fitting equation in the concentration range 0.1 - 1M was

$$\eta_{rel} = 1 + 0.175 \ C^{1/2} + 0.208 \ C + 1.23 \ C^2 \qquad 4-6$$

The standard errors in the y-intercept and in the coefficients of $C^{1/2}$, C and C^2 were $\pm\ 0.003$, $\pm\ 0.003$, $\pm\ 0.05$ and $\pm\ 0.003$ respectively. The correlation coefficient was 0.9995.

Table [4-1-3(b)] shows values of η_{rel} calculated using equations (4-5) and (4-6) and compared with experimental values based on $\eta_1 = 0.8937$ cP, $\rho_1 = 0.99707$ g cm^{-3} and $t_1 = 451.83_0 \pm 0.02$ sec. [see Table (3-2-2)].

The graphs of these two equations are shown in Figure (3-1-3).

For suspensions or solution of non-electrolytes the A coefficient in Jones-Dole equation is zero but equation (4-5) and (4-6) both yielded positive values of the A coefficient as expected[45,46] for electrolytes and indicated ion-ion interactions in dilute aqueous Thiaminium dichloride solutions. It was pointed out earlier that the A coefficients account for long-range coulombic forces between ions. The physical picture of the interaction is based on the Debye-Huckel ionic atmosphere. The electronic contribution to viscosities of electrolytes

solutions results from the stress transfer between the central ion and its atmosphere together with the frictional forces between ions and solvent molecules, since ionic interactions lead to ionic motions relative to solvent molecules.

The nature of the electrolyte studied by the author, clearly indicates that equation (2-26), as given by Onsager and Fuoss[7], should yield a theoretical value of the contribution of the $AC^{1/2}$ or $AI^{1/2}$ term and the value of A should be given by equation (2-27). The author found that these equations were not amenable to simple mathematical manipulation with the aim of obtaining a theoretical A value for comparison with the experimental value, nonetheless, these two approaches should yield A values that are practically equal.

The A coefficient in equation (4-5), 0.009 ± 0.0003, covers the concentration range 0 - 0.1M but the $AC^{1/2}$ term contributes little to the viscosity compared to the BC term within the concentration range considered for experimental measurements. A coefficients are more improtant below 0.002M. The contribution due to the $AC^{1/2}$ ranges between 0.03 to 0.3 % in the concentration range considered, while the BC term contributes 0.08 to 8.5 % in the same concentration range.

Equation (4-6) gives $AC^{1/2}$ and BC contributions as ranging from 6.5 to 8 % and 4 to 8.5 % respectively in the higher concentration range

mentioned earlier.

The viscosity B coefficients in both concentration ranges are 0.823 ± 0.010 and 0.228 ± 0.050. This coefficient is highly specific with respect to the electrolyte and temperature. It is more important above 0.002M, which for most experimental purposes in a modest laboratory makes B coefficient a more important measurement.

Strong ion-solvent interaction existed in this electrolyte solution as indicated by the positive values of B coefficient. The solvent molecules in the vicinity of the positive ions (neglecting contribution from the chloride anions) had undergone rearrangement giving rise to "hydrophobic hydration" of the water molecules by strengthening their hydrogren-bonds and thereby increasing the viscosity of water. The positive ions in aqueous Thiaminium dichloride solution were thus "Structure makers" or "hydrophobic ions".

B coefficients are fairly accurately additive properties of the constituent ions as mentioned ealier in section (2-2-3). From conductivity measurements, it is assumed that the ions present in solution were Thi^+, $ThiH^{2+}$, $ThiH_2^{3+}$, H^+ and Cl^-. Refering to equation (4-5), the B coefficient, 0.823, is a contribution of all these ions. Given the ionic B_i values[37] $B_{Cl^-} = -0.007$ and $B_{H^+} = 0.069$, the total ionic B_i value due to Thi^+, $ThiH^{2+}$ and $ThiH_2^{3+}$ is 0.761. From the values of α and β in section (4-1-5) it is clear

that this B value is due mainly to Thi^+ , $ThiH^{2+}$ and $ThiH_2^{3+}$ ionic species. A quick survey through the $Table^{37}$ of ionic B coefficients gave the author an impression that other than the singly charged ion, Thi^+, the value of $B_i = 0.761$ was large enough to allow for the existence of at least a doubly charge ion of the same size and shape as Thi^+, thus the existence of complex ions were evident even from viscosity measurements.

The B coefficients also contain contributions due to the size and shape of the ions, especially the large ions ($a^0 > 5 \times 10^{-8}$ cm) such as Thi^+, $ThiH^{2+}$ and $ThiH_2^{3+}$. This is the Einstein effect, which is always positive and increases with increasing ion size and non-sphericality. The Einstein equation obtained for this system in the dilute range was

$$\eta_{rel} = 1 + 5.5 \, \phi \qquad\qquad 4-7$$

This equation fitted experimetal relative viscosity values below 0.003M within $\pm$ 0.0003 units. ϕ was calculated using V and V_0 as defined for molal volume calculations. The value of 'a_1' in the Einstein equation indicates that the ionic species dealt with are not spherical.

TABLE 4-1-4   APPARENT MOLAL REFRACTIVE INDICES OF AQUEOUS
THAIMINIUM DICHLORIDE SOLUTIONS AT 25°C

C	m	ρ	nobs	[R]D
0.00103	0.00103	0.99726	1.33253	45.753
0.00198	0.00199	0.99737	1.33260	66.313
0.00262	0.00263	0.99746	1.33265	71.164
0.00299	0.00300	0.99750	1.33270	77.065
0.00415	0.00416	0.99764	1.33280	81.743
0.00504	0.00506	0.99775	1.33284	79.492
0.00598	0.00601	0.99785	1.33290	80.257
0.00702	0.00705	0.99798	1.33300	82.860
0.00828	0.00833	0.99807	1.33310	85.122
0.00906	0.00910	0.99816	1.33320	88.099
0.01964	0.01979	0.99933	1.33400	88.563
0.03000	0.03029	1.00039	1.33480	89.655
0.03509	0.03548	1.00094	1.33520	89.875
0.04146	0.04199	1.00149	1.33570	90.754
0.04528	0.04589	1.00198	1.33600	90.423
0.04910	0.04980	1.00250	1.33630	90.036
0.05006	0.05079	1.00252	1.33638	90.399
0.05039	0.05111	1.00258	1.33640	90.304
0.05897	0.05915	1.00346	1.33708	90.594
0.06439	0.06555	1.00346	1.33750	90.753
0.06821	0.06950	1.00443	1.33780	90.764
0.07330	0.07478	1.00498	1.33820	90.824
0.07712	0.07874	1.00542	1.33850	90.729
0.09368	0.09607	1.00674	1.33980	91.809
0.09627	0.09875	1.00734	1.33990	90.517
0.09750	0.10004	1.00751	1.34010	91.034
0.11342	0.11682	1.00917	1.34135	91.131
0.17583	0.18389	1.01544	1.34625	91.626
0.19042	0.19975	1.01752	1.34735	90.882
0.19939	0.20971	1.01803	1.34810	91.478
0.21212	0.22379	1.01939	1.34910	91.459
0.28981	0.31175	1.02737	1.35520	91.547
0.37713	0.41440	1.03727	1.36230	91.404
0.39934	0.44144	1.03930	1.36380	91.198
0.45920	0.51564	1.04541	1.36850	91.243
0.50377	0.57294	1.04919	1.37200	91.570
0.70627	0.84773	1.07134	1.38790	91.003
0.75388	0.91670	1.07664	1.39175	90.952
0.78205	0.95907	1.07919	1.39385	90.953
0.99538	1.30048	1.10110	1.41060	90.816

UNITS:-   C, mol l^{-1}; m, mol Kg^{-1}; ρ, g cm^{-3}; [R]D, cm^3
mol-1.

124

FIGURE 4-1-4(a). APPARENT MOLAL REFRACTIVITY, [R]D,
VERSUS C IN THE CONCENTRATION RANGE 0 - 1.0M

125
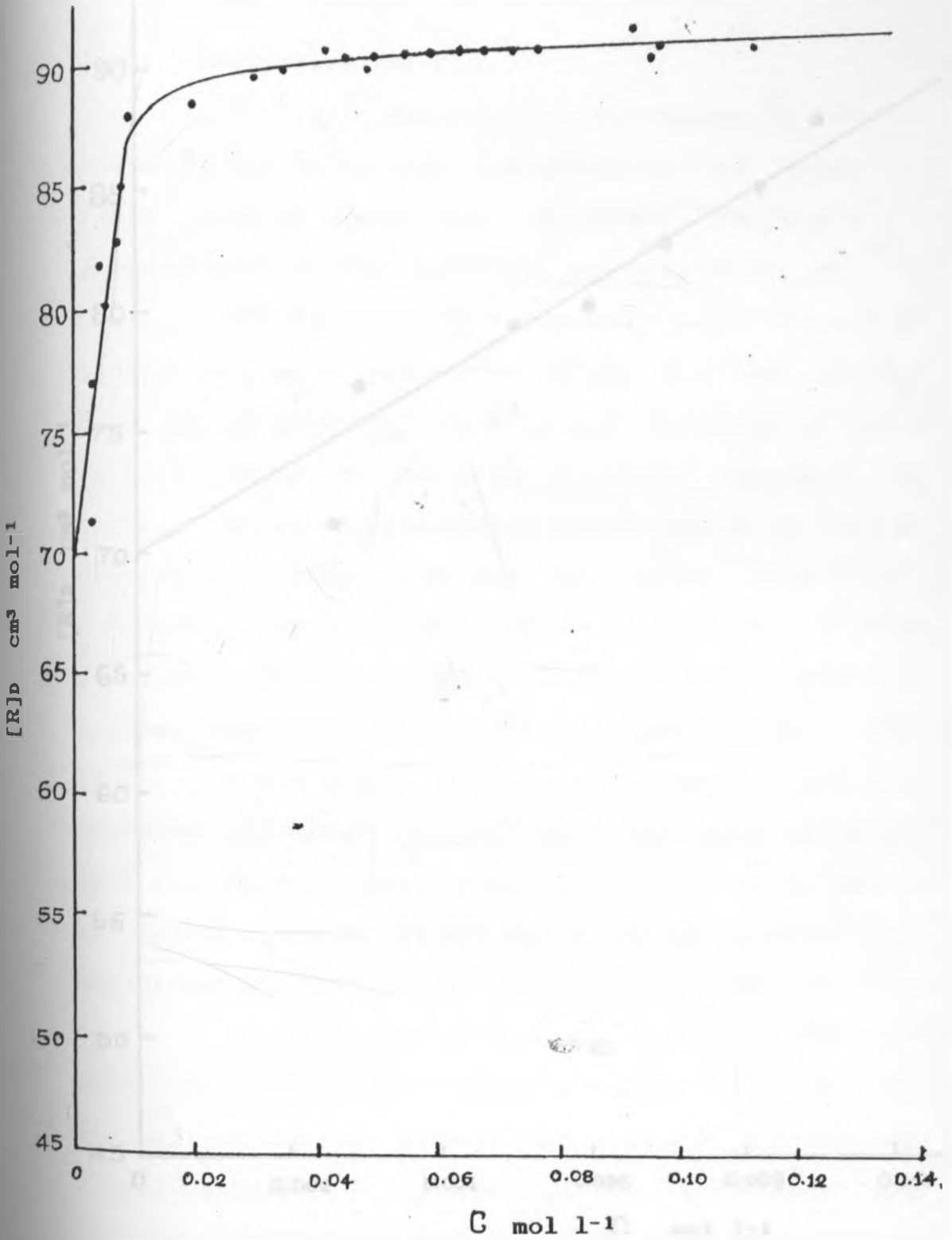
FIGURE 4-1-4(b). APPARENT MOLAL REFRACTIVITY, [R]D, VERSUS C IN THE CONCENTRATION RANGE 0 - 0.01M
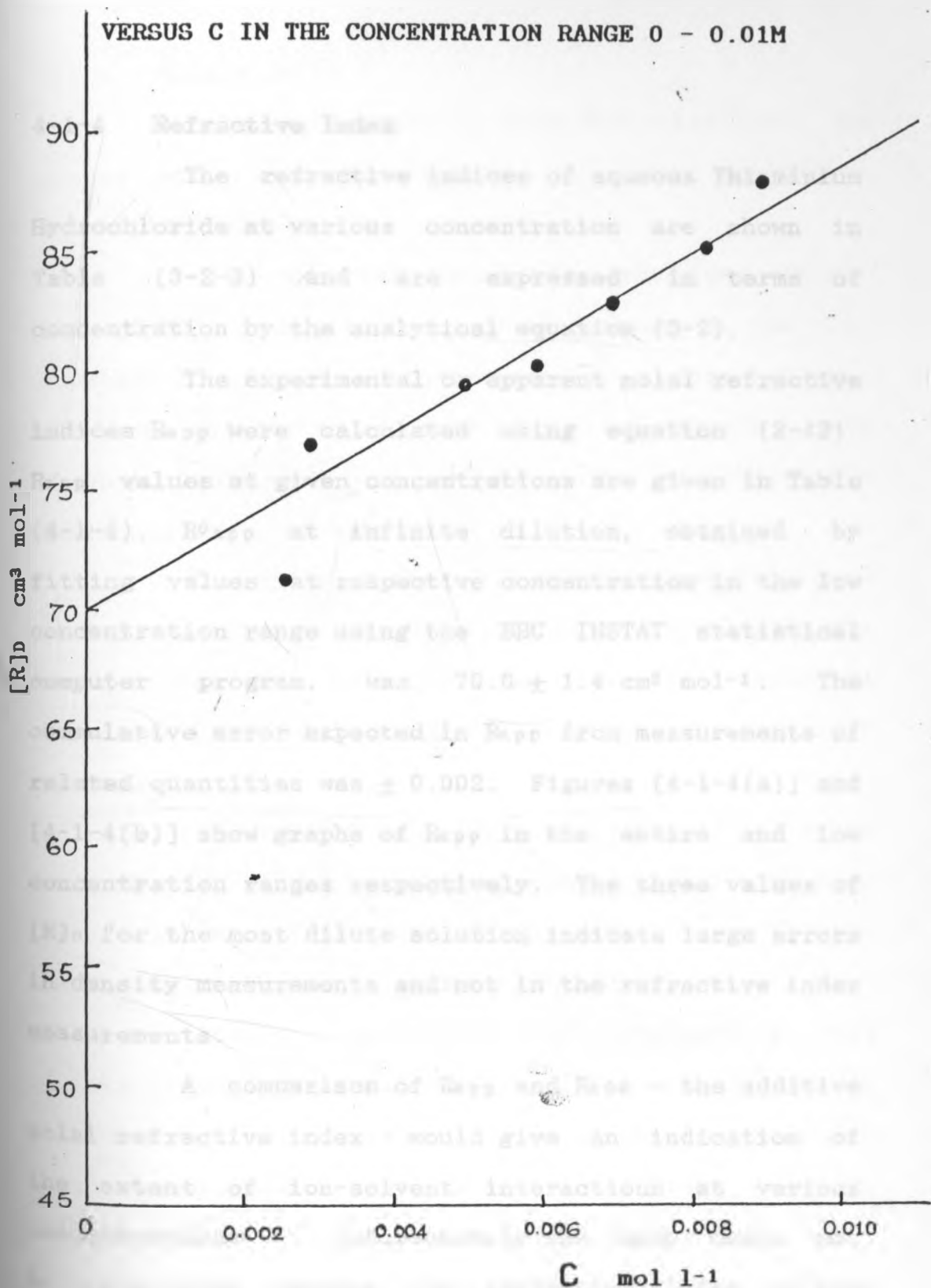
4-1-4   Refractive Index

The refractive indices of aqueous Thiaminium Hydrochloride at various concentration are shown in Table (3-2-3) and are expressed in terms of concentration by the analytical equation (3-2).

The experimental or apparent molal refractive indices R_{app} were calculated using equation (2-42). R_{app} values at given concentrations are given in Table (4-1-4). R^0_{app} at infinite dilution, obtained by fitting values at respective concentration in the low concentration range using the BBC INSTAT statistical computer program, was 70.0 ± 1.4 cm^3 mol^{-1}. The cummulative error expected in R_{app} from measurements of related quantities was ± 0.002. Figures [4-1-4(a)] and [4-1-4(b)] show graphs of R_{app} in the entire and low concentration ranges respectively. The three values of $[R]_D$ for the most dilute solution indicate large errors in density measurements and not in the refractive index measurements.

A comparison of R_{app} and R_{add} - the additive molal refractive index - would give an indication of the extent of ion-solvent interactions at various concentrations[54b]. Unfortunately the R_{add} could not be calculated because the refractive index of the solid Thiaminium dichloride is not yet known[89].

4-1-5 Conductivity

Literature survey to date indicates that no conductivity work has been done on aqueous Thiaminium dichloride solution.

Λ_{obs} were calculated using equations (2-48) and (2-49) from the measured resistance, R, the cell constant K and molar concentration, C. Λ_{obs} values, obtained within an accuracy of ± 0.5 S cm^2 mol^{-1}, are shown in Table [4-1-5(a)] and Figure (4-1-5) shows the variation of Λ_{obs} with $C^{1/2}$

The shape of the conductivity curve in Figure (4-1-5) neither ressembled that of a weak electrolyte nor a strong one. This indicated that the situation was not that of a simple electrolyte solution as it appears.

Theoretical calculations of Λ and Λ^o (later refered to as Λ_{fit} and Λ_{cal}^o respectively) were done using equations (2-67) and (2-61), with X added to the latter as explained in section (2-4-6).

Several mechanisms of complexation were initially postulated but the resulting equations for calculations of degrees of association (complexation) either yielded negative or complex values of α and/or β, or could not be easily solved.

The best scheme arrived at was the one given in section (2-4-6).

TABLE 4-1-5(a)   MOLAR CONDUCTIVITY VALUES OF AQUEOUS THIAMINIUM DICHLORIDE AT 25°C

C	R	Λ_{obs}
0.00005_1	34344.4	311.1
0.00006_3	28794.1	300.5
0.00007_6	24614.3	290.6
0.00008_3	22896.9	285.8
0.00009_8	20019.2	276.7
0.00009_8	19929.2	276.3
0.0010_3	19242.2	273.9
0.0010_6	18804.7	272.3
0.0012_3	16720.5	264.1
0.0014_1	15010.0	256.2
0.0015_7	13778.4	250.0
0.0017_0	12947.6	245.5
0.0018_1	12368.0	242.1
0.0019_6	11599.0	237.4
0.0019_8	11521.0	236.9
0.0026_2	8869.0	232.9
0.0041_5	5782.5	225.6
0.0050_4	4841.0	221.8
0.0082_9	3021.2	215.9
0.0098_2	2567.1	214.3
0.0196_4	1342.7	205.1
0.0200_2	1356.2	199.2
0.0300_7	927.1	194.0
0.0350_9	834.0	184.8
0.0414_6	747.5	174.5
0.0500_6	644.2	167.7
0.0618_3	532.3	164.3
0.0643_9	509.7	164.8
0.0682_1	485.6	163.4
0.0771_2	436.3	160.7
0.0986_8	374.1	154.3
0.1134_2	316.7	150.6
0.1758_3	225.7	136.3
0.1993_9	204.3	132.8
0.2121_2	195.2	130.6
0.2898_1	157.3	118.6
0.3771_3	130.2	110.1
0.3993_4	126.8	106.8
0.4592_0	116.6	101.0
0.5037_7	109.8	97.8
0.5655_4	104.4	91.6
0.5980_2	101.3	89.3
0.7062_7	95.8	80.0
0.7820_5	92.8	74.5
0.9953_8	89.0	61.1

UNITS:-   C, mol l^{-1};   R, Ohms; Λ_{obs}, S cm^2 mol^{-1}.

TABLE 4-1-5(b)   COMPARISON OF OBSERVED AND FITTED Λ
VALUES OF AQUEOUS THIAMINIUM DICHLORIDE SOLUTIONS BELOW
0.002M AT 25º C

C	α	β	Λ_{obs}	Λ_{fit}	Λ_{cal}
0.00005₁	0.3574	0.3544	311.1	317.0	526.5
0.00006₃	0.3985	0.3954	300.5	292.2	540.8
0.00007₆	0.4270	0.4239	290.6	274.9	548.0
0.00008₃	0.4378	0.4347	285.8	268.4	549.7
0.00009₈	0.4544	0.4513	276.7	258.4	550.7
0.00009₈	0.4549	0.4518	276.3	258.1	550.7
0.0010₃	0.4585	0.4554	273.9	255.9	550.5
0.0010₆	0.4608	0.4577	272.3	254.5	550.2
0.0012₃	0.4707	0.4676	264.1	248.5	548.0
0.0014₁	0.4778	0.4747	256.2	244.2	544.5
0.0015₇	0.4824	0.4793	250.0	241.4	541.0
0.0017₁	0.4852	0.4821	245.5	239.7	538.2
0.0018₁	0.4870	0.4839	242.1	238.6	535.9
0.0019₆	0.4892	0.4861	237.4	237.3	532.5
0.0019₈	0.4894	0.4863	236.9	237.2	532.2

UNITS:- C, mol l⁻¹; Λ_{obs}; Λ_{fit}; Λ_{cal}, S cm² mol⁻¹.
α and β are fractions.

Calculations based on K_1 = 1.585 X 10⁻⁵, K_2 = 6.310 X 10⁻¹⁰
mol l⁻¹, and Λ_{cal} = 532.7 ± 0.5 S cm² mol⁻¹.

In the calculation of the degrees of association, α and β, K_1 and K_2 values were varied within the vicinity of values derived from literature pK_a or pK_b values until reasonable values were fixed vis-a-vis guessed values of $\lambda^o_{Thi^+}$, $\lambda^o_{ThiH^{2+}}$, $\lambda^o_{ThiH_2^{3+}}$ and literature values[37] of $\lambda^o_{Cl^-}$ and $\lambda^o_{H^+}$. Values of α, β, K_1 and K_2 are shown in Table [4-1-5(b)]. The equilibrium constant values $K_1 = 1/K_{a1}$ and $K_2 = 1/K_{a2}$ $l\ mol^{-1}$ are of the order of those derived from pK_{a1} and pK_{a2} values[18] for Thiaminium dichloride, i.e $pK_{a1} = 4.8$ and $pK_{a2} = 9.2$. $l\ mol^{-1}$ respectively.

Table [4-1-5(c)] shows calculated values of Λ_{fit} using equation (2-67) and (2-61) together with $\lambda^o_{Thi^+} = 29.3 \pm 0.3$, $\lambda^o_{ThiH^{2+}} = 35.8 \pm 0.3$, $\lambda^o_{ThiH_2^{3+}} = 41.3 \pm 0.3$, $\lambda^o_{Cl^-} = 76.35$, $\lambda^o_{H^+} = 349.81$ and $\Lambda^o_{cal} = 532.7 \pm 0.5$ S cm^2 $(g\ equiv.)^{-1}$. The value of Λ^o_{obs}, 392.4 ± 0.8 S cm^2 $(g\ equiv.)^{-1}$, was obtained by fitting a curve to the graph of Λ_{obs} against $C^{1/2}$, using a BBC statistical program, and obtaining the value at infinite dilution. Λ^o_{cal} were calculated using the above equivalent ionic conductivities and Λ_{obs} values as explained earlier. The proposed scheme reasonably fitted the conductivity data in the concentration range 0.0005 in 0.002M and values were calculated using the computer program shown in appendix V.

Thiaminium dichloride solutions in water can be regarded as a mixture of equimolar Thiamine chloride and Hydrochloric acid solutions. But in this case the situation is further complicated by the fact that ionic complexation is seen to occur even at very low concentration as suggested by the reported values of pK_b.

The conductivity of a given total concentration of ions (or total ionic strength) are not additive in mixtures. This fact was first observed by Bray and Hunt[91]. The isoionic principle does not hold and the theory[7] for ionic conductivities in mixtures, for instance, in HCl-KCl mixture, predicts that the faster H^+ ions will be slowed down more than usual, while the slow K^+ will be accelerated in proportion and the Cl^- ions will practically move with their usual velocity as in 1:1 electrolyte solutions.

The value of Λ^o_{cal} at infinite dilution, 532.7 ± 0.5 S cm^2 (g equiv.)$^{-1}$, is thus an expected value. Furthermore Smith and Gortner[92] also reported an observed departure as large as 7 conductivity units on a Λ value of about 120 S cm^2 (g equiv.)$^{-1}$ at quite low concentrations.

The scheme provided in section (2-4-6) involved only tentative calculations that point to expressions of the form

$$\Lambda = \Lambda^o + \alpha C^{1/2} + \beta C \, logC + \gamma C + - - - - - \qquad 4-8$$

This is the type of equation expected from

theoretical treatments even more exact than those employed by Onsager and Fuoss[7].

The author has used equation (2-59), that applies to 1:1 electrolytes, to approximate λ_i values at finite concentrations instead of the more exact equation (2-62) applicable to mixtures because the involved mathematics was too rigorous and not worth it. Particularly when the minimum expected error in the measurement of Λ was relatively large, $\pm$ 0.5 S cm^2 equiv.$^{-1}$, and the presence of ions of higher valencies further complicated the situation. The data analysis was therefore simply based on an empirical extension of the limiting Onsager equations (2-60) and (2-61) to account for the proposed ionic complexation scheme.

The scheme fitted the observations quite well up to 0.002M as shown in Table [4-1-5(b)].

4-1-6 Diffusion Coefficient

R. Schneeberger, R. Stahl and M. Loncin[15] have reported diffusion coefficients at 25°C as 0.95 X 10^{-5} cm^2 s^{-1} for concentrations 0.01, 0.03 and 0.10 mol dm^{-3} respectively and 1.07 X 10^{-5} cm^2 s^{-1} at 0.07 mol dm^{-3}. They also reported variations of diffusion coefficient with temperature at 0.1 mol dm^{-3} as $[dD/d(T/\eta)]$ X 10^{11} = 0.313 Kg m K^{-1} s^{-2} and compared it with a theoretically calculated value from literature[93], 0.325. Values at 25, 30, 40, and 50°C

were reported as 0.95, 1.16, 1.37 and 1.77 X 10^{-5} cm^2 s^{-1} respectively.

It is evident that, contrary to expectation, some D values show no concentration dependence e.g at 0.01, 0.03 and 0.10 mol dm^{-3} the D values were all reported as 0.95 X 10^{-5} cm^2 s^{-1}. Their value at 0.03 mol dm^{-3} is lower than the author's while that at 0.1 mol dm^{-3} it is higher. The value obtained by the author at 0.03 mol dm^{-3} does not fall within the allowed range of the experimental method[64]. This measurement was done as a guide for the extrapolation of curves to infinite dilution.

The reasons for this discrepancy are that, firstly, the above authors did not have sufficient experimental data to obtain accurate $\bar{D}^o(\bar{C}_B)$ values for converting integral diffusion coefficients, $\bar{D}$, into D, and secondly, from the dimensions of their cell (β value was small) this author gathers that it would have taken them about a week to complete a run. Such a long duration for an experiment makes it very difficult to maintain the other variables under control.

The parameters needed for the calculations of experimental integral diffusion, $\bar{D}_{exp}$, using equation (2-84) were; duration, t, of a diffusion run, the differences between initial and final concentrations and the cell constant. All these were obtained as outlined in section (3-2-6) and are shown on Table [4-1-6(a)].

135

TABLE 4-1-6(a)   RAW DATA FOR CALCULATION OF INTEGRAL DIFFUSION COEFFICIENTS OF THIAMINIUM DICHLORIDE IN AQUEOUS SOLUTIONS AT 25°C, β = 3.274 cm^{-2}

TIME(t)	$C^0_B = \Delta C^0$	Ct_B	Ct_A	ΔCt	$\bar{D}_{exp}$
21960	0.0300_0	0.0196_2	0.0077_6	0.0118_7	1.29_0
21330	0.0300_0	0.0196_2	0.0074_4	0.0121_9	1.29_0
21690	0.0414_6	0.0311_7	0.0132_1	0.0179_6	1.17_8
21610	0.0414_6	0.0311_7	0.0132_1	0.0179_6	1.18_3
16285	0.0500_6	0.0401_5	0.0125_7	0.0275_8	1.11_8
16260	0.0500_6	0.0401_5	0.0125_7	0.0275_8	1.12_0
21690	0.0503_8	0.0375_8	0.0144_9	0.0230_9	1.09_8
21600	0.0503_8	0.0375_8	0.0144_9	0.0230_9	1.10_3
18050	0.0589_7	0.0472_0	0.0151_3	0.0320_7	1.03_1
16190	0.0589_7	0.0478_4	0.0138_5	0.0339_9	1.03_9
18060	0.0643_9	0.0516_9	0.0170_6	0.0346_3	1.04_8
18150	0.0643_9	0.0516_9	0.0170_6	0.0346_3	1.04_4
21640	0.0682_1	0.0532_9	0.0196_2	0.0336_7	0.99_6
21660	0.0682_1	0.0529_7	0.0196_2	0.0333_5	1.00_1
21670	0.0733_0	0.0581_0	0.0209_1	0.0372_0	0.95_6
21610	0.0733_0	0.0574_6	0.0202_7	0.0372_0	0.95_8
23140	0.0771_2	0.0593_8	0.0221_9	0.0371_9	0.96_3
22080	0.0771_2	0.0593_8	0.0209_1	0.0384_8	0.96_2
21690	0.0936_8	0.0722_1	0.0241_1	0.0480_9	0.93_9
21610	0.0936_8	0.0722_1	0.0241_1	0.0480_9	0.94_2
21960	0.0975_0	0.0786_2	0.0286_0	0.0500_1	0.92_9
21780	0.0975_0	0.0786_2	0.0282_8	0.0503_3	0.92_7
23040	0.0987_7	0.0760_5	0.0260_4	0.0500_1	0.90_2
18165	0.1134_2	0.0927_2	0.0266_8	0.0660_4	0.90_7
18240	0.1134_2	0.0927_2	0.0273_2	0.0654_0	0.92_2
18045	0.1758_3	0.1439_7	0.0375_8	0.1063_9	0.85_0
18030	0.1758_3	0.1439_7	0.0375_8	0.1063_9	0.85_1
18030	0.2121_2	0.1759_9	0.0465_6	0.1294_3	0.83_7
16215	0.2121_2	0.1791_9	0.0427_1	0.1364_8	0.83_1
22350	0.2898_1	0.2556_6	0.0936_8	0.1619_9	0.79_5
21660	0.2898_1	0.2579_0	0.0933_6	0.1645_4	0.79_8
18050	0.3993_4	0.3346_2	0.0837_4	0.2508_8	0.78_7
18000	0.3993_4	0.3352_6	0.0837_4	0.2515_2	0.78_4
16290	0.4592_0	0.3908_4	0.0856_7	0.3051_7	0.76_6
16450	0.4592_0	0.3908_4	0.0869_5	0.3038_9	0.76_7
14440	0.5037_7	0.4036_1	0.0516_9	0.3519_1	0.75_9
16230	0.5037_7	0.4109_5	0.0744_5	0.3365_0	0.75_9
21860	0.5980_2	0.4853_0	0.1350_1	0.3502_9	0.74_7
21660	0.5980_2	0.4865_7	0.1337_2	0.3528_5	0.74_4
18028	0.7062_7	0.5567_1	0.0965_6	0.4601_5	0.72_6
16200	0.7062_7	0.5694_5	0.0863_1	0.4831_5	0.71_6
21960	0.7820_5	0.6408_0	0.1715_1	0.4692_7	0.71_0
21720	0.7820_5	0.6414_3	0.1702_3	0.4712_0	0.71_2
21960	0.9953_8	0.7985_5	0.1964_8	0.6020_7	0.69_9
23040	0.9953_8	0.7877_4	0.2009_6	0.5867_9	0.70_1

UNITS:- t, sec.; C^0_B; Ct_B; Ct_A; ΔCt, mol l^{-1}, $\bar{D}_{exp}$ in cm^2 s^{-1} X 10^5.

136

TABLE 4-1-6(b)   SUCCESSIVE APPROXIMATE VALUES OF $\bar{D}^o(\bar{C}_A)$

$\bar{C}_A$	$\bar{D}^o(\bar{C}_A)$			
	1st	2nd	3rd	4th
0.0038_8	1.820	1.802	1.798	1.797
0.0037_2	1.821	1.802	1.798	1.797
0.0066_0	1.812	1.794	1.790	1.789
0.0066_0	1.812	1.794	1.790	1.789
0.0062_8	1.813	1.795	1.791	1.790
0.0062_8	1.813	1.795	1.791	1.790
0.0072_5	1.810	1.792	1.788	1.788
0.0072_5	1.810	1.792	1.788	1.788
0.0075_7	1.811	1.792	1.788	1.787
0.0069_3	1.809	1.793	1.789	1.789
0.0085_3	1.806	1.789	1.785	1.784
0.0085_3	1.806	1.789	1.785	1.784
0.0098_1	1.801	1.785	1.781	1.780
0.0104_5	1.799	1.783	1.779	1.779
0.0101_3	1.800	1.784	1.780	1.780
0.0110_8	1.797	1.782	1.778	1.777
0.0104_5	1.799	1.783	1.779	1.779
0.0120_6	1.794	1.779	1.775	1.774
0.0120_6	1.794	1.779	1.775	1.774
0.0143_0	1.787	1.773	1.769	1.768
0.0141_4	1.787	1.773	1.769	1.768
0.0130_2	1.791	1.776	1.772	1.772
0.0133_4	1.790	1.775	1.771	1.771
0.0136_6	1.789	1.773	1.771	1.771
0.0187_8	1.773	1.760	1.756	1.755
0.0187_9	1.773	1.760	1.756	1.755
0.0232_8	1.758	1.748	1.744	1.743
0.0213_6	1.765	1.753	1.749	1.748
0.0468_4	1.683	1.682	1.678	1.677
0.0466_8	1.683	1.682	1.678	1.678
0.0418_7	1.699	1.696	1.692	1.691
0.0418_7	1.699	1.696	1.692	1.691
0.0428_3	1.696	1.693	1.689	1.688
0.0434_7	1.694	1.691	1.687	1.687
0.0258_5	1.750	1.740	1.737	1.736
0.0372_2	1.714	1.709	1.705	1.704
0.0675_0	1.617	1.624	1.620	1.620
0.0668_6	1.619	1.626	1.622	1.621
0.0482_8	1.679	1.678	1.674	1.673
0.0431_5	1.695	1.692	1.688	1.687
0.0857_5	1.559	1.573	1.569	1.569
0.0851_1	1.561	1.575	1.571	1.570
0.0982_4	1.519	1.538	1.535	1.534
0.1004_8	1.512	1.532	1.528	1.528

UNITS:- C, mol l^{-1}; $\bar{D}^o(\bar{C}_A)$, cm^2 s^{-1} X 10^5.

TABLE 4-1-6(c)   COMPARISON OF FIRST, FINAL AND FITTED
VALUES OF $\bar{D}^o(\bar{C}_B)$

$\bar{C}_B$	$\bar{D}^o(\bar{C}_B)$		
	1st	Final	Fitted
0.15734	1.372	1.368	1.368
0.19053	1.295	1.292	1.291
0.21241	1.216	1.215	1.212
0.20975	1.215	1.211	1.214
0.23085	1.141	1.172	1.177
0.24104	1.158	1.155	1.155
0.24517	1.133	1.130	1.130
0.25619	1.090	1.106	1.109
0.26146	1.098	1.093	1.097
0.28826	1.068	1.062	1.055
0.29704	1.034	1.030	1.023
0.29595	1.029	1.031	1.035
0.32089	0.959	1.021	1.020
0.39998	0.939	0.957	0.961
0.44199	0.948	0.945	0.942
0.52342	0.889	0.912	0.910
0.60663	0.861	0.889	0.887
0.65265	0.837	0.868	0.867
0.67563	0.854	0.873	0.866
0.73737	0.790	0.854	0.844
0.79728	0.790	0.820	0.819
0.84409	0.813	0.789	0.793
0.94597	0.791	0.793	0.793

UNITS:-   C, mol l^{-1}; $\bar{D}^o(\bar{C}_B)$, cm^2 s^{-1} X 10^5.

These values are representatives of the duplicated

experimental data shown on Table [4-1-6(a)].

FIGURE 4-1-6(a). EXPERIMENTAL INTEGRAL DIFFUSION COEFFICIENT, $\bar{D}_{exp}$, VERSUS $(C^0_B)^{1/2}$ AND $\bar{D}^0(\bar{C}_B)$ VERSUS $(\bar{C}_B)^{1/2}$
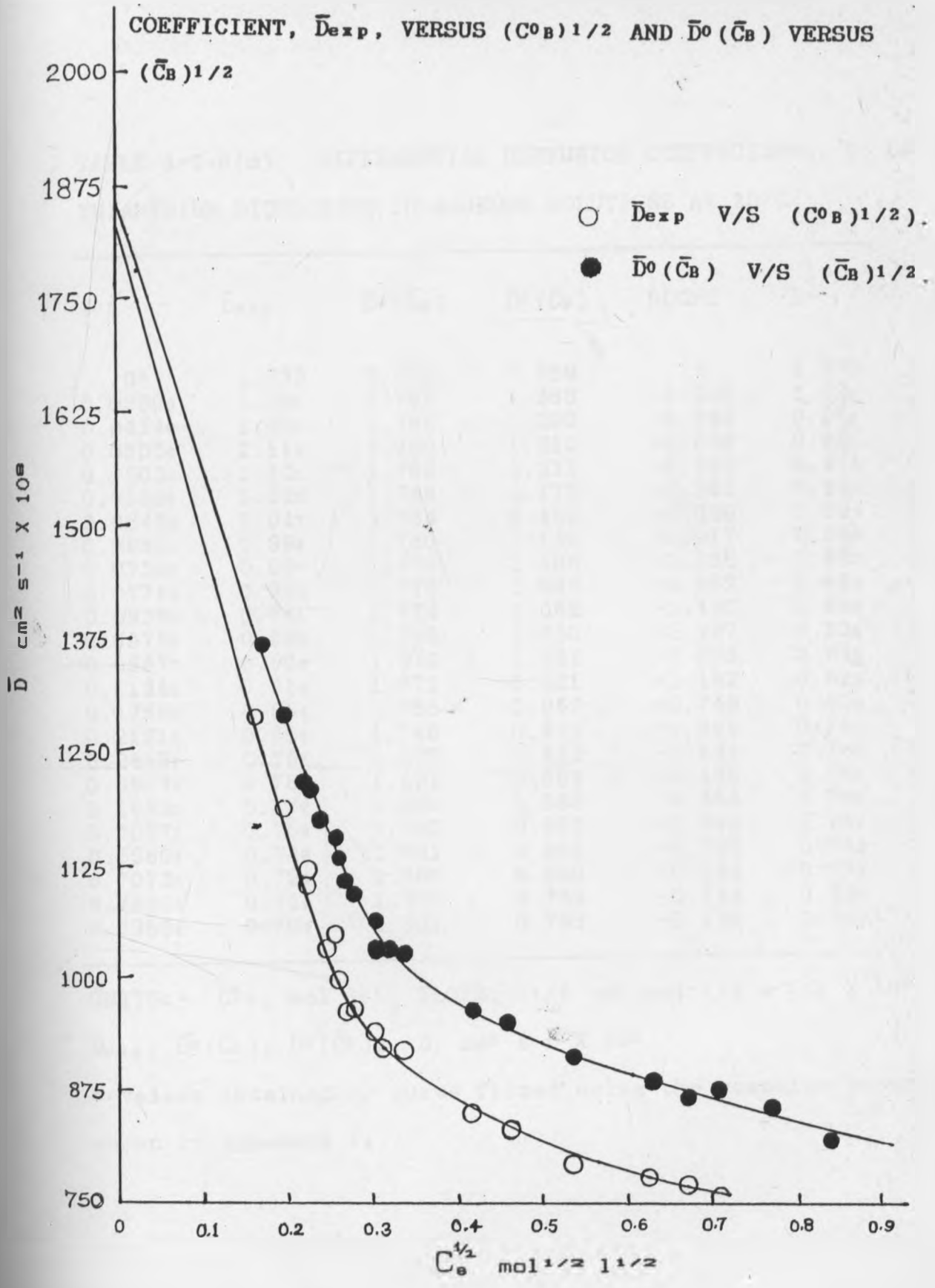
TABLE 4-1-6(d)   DIFFERENTIAL DIFFUSION COEFFICIENTS, D, OF THIAMINIUM DICHLORIDE IN AQUEOUS SOLUTIONS AT 25°C

C^0_B	$\bar{D}_{exp}$	$\bar{D}^0(\bar{C}_A)$	$\bar{D}^0(\bar{C}_B)$	SLOPE	D
0*	1.833	1.808	1.859	-	1.275
0.0300_0	1.29_0	1.797	1.368	-3.926	1.02_8
0.0414_6	1.18_1	1.789	1.292	-3.094	0.97_6
0.0500_6	1.11_9	1.790	1.215	-2.628	0.92_1
0.0503_8	1.10_1	1.788	1.211	-2.612	0.91_8
0.0589_7	1.03_5	1.788	1.172	-2.241	0.90_0
0.0643_9	1.047	1.784	1.155	-2.020	0.89_6
0.0682_1	0.99_8	1.780	1.130	-1.917	0.88_0
0.0733_0	0.95_7	1.779	1.106	-1.765	0.86_7
0.0771_2	0.96_2	1.778	1.093	-1.662	0.86_2
0.0936_8	0.94_1	1.774	1.062	-1.433	0.84_3
0.0975_0	0.92_6	1.768	1.030	-1.227	0.83_8
0.0987_7	0.90_2	1.772	1.031	-1.205	0.84_2
0.1134_2	0.91_6	1.771	1.021	-1.162	0.82_5
0.1758_3	0.85_4	1.755	0.957	-0.749	0.80_0
0.2121_2	0.83_3	1.746	0.945	-0.685	0.78_7
0.2898_1	0.79_7	1.678	0.912	-0.531	0.76_9
0.3993_4	0.78_5	1.691	0.889	-0.438	0.75_1
0.4592_0	0.77_7	1.688	0.868	-0.368	0.74_3
0.5037_7	0.75_9	1.720	0.873	-0.352	0.74_8
0.5980_2	0.74_6	1.621	0.854	-0.290	0.74_2
0.7072_6	0.72_0	1.680	0.820	-0.194	0.73_8
0.7820_5	0.71_3	1.570	0.789	-0.133	0.73_0
0.9953_8	0.70_0	1.531	0.793	-0.126	0.73_0

UNITS:- C^0_B, mol l^{-1}; SLOPE, $l^{1/2}$ cm^2 $mol^{-1/2}$ $s^{-1/2}$ X 10^5; $\bar{D}_{exp}$; $\bar{D}^0(\bar{C}_A)$; $\bar{D}^0(\bar{C}_B)$; D, cm^2 s^{-1} X 10^5.

* Values obtained by curve fitted using the computer program shown in appendix II.

FIGURE 4-1-6(b). DIFFERENTIAL DIFFUSION COEFFICIENT, D, VERSUS $C^{1/2}$ (OR $(C^0_B)^{1/2}$)
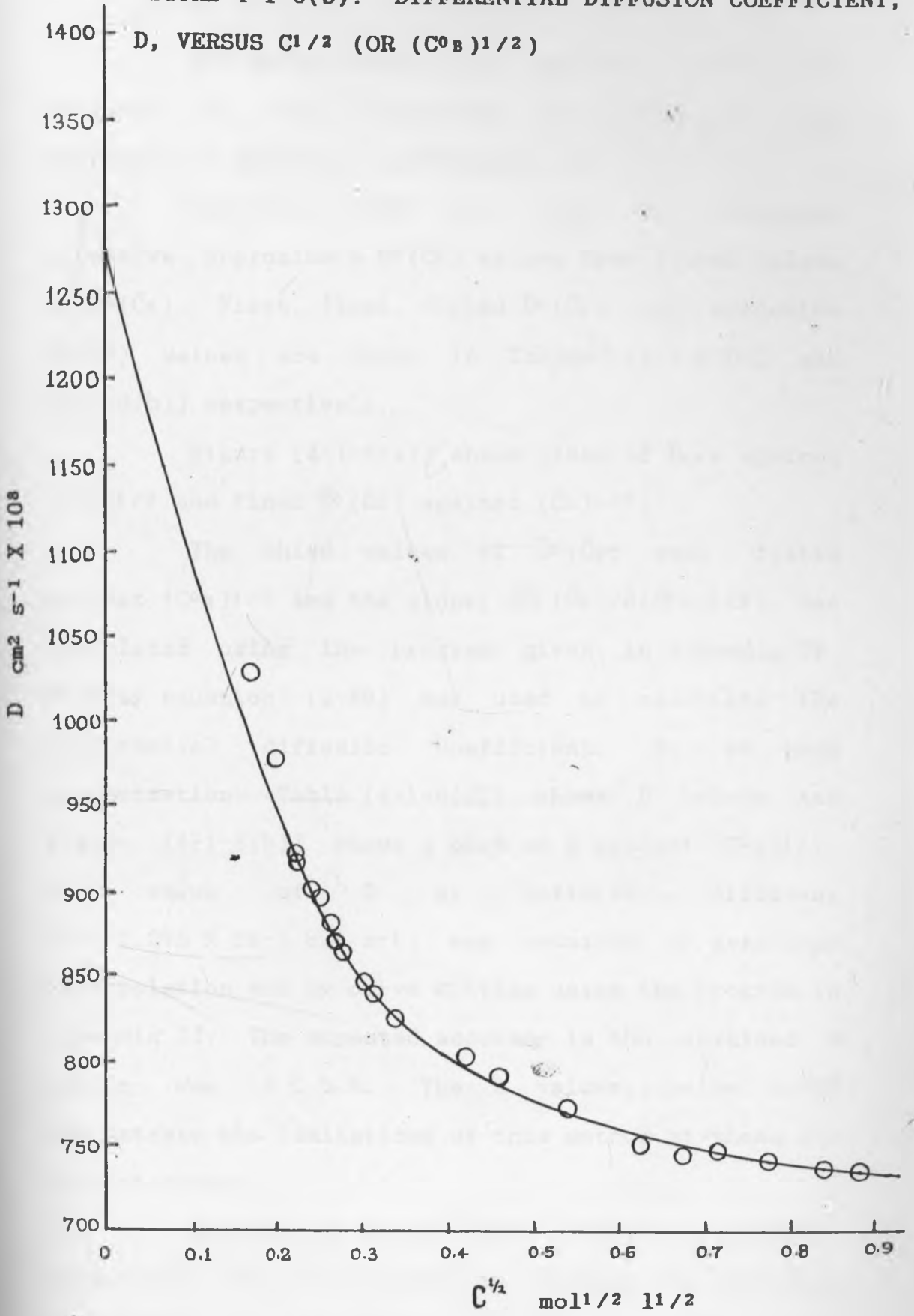
The method outlined in section (2-5-6) was followed in the conversion of $\bar{D}_{exp}$ into the differential diffusion coefficient, D.

Equation (2-88) was used to calculate succesive approximate $\bar{D}^0(\bar{C}_B)$ values from fitted values of $\bar{D}^0(\bar{C}_A)$. First, final, fitted $\bar{D}^0(\bar{C}_B)$ and succesive $\bar{D}^0(\bar{C}_A)$ values are shown in Tables [4-1-6(C)] and [4-1-6(b)] respectively.

Figure [4-1-6(a)] shows plots of $\bar{D}_{exp}$ against $(C^0_B)^{1/2}$ and final $\bar{D}^0(\bar{C}_B)$ against $(\bar{C}_B)^{1/2}$.

The third values of $\bar{D}^0(\bar{C}_B)$ were fitted against $(C^0_B)^{1/2}$ and the slope, $d\bar{D}^0(\bar{C}_B)/d(C^0_B)^{1/2})$, was calculated using the program given in appendix IV. Finally equation (2-89) was used to calculate the differential diffusion coefficient, D, at each concentration. Table [4-1-6(d)] shows D values and Figure [4-1-6(b)] shows a plot of D against $(C^0_B)^{1/2}$. The value of D at infinite dilution, $D^0 = 1.275 \times 10^{-5}$ cm^2 s^{-1}, was obtained by graphical extrapolation and by curve fitting using the program in appendix II. The expected accuracy in the obtained D values was $\simeq 0.5$ %. The D values, below 0.05M demonstrate the limitations of this method at these low concentrations.

Onsager and Fuoss[7] have derived equations, applicable to electrolytes in general, by including corrections to the simple theory of diffusion in

142

electrolyte solutions - which demands that the differential coefficients should depend only on the ratios of the ionic concentrations and remain constant when the concentrations are varied in the same proportion. When interionic forces are taken into account the above demand does not hold. The equation given by the authors mentioned above, was not expressed in experimentally measurable quantities and therefore a theoretical D^0 value could not be obtained for comparison.

4-2   CONCLUSION

The independent measurements and related derived quantities obtained for aqueous Thiaminium dichloride solutions at 25°C show that the constituent ions undergo strong interactions with each other and with the water molecules. This reveals part of the physical picture of the interactions, both coulombic and hydrodynamic, going on in systems that contain this electrolyte.

The following new and important data, on Vitamin B1 solutions, have emerged from this study.

(a). The equation for Density of solutions in the concentration range 0 - 0.5M. within an accuracy of ± 0.00008 g cm^{-3}, namely,

$$\rho = 0.99707 + 0.10684C - 0.00114 \, C^2 .$$

(b). The equations for the Apparent and Partial molal
       volumes in the concentration range 0.002 - 0.01M,

$$\phi = 157 + 640 \ m^{1/2} \ .$$

$$\overline{V} = 157 + 960 \ m^{1/2}.$$

Limits $= \pm 2 \ cm^3 \ mol^{-1}.$

(c). The Density of solid Thiaminium dichloride at
       $20^0 C$,

$$\rho = 1.4109 \pm 0.0005 \ g \ cm^{-3}$$

(d). The respective equations for Relative viscosities
       in the concentration range (0 - 0.1M) and
       (0.1 - 1M),

$$\eta_{rel} = 1 + 0.009 \ C^{1/2} + 0.823 \ C$$
Limits $= \pm 0.0009.$

$$\eta_{rel} = 1 + 0.175 \ C^{1/2} + 0.208 \ C + 1.23 \ C^2.$$
Limits $= \pm 0.005.$

(e). The Einstein's equation in the dilute range
       (below 0.003M),

$$\eta_{rel} = 1 + 5.5 \ \phi \ .$$
Limits $= \pm 0.0003.$

(f). The equation for Refractive index in the
       concentration range 0 - 1M,

$$n = 1.33247 + 0.07793C + 0.00047\ C^2.$$

$$\text{Limits} = -\ 0.00002\ \text{and}\ +\ 0.0002$$

(g). The Apparent Molal Refractivity at infinite dilution,

$$[R_{app}]^0_D = 70.0 \pm 1.4\ cm^3\ mol^{-1}.$$

(h). The electrolytic equivalent conductivities in the concentration range 0.00051 - 1M within an accuracy of ± 0.5 S cm^2 (g equiv.)$^{-1}$, and

$$\Lambda^0 = 532.7 \pm 0.5\ S\ cm^2\ equiv.^{-1}.$$

(i). The limiting ionic equivalent conductivities,

$$\lambda^0_{Thi^+} = 29.3 \pm 0.3$$
$$\lambda^0_{ThiH^{2+}} = 35.8 \pm 0.3$$
$$\lambda^0_{ThiH2^{3+}} = 41.3 \pm 0.3\ S\ cm^2\ (g\ equiv.)^{-1}.$$

(j). The association or ionic complexation constants.

$$K_1 = 1.585\ X\ 10^{-5}$$
$$K_2 = 6.310\ X\ 10^{-10}\ l\ mol^{-1}$$

(k). The diffusion coefficients in the concetration range 0.05 - 1M within $\pm$ 0.5%, and

$$D^0 = 1.275\ X\ 10^{-5}\ cm^2\ s^{-1}.$$

REFERENCES

1. GLASSTONE, S. "Textbook of physical Chemistry" 2nd Edn. D. Van Nostrand Company Inc. 1947, p.p. 887, Toronto, NY. London.

2. CONWAY, B. E., "Chemical Physics of ionic Solutions", Ch.1, Eds. CONWAY B. E and BARRADAS (The Electrochemical Society, 1964), John Wiley and Sons Inc., NY., London, Sydney.

3. DEBYE, P. and HUCKEL, E., Phys. Z., **24**, 48, 185, 305 (1923); **25**, 97 (1924); Trans. Farad. Soc., **23**,334 (1927); ONSAGER. L., Phys. Z., **27**, 388 (1926); **28**, 277 (1927); Trans. Farad. Soc. **23**, 341 (1927).

4. KIRKWOOD, J. G. and POIRIER, J. G., J. Chem. Soc., **58**, 591 (1954).

5. MAYER, J. E., J. Chem. Phys., **18**, 1426 (1950).

6. (a) FALKENHAGEN, H. K. and DOLE, M., Phys. Z., **30**, 611 (1929); (b) FALKENHAGEN, H. K., Phys. Z., **32**, 745 (1931).

7. ONSAGER, L. and FUOSS, R. M., J. Phys. Chem., **36** 2689 (1932).

8. BRONSTEAD, J. N., J. Amer. Chem. Soc., **42**, 761 (1920); **44**, 877, 938 (1922); **45**, 2898 (1923).

9. GUGGENHEIM, E. A. and TURGEON, J. C., Trans. Farad. Soc., **51**, 747 (1955).

10. MUKERJEE, P., J. Phys. Chem., **65**, 740 - 746 (1961).

11. COURTURE, A. M. and LAIDLER, K. J., Can. J. Chem., **35**, 207 (1957).

12. CONWAY, B. E., VERRAL, R. E. and DESNOYERS, J. E., Zeit. Phys. Chem., (Leipzig) (1965) [Falkenhagen Anniversary Volume].

13. HALLIWELL, H. F. and NYBURG, S. C., Trans. Farad. Soc., **59**, 1126 (1963).

14. WILLIAMS, R. R., "Vitamin B1 and its uses in Medicine", Macmillan, 1938.

15. SCHNEEBERGER, R., STAHL, R. and LONCIN, M., Lebensm - Wiss. Technol., **8**(5), 222-4 (1975), *Ger*.

16. SHAMIM, M. and BAKI, S. M. A., Aust. J. Chem., **33**, 1857-61 (1980).

17. YAO, SHOUZHUO, LIU and JIANHUA (New Materials Res. Inst.), Hunan Univ. Changsha, China/Huaxue Xuebao, **43**(7), 611-19 (1985).

18. DAWSON, R. M. C., ELLIOTT, D. C., ELLIOTT, W. H., and JONES, K. M, Eds., "Data for Biochemical research", 2nd Edn., p.p. 210, Oxford, Clarendon Press (1969).

19. WILLIAMS, R. R. and RUEHLE, A. E., J. Amer. Chem. Soc., **57**, 1856 (1935).

20. (a). WILLIAMS, R. R., WATERMAN, R. E. and KERESZTESY, J. C., J. Amer. Chem. Soc., **56**, 1187 (1934); (b). ELDERFIELD, R. C., Edr., "Heterocyclic Compounds", Vol. 5, p.p. 653 (1957), NY. John Wiley and Sons. Inc., London, Chapman and Hall Ltd..

21. ROBINSON, F. A., "The Vitamin Cofactor of enzyme systems", 1st Edn., Ch. 2, Pergamon press, Oxford, London, Edinburgh, NY, Toronto Paris (1966).

22. WILLIAMS, R. R., J. Amer. Chem. Soc., **57**, 229 (1935); WILLIAMS, R. R., WATERMAN, R. E., KERESZETESY, J. C. and BUCHMAN, E. R.; *ibid.*, 536.

23. WILLIAMS, R. R., BUCHMAN, E. R., and RUEHLE, A. E., *ibid.*, 1093.

24. WILLIAMS, R. R., *ibid.*; **58**, 1063 (1936); CLINE, J. K., WILLIAMS, R. R., RUEHLE, A. E. and WATERMAN, R. E., *ibid.*, **59**, 530 (1937).

25. WILLIAMS, R. R., RUEHLE, A. E. and FINKELSTEIN, J., *ibid.*, 526.

26. CLINE, J. K., WILLIAMS, R. R. and FINKELSTEIN, J., *ibid.*, 1052.

27. BUCHMAN, E. R., WILLIAMS, R. R. and KERESZTESY, J. C., *ibid.*, **57**, 1849 (1935).

28. WOHMANN, M., Annalen., **259** , 299 (1890).

29. WINDAUS, A., TSCHESCHE, R. and GREWE, R. Z. Physiol. Chem., **228**, 27 (1934).

30. CLARKE, H. T. and GURIN, S., J. Amer. Chem. Soc., **57**, 1876 (1935).

31. (a). HORNE, R. A., Edr., "Water and aqueous solutions - structures, thermodynamics and transport processes", Ch. 12 and 13, contributions by MILLERO, F. J., Wiley-Interscience, NY., London, Sydney, Toronto. (b). WEISSBERGER, A., Edr., **Physical methods in Organic chemistry**,

Vol. I, Part I, 2nd Edn, Contributions by
BAUER, N. and LEWIN, S. Z., "Determination of
density", Ch. IV, p.p. 131, Wiley
Interscience, NY., London (1971); (c).
MacINNES, D. A., "The principles of
electrochemistry", 1961 Edn., p.p. 82-83, Dover
publications Inc., New York.

32. MASSON, D. O., Phil. Mag., 81, 218 (1929).

33. (a). STOKES, R. H. and MILLS, R., **International
Encyclopedia of Physical Chemistry and chemical
physics**, "Viscosity of electrolytes and related
properties", Chap. 1, Pergamon press Oxford 1965.
(b). DUNCAN, T., "Advanced physics materials and
mechanics", p.p. 362 (1977); Ref. 31a, Ch. 17,
p.p. 701.

34. (a). STOKES, Trans. Camb. Phil. , 8, 287 (1845);
(b). LAMB, "Hydrodynamics", 6th Edn., Ch. XI,
Cambridge University press, 1932; M1LNE-THOMSON,
"Theoretical hydrodynamics", 2nd Edn., Macmillan,
1949.

35. POISEUILLE, Mem. Savants Etrangers, 7, 105
(1841); *ibid.*, 9, 433 (1846).

36. HAGENBACH, Ann. Phys., Lpz. (Pogg. Ann.), 109, 385
(1860).

37. ROBINSON, R. A. and STOKES, R. H., "Electrolyte
solutions", 2nd Edn. (Revised), Appendix,
Butterworths London 1970.

38. GRUNEISEN, Wiss. Abhandl. Physik-tech.

Reichanstat., **4** 239 (1905).

39. JONES, G. and DOLE, M., J. Amer. Chem. Soc., **51**, 1950 (1929); *ibid.*,2950-2964.

40. DESNOYERS, J. E. and PERRON, G., J. Sol. Chem., **1**, 199-212 (1972); WEN, W. Y., TAKEGUCHI, N. and WILSON, D. P., *ibid.*, **3**, 103-117 (1974).

41. FALKENHAGEN, H. K., and VERNON, E. L., Phil. Mag., **14**, 537 (1932).

42. HARNED, H. S., and OWEN, B. B., "The physical chemistry of Electrolytic solutions", 3rd Edn., p.p. 240, Reinhold Publishing Corp, N.Y., 1958.

43. FALKENHAGEN, H. K., and KELBG, G., Z. Elecktrochem., **56** 834 (1952).

44. PITTS, E., Proc. roy. Soc., **A217**, 43 (1953).

45. Ref. 33, Ch. 3, p.p. 30.

46. PHANG, S., Sains, Mal., **5**(2), 103 (1976); Mal. J. Chem., **4**, (1976); Aust. J. Chem., **25**, 1575 (1972).

47. CRICKARD, K. and SKINNER, J. F., J. Phys. Chem., **73**, 2060 (1969).

48. KAMINSKY, M., Disc. Farad. Soc., **24**, 171 (1957); KAY, R. L., VITUCCIO, T., ZAWOYSKI, C. and EVANS, D. F., *ibid.*, **70**, 2336 (1966).

49. EINSTEIN, A., Ann. Phys. Lpz., **19**, 289 (1906); *ibid.*, **34**, 591 (1911); EINSTEIN, A., "Investigations on the theory of the Brownian Movement", 1929, Dover publications, Inc., N.Y., p.p. 55, Translated by COWPER, A. D.

50. HOLTZER, A. and EMERSON, M. F., , J. Phys. Chem.

73, 26-33 (1969).

51. EIRICH, F. R., Edr., "Rheology, Theory and Applications", Vol.1, Academic Press, NY (1956); FORD, T. F., J. Phys. Chem., **64**, 1168 (1960).

52. VAND, V., *ibid.*, **52**, 277 (1948); *ibid.*, 314.

53. THOMAS, D. G., J. Colloid. Sci., **20**, 247 (1965).

54. (a). FINDLAY, A. (KITCHENER, J. A., Edr.), "Practical Physical Chemistry", 8th Edn., Ch. 8, Sec 8E, Longmans (1953); (b). WEISSBERGER, A., Edr. **Physical methods in Organic chemistry**, Vol. I, Part II, 2nd, Contributions by BAUER, N., FAJAN, K. and LEWIN, S. Z., "Refractometry", Ch. XVIII, Wiley Interscience, NY. (1971).

55. MOELWYN-HUGHES, E. A., "Physical Chemistry", 2nd Rev. Edn., p.p. 390, Pergamon press, Oxford-London, NY, Paris (1961).

56. ARRHENIUS, S., J. Amer. Chem. Soc., **34**, 353 (1912); Ref. 31b, p.p. 15, 40, 322.

57. KOHLRAUSCH, F., Ann. Phys., **6**, 1 (1879).

58. ARRHENIUS, S., Z. Phys. Chem., **1**, 481 (1887); Phil. Mag., **26**, 81 (1888).

59. SHEDLOVSKY, T., BROWN, A. S. and MacINNES, D. A., Trans. Electrochem. Soc., **66**, 165 (1934); SHEDLOVSKY, T., J. Amer. Chem. Soc., **54**, 1405 (1932); SHEDLOVSKY, T. and BROWN, A. S., *ibid.*, **56**, 1066 (1934).

60. Ref. 37, p.p. 143-155.

61. PRUE, J. E. and SHERRINGTON, P. J., Trans. Farad.

Soc., **57**, 1795 (1961).

62. SELVARATNAM, M. and SPIRO, M., *ibid.*, **61**, 361 (1965); (b). PETHYBRIDGE, A. D. and PRUE, J. E., *ibid.*, **63**, 2019 (1967); (c). SHAMIM, M. and SPIRO, M., *ibid.*, **66**, 2863 (1970); SHAMIM, M. and SENG, C. E., Z. Phys. Chem., **128**, 221-224 (1981).

63. FINAR, I. L., "Organic Chemistry", Vol. II, p.p. 608, Table 12.2, 5th Edn., London Longman, 1975.; HURST, D. T., "An introduction to the chemistry and biochemistry of pyrimidines, purines and pteridines.", p.p. 27, John - Wiley and Sons, Chochester, N.Y., Brisbane, Toronto.

64. Ref. 37, p.p. 285.

65. NERNST, W., Z. Phys. Chem., **2**, 613 (1888); HARTLEY, G. S., Phil. Mag., **12**, 473 (1934).

66. CHRISTOPHER, J. D. F. and HURCHINSON, H. P., I. E. C. Fundamentals, **10**, 303 (1971).

67. GORDON, A. R., Ann. NY. Acad. Sci., **46**, 285 (1945).

68. STOKES, R. H., J. Amer. Chem. Soc., **72**, 763 (1950); *ibid.*, 2243.

69. Ref. 54a, Ch. 3, p.p. 37.

70. Ref. 33, p.p. 20; Ref. 31a.

71. WEISSBERGER, A., Edr., **Physical methods in Organic chemistry**, Vol. I, Part II, Ch. XVI, 3rd Edn, Contributions by GEDDES, A. L. and PONTIUS, R. B., "Determination of diffusivity", Wiley Interscience, NY. (1971); Ref. 64.

72. Ref. 54a, Ch. 10, Sec. 10A, p.p. 205.

73. WEISSBERGER, A., Edr., **Physical methods in Organic chemistry**, Vol. I, Part IV, Ch. XLV, 2nd Edn., Contributions by SHEDLOVSKY, T., "Conductometry", Wiley Interscience, NY. (1971).

74. JONES, G. and BOLLINGER, G. M., J. Amer. Chem. Soc., **53**, 411 (1931).

75. KOHLRAUSCH, F., Wied. Ann., **60**, 315 (1897).

76. JONES, G. and BOLLINGER, G. M., J. Amer. Chem. Soc., **57**, 280 (1935).

77. KULBAUM, F. and LUMMER, O., Verh. Phy. Ges. Berlin, **14**, 56 (1970).

78. WENDT, R. P. and SHAMIM, M., J. Phys. Chem., **74**, 2770 (1970).

79. JAGANYI, D., Msc. Thesis, Dept. of Chem., University of Nairobi.

80. JAMES, A. M., "Practical Physical Chemistry", 2nd Edn., p.p. 22, J & A Churchill Ltd., 104 Gloucester Place, London W1, 1953; Ref. 85, p.p. 913, 915.

81. JONES, G. and BRADSHAW, B. C., J. Amer. Chem. Soc., **55**, 1780 (1953).

82. Ref. 80, p.p. 45-47; SHEDLOVSKY, T., *ibid.*, **54**, 1411 (1932); LIND, J. E., ZWOLENIK, J. J. and FUOSS, R. M., *ibid.*, **81**, 1557 (1959).

83. STOKES, R. H., *ibid.*, **73**, 3527 (1951).

84. MILLS, R. and WOOLF, L. A., "The diaphragm cell",

p.p. 47, Table 5.1. The Australian National University. 1968; WENDT, R. P. and SHAMIM, M., "Diffusion in aqueous ternary saline solutions", Research and development report Nº 504, p.p. 39, Loyola state University, New Orleans (1969).

85. VOGEL, A. I., "A text book of quantitative inorganic analysis including elementary instrumental analysis, p.p. 931, 3rd Edn., E.L.B.S. and Longmann, 1968.

86. SQUIRES, G. L., "Practical Physics", McGraw-Hill, London 1968.

87. REDLICH, O. and MEYER, D. M., Chem. Rev., **66**(3), 221 (1964).

88. BENSON, S.W. and COPELAND, C. S., J. Phys. Chem., **65**, 1194 (1962).

89. "Hand book of chemistry and physics.", 57th Edn., p.p. C543, Chemical Rubber Co., Cleveland, Ohio. 1976-77.

90. Ref. 55, p.p. 807.

91. BRAY and HUNT, J. Amer. Chem. Soc., **33**, 781 (1911).

92. SMITH, A. K. and GORTNER, R. A., J. Phys. Chem., **37**, 79 (1933).

93. BARNES, C., J. Appl. Phys., **5**, 4 (1934).

L.
```
  10 MODE 0
  20 REM FILE "DENSOL"
  30 REM CALCULATION OF THE DENSITY  OF THIAMINE-HCL SOLUTIONS
  40 DIM WT(50),WT2(50),DENS(50),DENS2(50),CONC(50)
  50 DATA 25.60035,25.60498,25.60700,25.60704,25.61001,25.61012,25.612445
  60 DATA 25.61500,25.61506,25.61785,25.62030,25.62362,25.62615,25.62829
  70 DATA 25.63144,25.65851,25.68568,25.69984,25.71401,25.72669,25.74002
  80 DATA 25.74054,25.74205,25.76469,25.7788,25.78949,25.80330,25.81496
  90 DATA 25.84902,25.86430,23.76299,25.91152,26.07245,23.99940,26.13923
 100 DATA 26.17402,26.37914,24.46571,26.68605,26.84288,26.94007,27.21778
 110 DATA 25.25091,27.50958,25.39536,27.71125,28.27454
 120 FOR I%=1 TO 47
 130 READ WT(I%)
 140 NEXT I%
 150 DATA .00000000,.00098208,.00102618,.0019641607,.00198137,.00261816
 160 DATA .0029900955,.0041462505,.004910418,.00503798,.005980191,.0070189168
 170 DATA .0082925018,.0090566528,.009820836,.019641672,.030000245,.035094584
 180 DATA .041462509,.045283264,.049104,.0500592,.0503776,.0589743,.064387
 190 DATA .0682077,.0733021,.0771228,.0936794,.0962687,.0975002,.113420056
 200 DATA .1758257,.1904187,.199387,.2121228,.2898115,.3771312,.3993398
 210 DATA .4591983,.5037738,.565537,.5980191,.7062738,.753875,.7820521
 220 DATA .9953775
 230 FOR J%=1 TO  47
 240 READ CONC(J%)
 250 NEXT J%
 260 PRINT TAB(5);"CONCENTRATION";TAB(25);"APP.WT.";TAB(40);"CORR.WT.";TAB(55);
          "DENSITY";TAB(70);"BLT.VOL."
 270 PRINT
 280 V=25.7028127
 290 FOR J%=1 TO 47
 300 DENS(J%)=WT(J%)/V
 310 PRINT TAB(40);WT(J%);TAB(55);DENS(J%)
 320 FOR K%=1 TO 5
 330 WT2(J%)=WT(J%)+.0012*WT(J%)*((1/DENS(J%))-(1/8.4))
 340 DENS(J%)=WT2(J%)/V
 350 Z=GET
 360 PRINT TAB(40);WT2(J%);TAB(55);DENS(J%)
 370 NEXT K%
 380 Z = GET
 390 PRINT TAB(5);CONC(J%);TAB(25);WT(J%);TAB(40);WT2(J%);TAB(55);DENS(J%);TAB(
70);V
 400 PRINT
 410 IF  J%=30 OR J%=33 OR J%=37 OR J%=42 OR J%=44 THEN  440
 420 V=25.7028127
 430 GOTO 450
 440 V=23.61061175
 450 NEXT J%
 460 END
```

```
> L.
  10CLS
  20 VDU6
  30DIM P(30),R(30),T(30),U(30),V(30),W(30),X(30),Y(30),Z(30)
  40DIM A(30),B(30),C(30),D(30),F(30),G(30),L(30),Q(30),S(30)
  50DIM A$(2),I$(3),Q$(3)
  60REM ARRAY SIZES LIMIT PROGRAM TO A MAXIMUM OF 100 DATA POINTS.
  70REM THE NUBER OF DATA POINTS SHOULD BE AT LEAST 2 GREATER THAN THE
  80REM MAXIMUM ORDER OF THE POLYNOMIAL.
  90PRINT "PROGRAM TO FIT A POLYNOMIAL TO A SET OF POINTS"
  100PRINT "======= == === = ========== == = === == ======"
  110PRINT
  120PRINT "WOULD YOU LIKE FULL INSTRUCTIONS.";
  140GOSUB 3720
  150LET I$ = Q$
  160IF I$ = "NO" THEN 190
  170PRINT "TYPE IN A PAIR OF X & Y VALUES & WEIGHT SEPARATED BY COMMAS"
  180PRINT "THEN PRESS RETURN, TYPE THE NEXT PAIR OF VALUES ETC"
  190PRINT "TERMINATE DATA WITH 999,999,999"
  200PRINT
  210 INPUT "HOW MANY DATA HAVE YOU ? " SUMM
  220PRINT "STARTING DATA"
  230 CHANL=OPENOUT "COEFFS"
  231 XX=OPENIN "TRY"
  240PRINT " X, Y, WEIGHT"
  250LET N = 0
  260 I1=0
  270 REPEAT
  280 I1 =I1+1
  290 INPUT£XX ,X(I1),Y(I1),W(I1)
  295 PRINT X(I1),Y(I1),W(I1)
  300  IF ABS(X(I1) - 999) + ABS(Y(I1) - 999) = 0 THEN 390
  310  IF W(I1) >= 0 THEN 340
  320  PRINT "NEGATIVE WEIGHTS ARE IMPOSSIBLE - RETYPE LAST LINE"
  330  GOTO 290
  340  LET N = N + 1
  350 UNTIL I1 = SUMM
  355 CLOSE£XX
  360PRINT "PROGRAM CAN HANDLE MAXIMUM OF 100 VALUES"
  370REM CHECK THAT THERE ARE AT LEAST 2 POINTS
  390IF N < 2 THEN 1170
  400PRINT
  410REM CALL SUBROUTINE TO CHECK THAT DATA ARE CORRECT
  420GOSUB 2870
  430PRINT
  440REM CALCULATE MAXIMUM ORDER BASED ON NUMBER OF DATA POINTS
  450LET N9 = 9
  460IF N - 2 >= 9 THEN 480
  470LET N9 = N - 2
  480IF I$ = "YES" THEN 510
  490PRINT "TYPE ORDER REQUIRED"
  500GOTO 560
  510PRINT "TYPE IN THE ORDER REQUIRED IN THE RANGE 1 -"; N9; " OF THE"
  520PRINT "ONE SPECIFIC POLYNOMIAL REQUIRED."
  530PRINT "OR TYPE 0 IF ALL THE POLYNOMIALS FROM ORDER 0 -";N9;"ARE TO"
  540PRINT "BE EXAMINED, AND THE ONE WHICH FITS BEST REPORTED,"
  550PRIN
```

```
550PRINT "THEN PRESS RETURN."
560INPUT L
570IF L <> INT(L) THEN 600
580IF L < 0 THEN 600
590IF L <= N9 THEN 630
600PRINT "INCORRECT VALUE TYPED"
610GOTO 510
620REM SET THE MAXIMUM ORDER TO 9, IE M1 (MAXORDER+1) TO 10
630LET M1 = 10
640IF L <= 0 THEN 660
650LET M1 = L + 1
660LET I = N - 1
670IF M1 <= I THEN 700
680LET M1 = I
690REM CALL SUBROUTINE TO FIT THE POLYNOMIAL
700GOSUB 1280
710LET M2 = M1 - 1
720PRINT
730IF L = 0 THEN 760
740PRINT "ORDER OF POLYNOMIAL SPECIFIED ="; N2
750GOTO 790
760PRINT "MAXIMUM ORDER OF POLYNOMIAL TESTED FOR ="; M2
770PRINT "ORDER OF BEST POLYNOMIAL FOUND ="; N2
780PRINT
790PRINT "POLYNOMIAL ORDER   GOODNESS OF FIT"
800FOR I = 1 TO M1
810   PRINT TAB(1);I - 1; TAB(10); G(I)
820NEXT I
830PRINT
840PRINT "COEFFICIENTS OF THE BEST OR SPECIFIED ORDER POLYNOMIAL"
845 VDU3
850 VDU2
860PRINT "(Y = A + B*X + C*X^2 + D*X^3 +...)"
870LET N3 = N2 + 1
880FOR I = 1 TO N3
890   READ A$
900   PRINT A$; TAB(5); F(I)
905 PRINT£CHANL, F(I)
910NEXT I
911 *SPOOL A11
912 PRINT "REA X1"
913 FOR I = 1 TO N3
914 PRINT F(I)
915 NEXT
916 PRINT "EOF"
917 *SPOOL
920 VDU3
930DATA "A=", "B=", "C=", "D=", "E=", "F=", "G=", "H=", "I=", "J="
940RESTORE
950PRINT
960PRINT "WOULD YOU LIKE A TABLE OF RESIDUALS"
970GOSUB 3710
980IF Q$ = "NO" THEN 1080
985 VDU2
990PRINT TAB(0);"X";TAB(10);"Y";TAB(25);"Y(CALC)";TAB(40);"DIFF"
1000LET R2 = 0
1010FOR I
```

```
             = 1 TO N
1020   PRINT TAB(0);X(I);TAB(10);Y(I);TAB(25);Z(I);TAB(40);R(I)
1030   LET R2 = R2 + R(I) ^ 2
1040NEXT I
1050PRINT
1060PRINT "SUM OF ERRORS SQUARED ="; R2
1070PRINT
1075 VDU3
1080PRINT "WOULD YOU LIKE ANOTHER RUN";
1090GOSUB 3710
1100IF Q$ = "NO" THEN 1200
1110LET I$ = "NO"
1120PRINT "WOULD YOU LIKE TO TRY ANOTHER ORDER WITH THE SAME DATA"
1130GOSUB 3710
1140IF Q$ = "YES" THEN 390
1150GOTO 190
1160REM ENTER IF THERE ARE NOT ENOUGH POINTS
1170PRINT "RUN TERMINATED - NOT ENOUGH DATA POINTS"
1180GOTO 1080
1190REM TERMINATE JOB
1200IF I$ = "NO" THEN 1240
1205 VDU2
1210PRINT "REMEMBER THAT YOU MUST NOT EXTRAPOLATE BEYOND THE"
1220PRINT "DATA POINTS, AND ALSO THAT INTERPOLATION BETWEEN"
1230PRINT "POINTS IS DANGEROUS WITH HIGH ORDER POLYNOMIALS."
1240PRINT "END OF JOB"
1241 CLOSE £0
1245 CHAIN"DERIVE"
1250STOP
1260REM SUBROUTINE TO CALCULATE A WEIGHTED LEAST SQUARES POLYNOMIAL
1270REM BY FORSYTHE"S METHOD USING ORTHOGONAL POLYNOMIALS.
1280LET M3 = M1 - 1
1290LET N2 = M3
1300FOR I = 1 TO M1
1310   LET C(I) = 0
1320NEXT I
1330LET Q(1) = 0
1340LET D(1) = 0
1350LET D(2) = 0
1360LET A(1) = 1
1370LET D2 = 0
1380LET P1 = 0
1390LET S1 = 0
1400LET G1 = 0
1410LET I1 = 0
1420LET S2 = W(1)
1430REM FIND THE MAXIMUM AND MINIMUM X & Y
1440LET X9 = X(1)
1450LET X1 = X(1)
1460LET Y9 = Y(1)
1470LET Y1 = Y(1)
1480FOR I = 2 TO N
1490   IF X(I) = X9 THEN 1510
1500   LET X9 = X(I)
1510   IF X(I) >= X1 THEN 1530
```

```
1520    LET X1 = X(I)
1530    IF Y(I) <= Y9 THEN 1550
1540    LET Y9 = Y(I)
1550    IF Y(I) >= Y1 THEN 1570
1560    LET Y1 = Y(I)
1570    LET S2 = S2 + W(I)
1580NEXT I
1590REM CHECK THAT SUM OF WEIGHTS IS NOT ZERO
1600IF S2 = 0 THEN 2840
1610LET Y3 = (Y9 + Y1) / 2
1620LET Y4 = (Y9 - Y1) / 2
1630IF Y4 > 0 THEN 1680
1640LET F(1) = Y(1)
1650LET N2 = 0
1660GOTO 2820
1670REM SCALE Y TERMS INTO THE RANGE +1 TO -1
1680FOR I = 1 TO N
1690    LET V(I) = (Y(I) - Y3) / Y4
1700    LET D2 = D2 + W(I) * V(I) ^ 2
1710    LET P(I) = 1
1720    LET T(I) = 0
1730    LET P1 = P1 + W(I) * V(I)
1740    LET S1 = S1 + W(I)
1750NEXT I
1760LET S(1) = P1 / S1
1770LET C(1) = S(1)
1780LET D2 = D2 - S(1) * P1
1790LET G(1) = ABS(D2 / (N - 1))
1800LET A1 = 4 / (X9 - X1)
1810LET B1 = -2 - A1 * X1
1820REM SCALE X TERMS INTO THE RANGE +2 TO -2
1830FOR I = 1 TO N
1840    LET U(I) = A1 * X(I) + B1
1850NEXT I
1860REM START LOOP FOR EACH ORDER
1870FOR I = 1 TO M3
1880    LET D1 = 0
1890    FOR J = 1 TO N
1900       LET D1 = D1 + W(J) * U(J) * P(J) ^ 2
1910    NEXT J
1920    REM L IS FORSYTHES ALPHA
1930    LET L(I + 1) = D1 / S1
1940    LET W2 = S1
1950    LET S1 = 0
1960    LET P1 = 0
1970    REM STORE VALUE OF CURRENT ORTHOGONAL POLYNOMIAL IN P( )
1980    REM AND OF PREVIOUS ORTHOGONAL POLYNOMIAL IN T( )
1990    FOR J = 1 TO N
2000       LET D1 = Q(I) * T(J)
2010       LET T(J) = P(J)
2020       LET P(J) = (U(J) - L(I + 1)) * P(J) - D1
2030       LET S1 = S1 + W(J) * P(J) ^ 2
2040       LET P1 = P1 + W(J) * V(J) * P(J)
2050    NEXT J
2060    REM Q IS FORSYTHES BETA
2070    LET Q(I + 1) = S1 / W2
```

```
2080    LET S(I + 1) = P1 / S1
2090    LET D2 = D2 - S(I + 1) * P1
2100    LET G(I + 1) = ABS(D2 / (N - I - 1))
2110    IF L > 0 THEN 2280
2120    REM ENTER IF PROGRAM HAS TO DECIDE ON BEST ORDER (L = 0)
2130    IF I1 = 1 THEN 2230
2140    IF G(I + 1) < G(I) THEN 2280
2150    REM ENTER IF A MINIMUM DETECTED
2160    LET N2 = I - 1
2170    LET I1 = 1
2180    LET G1 = G(I)
2190    FOR J = 1 TO M1
2200      LET B(J) = C(J)
2210    NEXT J
2220    GOTO 2280
2230    IF G(I + 1) >= 0.6 * G1   THEN 2280
2240    LET I1 = 0
2250    LET N2 = M3
2260    REM BUILD COEFFICIENTS OF J TH ORDER TERM IN A( ) & SUM TO FORM
2270    REM EXPLICIT POWER SERIES IN C( )
2280    FOR J = 1 TO I
2290      LET D1 = D(J + 1) * Q(I)
2300      LET D(J + 1) = A(J)
2310      LET A(J) = D(J) - L(I + 1) * A(J) - D1
2320      LET C(J) = C(J) + S(I + 1) * A(J)
2330    NEXT J
2340    LET C(I + 1) = S(I + 1)
2350    LET A(I + 1) = 1
2360    LET D(I + 2) = 0
2370    IF I1 = 0 THEN 2420
2380    IF I <> M3 THEN 2420
2390    FOR J = 1 TO M1
2400      LET C(J) = B(J)
2410    NEXT J
2420NEXT I
2430LET D(1) = 1
2440LET B(1) = 1
2450LET F(1) = C(1)
2460FOR I = 2 TO M1
2470    LET D(I) = 1
2480    LET B(I) = B1 * B(I - 1)
2490    LET F(1) = F(1) + C(I) * B(I)
2500    REM WORK OUT EXPLICIT POWER SERIES IN UNSCALED X, & ADD
2510    REM INTO THE COEFFICIENTS F( ) THE RELEVANT CONTRIBUTIONS
2520NEXT I
2530FOR J = 2 TO M1
2540    LET D(1) = D(1) * A1
2550    LET F(J) = C(J) * D(1)
2560    LET K1 = 2

2570    LET J1 = J + 1
2580    IF J1 > M1 THEN 2660
2590    FOR I = J1 TO M1
2600      LET D(K1) = A1 * D(K1) + D(K1 - 1)
2610      LET F(J) = F(J) + C(I) * D(K1) * B(K1)
2620      LET K1 = K1 + 1
2630    NEXT I
```

160

```
2640NEXT J |
2650REM CALCULATE YCALC & RESIDUAL FOR EACH POINT (ON ORIGINAL SCALE).
2660FOR I = 1 TO N
2670   LET J = N2 + 1
2680   LET Y5 = F(J)
2690   IF N2 = 0 THEN 2730
2700   FOR K = 1 TO N2
2710     LET Y5 = F(J - 1) + (X(I) * Y5)
2720     LET J = J - 1
2730   NEXT K
2740   LET Z(I) = Y5 * Y4 + Y3
2750   LET R(I) = (V(I) - Y5) * Y4
2760NEXT I
2770REM CONVERT COEFF ARRAY F( ) BACK TO ORIGINAL SCALE
2780LET F(1) = (F(1) * Y4) + Y3
2790FOR I = 2 TO M1
2800   LET F(I) = F(I) * Y4
2810NEXT I
2820RETURN
2830REM ENTER IF ERRORS DETECTED
2840PRINT " JOB TERMINATED BY PROGRAM BECAUSE SUM OF WEIGHTS = 0"
2850STOP
2860REM SUBROUTINE TO CHECK THAT DATA ARE CORRECT & ALTER IF NECESSARY
2870PRINT "ARE THE DATA VALUES ENTERED CORRECT?";
2880REM A4 SHOULD BE SET TO THE NUMBER OF LINES ON THE VDU
2890LET A4 = 20
2900GOSUB 3710
2910IF Q$ = "YES" THEN 3690
2920PRINT "HERE IS A LIST OF THE CURRENT DATA"
2930 VDU2
2940PRINT TAB(0);"LINE";TAB(5);"X";TAB(20);"Y";TAB(30);"WEIT"
2950FOR I = 1 TO N
2960   PRINT TAB(1);I;TAB(5);X(I);TAB(20);Y(I);TAB(30);W(I)
2970   IF INT(I / (A4 - 1)) * (A4 - 1) <> I THEN 3010
2980   PRINT "WOULD YOU LIKE TO CONTINUE LISTING";
2990   GOSUB 3710
3000   IF Q$ = "NO" THEN 3030
3010NEXT I
3020 VDU3
3030PRINT "TYPE R TO REPLACE";
3040IF I$ = "NO" THEN 3060
3050PRINT " AN EXISTING LINE OF DATA"
3060IF N = 100 THEN 3110
3070PRINT TAB(5); "A TO ADD";
3080IF I$ = "NO" THEN 3100
3090PRINT " AN EXTRA LINE"
3100IF N = 1 THEN 3140
3110PRINT TAB(5); " D TO DELETE";
3120IF I$ = "NO" THEN 3140
3130PRINT " AN EXISTING LINE"
3140PRINT TAB(5); " L TO LIST";
3150IF I$ = "NO" THEN 3170
3160PRINT " THE DATA"
3170PRINT "  OR C TO CONTINUE";
3180IF I$ = "NO" THEN 3200
3190PRINT " THE CALCULATION"
```

```
3200INPUT Q$
3210IF Q$ = "R" THEN 3310
3220IF N = 100 THEN 3250
3230IF Q$ = "A" THEN 3450
3240IF N = 1 THEN 3260
3250IF Q$ = "D" THEN 3550
3260IF Q$ = "L" THEN 2920
3270IF Q$ = "C" THEN 3690
3280PRINT "REPLY '"; Q$; "' NOT UNDERSTOOD."
3290GOTO 3030
3300REM REPLACE LINE
3310PRINT "TYPE THE LINENUMBER OF THE LINE TO BE REPLACED";
3320INPUT I
3330IF I <> INT(I) THEN 3350
3340IF (I - 1) * (I - N) < = 0 THEN 3380
3350PRINT "LINENUMBER MUST BE AN INTEGER IN THE RANGE 1 -"; N
3360PRINT "RE-";
3370GOTO 3310
3380PRINT "TYPE THE CORRECT LINE TO REPLACE THE ONE WHICH IS WRONG:"
3390PRINT "X, Y, WEIGHT"
3400INPUT X(I), Y(I), W(I)
3410IF W(I) >= 0 THEN 3520
3420PRINT "NEGATIVE WEIGHTS ARE IMPOSSIBLE - LAST LINE REJECTED"
3430GOTO 3380
3440REM ADD A NEW LINE
3450LET N = N + 1
3460PRINT "TYPE THE ADDITIONAL LINE OF DATA AS SHOWN:"
3470PRINT "X, Y, WEIGHT"
3480INPUT X(N), Y(N), W(N)
3490IF W(N) >= 0 THEN 3520
3500PRINT "NEGATIVE WEIGHTS ARE IMPOSSIBLE - LAST LINE REJECTED"
3510GOTO 3460
3520PRINT "OK"
3530GOTO 3030
3540REM DELETE A LINE
3550PRINT "TYPE THE LINENUMBER OF THE LINE TO BE DELETED"
3560INPUT J
3570IF (J - 1) * (J - N)
3580IF J = INT(J) THEN 3610
3590PRINT "LINENUMBER MUST BE AN INTEGER IN THE RANGE 1 -"; N
3600GOTO 3550
3610FOR I = J + 1 TO N
3620   LET X(I - 1) = X(I)
3630   LET Y(I - 1) = Y(I)
3640NEXT I
3650LET N = N - 1
3660PRINT "OK"
3670IF J > N THEN 3030
3680GOTO 2920
3690RETURN
3700REM SUBROUTINE TO CHECK REPLIES
3710IF I$ = "NO" THEN 3730
3720PRINT " TYPE YES OR NO $ PRESS RETURN."
3730PRINT
3740INPUT Q$
3750IF Q$ = "YES" THEN 3790
3760IF Q$ = "NO" THEN 3790
3770PRINT "REPLY '"; Q$; "' NOT UNDERSTOOD.";
3780GOTO 3720
3790RETURN
3800END
```

APPENDIX III

```
  5 VDU 3
 10 CLS
 20 REM  VDU6
 30 PRINT "PROGRAMME INTER2 FOR INTEGRATION OF AREA BETWEEN
    THE VALUES LO & UP"
 40 PRINT
 50 A=0:B=0:C=0:D=0:E=0:F=0:G=0:H=0:I=0:J=0:NUM=1:
    SUMMY=0:SUMM1=0
 60 VDU2
 70 FILE=OPENIN "COEFFS"
 80 INPUT "LOWER LIMIT VALUE   ",LO
 90 INPUT "UPPER LIMIT VALUE   ",UP
100 REPEAT
130 INPUT£FILE,COEFFICIENT
140 ON NUM GOTO 150,190,230,270,310,350,390,430,470,510
150 A=COEFFICIENT
160 SUMMY = SUMMY + (COEFFICIENT * (UP^NUM)/NUM)
170 SUMM1 = SUMM1 + (COEFFICIENT * (LO^NUM)/NUM)
180 GOTO 540
190 B=COEFFICIENT
200 SUMMY = SUMMY + (COEFFICIENT * (UP^NUM)/NUM)
210 SUMM1 = SUMM1 + (COEFFICIENT * (LO^NUM)/NUM)
220 GOTO 540
230 C=COEFFICIENT
240 SUMMY = SUMMY + (COEFFICIENT * (UP^NUM)/NUM)
250 SUMM1 = SUMM1 + (COEFFICIENT * (LO^NUM)/NUM)
260 GOTO 540
270 D=COEFFICIENT
280 SUMMY = SUMMY + (COEFFICIENT * (UP^NUM)/NUM)
290 SUMM1 = SUMM1 + (COEFFICIENT * (LO^NUM)/NUM)
300 GOTO 540
310 E=COEFFICIENT
320 SUMMY = SUMMY + (COEFFICIENT * (UP^NUM)/NUM)
330 SUMM1 = SUMM1 + (COEFFICIENT * (LO^NUM)/NUM)
340 GOTO 540
350 F=COEFFICIENT
360 SUMMY = SUMMY + (COEFFICIENT * (UP^NUM)/NUM)
370 SUMM1 = SUMM1 + (COEFFICIENT * (LO^NUM)/NUM)
380 GOTO 540
390 G=COEFFICIENT
400 SUMMY = SUMMY + (COEFFICIENT * (UP^NUM)/NUM)
410 SUMM1 = SUMM1 + (COEFFICIENT * (LO^NUM)/NUM)
420 GOTO 540
430 H=COEFFICIENT
440 SUMMY = SUMMY + (COEFFICIENT * (UP^NUM)/NUM)
450 SUMM1 = SUMM1 + (COEFFICIENT * (LO^NUM)/NUM)
460 GOTO 540
470 I=COEFFICIENT
480 SUMMY = SUMMY + (COEFFICIENT * (UP^NUM)/NUM)
490 SUMM1 = SUMM1 + (COEFFICIENT * (LO^NUM)/NUM)
500 GOTO 540
510 J=COEFFICIENT
520 SUMMY = SUMMY + (COEFFICIENT * (UP^NUM)/NUM)
530 SUMM1 = SUMM1 + (COEFFICIENT * (LO^NUM)/NUM)
540 NUM = NUM+1
550 UNTIL EOF£(FILE)
560 NUM =1:PTR£FILE =0
570 IF UP=10 THEN  580 ELSE  PRINT "DO = "; (SUMMY-SUMM1)/UP:
    SUMMY=0:SUMM1=0:GOTO 80
580 INPUT "DO YOU WANT TO LOAD MIRPOLY  Y/N ?"  A$
590 IF A$="Y"  THEN CLOSE£0:VDU3:CHAIN "MIRPOLY" ELSE VDU3:STOP
```

163

```
10 VDU 3
20 CLS
30 REM   VDU6
40 DIM X(44),Y(44),WT(44)
50 PRINT "PROGRAMME DERIVE FOR FINDING THE SLOPE OF A CURVE AT X=RC"
60 PRINT
70 PRINT TAB(0);"ROOTCONC";TAB(15);"SLOPE"
80 A=0:B=0:C=0:D=0:E=0:F=0:G=0:H=0:I=0:J=0:NUM=1:SLOPE=0
90 VDU2
100 FILE=OPENIN "COEFFS"
110 YY=OPENIN "TRY"
120 FOR I=1 TO 44
130 INPUT#YY,X(I),Y(I),WT(I)
140 RC=X(I)
150 REPEAT
160 INPUT#FILE,COEFFICIENT
170 ON NUM GOTO 180,210,240,270,300,330,360,390,420,450
180 A=COEFFICIENT
190 SLOPE = SLOPE + ((NUM-1)*COEFFICIENT * (RC^(NUM-2)))
200 GOTO 470
210 B=COEFFICIENT
220 SLOPE = SLOPE + ((NUM-1)*COEFFICIENT * (RC^(NUM-2)))
230 GOTO 470
240 C=COEFFICIENT
250 SLOPE = SLOPE + ((NUM-1)*COEFFICIENT * (RC^(NUM-2)))
260 GOTO 470
270 D=COEFFICIENT
280 SLOPE = SLOPE + ((NUM-1)*COEFFICIENT * (RC^(NUM-2)))
290 GOTO 470
300 E=COEFFICIENT
310 SLOPE = SLOPE + ((NUM-1)*COEFFICIENT * (RC^(NUM-2)))
320 GOTO 470
330 F=COEFFICIENT
340 SLOPE = SLOPE + ((NUM-1)*COEFFICIENT * (RC^(NUM-2)))
350 GOTO 470
360 G=COEFFICIENT
370 SLOPE = SLOPE + ((NUM-1)*COEFFICIENT * (RC^(NUM-2)))
380 GOTO 470
390 H=COEFFICIENT
400 SLOPE = SLOPE + ((NUM-1)*COEFFICIENT * (RC^(NUM-2)))
410 GOTO 470
420 I=COEFFICIENT
430 SLOPE = SLOPE + ((NUM-1)*COEFFICIENT * (RC^(NUM-2)))
440 GOTO 470
450 J=COEFFICIENT
460 SLOPE = SLOPE + ((NUM-1)*COEFFICIENT * (RC^(NUM-2)))
470 NUM = NUM+1
480 UNTIL EOF#(FILE)
490 NUM =1:PTR#FILE =0
500 PRINT TAB(0);X(I);TAB(15);SLOPE
505 SLOPE =0
510 NEXT I
520 CLOSE#0
530 VDU3
550 INPUT "DO YOU WANT TO LOAD MIRROR  Y/N ?"  A$
560 IF A$<>"Y" THEN 590
580 CHAIN "MIRROR"
590 END
```

```
10 MODE 0
20 REM FILE "SUPER3"
30 REM CALCULATION OF EXPERIMENTAL CONDUCTIVITY OF THIAMINE-HCL SOLUTIONS
40 DIM CONC(20),REST(20),ALPHA(20),Y(20),Y1(20),BETA(20),IS(20)
50 DATA .00050625,.000625,.00075625,.0008265625,.0009765625,.00098208
60 DATA .00102618,.00105625,.001225,.0014063,.00157014,.0017016,.00180625
70 DATA .0019641607,.00198137
80 FOR I%=1 TO 15
90 READ CONC(I%)
100 NEXT I%
110 DATA 34344.4,28794.1,24614.3,22896.9,20019.2,19929.2,19242.2,18804.7
120 DATA 16720.5,15010.0,13778.4,12947.6,12368.0,11599.0,11521.9
130 FOR J%=1 TO 15
140 READ REST(J%)
150 REM PRINT TAB(1);J%;TAB(5);REST(J%);TAB(20);CONC(J%)
160 NEXT J%
170 ZT=1:ZTH1=2:ZTH2=3:ZH=1:ZCL=1
180 B1=.2300  :B3=.3291E8  :A0=1E-3
190 FOR KA=10^(-4.8) TO 10^(-4.7) STEP 5E-8
200 REM READ KA
210 FOR KB=10^(-9.2) TO  10^(-9.1) STEP 5E-13
220 REM READ KB
230 K2= (1/KA): K3= (1/KB)
240 REM PRINT "PRESS ANY KEY FOR RUN OF K2 =";K2
250 REM W$=GET$
260 PRINT TAB(5);"MOLALITY";TAB(22);"ALPHA";TAB(37);"BETA";TAB(50);"ITERATES";
    TAB(65);"RESIST"
270 FOR L%=1 TO 15
280 ALPHA(L%)=1 :TEST1=1 :SUM =0 :TEST2=0 :BETA(L%) =0
290 REM CALCULATIONS OF LOG fi
300 IS(L%)=(ALPHA(L%)+(2*(1+BETA(L%))))*CONC(L%)
310 Y(L%)=SQR(IS(L%))/(1+(B3*A0*SQR(IS(L%))))
320 Y1(L%)=SQR(IS(L%))/(1+((B3*A0)-B1)*SQR(IS(L%)))
330 A=(-0.5115*(ZT^2)*IS(L%))  :FT=10^A
340 B=(-0.5115*(ZTH1^2)*IS(L%))  :FTH1=10^B
350 C=(-0.5115*(ZTH2^2)*IS(L%)):FTH2=10^C
360 D=(-0.5115*(ZH^2)*IS(L%)):FH=10^D
370 E=(-0.5115*(ZCL^2)*IS(L%)):FCL=10^E
380 REM CALCULATION OF LAMBDA
390 R=K2*(CONC(L%))^2*FT*FH:R1=(R*(BETA(L%)-2))-FTH1:R2=R-(BETA(L%)*(R-FTH1))
400 GOSUB 900
410 REM PRINT"ALPHA"TAB(4);CONC(L%);TAB(20);SOLN1;TAB(35)SOLN2
420 ALPHA(L%) =SOLN2:REM ALPHA(L%)=SOLN1
430 REM CALCULATION OF BETA
440 R=K3*(CONC(L%))^2*FTH1*FH:R1=-(R+FTH2):R2=R*(ALPHA(L%)-ALPHA(L%)^2)
450 GOSUB 900
460 REM PRINT"BETA" TAB(4);CONC(L%);TAB(20);SOLN1;TAB(35)SOLN2
470 BETA(L%)=SOLN2:REM BETA(L%)=SOLN1
480 IF ABS(TEST1-ALPHA(L%))<0.0000001 AND ABS(TEST2-BETA(L%))<0.0000001 THEN
    510
490 SUM =SUM+1:TEST1=ALPHA(L%) :TEST2=BETA(L%)
500 GOTO  300
510 PRINT TAB(4);CONC(L%);TAB(20);ALPHA(L%);TAB(35);BETA(L%);TAB(53);SUM;
    TAB(65);REST(L%)
520 NEXT L%
530 RESTORE
540 J=5.40859188
550 TIDLAM2 = 0
560 REM FITTING OF LAMBDA VALUES AS PER EXISTING THEORY
570 FOR LTH20=41.25 TO 42 STEP .25
```

```
580 FOR LTH10=35.5 TO 36 STEP .25
590 FOR LT0=29 TO 29.5 STEP .25
600 B1=.23:B2=60.65:LH0=349.81:LCL0=76.35:A0=1E-3:E=78.54:T=298.16:N=8.937E-3
605 IDLAM1=LH0+LCL0+LT0+LTH10+LTH20
610 REM INPUT "LAMBDA VALUE AT INFINITE DILUTION ";IDLAM2
620 PRINT TAB(1);"CONC";TAB(16);"ROOTC";TAB(28);"INF.DIL.L";TAB(40);"I/D.L.CA"
    ;TAB(56);"EXLAM";TAB(70);"EXLAM.CAL"
630 FOR L%=1 TO 15
640 LCL=LCL0-((B1*LCL0)+(.5*B2))*Y(L%)
650 LT=LT0-((B1*LT0)+(.5*B2))*Y(L%)
660 LH=LH0-((B1*LH0)+(.5*B2))*Y(L%)
670 LTH1=LTH10-((B1*LTH10)+(.5*B2))*Y(L%)
680 LTH2=LTH20-((B1*LTH20)+(.5*B2))*Y(L%)
690 EXLAM=(J*1000)/(REST(L%)*CONC(L%)):CONCSQR=SQR(CONC(L%))
700 X=((ALPHA(L%)*LT)+((ALPHA(L%)+BETA(L%))*LH)-(2*(ALPHA(L%)-BETA(L%))*LTH1)-
    (3*BETA(L%)*LTH2))
710 EXLAM2=IDLAM1-(((B1*IDLAM1)+B2)*Y(L%))-X:IDLAM2=EXLAM+(((B1*EXLAM)+B2)*Y1(
    L%))+X
720 TIDLAM2 = TIDLAM2 + IDLAM2
730 PRINT TAB(1);CONC(L%);TAB(15);CONCSQR TAB(29);IDLAM1;TAB(40);IDLAM2;
    TAB(54);EXLAM;TAB(68);EXLAM2
740 NEXT L%
750 B=GET
760 IF ABS((TIDLAM2/15)-IDLAM1)>0.01 THEN 800
770 PRINT "AVERAGE IDLAM2 ",TIDLAM2/15
780 IDLAM1 = TIDLAM2/15
790 TIDLAM2=0
800 IDLAM1=LH0+LCL0+LT0+LTH10+LTH20
810 PRINT TAB(1);"HLAM.";TAB(14);"TLAM.";TAB(27);"CLLAM";TAB(40);"THLAM.";
    TAB(53);"TH2LAM.";TAB(67);"ION RAD"
820 PRINT TAB(1);LH0;TAB(14);LT0;TAB(27);LCL0;TAB(40);LTH10;TAB(53);LTH20;
    TAB(67);A0
830 REM PRINT TAB(1);LH;TAB(14);LT;TAB(27);LCL;TAB(40);LTH1;TAB(53);LTH2;
    TAB(67); A0
840 PRINT KA    , KB
850 NEXT LT0
860 NEXT LTH10
870 NEXT LTH20
880 Q=GET:RESTORE:NEXT KB
890 RESTORE : NEXT KA:END
900 REM SUBROUTINE TO SOLVE QUADRATIC EQUATION
910 DIS=(R1)^2-(4*R*R2)
920 IF DIS<>0 THEN 960
930 PRINT "BOTH ROOTS ARE EQUAL ,AND HAVE THE SAME VALUE:"-R1/(2*R)
940 GOTO  1020
950 PRINT
960 IF DIS>0 THEN 990
970 PRINT "THIS EQUATION DOES NOT HAVE REAL ROOTS"
980 GOTO 1020
990 DIS2=SQR(DIS)
1000 IF R1 >=0 THEN 1010
1010 SOLN1=((-R1)+DIS2)/(2*R): SOLN2=((-R1)-DIS2)/(2*R)
1020 RETURN
```