A MEASUREMENT OF CRYOSCOPIC AND TRANSFERENCE NUMBERS OF BARBITURIC ACID AND SODIUM BARBITAL.

BY

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

March 1990

DECLARATION

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

Signed ......Antipa......

P. O ANTIPA

Date ......17-7-91......

This work has been presented for examination with my approval as the project supervisor

Signed..M. Shamim......

Dr. MOHAMMED SHAMIM

Date ..18.7.1991......

DEDICATION

To my dear wife, Rosa

ACKNOWLEDGHEMENTS

I wish to express my sincere appreciation to Dr. M. Shamim, my supervisor, who initiated this work, for his guidance, patience and invaluable advise during the carrying out of this investigation.

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

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ABSTRACT

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

Inspite of age-long use of these compounds, it was surprising to note that the only physico-chemical data available on these chemicals are the density, viscosity. refractive index, conductance and diffusion coefficient measurments of barbituric acid and Sodium Barbital at 25° C. It thus became the objective of the present project to produce additional physico-chemical data on these pyrimidines so as to have a better understanding of the mode of physiological action of these medicines.

Accordingly cryoscopic and transference measurements were undertaken in aqueous Barbituric acid and Sodium Barbital.

The investigation has shown that Barbituric Acid dimerizes in solution to give ionic species, $(B_2)^{2-}$ with an equivalent conductance of 40.0 ± 0.1 S cm^2 $equiv.^{-1}$ and a formation constant of 3.0 ± 0.1 kg Mol^{-1} while the transferesnce number for the B^- ions was found to be 0.0584 ± 0.01

conductance of 39.8 S cm^2 $equiv.^{-1}$ for the B^{*-} ions and the average transference numbers of 0.4416 ± 0.01 for the same B^- ions.

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LIST OF SYMBOLS

a^o	Distance of closest approach of ions
a	Activity.
a_{HB}	Activity coefficients of Barbituric Acid, HB
a_{NaB^*}	Activity coefficient of Sodium Barbital, NaB*
A	Constant of DHO limiting law
B_1	Parameter of DHO limiting equation
B_2	Parameter of DHO limiting equation
B_3	Parameter of DHO limiting equation
c	normality of solution as a whole
C_i	Normality of solution i
D_{2-}	Algebraic representation of dimeric anion
F	Faraday constant
g	Weight of solute, g
G	Weight of solvent, g
G	Molar free energy, J mol^{-1}
G_o	Standard molar free energy, J mol^{-1}
J	Difference of the molal heat capacities of liquid wate and ice, J K^{-1} Molal^{-1}
K_f	Molal freezing point depression
$\bar{L}$	Latent heat of fusion of water
L_o	Latent heat of fusion of water freezing point of water

m	Molality, mol Kg^{-1}
M	Molecular weight of solute
M^{o}	Molecular weight of solvent
n	Total number of species
R	Universal gas constant, 8.3142 J K^{-1} mol^{-1}
T	Absolute temperature, K
T_{B^-}	Transport number of B- ions
T_{B^-}	Transport number of B* ions
T_{H^+}	Transport number of H+ ions
T_{Na^+}	Transport number of Na+ ions
T_o	Freezing point of pure solvent, ^{o}C
T_f'	Freezing point of solution, ^{o}C
t_i	Transport number of species i
T_R	Transport number of ion constituent R
U_i	Mobility of species i
Z_+Z_-	Algebraic charge number of positive and negative ions
Z_i	Algebraic charge number of ions i
α	Degree of dissociation
β	Degree of formation
γ_i	Activity coefficient of ion i
$\gamma_\pm$	Mean activity coefficient
δ	Degree of hydrolysis, $degree^{-1}$
T_f	Freezing point depression
λ_i	Equivalent conductance of species i

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CHAPTER 1

1-1-0 INTRODUCTION

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

It is surprising that physico-chemical data on these substances and it's parent compound, Barbituric Acid, are practically non-existent. An up-to-date literature review (1907-1978) reveals that only density, viscosity, refractive index, partial molar volume, diffusion and conductances at 25°C have been studied by D. Jaganyi and M. Shamim(1). Sodium Barbital have been investigated by some workers but within narrow limits. Robert Taft and Helen Patton(2) have studied conductance, viscosity, density and refractive index of this compound in aqueous solution at 30°C. The solubility (2,3) of the salt has been reported as 17.3% by weight at 30°C and 17.8% at 25°C. The limiting equivalent conductance(2) of the salt has been reported to be 82.5 S cm^2 equiv-1 at 30°C and hence a limiting conductance of the diethyl barbiturate ion has been deduced to be 26.3 S cm^2 equiv-1. Conductance, density, refractive index, viscosity, diffusion and partial molar volume have also been studied at 25°C by D. Jaganyi and M. Shamim(1). The density(4), of solid Sodium Barbital has been found to be 1.202 g/cm^3.

1-1-1 THE OBJECTIVE

The scarcity of basic but related physico-chemical data like the freezing point depression and transference numbers made it desirable to study such aspects of these pyrimidines. Barbituric acid and it's Sodium diethyl derivative (Barbital) were chosen to investigate their behaviour in aqueous solutions at 25°C by measuring depression in freezing point and transference numbers. As with most organic acids and their salts, it was expected that these compounds will show strong ion-ion and ion-solvent interactions and undergo complex ion formation. If it is so, the information will give a better picture of the structural nature of the individual ions in the solution and hence their mode of physiological action.

1-1-2 DIMERIZATION.

A variety of physico-chemical measurements in many electrolyte solutions have shown that the concentration dependence of certain properties do not comply with the theoretical expectations. Almost in all cases such departures from the theory have been explained in terms of some kind of complex ion formation.

Selvaratnam and Spiro(4) have explained the anomalous concentration dependence of measured transference numbers in aqueous orthophosphoric acid solutions by postulating triple ions ($H_2PO_4.H^+.H_2PO_4$). likewise a kinetic, cryoscopic and potentiometric study by Pethybridge and Prue(5) in aqueous iodic acid solutions revealed the presence of similar triple ions, namely ($IO_3.H^+.IO_3$). Analogous triple ions have been identified in aqueous tartaric acid solutions by Shamim and Spiro(6) from their transference number measurements. Recently, transference number(6), conductance and cryoscopic(7) measurements in picric acid and potassium picrate solutions have shown the presence of dimeric picrate anions $(Pic)_2^{2-}$

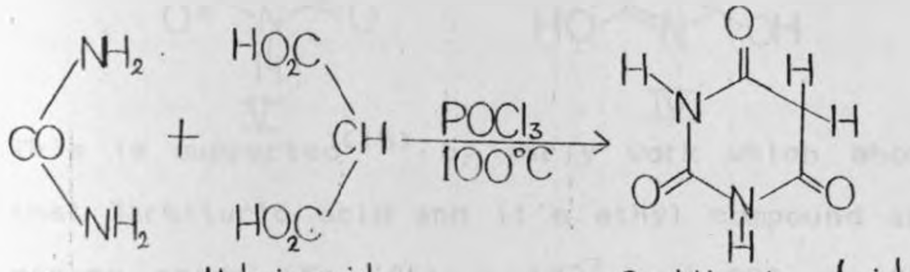
The phenomenon of dimerization in aqueous solutions is not something new. It has long been studied and is still a subject of active interest.

Several groups(8-11) have shown that carboxylic acids and their salts dimerize in aqueoussolutions. Farrer and Rossotti(12) have described hydrolytic equilibrium in sodium acetate and suggested the formation of $(CH_3COOH)_2$ and $(CH_3COO)_2H^-$ to explain their experimental results. They have also shown that higher oligomers form in solution of the acid, with dimerization being the major process occuring in the low concentration range. However, formation of carboxylic dimers and homoconjugated anions cannot be neglected even in aqueous solutions at higher concentrations of acid and salt(13)

1-2-0 CHEMISTRY OF THE COMPOUNDS

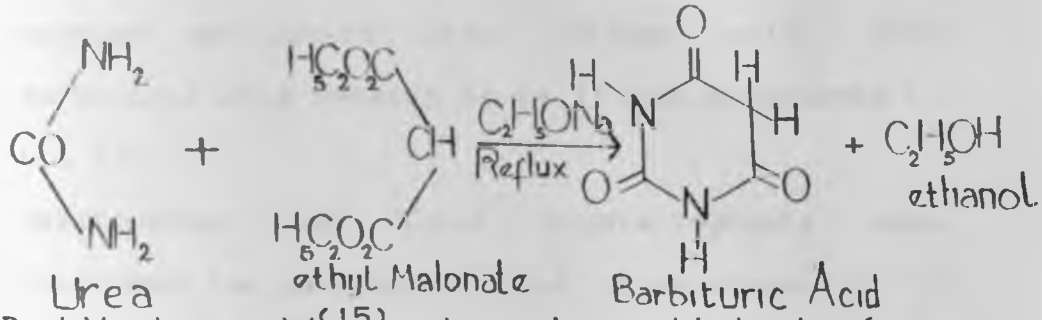
1-2-1 BARBITURIC ACID

Barbituric acid, 2:4:6-trihydroxypyrimidine (malonglurea) was originaly prepared by condensing urea with malonic acid with either phosphonyl chloride at 100°C (14-18) or acetyl anhydride (19)

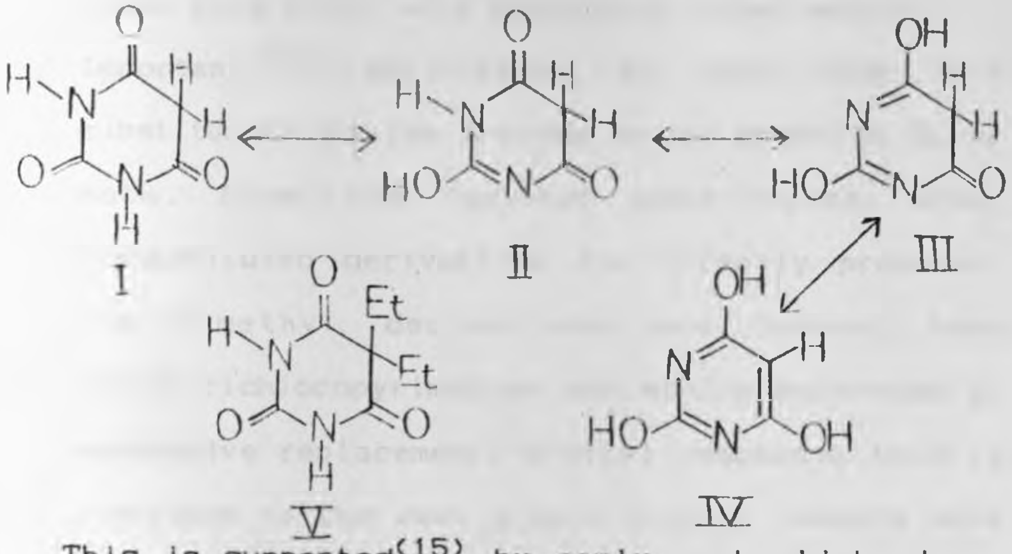


Urea Malonic acid Barbituric Acid

A much better synthesis is to reflux ethyl malonate with urea in ethanoic solution in the presence of sodium ethoxide as a condensing agent(15,18,20,21)



Barbituric acid(15) is also obtained from 2:4:6-triamino-hydroxy and triamino-pyrimidines by hydrolysis of the amino groups by hot mineral acid. Structure IV(15,18,22) represents Barbituric acid as 2:4:6-trihydroxypyrimidine, and this structure has been proposed because of the acidic nature of Barbituric acid.


I
II
III
IV
V

This is supported(15) by early work which shows that Barbituric acid and it's ethyl compound are strong acids (Ka 1051 x 10^{-7} and 383 x 10^{-7} respectively) whilst the 5,5-diethyl compound is a weak acid (Ka 0.37 x 10-7) and considered to have structure V(23).

On the other hand(18) Barbituric acid contains an active methylene group, since it readily forms an oximino derivative with nitrous acid. Thus Barbituric acid behaves as if it has structures I, II, III.

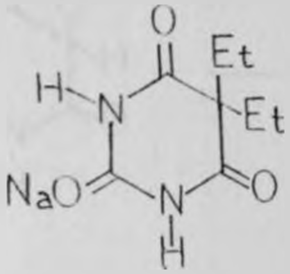
Spectroscopy and X-ray crystallography have confirmed the predominance of trioxo-form. It is planar but does not contain a cyclic π-electron system.

Barbituric acid(15,17) is a colourless crystalline solid with m.p. 243°C (dec), and it is not very soluble in water. It is a dibasic giving an insoluble salt prepared from ammonium salt and it forms crystaline acid salts with other metals.

Important(24) derivatives of the acid have substituents on the N-atoms or at position 5, or both. From the various substituted urea, N-substituted derivatives are directly prepared. The O-methyl derivatives are formed from 2:4:6-trichloropyrimidine and sodium methoxide by successive replacement, O-alkyl compounds tend to rearrange to the more stable N-alkyl isomers when heated with the appropriate alkyl halide.

1-2-2 SODIUM BARBITAL

Sodium(25) Barbital (medicinal) has the structure shown below:



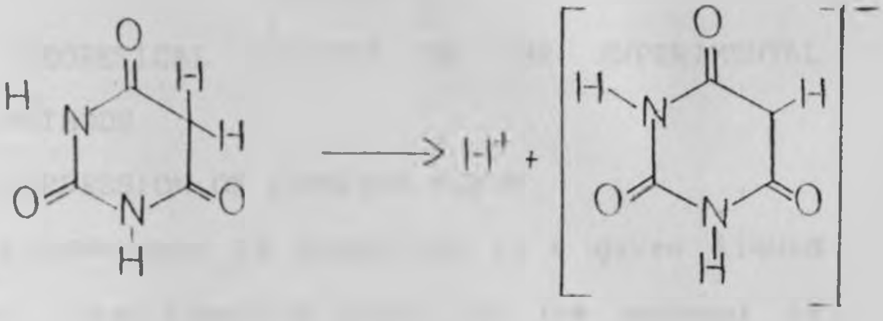
The dry salt itself is very light and fine. Aqueous solutions of sodium barbital are clear, colourless alkaline liquids. The salt undergoes hydrolysis in aqueous solutions and is also very unstable at a temperature above 90°C, decomposing rapidly to give ammonia.

Sodium barbital is a sodium derivative of barbitane (veronal)(26) which is prepared by condensing ethyl malonate with ethyl iodide in the presence of sodium ethoxide to give ethyl diethyl malonate. Upon allowing the latter to react with urea in the presence of an alcoholic solution of sodium ethoxide veronal (diethyl-barbituric acid or diethylmalonylurea) is produced.

$$CH_2(COOC_2H_5)_2 + 2NaOC_2H_5 + 2C_2H_5I \text{ ---> } (C_2H_5)_2C(COOC_2H_5)_2 + 2NaI + 2C_2H_2OH$$

Since the anions of the two compounds differ, the author has used B^- to represent the anion of Barbituric acid as ($B^- = (C_4H_3N_2O_3)-$) and B^{*-} for the anion of sodium barbital i.e. ($B^{*-} = [(C_2H_5)_2C_4H_3N_2O_3]-$), in this work.

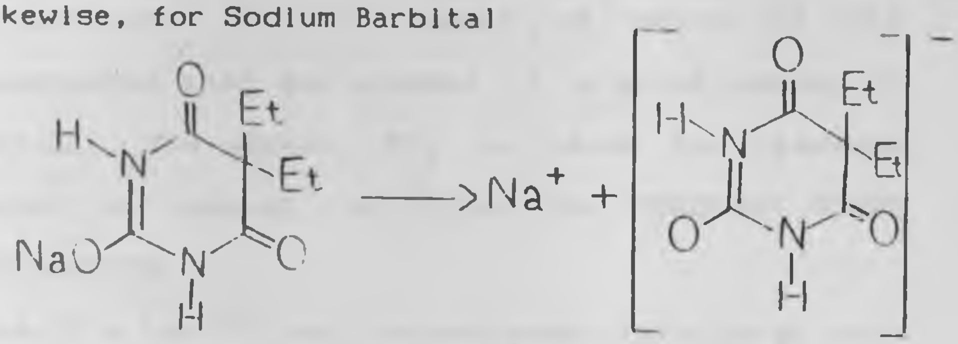
The dissociation scheme can thus be represented as



or

HB--------------------> H+ + B-

Likewise, for Sodium Barbital



or

NaB* --------------------> Na$^+$ + B*-

CHAPTER 2

2-1-0 THEORETICAL ASPECTS OF THE EXPERIMENTAL METHODS

2-1-1 DEPRESSION OF FREEZING POINT

When a substance is dissolved in a given liquid solvent, the freezing point of the solvent is lowered. This phenomenon constitutes a colligative property, the magnitude of which is proportional to the number of moles of the substances that are present in a given amount of solvent. The amount, DT_f, by which the freezing point is lowered, is called the FREEZING POINT DEPRESSION.

Raoult's law(27) and thermodynamic considerations, with special reference to the Clausius-Clapeyron(28) equation, give an equation for the freezing-point depression of solutions, namely

$$DT_f = \frac{m\ M_o R T_o}{1000 L_o} \tag{2-1}$$

where the freezing-point depression, DT_f is equal to the difference of the freezing point of the solvent, T_o and of solution, T_f; m represents the concentration of the solution in mol Kg^{-1}, R the universal gas constant, M_o the molecular mass of the solvent, L_o the latent heat of fusion of the solvent at T_o and K_f the molal freezing-point depression expected for a one molal solution. Alternatively (2-1) can be written as

$$DT_f = \frac{M_o g R T_o}{M G L_o} = \frac{1000 g K_f}{MG} \qquad (2\text{-}2)$$

where M is the molecular weight of the solute while G and g are the actual weights of solvent and solute used respectively.

Further refinements(29) of the expressions (2-1) and (2-2) give

$$DT_f = \frac{m K_f}{(1 + \varepsilon\, DT_f)} \qquad (2\text{-}3)$$

and

$$DT_f = \frac{1000 g K_f (1 - \varepsilon DT_f)}{MG} \qquad (2\text{-}4)$$

where ε is a correction constant for DT_f in deg^{-1}. The author has employed equations (2-3) and (2-4) to interpret the depression in freezing point.

2-1-2 DEVIATIONS FROM THE DEPRESSION IN FREEZING POINT LAW

The depression of freezing point is based on Raoult's Law for ideal binary solutions which are characterized by small solvent-solvent, solute-solute and solvent-solute interactions. In addition, the molecular volume of each species should be the same and there should be no volume and heat changes on mixing the two. In practice, most systems encountered are non-ideal. Nevertheless, Raoult's Law applies equally well for dilute non-ideal solutions where the mole fraction of the solvent approaches unity. However, this only holds if the solute retains it's molecular identity in the solution. Otherwise, within the limitations of dilute solutions, deviation from the depression of freezing point law may arise due to the following reasons:

(a) The solute dissociates to form two or more molecules or ions, thus increasing the effective number of particles in solution. The depression would be greater since the colligative property is dependent on the number, rather than the nature of the solute present.

Hexaphenylethane dissolved in napthalene dissociates partially to form the triphenylmethyl radical, and the observed melting points for the mixture are lower than those of benzene in napthalene(30). The phenomenon corresponds to most weak and strong electrolytes in which ionization increases the effective number of solute particles.

(b) The solute associates to form dimers or trimers, hence the effective number of the solute molecules is reduced and the observed depression will be lower than that predicted for the ideal case. One good example is acetic acid. It's lowering of the melting point of napthalene is less than that of benzene or biphenyl, both of which show essentially ideal behaviour in napthalene(31,32).

(c) The solvent A and solute B combine partially in the liquid phase to form a third substance AB. The formation of AB does not increase the number of the solute molecules in the solvent but decreases the number of solute molecules and free solvent. The mole fraction of solvent is, therefore, smaller, and the mole fraction of the solute greater than expected; hence the depression of freezing point is greater than that predicted by the freezing point law. M-Dinitrobenzene forms such a molecular compound with napthalene$^{(32)}$ and picric acid in napthalene$^{(33)}$ shows a similar deviation.

2-1-3 MODIFICATION OF THE DEPRESSION OF FREEZING POINT EQUATION

The general form of the depression of freezing point expression for ideal binary solutions has been derived as

$$DT_f = mK_f \qquad (2\text{-}1)$$

and the more accurate form as

$$DT_f = \frac{mK_f}{(1 + \varepsilon_a DT_f)} \qquad (2\text{-}3)$$

In the event of non-ideal conditions, where the interactions in the solutions results in a change in the number of solute molecules, the depression is found to vary accordingly; increasing with increase in the number of solute fragments and decreasing with a decrease. For a strong electrolyte such as NaCl(34) where complete dissociation takes place, the depression in freezing point has been observed to be twice of that expected for an ideal case. In general, to accomodate all different species present in a solution, equations(2-1) and (2-3) should be modified accordingly, i.e

$$DT_f = nmK_f \qquad (2\text{-}5)$$

and

$$DT_f = \frac{nmK_f}{(1+ \varepsilon DT_f)} \qquad (2\text{-}6)$$

where n is the effective number of solute species (molecules or ions) present in the solution at equilibrium.

For a 1:1 electrolyte solution, n equals 2. However, if Barbituric acid behaves as proposed below:

$$HB \xrightleftharpoons{\alpha} H^+ + B^- \qquad (2\text{-}7)$$

$$B^- + B^- \xrightleftharpoons{\beta} D^{2-} \qquad (2\text{-}8)$$

where α is the degree of dissociation for step (2-7) and β is the degree of formation for step (2-8) respectively, then the concentration of each species in a m molal solution will be:

$[H^+]=m\alpha \quad [B^-]=m(\alpha-2\beta) \quad [D^{2-}]=\beta m \quad [HB]=m(1-\alpha)$

Thus the total number of solute-solute would be

$$nm = (1+\alpha-\beta)m \qquad (2\text{-}9)$$

where

$$n = 1+\alpha-\beta$$

Substituting (2-9) into equations (2-5) and (2-6) we obtain

$$DT_f = (1+\alpha-\beta)mK_f \qquad (2\text{-}10)$$

and

$$DT_f = \frac{(1+\alpha-\beta)mK_f}{(1+\varepsilon\, DT_f)} \qquad (2\text{-}11)$$

where K_f and ε for water(35,36) are 1.860 degree molal^{-1} and 0.54×10^{-3} degree^{-1} respectively. The calculations for α and β, by successive approximations, were carried out in the following way:

(a) From equation (2-7)

$$K_A = \frac{a_{H+}\cdot a_{B-}}{a_{HB}} = \frac{(m\alpha\ .\ \gamma_{H+})m(\alpha-2\beta)\ \gamma_{B-}}{a_{HB} \qquad m(1-\alpha)\ \gamma_{HB=1}} \qquad (2\text{-}12)$$

which gives

$$\alpha = \frac{-(K_A-2m\beta\quad\gamma^2)+((K_A-2m\beta\quad\gamma^2)^2+4m\quad\gamma^2K_A)^{1/2}}{2m\gamma^2} \qquad (2\text{-}13)$$

Here $K_A=1.01 \times 10^{-4}$ mol kg^{-1}: the first dissociation constant of Barbituric acid $^{(37)}$.

(b) From equation (2-8) we get the formation constant of dimeric anions.

$$K_D \qquad \frac{m\beta\quad D2-}{m(\alpha-2\beta)\,\gamma_{D2-}\ m(\alpha-2\beta)\,\gamma_{D2-}} \qquad (2\text{-}14)$$

which yields

$$\beta = \frac{(4\,\alpha m K_{D^{2-}}\,\gamma_{D^{2-}}+\gamma_{D^{2-}})\ +\ ((4\,\alpha m K_{D^{2-}}\gamma_{D^{2-}}+\gamma_{D^{2-}})^2}{8mK_D\quad D}$$

$$\frac{-\,16\,\alpha^2 m^2 K_{D^{2-}}\,\gamma_{D^{2-}})^{1/2}}{8mK_{D^{2-}}\,\gamma_{D^{2-}}} \qquad (2\text{-}15)$$

The calculations were initiated by assuming $\alpha=1$, $\beta=0$, to get an initial value of α from (2-13). The value so obtained was substituted in equation (2-15) to obtain a β value. The iteration was continued until α and β were internally consistent and constant. The author has employed a Basic program (APPENDIX 1) to compute α and β values for the entire concentration range studied using K_D ranging from 2.8-4.0 mol kg^{-1}. It was tested that any initial value of α , in the range 0-1, would converge to yield identical final α and β values.

The activity coefficients appearing in the equations were obtained using equation

$$\log \gamma_i = -0.4918|z^2| f(I)$$

or

$$\log \gamma_{\pm} = -0.4918|z_+z_-| f(I) \qquad (2\text{-}16)$$

where

$$f(I) = \frac{I^{1/2}}{1+B_3a^oI^{1/2}}$$

with I being the ionic strength ($\alpha + \beta$)m, B_3 and a^o are constants taken as 0.3248×10^8 and $5A^0$ respectively(35).The activity coefficients for dimeric anions were obtained using

$$\log \gamma_{D^{2-}} = \frac{-A\ z_D\ I^{1/2}}{1+B_3a^oI^{1/2}} = \frac{-4AI^{1/2}}{1+B_3a^oI^{1/2}} \qquad (2\text{-}17)$$

Let's now consider Sodium Barbital, NaB*, which is a strong 1:1 electrolyte. Accordingly, it's dissociation in solution can be written as:

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

since the salt undergoes hydrolysis the subsequent equilibrium must be

$$B^{*-} + H_2O \overset{\delta}{\rightleftharpoons} HB^{*} + OH^{-}$$

where δ is the degree of hydrolysis.

The concentration of each species in a m molal of NaB^{*} solution would be :

$$[Na^{+}] = m, \quad [B^{*-}] = m(1-\delta),$$
$$[HB^{*}] = m\delta \quad [OH^{-}] = m\delta \qquad (2\text{-}18)$$

Thus the total number of ions and molecules will be:

$$m + m(1-\delta) + m\delta + m\delta = 2m + m\delta$$
$$= m(2 + \delta) \qquad (2\text{-}19)$$

Substituting the concentration values of the species in (2-9) we obtain

$$DT_f = (2 + \delta)mK_f \qquad (2\text{-}20)$$

and

$$DT_f = \frac{(2+ \delta)mK_f}{(1+ \& DT_f)} \qquad (2\text{-}21)$$

K_f and $\mathcal{E}$ for water (35,36), are 1.86 degree mol^{-1} and 0.54×10^{-3} degree respectively as mentioned for Barbituric acid. The degree of hydrolysis (37), 6.47×10^{-7} was found to affect only the fifth and sixth decimal places and was thus neglected in this work.

2-1-4 ACTIVITY COEFFICIENTS: BASIC CONCEPTS AND DEFINITIONS

For ideal solutions, the molal free energy $\bar{G}$ of any component in the liquid is

$$\bar{G} = \bar{G}_o + RT \ln(P) \qquad (2\text{-}22)$$

where P is the partial pressure of the component in the vapour phase in equilibrium with the solution; and $\bar{G}_o$ is the standard molal free energy (under one atmosphere). According to Henry's Law, the vapour pressure of a solute is proportional to it's mole fraction x in a dilute solution. Hence (2-22) becomes

$$\bar{G} = \bar{G}_o + RT \ln(x) \qquad (2\text{-}23)$$

Since for dilute solutions the mole fraction is proportional to the concentration m, (2-23) may be rewritten as

$$\bar{G} = \bar{G}_o + RT \ln(m) \qquad (2\text{-}24)$$

For use in real, non-ideal situations, (2-24) is modified by the introduction of activity coefficient; thus

$$\bar{G} = \bar{G}_o + RT\ln(m\gamma) \qquad (2\text{-}25)$$

At infinite dilution the system tends towards ideal behaviour where γ approaches unity. The product $(m\gamma)$ is called the activity of a particular component and is represented by the symbol ʻaʼ, i.e.

$a = (m\gamma)$ so that

$$\bar{G} = \bar{G}_o + RT\ \ln(a) \qquad (2\text{-}26)$$

2-1-5 ACTIVITY COEFFICIENTS FROM CRYOSCOPIC MEASUREMENTS

The condition for ice to be in equilibrium with pure liquid water (A) at the freezing point T_o is that the molal free energy is the same in each phase; i.e.

$$\bar{G}_{ice(T_o)} = \bar{G}_{A(T_o)} \qquad (2\text{-}27)$$

As solution always has a lower freezing point, T_f; the condition for equilibrium is given by:

$$\bar{G}_{ice(T_f)} = \bar{G}_{A(T_f)} = \bar{G}_{A(T_f)} + RT_f(a_A) \qquad (2\text{-}28)$$

where $\bar{G}_{A(T_f)}$ is the molal free energy of the solvent at T_f. The increase in free energy of a mole to become pure liquid water at T_f is given by

$$\bar{G}_{T_f} = \bar{G}_{A(T_f)} - \bar{G}_{ice(T_f)} \qquad (2\text{-}29)$$

From the Gibb's-Helmholtz equation

$$\frac{d}{dT}\left(\frac{D\bar{G}}{T}\right) = \frac{-L}{T^2} \qquad (2\text{-}30)$$

where L is the latent heat of fusion of one mole of ice. It follows, therefore that

$$-R \ln (a_A) = \frac{D\,GT_f}{T_f} = -\int_{T_o}^{T_f} \frac{L\,dT}{T^2} \qquad (2\text{-}31)$$

The latent heat of fusion can be written as a function of temperature

$$\bar{L} = \bar{L}_o + \bar{J}\,(T_f - T_o)$$

where $\bar{L}_o$ is the latent heat of fusion at T_o and $\bar{J}$ the difference of molal heat capacities of liquid water and ice. In most work J can be assumed to be independent of temperature. Then

$$-\ln(a_A) = \frac{1}{R}\,(L_o - JT_o)\left[\frac{1}{T_f} - \frac{1}{T_o}\right] + \frac{J}{R}\,\frac{\ln T_o}{T_f} \qquad (2\text{-}32)$$

Introducing the depression of freezing point $DT_f = T_o - T_f$, we obtain

$$-\ln (a_A) \quad \frac{\bar{L}_o DT_f}{RT^2} + \left[\frac{\bar{L}_o}{RT} - \frac{\bar{J}}{2R} \right] \frac{DT_f}{T_o} \qquad (2\text{-}33)$$

By Gibb's-Duhem equation where

$$m \ln (a_A) + m \ln(a_B) = 0,$$

$$d\ln (a_B) = \frac{1000 L_o . dDT_f}{M_A R T_o \quad m} + \frac{2000}{M_A R T_o} \left[\frac{L_o}{T_o} - \frac{J}{2} \right] \frac{DT_f dDT_f}{m}$$

$$\frac{dDT_f}{K_f m} + \frac{DT_f dDT_f}{m} \qquad (2\text{-}34)$$

(M_A = molecular mass of water)

where $K_f^{(35)}$ and $\varepsilon^{(36)}$ for water are 1.86 degree molal^{-1} and 0.54 x 10-3 deg^{-1} respectively. The integration of (2-33) is facilitated by introducing a function defined by

$$j = 1 - \frac{DT_f}{nK_f m} \qquad (2\text{-}35)$$

Then

$$\frac{d\ DT_f}{nK_f m} = -dj + (1-j)d\ln(m)$$

$$d\ln\gamma = -dj - j\,d\ln(m) + \frac{\varepsilon DT_f d\ DT_f}{nm}$$

$$-\ln\gamma = j + \int_0^m j\ d\ln(m) - \varepsilon\int_0^{\Delta T_f}\frac{DT_f dDT_f}{nm} \qquad (2\text{-}36)$$

The second term $\int_0^m j\ d\ln(m)$ is the most important and is obtained graphically from a plot of j/m versus m(37) and using the Simpon's rule(38). The area under the curve is divided into an even number of strips of width h. It is then calculated using the equation

$$\begin{aligned}\text{Area} = h/3\ (&\Sigma\text{first and last coordinates} \\ &+ 4(\Sigma\text{ even ordinates}) \\ &+ 2(\Sigma\text{ remaining odd ordinates}))\end{aligned} \qquad (2\text{-}37)$$

The last term in (2-36) is equivalent to

$$\varepsilon K_f \int_0^{DT_f} (1 - j)\ d\ DT_f$$

and may also be obtained graphically using the method described above. However, it's contribution is very small and is generally ignored(39).

2-1-6 THE DEBYE-HUCKEL LIMITING LAW

Since the Debye-Huckel equation would be used to calculate activity coefficients in the present work, it is therefore appropriate to discuss the law in some detail. The Debye-Huckel Limiting Law takes the general form:

$$\log \gamma_i = -A \left| Z^2 \right| I^{1/2} \qquad (2\text{-}38)$$

which expresses the variation of γ_i -the activity coefficient of a single ion with the ionic strength I of the solution, A is the constant of Debye-Huckel equation for the activity coefficient and Z is the absolute value of the valency of the ions. In practise, it is impossible to evaluate the activity coefficient of a single ionic species because the law of electroneutrality forbids a single ion to exist independently in solution. Experimental measurements yield the mean activity coeficient γ which is given as

$$\log \gamma = - A \left| Z_+ Z_- \right| I^{1/2} \qquad (2\text{-}39)$$

where Z+, Z- are the valencies of the cation and anion respectively.

The Debye-Huckel Limiting Law has been derived by regarding an ion as a point charge surrounded by an oppositely charged ionic atmosphere. This only holds at low concentrations. At appreciable concentrations, the thickness of the ionic clouds becomes comparable to the radius of the ion. To accomodate this situation, equation (2-39) was modified to

$$\log \gamma = \frac{- A \left| Z_+ Z_- \right| I^{1/2}}{1 + B_3 a^o I^{1/2}} \qquad (2\text{-}40)$$

where A, B_3 are constants depending on the nature of solvent and temperature and 'a^o' is the distance of closest approach between the ions. The equation (2-39) is known as the Debye-Huckel-Onsager Limiting Law.

2-2-0 TRANSFERENCE NUMBER.

2-2-1 Introduction and Definitions

The electrical conductance of an electrolyte solution measures the ability of the solution as a whole to carry an electric current. A transference or transport number, on the other hand, is a measure of the relative transfer of a particular constituent in the solution when an electric current is passed. The common definition runs as: The transference or transport number, t_i of a species `i` in a given electrolyte solution is the fraction of the total current carried in the solution by that species.

The above definition is called the "electric transport number".(40,41,42,43) and is the definition found in most textbooks and some papers in the literature. It follows that t_i is dimensionless, positive for an ionic species and zero for all uncharged molecular species, and that:

$$\sum_i t_i = 1 \tag{2-41}$$

The transport number, t_i is related to the concentrations, charges and mobilities of the ionic and molecular species in the solution as shown:

$$t_i = \frac{u_i\ m_i\ |z_i|}{u_i\ m_i\ |z_i|} = \frac{\lambda_i\ m_i\ |z_i|}{\sum_i \lambda_i\ m_i\ |z_i|} = \frac{\lambda_i\ C_i}{\sum_i \lambda_i\ C_i} = \frac{\lambda_i C_i}{\Lambda_c} \tag{2-42}$$

where u_i is the mobility of the species i (cm s^{-1}), λ_i is the equivalent conductance (cm^2 ohm^{-1} gram-equiv^{-1}), m_i is the molality (mol kg^{-1}), C_i is the normality. (gram equiv. litre^{-1}),

Z_i is the algebraic charge number, Λ the conductance and c the normality of the solution as a whole.

The various terms in equation (2-42) can be derived from each other using the relations

$$C_i = m_i \, |z_i| \qquad (2\text{-}43)$$

$$\lambda_i = u_i \; F \qquad (2\text{-}44)$$

$$\Lambda c = \sum_i \lambda_i \; c_i \qquad (2\text{-}45)$$

where F is the Faraday constant (96,500 coulombs gram-equiv.$^{-1}$).

As an example, in aqueous solution of oxalic acid there are present as solutes the (hydrated) ionic species H^+, $HC_2O_4^-$, and $C_2O_4^{2-}$, and the molecular species $H_2C_2O_4$. From equation (2-42):

$$t_{H^+} = \lambda_{H^+} \, m_{H^+} / \Lambda c$$

$$t_{HC_2O_4^-} = \lambda_{HC_2O_4^-} \, m_{HC_2O_4^-} / \Lambda c$$

$$t_{C_2O_4^{2-}} = \lambda_{C_2O_4^{2-}} \, m_{C_2O_4^{2-}} / \Lambda c$$

$$t_{H_2C_2O_4} = 0$$

$$\Lambda c = \lambda_{H^+} m_{H^+} + \lambda_{HC_2O_4^-} m_{HC_2O_4^-} + 2\lambda_{C_2O_4^{2-}} m_{C_2O_4^{2-}}$$

It is not often realized that the electrical transport number can be derived from experimental data only if the electrolyte is strong, i.e. if there is complete dissociation into ions and no complex ion formation takes place. In some cases, the electrical transport number can be approximately calculated from experimental data(42).

In many instances it cannot be obtained at all no matter how much experimental information is available, so that the practical utility of the above definition is limited. This is because the electrical transport number is defined as the property of an individual ionic or molecular species, and in the laboratory, only the overall transfer of electrolyte can be measured. In order to define a directly observable number it is necessary to introduce the term 'ion constituent' which is the ion-forming portion of an electrolyte without reference to the extent to which it may actually exist in the dissociated state. As an illustration, in the aqueous oxalic acid solution the hydrogen ion constituent (H^+) exists only partly in the form of free (hydrated) H^+ and exists also in the form of species as (hydrated) $HC_2O_4^-$ and $H_2C_2O_4$. It is the concentration of H^+ ion-constituent, not of H^+, that is determined by chemical analysis such as titration with alkali. Similarly, $C_2O_4^{2-}$ ion constituent exists in the form

$C_2O_4^{2-}$, $HC_2O_4^-$, and $H_2C_2O_4$. The species chosen as ion constituents must not dissociate into smaller particles under experimental conditions.

It is now possible to give a second definition, which is often used in literature and which the author has employed in this work.

" The transference number T_R of a cation or anion constitient R is the net number of gram-equivalents of that ion constituent that crosses an imaginary plane in the solution, in the direction of the cathode or anode respectively, when one faraday of electricity (96,500 Coulombs) passes across that plane" (43-50). (2-46)

This is the "ion constituent transference number" (42) or simply the "transference number". The plane is usually taken as fixed with respect to the solvent, and the transference numbers are measured on this basis. It follows that:

$$\sum_R T_R = 1 \qquad (2\text{-}47)$$

because the total number of gram-equivalents of all the ion constituents so transferred in both directions equals the number of faradays of electricity passed through the solution. In terms of the properties of the species:

$$T_R = \frac{\left(\frac{z_R}{z_R}\right) U_i m_i n_{R,i} \left(\frac{z_R}{z_R}\right)}{U_i m_i z_i} = \frac{\left(\frac{z_R}{z_R}\right) \sum_i \lambda_i m_i n_{R,i} \left(\frac{z_R}{z_R}\right)}{\sum_i \lambda_i m_i z_i}$$

$$= \frac{\left(\frac{z_R}{z_R}\right) \sum_i \lambda_i c_i \left(\frac{n_{R,i}}{z_i}\right)}{\sum_i \lambda_i c_i} \qquad (2\text{-}46)$$

where $n_{R,i}$ is the number of gram-equivalent of ion constituent R in one gram-formula-weight of species i.

The term (Z_R / Z_R) is (+1) or (-1) for a cation or an anion constituent respectively.

The electrical transport number and the transference number becomes identical numerically for strong 1:1 electrolytes. A particularly simple form results from a strong univalent electolyte like sodium acetate in water:

$$T_{Na} = t_{Na} = Na+ / (Na+ + OAc-)$$
$$= 1 - T_{OAc} = 1 - t_{OAc}$$

Since strong electrolytes are completely dissociated at infinite dilution, the limiting transference or electrical transport numbers can be calculated from tables of ionic conductances(51). The ion constituent transference number, unlike the electrical transport number, is directly obtained from experimental data without any prior knowledge about the detailed composition of the solution.

2-2-2 CONCENTRATION DEPENDENCE OF TRANSFERENCE NUMBERS

According to the Debye-Huckel-Onsager theory the mobility of ions should change with concentration. The transference numbers, therefore, provide a very good test of the theory.

The relationship between the transference number of any ion-constituent and the concentration can be obtained using the conductance equation

$$\lambda_i = \lambda_i^{\circ} - \frac{B_1 \quad {}_i + 1/2\ B_2\ I^{1/2}}{1 + B_3\ a^{\circ}\ I^{1/2}} \qquad (2\text{-}48)$$

The transference number of the +ve ion-constituent, T+, of an electroltye can thus be written as:

$$T_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{\lambda^{0} - (B_1 \quad {}_+ + 1/2\ B_2)\ I^{1/2}}{\lambda^{0} - (B_1\ {}^{0} + B_2\ )\ I^{1/2}} \qquad (2\text{-}49)$$

In this equation, the viscosity correction cancels out as it appears both in the numerator and the denominator. By differentiating equation (2-48) with respect to $c^{1/2}$, and including the condition that c approaches zero, gives;

$$\left(\frac{dT_+}{d\,c^{1/2}}\right)_{c \dashrightarrow 0} = \frac{T^o - 0.5B_2}{\Lambda^o} \qquad (2\text{-}49)$$

in which

$$T_+^o = \frac{\lambda_+^o}{\lambda_+^o + \lambda_-^o}$$

It shows that when T_+ is close to 0.5, T_+ will not vary with concentration, but will do so the more it differs from 0.5. The literature results have been found to follow equation (2-49) very closely.

2-2-3 METHODS OF MEASURING TRANSFERENCE NUMBERS

There are 3 methods of measuring transference numbers.

(i) Moving Boundary method

The moving boundary method (52-54) for measuring transference numbers has been used successfully for both strong and weak electrolytes. The theory of this method has been extended to systems of strong electrolytes (55) and buffer(56) mixtures. Lodge(57) was the first person who demonstrated the possibility of following the boundary visually. Subsequent work by Whetman(58) , Nernst(59), Masson(60), Denison and Steele(61), made substantial improvements in the method. The work of Cady(62,63), Smith(64), McInnes and Longsworth(65,66) made it capable of producing data of high accuracy.

In the direct moving boundary method , an electric current maintains and moves a fairly sharp boundary between the solution under investigation (leading solution) and the following or indicator solution. The movement of the boundary can be easily followed visually because of the difference in the refractive indices of the two solutions. Under the influence of the applied potential, the boundary moves upwards or downwards depending upon whether the indicator solution behind the boundary is heavier or lighter than the leading solution.

(ii) E.M.F. Method

This is a theoretically sound method. It involves measurement of the e.m.f. of a concentration cell with transference (E_t) and the e.m.f. of a related cell without transference (E). The transference number T_R of the ion-constituent R is related to E_t and E by the following equation:

$$T_R = \frac{E_t}{E} \qquad (2-50)$$

This method is useful for a survey over a wide range of temperature and concentration.

(iii) The Hittorf's Method

Since the Hittorf's method has been employed in this work it is desirable to describe the theory of this method in some detail;

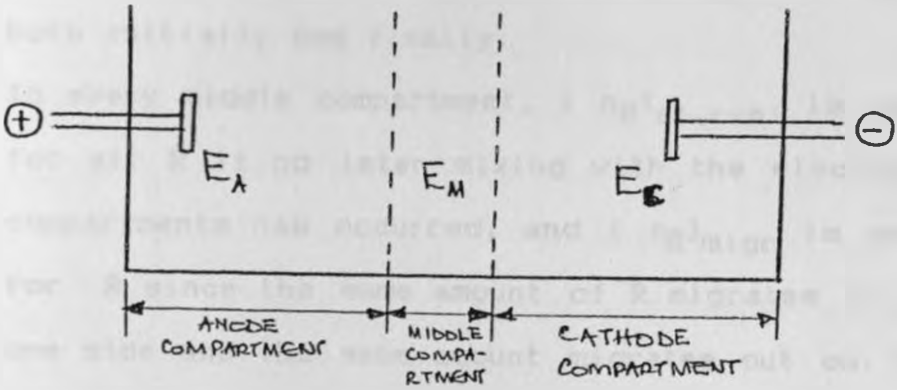
2-2-4 THE HITTORF'S METHOD

In this method, a known quantity of electricity is passed through a cell filled with the solution whose transference numbers are to be determined. The solutions in various sections of the cell are then separated, weighed, and quantitatively analyzed. The method is sometimes called the "analytical or gravimetric " method.

In Fig (2-2-1), E_A and E_C are the anodic and cathodic electrode sections or compartment of a general Hittorf cell. M_A, M_m and M_C are the three middle sections

(anode middle, middle middle, cathode middle). The dotted lines stand for the boundaries which, for the reason given in (2-2-1), are considered fixed with respect to the solvent throughtout the experiment. It follows from the conservation of mass that in every compartment:

Fig (2-2-1): Schematic diagram of a Hittorf cell



$$[n_R]_{final} = [n_R]_{initial} + [\ n_R]_{el.rxn.} + [n_R]_{migr.} \qquad (2\text{-}51)$$

where n_R is the number of gram-equivalents of ion constituent R in solution, referred to a fixed weight of solvent so that definition for transference number given by equation (2-46) can be applied. The last two terms in equation (2-51) stand for the changes resulting from the electrode reactions, el. rxn., and migrations respectively. Equation (2-51) can be written for every ion constituent present, but the resulting equations are related by the necessity for electroneutrality both initially and finally.

In every middle compartment, $[\ n_R]_{el.rxn.}$ is zero for all R if no inter mixing with the electrode compartments has occurred, and $[\ n_R]_{migr}$ is zero for R since the same amount of R migrates in on one side and the same amount migrates out on the other side, so that:

$$[\text{middle compartment}] \quad [n_R]_{final} = [n_R]_{initial} \qquad (2\text{-}52)$$

In every experiment the validity of equation (2-52) should be tested by comparing the initial and the final concentrations in the middle compartment, for incorrect values of the transference numbers are obtained unless all the concentration changes are localized in the electrode compartments.

In the anode or cathode compartment, $[n_R]_{final}$ and the mass of solvent are found from the final concentration and weight of the electrode compartment solution. $[n_R]$ $_{initial}$ the number of gram-equivalents of ion constituent R initially dissolved in this same mass of solvent, is then calculated either from the known initial concentration or, using equation (2-52), from the final concentrations in the middle sections. The value of $[n_R]_{el.rxn.}$ - which can be calculated by applying Faraday's laws of electrolysis to the known electrode reaction is proportional to q, the number of faradays of electricity passed through the cell. Similarly, from equation (2-46) in section (2-2-1), $(n_R)_{migr.}$ is proportional to q and depends on T_R, the transference number of R. Hence equation (2-51) becomes:

$$
\begin{aligned}
\text{[Anode or cathode compartment]} &= [(n_R]_{final} - [n_R]_{initial} \\
&= [\ n_R]_{el.rn.} + [\ n_R]_{migr.} \\
&= q\phi_R \qquad (2\text{-}51)
\end{aligned}
$$

The change in n_R per faraday, is a function of T_R as shown in the following example:

Jones and Dole(67) electrolyzed aqueous $BaCl_2$ solutions at 25°C, using Ag anode and AgCl cathode. In their sixteenth run they passed 0.024644 faradays of electricity through a 0.24745 molar (4.949 wt.%) solution of $BaCl_2$ (gram-equiv.wt. 104.137). The final concentrations in the middle compartments M_A, M_M, M_C were 4.946, 4.947 4.946 wt.%, so that no appreciable mixing has occurred, and the initial concentration may be taken as 4.947 wt.% $BaCl_2$. The anode solution after the run weighed 121.58g and contained 4.148 wt.% $BaCl_2$ or 5.043g $BaCl_2$ and 116.54g of water. Thus in the anode compartment:

$[n_{BaCl}]_{final}$ = 5.043/104.137 = 0.04842 gram-equiv.

$[n_{BaCl}]_{initial}$ =

= (4.947 x 116.54) / ((100-4.947) x 104.137)

= 0.05824 gram-equiv.

T_{Ba} = (0.04842 - 0.05824) /(-0.024644) = 0.398

The same result is obtained by an analogous examination of the cathode compartment.

CHAPTER 3

EXPERIMENTAL PROCEDURES

3-1-0 CHEMICALS

3-1-1 DISTILLED WATER

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

3-1-2 SODIUM CHLORIDE

B.D.H. A.R grade sodium chloride was used without any purification.

3-1-3 SODIUM HYDROXIDE

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

3-1-4 SILVER NITRATE

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

3-1-5 OXALIC ACID

B.D.H. A.R grade oxalic acid was used without any purification.

3-1-6 BARBITURIC ACID

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

3-1-7 SODIUM BARBITAL

B.D.H. A.R grade Sodium Barbital was dried for 30 hours at 90°C in a temperature controlled oven. Shaking of the salt was done occassionally to remove any trapped vapour. The dried salt was powdery and free of lumps.

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

3-1-8 ETHANOL

A.R grade ethanol was used without any purification, for cleaning the cathode section of Hittorf's cell before and after every electrolysis prior to drying in the oven.

3-1-9 PREPARATION OF SILVER CHLORIDE AND OTHER SOLUTIONS

(a) Silver Chloride

Equimolar solutions of NaCl and $AgNO_3$ were prepared and were mixed together to obtain AgCl precipitates. The AgCl so obtained was thoroughly washed with conductivity water on filter paper and dried. The white precipitates of AgCl turned grey after drying and exposure to light and air.

(b) Barbituric Acid

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

(c) Sodium Barbital

Solutions of sodium barbital were prepared by weighing B.D.H. A.R grade sodium barbital and transfered it into a calibrated volumetric flask. The weighing bottle was wiped out using tissue paper and the funnel used to transfer the salt was wide enough to transfer the salt right into the neck of funnel to prevent the salt particles from being blown away. This was necessary as the dry salt is so light and fine that it adheres to any vessel used in weighing. The difficulty was overcome by wiping the weighing vessel dry with tissue paper, so that the amount sticking to it is minimal. Since the weights are determined by the difference of weights, the difference in weigts, the amount sticking made no difference. The solutions were made up with water at 25°C

(d) Oxalic Acid

Solutions of oxalic acid were prepared by weighing B.D.H. A.R grade oxalic acid and transfering into a calibrated volumetric flask.

The solutions were made up with water at 25°C.

(e) Sodium Hydroxide

A roughly weighed amount of sodium hydroxide was dissolved in distilled water and stored in a one-litre volumetric flask. Soda-lime guard tube was used to protect the solution from atmospheric carbon dioxide. The concentration of the solution so prepared was determined by titration against oxalic acid.

3-1-10 CALIBRATION OF MEASURING FLASKS

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

Three measuring flasks of 250 ml capacity were calibrated. For the purpose of identification, different marks were etched on different flasks.

To calibrate a flask, it was thoroughly cleaned using chromic-sulphuric acid cleansing mixture followed by several rinses with distilled water. The flask was then filled with air-free distilled water and was equilibrated in a constant temperature bath for an hour. After the flask had attained the temperature of the bath, the meniscus was brought upto the calibration mark with the help of a 1-ml pipette. Any drop of water sticking to the neck of the flask above the calibration mark was removed by wrapping a tissue paper on a glass rod and inserting it into the neck of the flask to absorb the sticking droplets. The flask was then weighed and the exact volume calculated by dividing the mass of water in the flask by the density of water at 25°C. The density of water at 25°C was taken as 0.99707 g cm^{-3}. The mass of the water in the flask was determined by weighing the dried flask, which was then cooled to room temperature while in a dessicator containing silica gel. The difference of the two weighings gave the mass of the water.

3-2-0 DEPRESSION OF FREEZING POINT APPARATUS

Depression of freezing point is a popular method used for the molecular weights determinations. The apparatus and the procedure are described in almost all physical chemistry texts.(68-70)

The conventional apparatus consists of essentially two test-tubes, one held inside the other, which are placed in a cooling bath of ice-common salt mixture. The bath is covered with a lid which has holes for the tubes to pass through in the middle and a bath stirrer and a thermometer to pass on the side. The inner tube is fitted with a Beckmann thermometer and a single-ring glass stirrer. Stirring is done manually by an up and down movement of the stirrer through the solution. This causes tremendous fatigue and invariably causes splashing of solvent or solution. Usually a known amount (weight) of solvent is introduced in the inner tube and it's freezing point determined. Having done so, a known amount (weight) of solute is added through the side arm. During freezing point determination of solvent, the interior walls of the side arm accumulates a lot of water vapour and it becomes difficult to introduce all the solute accurately. Some of the substances get stuck on the wall of the moist arm and hence an unknown amount (less than what was weighed) goes into solution. Morever, dissolving the added substance properly causes another problem. Apart from the above mentioned difficulties, maintaning a constant temperature of the cooling bath constitutes another problem. An ice-common salt mixture does not keep temperature constant for long.

For the present work, the apparatus was modified to overcome these difficulties. The whole assembly is shown in Fig.(3-2-1)

The single glass stirrer was replaced by a seven-ring perspex-nylon stirrer Fig. (3-2-2). There was no side-arm(71), and the solutions were prepared in a volumetric flask and transferred into the inner tube. After each experiment, the inner tube together with the solution was replaced by another thoroughly washed and dried tube filled with a new solution of a different concentration. The ice-salt mixture was renewed after each experiment and it´s temperature kept constant by stirring every now and then.

Figure(3-2-1): THE FREEZING POINT APPARATUS

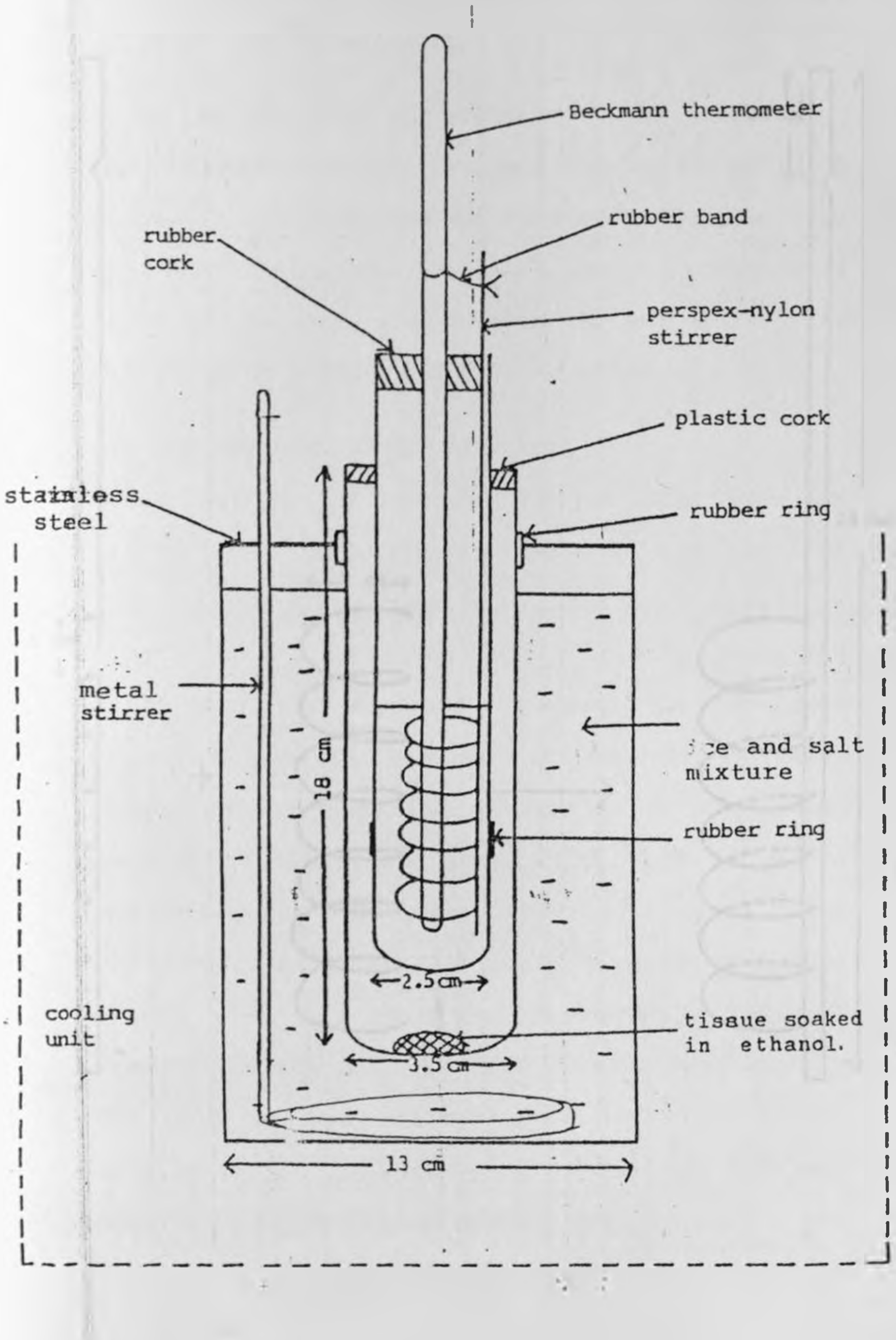
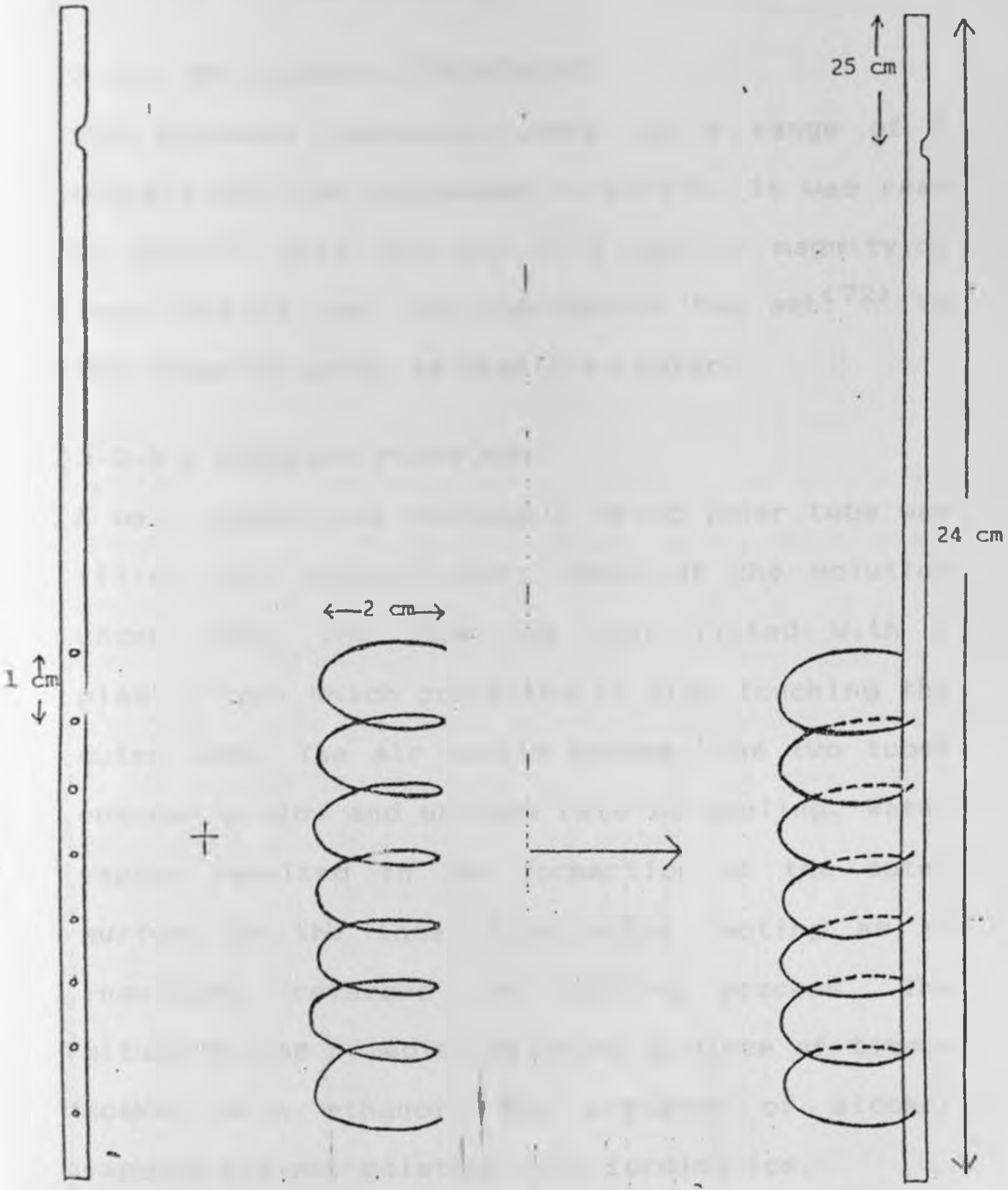


Fig. (3-2-2): THE PERSPEX-NYLON STIRRER



3-2-1 THE PERSPEX-NYLON STIRRER

This stirrer was specially improvised(37) to reduce the awful pain of stirring and splashing of solution during stirring.

3-2-2 THE BECKMANN THERMOMETER

The Beckmann themometer used had a range of 5 degrees and was graduated in 0.01°C. It was read to 0.001°C with the aid of a special magnifying lens. Before use, the thermometer was set(72) to the freezing point of distilled water.

3-2-3 A FREEZING POINT RUN

A well washed and thoroughly dried inner tube was filled with approximately 40mls of the solution under test. The tube was then fitted with a plastic cork which prevented it from touching the outer tube. The air mantle between the two tubes ensured a slow and uniform rate of cooling. Water vapour resulted in ice formartion on the outer surface of the inner tube which, acting as an insulator, retarded the cooling process. The situation was remedied by using a piece of tissue soaked with ethanol. The presence of alcohol vapours prevent moisture from forming ice.

The solution was stirred continously by slight tapping of the stirrer at a rate of 40 taps per minute. Temperature readings were taken at one minute interval. The solution was found to supercool considerably until the stage of nucleation when the latent heat of crystallization causes a sudden and sharp increase in the temperature. After this point, the temperature readings were taken for another 10-15 minutes.

The inner tube was taken out and the frozen solution melted by holding it in the hand and also by vigorous stirring of the solution. The tube was placed back into position for the second set of readings. The process was repeated 3 to 4 times with each solution and that of the water which was used to prepare the solution.

From the temparature-time data, cooling curves were drawn and the depression of freezing point was determined from the difference between the freezing points of solvent and solution.

3-2-4 SUPERCOOLING

Supercooling has been quoted as an important source of error(73) in the depression of freezing point experiments. It has been recommended that supercooling should not exceed 0.3-0.5°C(68) and is best if kept below 1° (71). If there is too much of supercooling, a large quantity of ice would separate out at the freezing point of the solution. Hence the concentration of the solution will be changed appreciably and the freezing point will not be that of the solution prepared.

In this work, almost all the experiments gave a supercooling of less than 0.5°. Calibration runs were carried out to check the effect of supercooling. The author's experiments on NaCl yielded depression data identical with those obtained in an earlier study(34). The results are given in table (3-1a)

3-3-0 MEASUREMENT OF TRANSFERENCE NUMBERS

3-3-1 ANALYSIS

Equation (2-51) shows that the transference number depends upon a relatively small difference between two concentrations, and thus the accuracy of the final result depends mainly upon the accuracy of the analyses. Any suitable analytical procedure may be used- gravimetric, volumetric, colorimetric etc.

After a run, sample from the middle compartment is analyzed first and if the concentration differs appreciably from the initial concentration, the run was rejected. If, however, the concentration was the same, then, depending upon the system, the number of gram-equivalents of one or more ion-constituents or of the electrolyte as a whole, in one or both compartments, was determined

Table (3-1a): Freezing Point Depressions
In Aqueous NaCl Solution

m	T_f(a)	T_f(b)
0.01	0.036	0.0361
0.02	0.070	0.0714
0.05	0.177	0.1758

(a) Experimental data

(b) Calcuated data

determined by isolating the compartments from each other after a run by closing the stopcork. 10 mls of solution in the anode or cathode was carefully pipetted out and titrated against a base or acid using a microburette.

3-3-2 ELECTRODES

The following are the criteria used for selecting the electrodes in this work:

(1) The electrodes reaction should be known, so that equation (2-51) can be derived by an examination of the cell processes. Secondary reactions were reduced by using electrodes of large surface area.

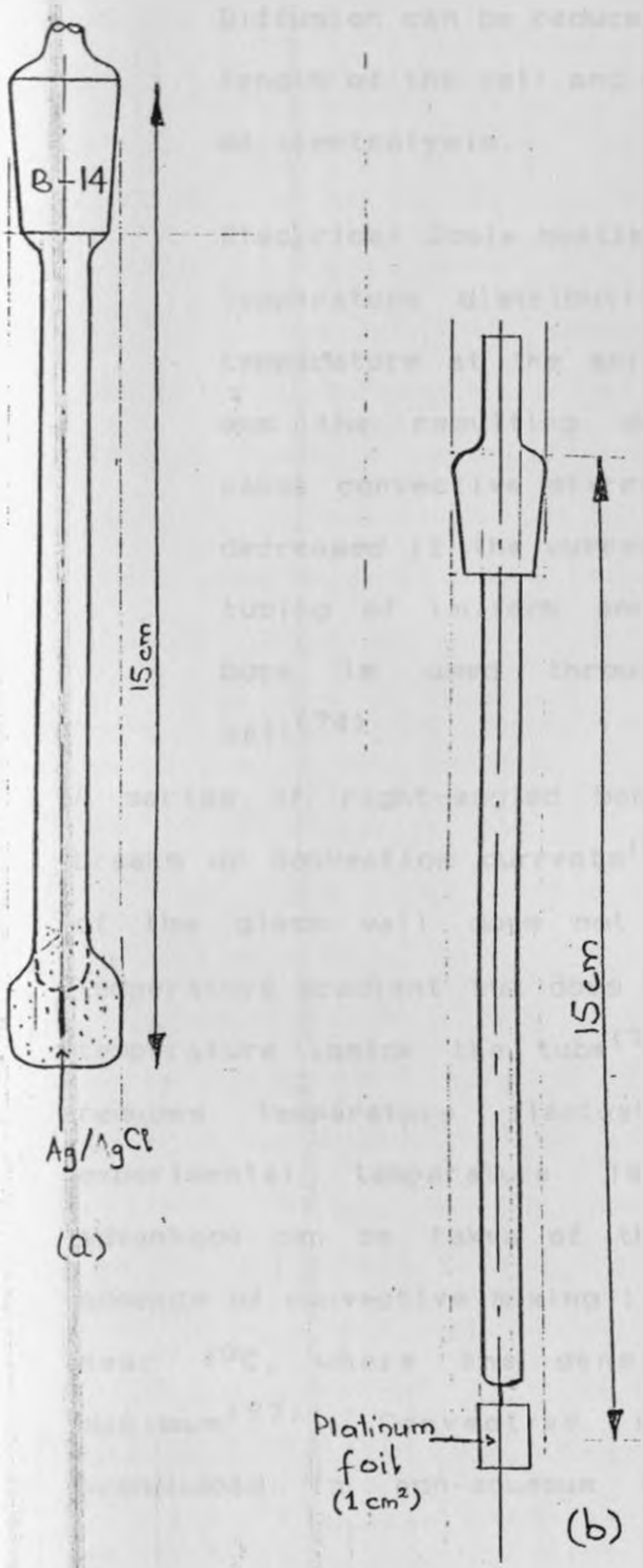
(2) An ideal electrode reaction introduces no foreign ions into solution(74). If any ions are introduced, they must not interfere with the analysis of the solution nor must they reach the middle compartments.

(3) If possible, the electrode reaction should not be associated with any physical action tending to stir and mix the solution, such as gas evolution or the formation of any precipitate that does not adhere to the electrode(74). The evolution of gas was unavoidable and it′s effect was reduced by the design of the cell used in this work.

For Barbituric acid work, the cathode, Ag/AgCl, was made by covering a platinum wire with molten Silver Chloride which solidifies immediately to give the required electrode. The Platinum wire was sealed at the end of an extended B-14 cone which was introduced into the compartment and restrained from being completely closed by using two thin pieces of wire. This was done to allow the escape of the gas evolved at the electrode. (Fig 3-3-1a) shows the cathode used for barbituric acid. The anode was a large Platinum foil electrode of a large surface area (Fig 3-3-1b).

For Sodium Barbital work, both the anode and cathode were Platinum foils of large surface areas (Fig. 3-3-1b)

Fig. (3-3-1): THE ELECTRODES



3-3-3 DISTURBING EFFECTS.

The various effects which cause mixing between compartments can be decreased . as follows:

> Diffusion can be reduced by increasing the length of the cell and decreasing the time of electrolysis.
>
> Electrical Joule heating sets up a radial temperature distribution with a maximum temparature at the axis of the tube(75), and the resulting density differences cause convective stirring. The effect is decreased if the current is small and if tubing of uniform and moderately large bore is used through-out the whole cell(74).

A series of right-angled bends in the tubing breaks up convection currents(76). The thickness of the glass wall does not alter the radial temperature gradient but does influence the mean temperature inside the tube(75). Thermostatting reduces temparature flactuations . If the experimental temparature is not important, advantage can be taken of the almost complete absence of convective mixing in aqueous solutions near 4°C, where the density of water is maximum(77). Convective stirring becomes pronounced in non-aqueous solutions of low conductance, and a preliminary investigation by means of coloured indicators displays the extent of the effect(78).

Electrical migration of ions introduced by the electrode reactions into the middle compartment was reduced by increasing the volumes of the electrode compartments and by decreasing the quantity of electricity passed through the cell.

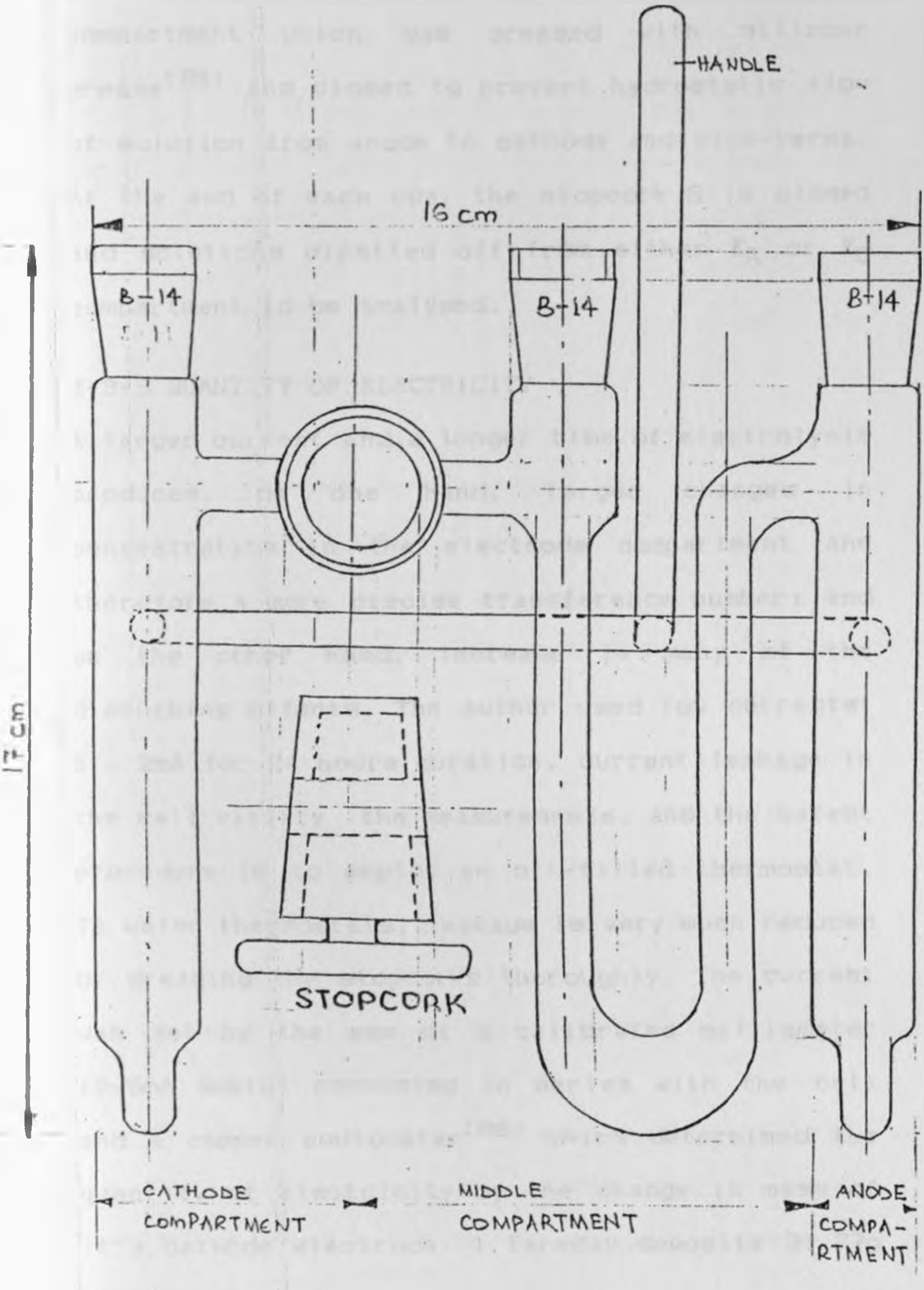
Vibration disturbances, if serious, are reduced by hanging from a special suspension(79) or by standing the cell or the thermostat on a plate over rubber stoppers or a thick rubber mat(80).

The changed solubility of air in the solution at the experimental temperature may lead to the formation of air bubbles. This was overcomed by partially degassing the solution just prior to filling, by shaking it for a few moments at a reduced pressure.

3-3-4 CELL DESIGN

In a large cell many of the above disturbing effects would be eliminated although the change in molarity in the electrode compartments per faraday would be needed. The cell used in this. Fig.(3-3-2) work was made of pyrex glass and took into consideration the above conditions and was a modification of other cells used in transference number measurements(71,81-84).

Fig. (3-3-2): THE HIRTOFF'S CELL



The stopcork, S, had a bore of the same size as the rest of the cell to reduce Joule heating. The cell has a ground glass joint in the middle compartment which was greased with silicone grease(85) and closed to prevent hydrostatic flow of solution from anode to cathode and vice-versa. At the end of each run, the stopcork S is closed and solutions pipetted off from either E_A or E_C compartment to be analysed.

3-3-5 QUANTITY OF ELECTRICITY

A larger current and a longer time of electrolysis produces, on one hand, larger changes in concentration in the electrode compartment and therefore a more precise transference number; and on the other hand, increase in many of the disturbing effects. The author used low currents: 0 - 2mA for 24 hours duration, current leakage in the cell vitiate the measurements, and the safest procedure is to employ an oil-filled thermostat. In water thermostats, leakage is very much reduced by greasing the stopcorks thoroughly. The current was set by the use of a calibrated milliameter (0-5mA scale) connected in series with the cell and a copper coulometer(86) which determimed the quantity of electricity by the change in mass of it's cathode electrode. 1 Faraday deposits 31.77g of copper.

3-3-6 THE POWER SUPPLY ,

The author used a stabilized power unit type R2130 AEI capable of producing 600V D.C. to pass current through the cell.

3-3-7 TITRATIONS

An A-grade milliburette of 5-ml capacity and a 10-ml pipette were used to read volumes of Barbituric acid, Sodium Barbital, Sodium Hydroxide and Oxalic acid. For all solutions, triplicate titrations were carried out to check the reproducibility of the titrations. The reproducibility of the titrations were within 0.5%

3-3-8 TRANSFERENCE MEASURMENTS RUN

(a) CELL FILLING

A clean and dried Hittorff's cell was firmly clamped onto a stand. The big stopcork S was lubricated with silicone grease and placed in the position. The solution was very carefully poured not to have any bubbles formed in the cell. The level of the solution kept just upto the ground glass joints of the cell. The electrodes were then put in and the stop cork S was opened .

(b) The coulometer is then placed outside the thermostatic tank and connected in series with the cell. The power was then switched on and the voltage adjusted to pass the desired current as shown on the milliameter.

(c) Washing the cell

After the experiment, the cell was taken out of the tank and the outer surfaces washed clean with teepol solution. The cell was clamped in an inverted position on a retort stand. The greased parts of the cell were first wiped out with tissues moistened with carbon tetrachloride.

The cell was put back in an upright position and was thoroughly washed out with teepol solution. The cell was then soaked for half-an-hour. Finally, the cell thoroughly rinsed with double-distilled water.

The cell so washed clean was checked for cleanliness. A careful look into the cell against the light was found adequate enough to spot the unclean areas, if any, of the cell.

CHAPTER 4

RESULTS AND DISCUSSION

4-1-0 CRYOSCOPIC RESULTS.

4-1-1 BARBITURIC ACID

Table (4-1-1) depicts the results of theoretical and experimental depression of freezing points in aqueous Barbituric Acid, and Figure (4-1-1) shows the concentration dependence. It is obvious from the Table (4-1-1) and the Figure (4-1-1), that the two sets of figures do not agree and show a pronounced departure. Had Babituric acid been behaving as a 1:1 electrolyte the two figures at each concentration would have been the same. It is to be noted that the deviation is noticeable even at the lowest concentrations and progressively increases with concentration.

The discrepancy, it has been found, can be explained by postulating a dimeric anionic species $(B_2)^{2-}$ in these solutions which comes into being following the equilibrium reactions given by (2-7), and (2-8), as mentioned earlier.The explanation requires intricate calculations which requires a set of α and β values that fit best with the experimental data. To obtain these values a computer program (APPENDIX 1) was used with K_D values ranging from 2.8 to 4.0 Kg mol^{-1}. It was found that a K_D value of 3.0 Kg mol^{-1}

produced α and β values which, on substitution into equation (2-6), yielded calculated T_f(calc.) values which agreed very well with the observed T_f(exptl) results. TABLE (4-1-2) records the and values so obtained and compares T_f(calc.) with T_f(exptl).It is apparent that the two sets of values agree within an average value of +/-(0.0005) which is well within the limits of accuracy obtainable from the Beckmann thermometer employed in the cryoscopic measurements. At concentrations higher than 0.020 m the dissolved Barbituric acid separated out due to the low solubility at $0^{o}C$ thus affecting the concentration of the solution and giving a much lower giving T_f and were therefore ignored. The dimerization postulate thus explains very well the causes of deviations from theoretical expectations.

TABLE (4-1-1): THEORETICAL AND EXPERIMENTAL CRYOSCOPIC RESULTS IN AQUEOUS BARBITURIC ACID SOLUTIONS

Conc(m)	T_f(1:1)	T_f(exptl)	T_f(1:1)-T_f(exptl)
0.001973	0.00734	0.004	0.003
0.002999	0.01116	0.007	0.004
0.004143	0.0154	0.009	0.006
0.005999	0.0223	0.013	0.019
0.008021	0.0298	0.017	0.013
0.008076	0.0300	0.017	0.013
0.010012	0.0372	0.020	0.017
0.010522	0.0391	0.021	0.018
0.019961	0.0742	0.040	0.034
0.020205	0.0755	0.0404	0.036

Units: m, mol Kg^{-1}; T_f(1:1), T_f(exptl), ^oC

Fig. (4-1-1):

Theoretical And Experimental DT_f Vs Mol.

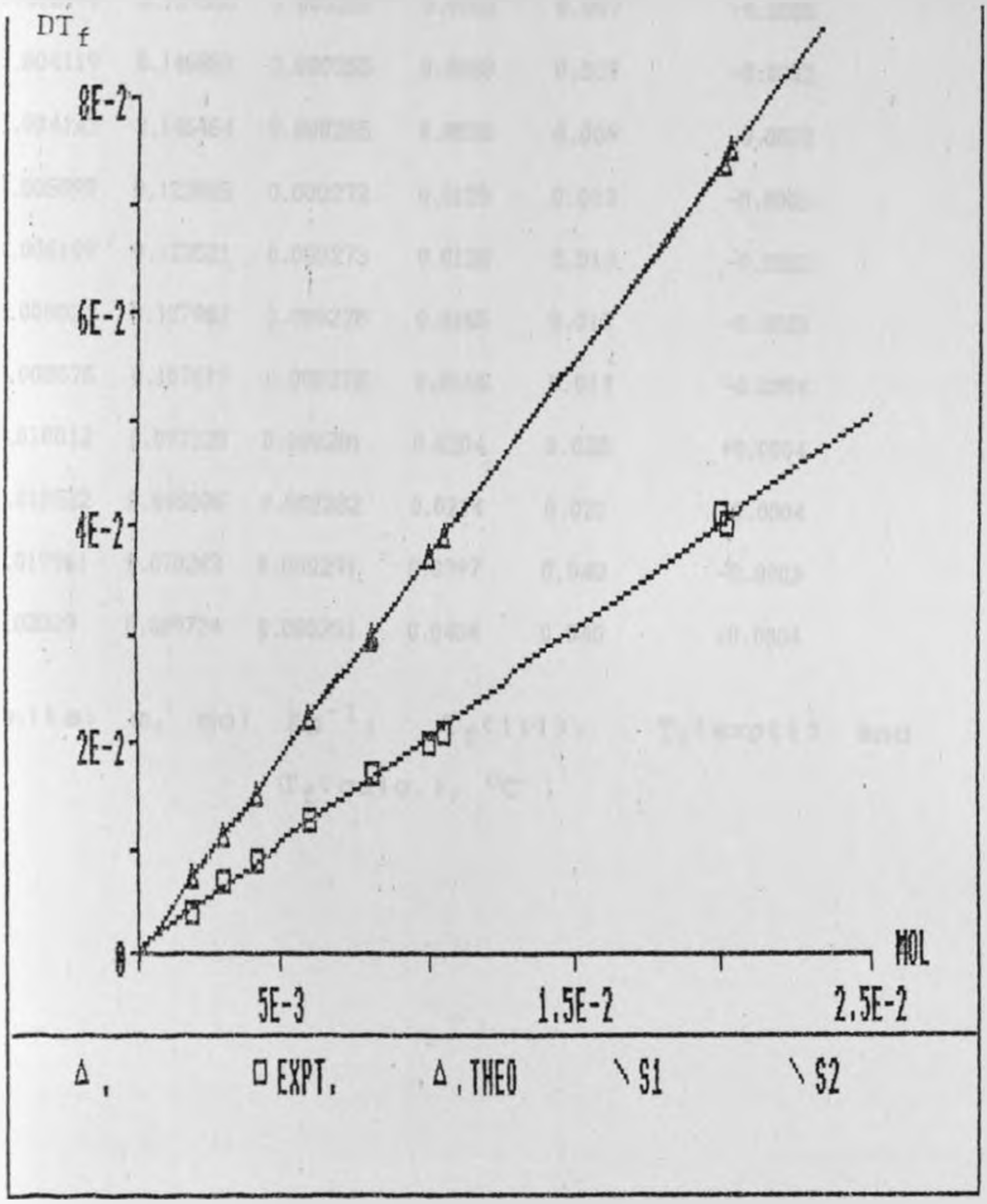


TABLE (4-1-2) : α and β VALUES WITH K_D = 3.0 Kg mol^{-1} T_f(calc.) COMPARED WITH T_f(exptl)

m	α	β	T_f(calc)	T_f(exptl)	T_f(calc) - T_f(exptl)
0.001973	0.204304	0.000204	0.0044	0.004	+0.0004
0.002999	0.169566	0.000257	0.0065	0.007	-0.0005
0.004119	0.146852	0.000265	0.0088	0.009	-0.0002
0.004143	0.146464	0.000265	0.0088	0.009	-0.0002
0.005999	0.123555	0.000272	0.0125	0.013	-0.0005
0.006109	0.122521	0.000273	0.0128	0.013	-0.0002
0.008021	0.107962	0.000278	0.0165	0.017	-0.0005
0.008076	0.107619	0.000278	0.0166	0.017	-0.0004
0.010012	0.097328	0.000281	0.0204	0.020	+0.0004
0.010522	0.095086	0.000282	0.0214	0.021	+0.0004
0.019961	0.070267	0.000291	0.0397	0.040	-0.0003
0.02029	0.069724	0.000291	0.0404	0.040	+0.0004

Units: m, mol Kg^{-1}; T_f(1:1), T_f(exptl) and T_f(calc.), °C

4-1-2 SODIUM BARBITAL

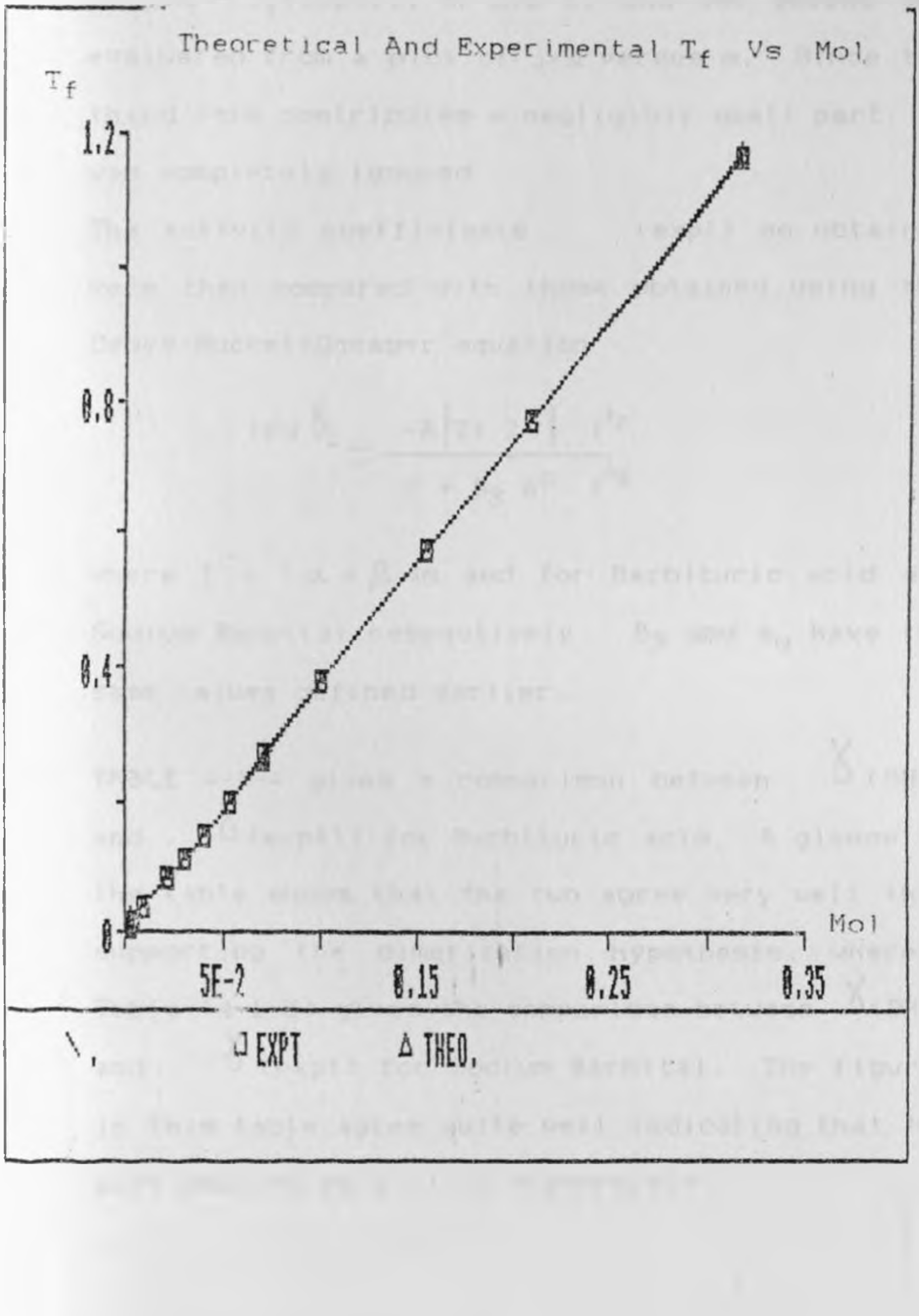
Table (4-1-3) shows the results of the theoretical and experimental depression of freezing points in aqueous Sodium Barbital and Figure (4-1-2) shows the concentration dependence. Since NaB^* behaves as a (1:1) electrolyte it can be seen, from the table and graph, that the two sets of figures agree within +/-0.001 - the limit of accuracy obtainable from the thermometer employed.

TABLE (4-1-3) : THEORETICAL AND EXPERIMENTAL CRYOSCOPIC RESULTS IN AQUEOUS SODIUM BARBITAL

m	T_f(1:1)	T_f(exptl)	T_f(1:1)-T_f(EXPT)
0.003442	0.0128	0.013	-0.0002
0.005062	0.0188	0.019	-0.0002
0.010049	0.0374	0.037	+0.0004
0.021813	0.0811	0.081	+0.0001
0.030378	0.1129	0.113	-0.0001
0.040445	0.1504	0.150	+0.0004
0.05364	0.1995	0.200	-0.0005
0.071726	0.2668	0.270	-0.0002
0.102046	0.3795	0.380	-0.0005
0.15427	0.5737	0.574	-0.0006
0.2071224	0.7702	0.770	+0.0002
0.315128	1.172	1.170	+0.002

Units: m, mol Kg^{-1}; T_f(1:1), T_f(exptl) ^oC

Fig. (4-1-2):


Theoretical And Experimental T_f Vs Mol
T_f
1.2
0.8
0.4
0
Mol
5E-2
0.15
0.25
0.35
□ EXPT
Δ THEO.

4-1-3 ACTIVITY COEFFICIENTS RESULTS FROM CRYOSCOPIC MEASUREMENTS

The observed freezing-point depressions, T_f(exptl), were substituted into equation (2-36). The first term was obtained by direct substitution of the T_f(exptl), m and Kf and the second was evaluated from a plot of j/m versus m. Since the third term contributes a negligibly small part, it was completely ignored.

The activity coefficients (expt) so obtained were then compared with those obtained using the Debye-Huckel-Onsager equation

$$\log \gamma_i = \frac{-A\left|Z_+ \; Z_-\right| \; I^{1/2}}{1 + B_3 \; a^o \; I^{1/2}}$$

where I = (α + β)m and for Barbituric acid and Sodium Barbital respectively. B_3 amd a_o have the same values defined earlier.

TABLE 4-1-4 gives a comparison between γ(DHO) and γ(exptl) for Barbituric acid. A glance at the table shows that the two agree very well thus supporting the dimerization hypothesis, whereas Table (4-1-5) gives the comparison between γ(DHO) and γ(expt) for Sodium Barbital. The figures in this table agree quite well indicating that the salt behaves as a (1:1) electrolyte.

TABLE (4-1-4):ACTIVITY COEFFICIENTS FROM DHO AND CRYOSCOPIC MEASUREMENTS IN AQUEOUS BARBITURIC ACID WITH K_D=3.0

m	DHO	(expt)	(DHO)- (expt)
0.001973	0.978	0.977	0.001
0.002999	0.976	0.974	0.002
0.004143	0.974	0.972	0.002
0.005999	0.971	0.971	0.000
0.008021	0.969	0.968	0.001
0.008076	0.969	0.967	0.002
0.010012	0.967	0.967	0.000
0.010522	0.967	0.967	0.000
0.019961	0.961	0.963	0.002

Units: m, mol Kg^{-1}

TABLE (4- -5): ACTIVITY COEFFICIENTS FROM DHO AND EXPERIMENTAL MEASUREMENTS IN AQUEOUS SODIUM BARBITAL

m	γ_{DHO}	$\gamma_{(exptl)}$	$\gamma_{(DHO)}- \gamma_{(exptl)}$
0.003442	0.921	0.920	0.001
0.005062	0.894	0.891	0.003
0.010049	0.878	0.879	-0.001
0.0218128	0.838	0.838	0.000
0.030378	o.819	0.816	0.003
0.040445	0.802	0.803	-0.001
0.05364	0.783	0.786	-0.003

Units: m, mol Kg^{-1}

4-2-0 TRANSFERENCE NUMBERS

4-2-1 TRANSFERENCE NUMBERS RESULTS IN BARBITURIC ACID SOLUTIONS

An ideal transference number work entails measurement of both anion and cation constituent transference numbers. This provides an internal check on the accuracy of the value measured because these should satisfy the condition

$$\sum_{R} T_R = 1 \qquad (2\text{-}47)$$

For Hittorf's method, this amounts to accurately determining the final concentrations in both the anode and cathode compartments. The solution from the anode was titrated with oxalic acid and a drop was enough to give a colour change but the solution from the cathode, where the H^+ ions migrated to, required measurable amounts of alkaline solution. The author was able to accurately determine the final concentration in the cathode compartment and hence worked out the transference mumber of H^+ ions from which the transference number of B^- ions were calculated using the relation (2-47). The electrolysis in these experiments were done for a minimum period of twenty-four hours at 0.2mA, 0.3mA 0.5mA for the given concentrations. The lower concentrations were studied at 0.2mA and 0.3mA only due to it's high resistance while the rest were studied at the three different currents to ensure that the transference numbers do not change with the duration of the experiment and current.

Tranference Numbers in aqueous solutions of Barbirturic acid obtained at different currents are shown in Table (4-2-1)

Table 4-2-1: TRANSFERENCE NUMBERS OF BARBITURIC ACID AT SELECTED CONCENTRATIONS AND CURRENTS

HB (M)	Current I	TH+	TB-
0.00197	0.2	0.9402	0.0598
0.00197	0.3	0.9403	0.0597
	At zero current	0.9400	0.0600
0.00299	0.2	0.9421	0.0579
0.00299	0.3	0.9421	0.0579
0.00299	0.4	0.9422	0.0578
	At zero current	0.9420	0.0580
0.004106	0.2	0.9420	0.058
0.004106	0.3	0.9422	0.0578
0.004106	0.4	0.9424	0.0576
	At zero current	0.9416	0.0584
0.00598	0.2	0.9430	0.057
0.00598	0.3	0.9431	0.0569
0.00598	0.5	0.9431	0.0569
	At zero current	0.9429	0.0571
0.007994	0.2	0.9423	0.0577
0.007994	0.3	0.9425	0.0575
0.007994	0.5	0.9428	0.0572
	At zero current	0.9420	0.0580
0.009978	0.2	0.9420	0.058
0.009978	0.3	0.9422	0.0578
0.009978	0.5	0.9424	0.0576
	At zero current	0.9417	0.0583
0.01988	0.2	0.9418	0.0582
0.01988	0.3	0.9420	0.0580
0.0988	0.5	0.9426	0.0574
	At zero current	0.9413	0.0587

Units: M,mol l-1; I,mA

Fig. (4-2-1):

T_{H+} Vs Current I At HB Concentration of 0.00197

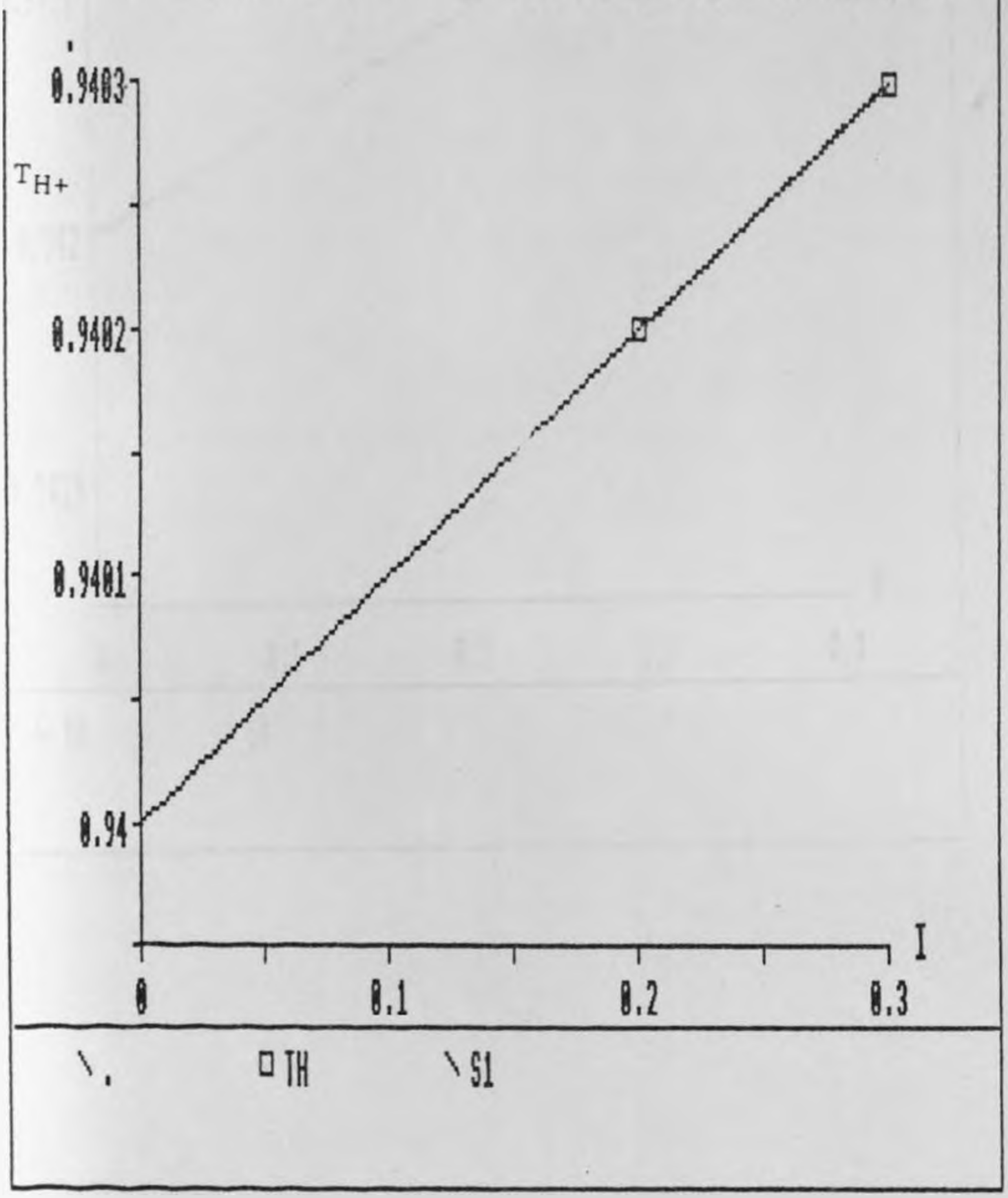


Fig. (4-2-2):

T_{H+} Vs I At HB Concentration of 0.00299

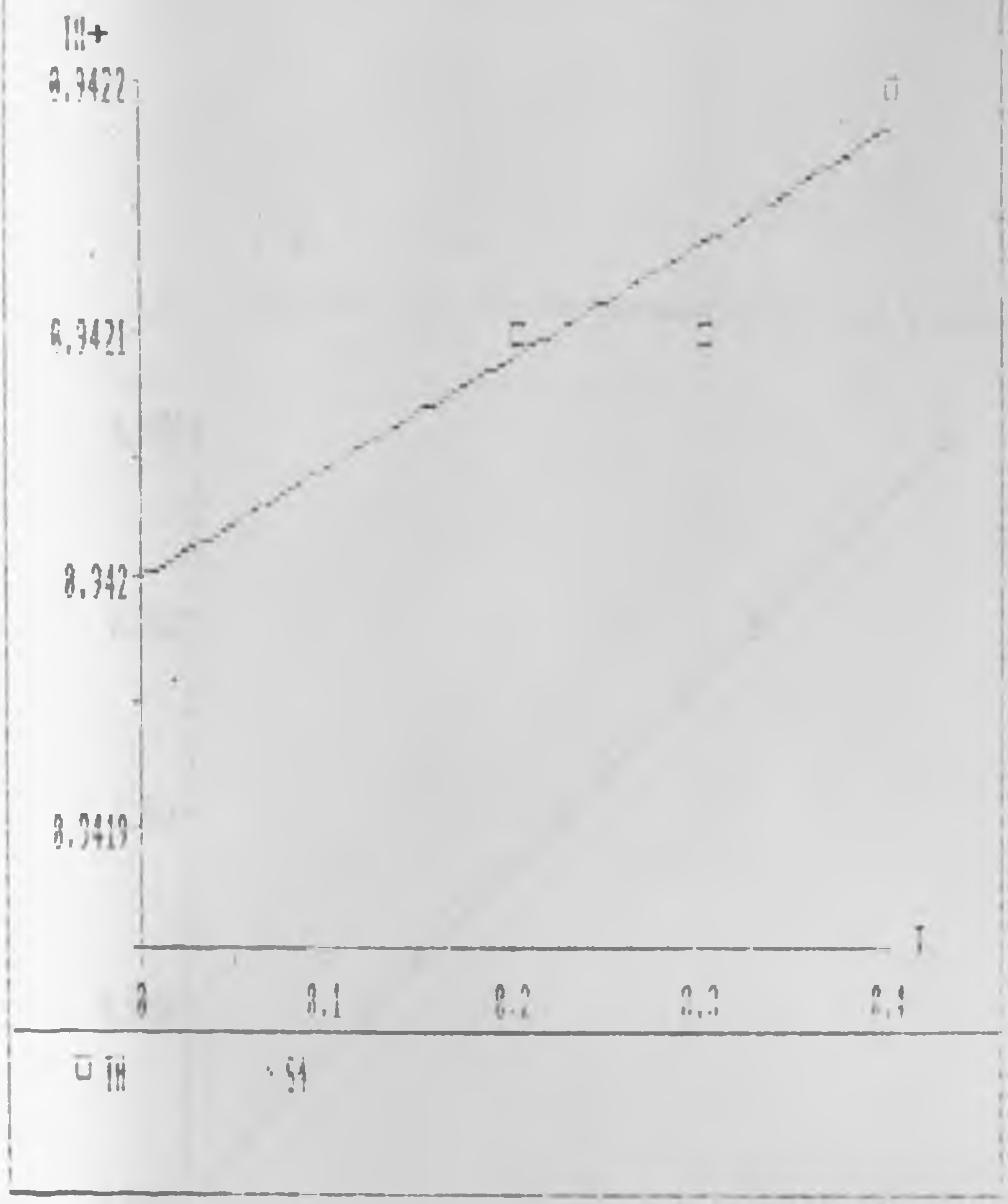


Fig. (4-2-3):

T_{H+} Vs I At HB Concentration of 0.004106

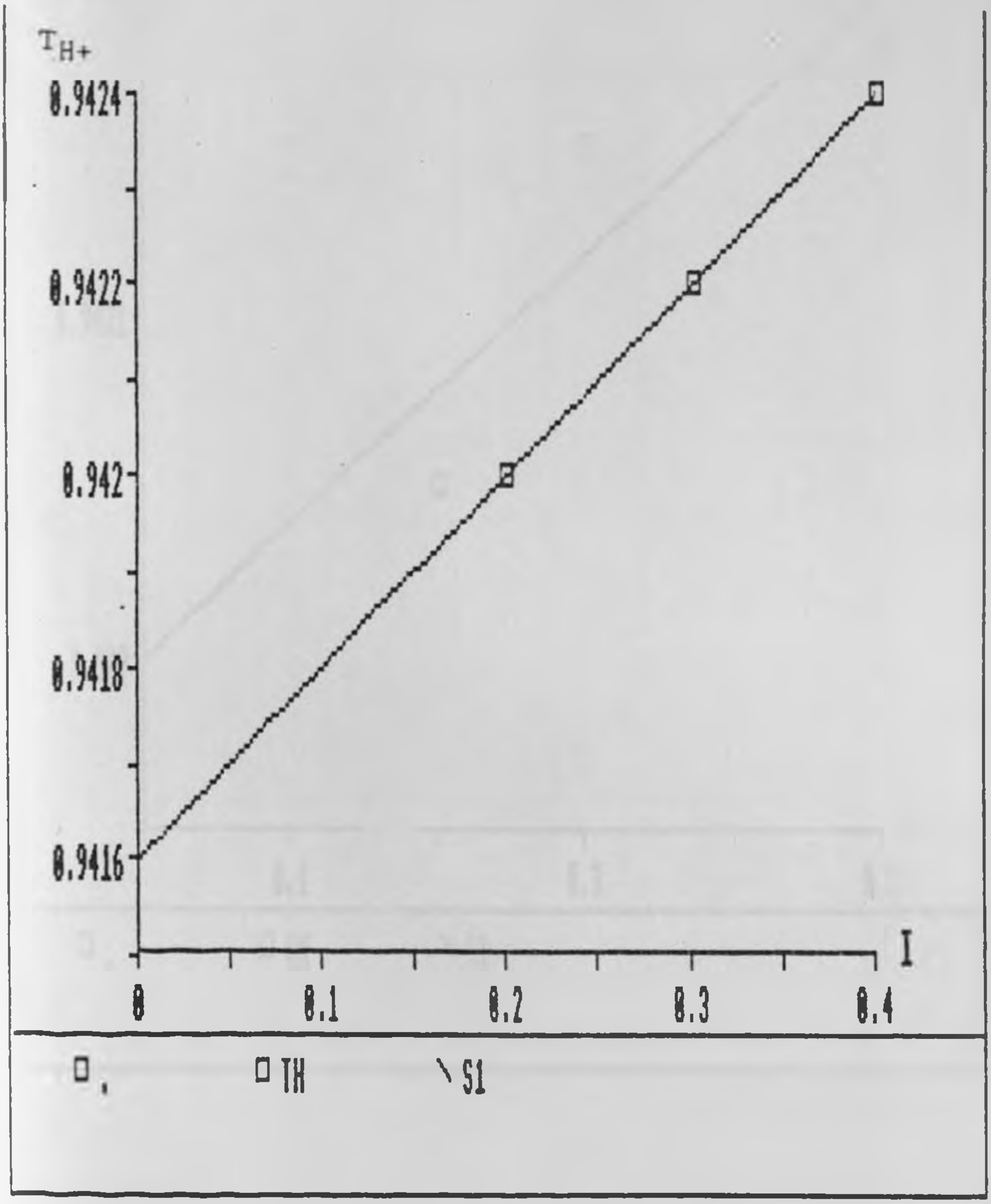


Fig. (4-2-4):

T_{H+} Vs I At HB Concentration of 0.00598

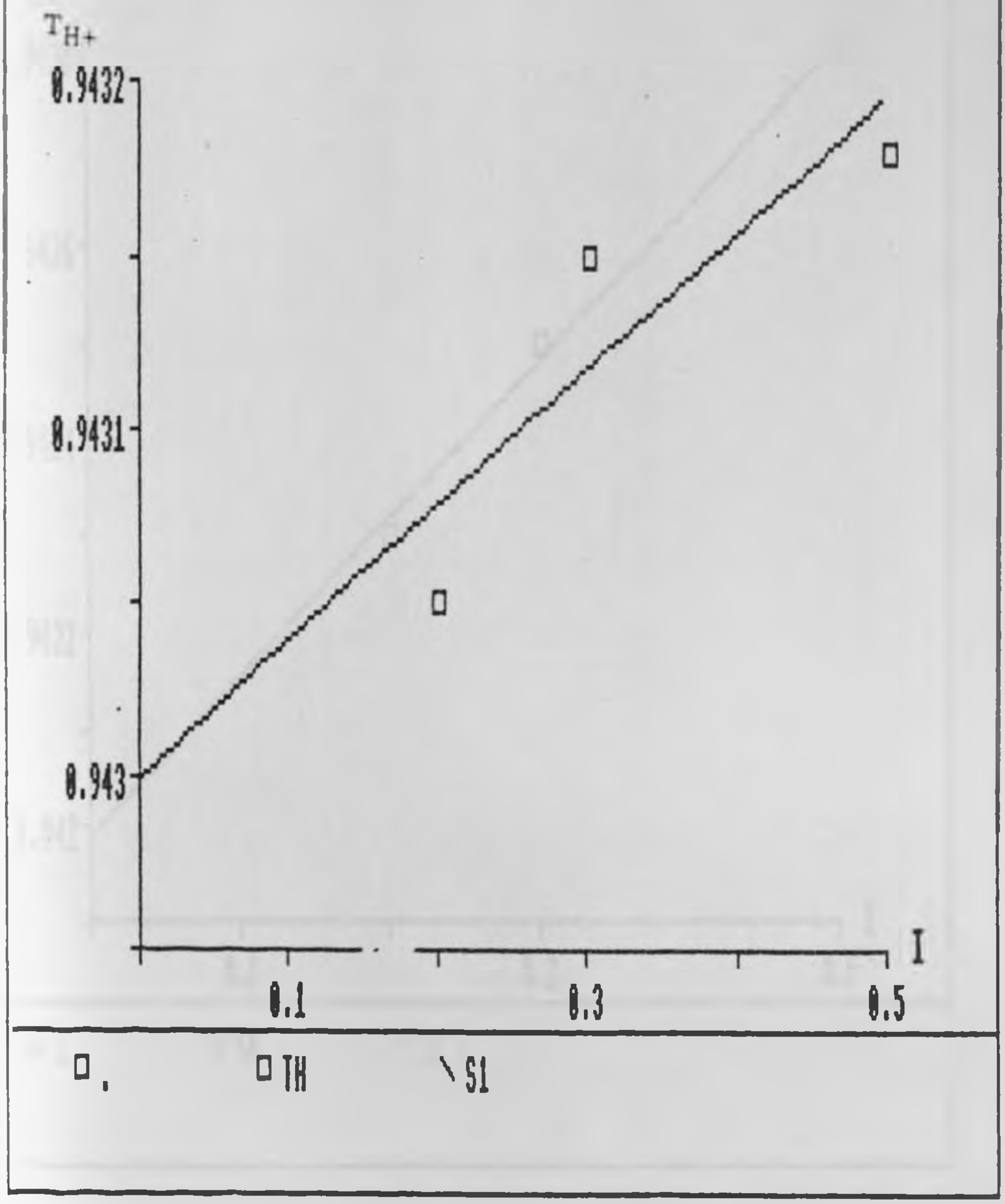


Fig. (4-2-5):

T_{H+} Vs I At HB Concentration of 0.007994

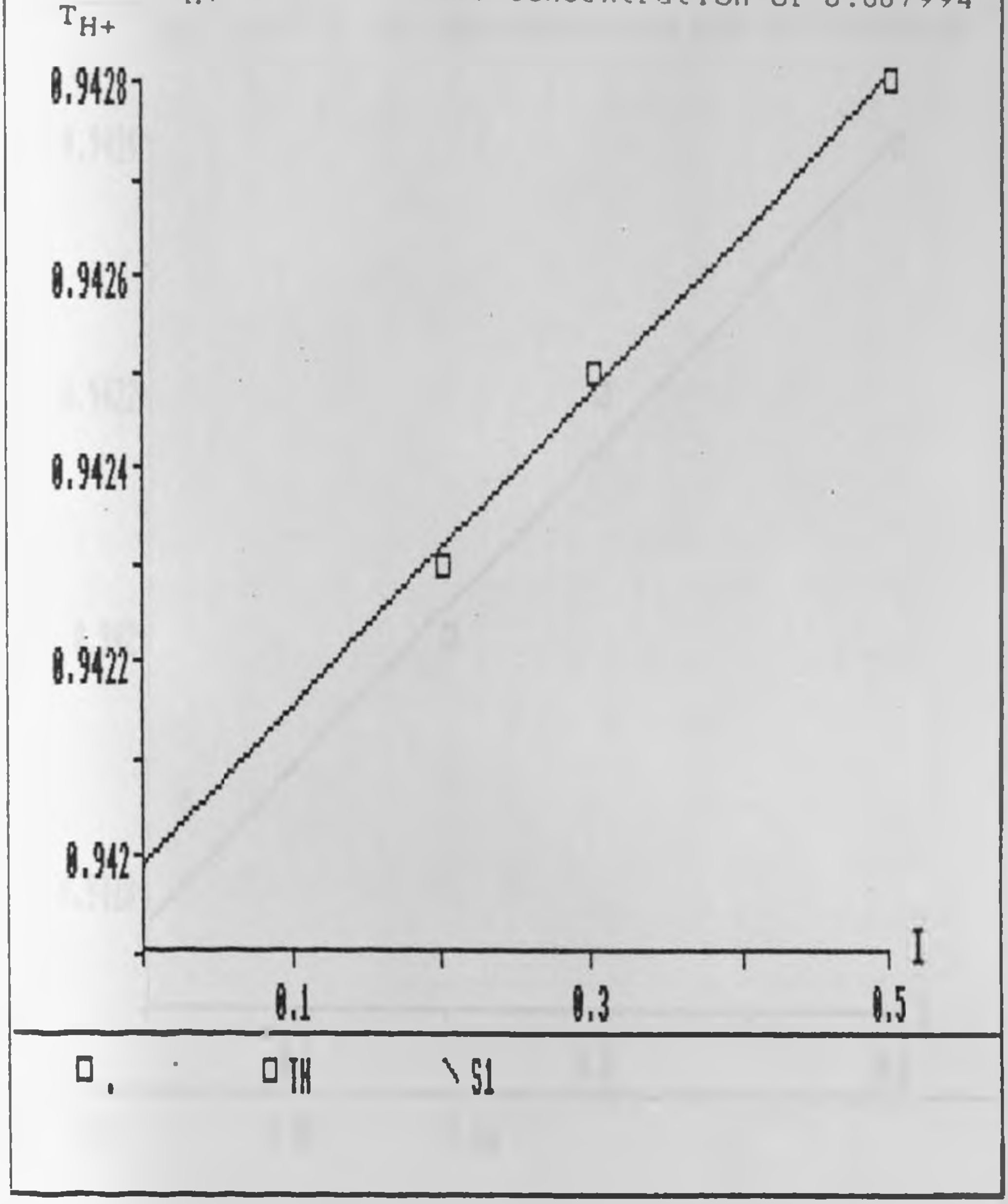


Fig. (4-2-6):

T_{H+} Vs I At HB Concentration of 0.009978

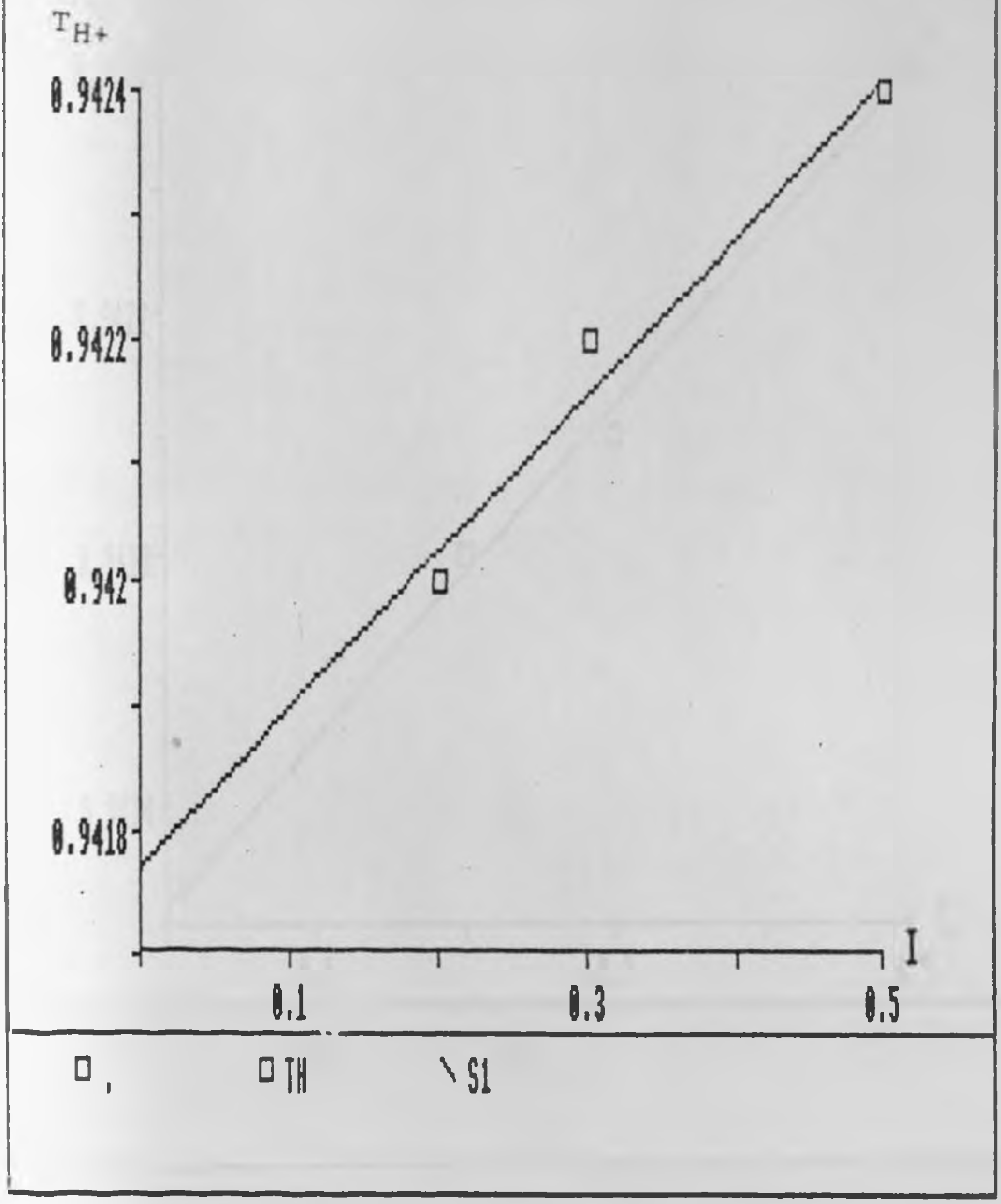


Fig. (4-2-7):

T_{H+} Vs I At HB Concentration of 0.01988

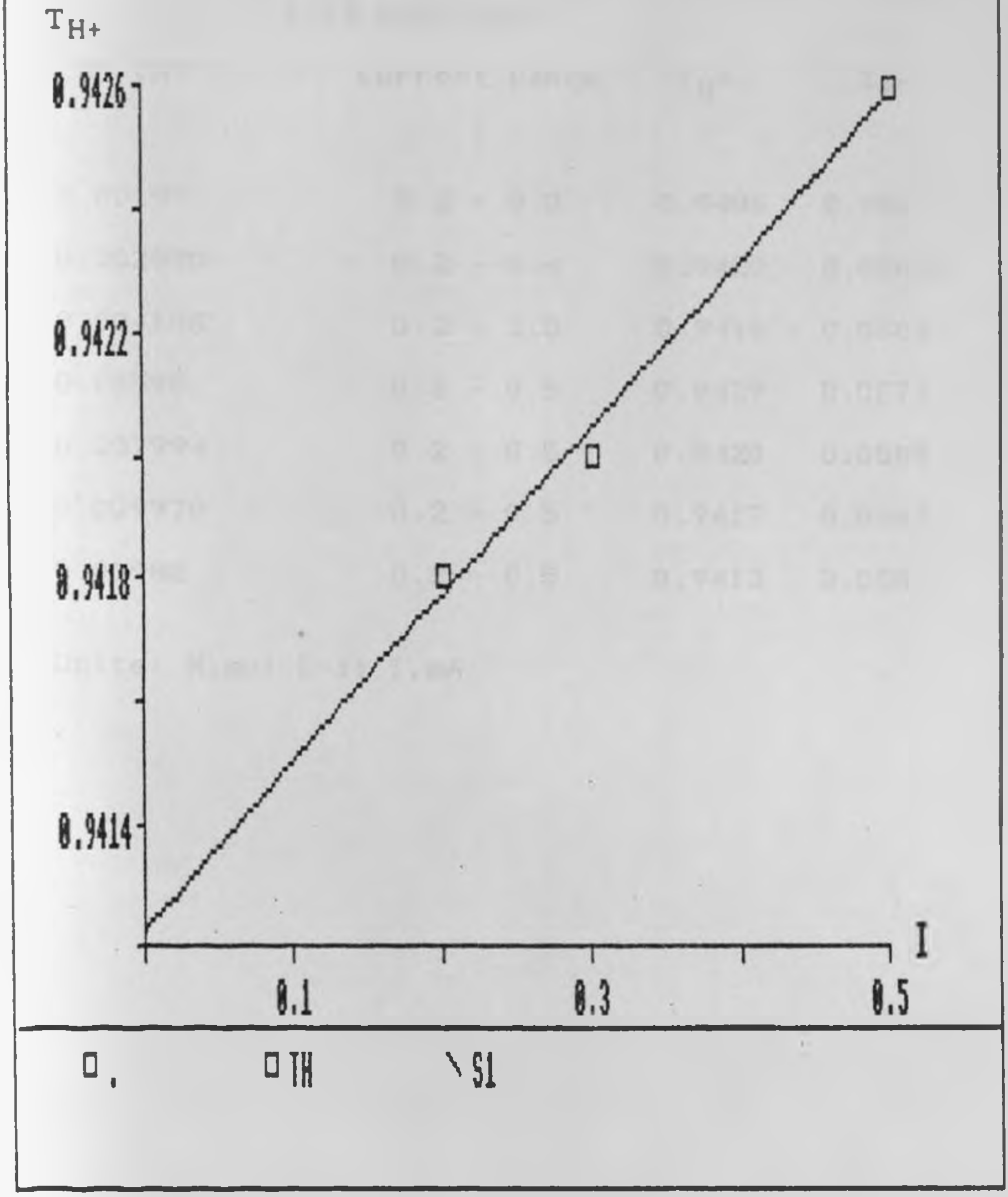


Table 4-2-2 TRANSFERENCE NUMBERS AT ZERO CURRENTS IN DIFFERENT CONCENTRATIONS BARBITURIC ACID SOLUTIONS

HB (M)	Current Range I	T_{H^+}	T_{B^-}
0.00197	0.2 - 0.3	0.9400	0.0600
0.002990	0.2 - 0.4	0.9420	0.0580
0.004106	0.2 - 0.5	0.9416	0.0584
0.00598	0.2 - 0.5	0.9429	0.0571
0.007994	0.2 - 0.5	0.9420	0.0580
0.009978	0.2 - 0.5	0.9417	0.0583
0.01988	0.2 - 0.5	0.9413	0.0587

Units: M,mol L-1; I,mA

The values of transference numbers at zero current for each concetrations is shown in Table (4-2-2). It becomes obvious that the T_{H^+} values increase with concentration as expected. However, the magnitude of variation does not follow the theory. A plot of T_{H^+} against M is shown in figure (4-2-8) which depicts a typical concentration dependence in the presence of complex ion formation. The plot on extrapolation to zero concentration yielded TH+ equal to 0.9170 which using the equation :

$$T_{H^+} = \frac{\lambda^o_{H^+}}{\lambda^o_{H^+} + \lambda^o_{B^-}}$$

and $\lambda^o_{H^+} = 349.8\ cm^2\ ohm^{-1}$ gives :

$$T^o_{H^+}\ (\lambda^o_{H^+} + \lambda^o_{B^-}) = \lambda^o_{H^+}$$

$$T^o_{H^+}\ (349.8 + \lambda^o_{B^-}) = 349.8$$

$$\lambda^o_{B^-} = \frac{349.8 - (0.9170 x 349.8)}{0.9170}$$

$$= 22.72\ S\ cm^2\ equiv.^{-1}$$

From a consideration of equilibrium equations (2-7) and (2-8) which have been used to explain the concentration dependence of the depression in

The values of transference numbers at zero current for each concetrations is shown in Table (4-2-2). It becomes obvious that the T_{H^+} values increase with concentration as expected. However, the magnitude of variation does not follow the theory. A plot of T_{H^+} against M is shown in figure (4-2-8) which depicts a typical concentration dependence in the presence of complex ion formation. The plot on extrapolation to zero concentration yielded TH+ equal to 0.9170 which using the equation :

$$T_{H^+} = \frac{\lambda^o_{H^+}}{\lambda^o_{H^+} + \lambda^o_{B^-}}$$

and $\lambda^o_{H^+} = 349.8 \text{ cm}^2 \text{ ohm}^{-1}$ gives :

$$T^o_{H^+} \; (\lambda^o_{H^+} + \lambda^o_{B^-}) = \lambda^o_{H^+}$$

$$. \; T^o_{H^+} \; (349.8 + \lambda^o_{B^-}) = 349.8$$

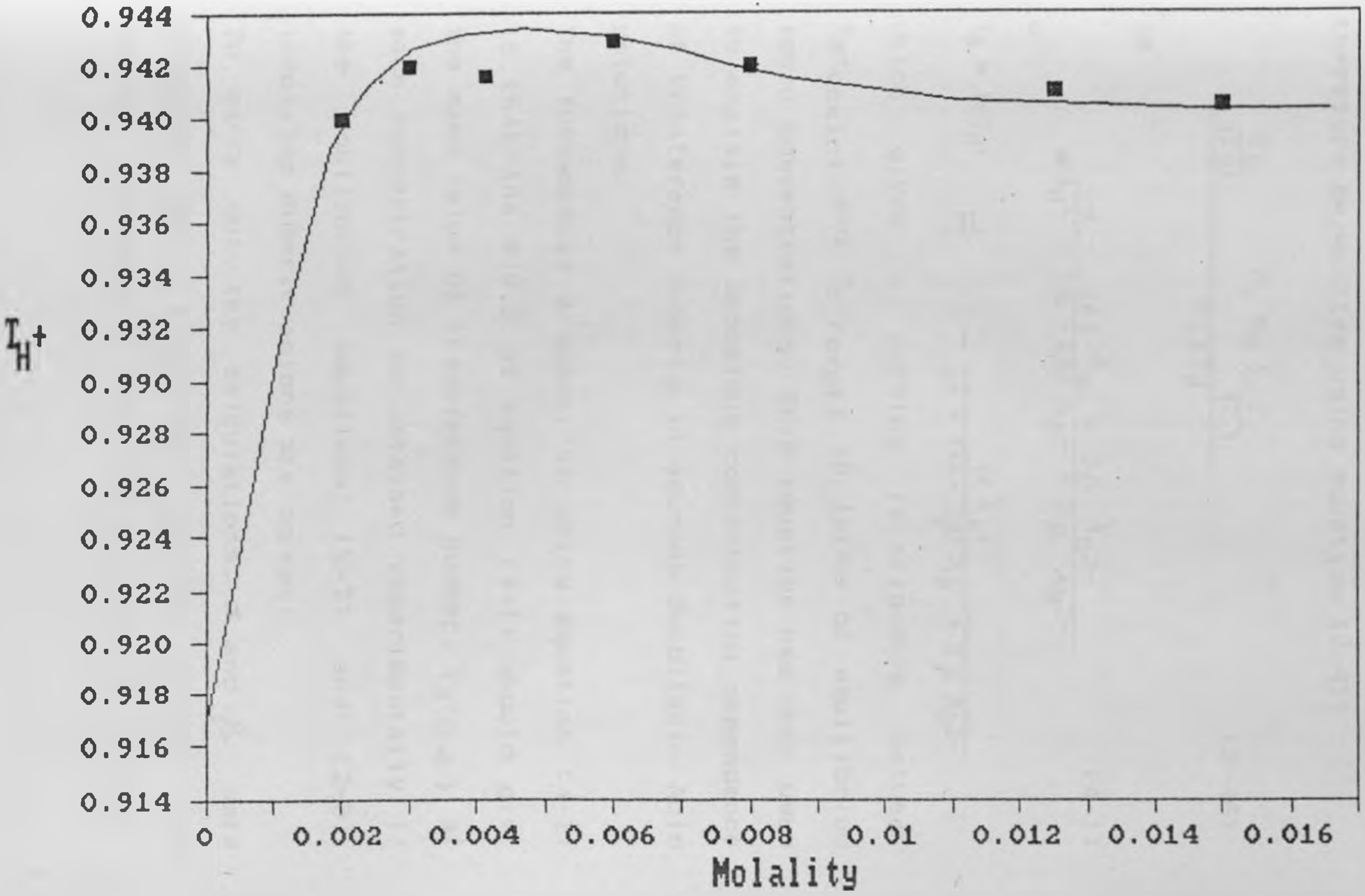
$$\lambda^o_{B^-} = \frac{349.8 - (0.9170x349.8)}{0.9170}$$

$$= 22.72 \text{ S cm}^2 \text{ equiv.}^{-1}$$

From a consideration of equilibrium equations (2-7) and (2-8) which have been used to explain the concentration dependence of the depression in

Fig (4-2-8)

Transference Number Vs. Concentration



freezing point, it is clear that B^- ion exists as $(B_2)^{2-}$ in aqueous acid solutions.

The transeference number of B^- constituent can therefore be written using equation (2-41)

$$\frac{\frac{Z_p}{|Z_p|} \qquad M_i \; N_R \lambda_i \frac{Z_i}{|Z_i|}}{M_i \, |Z_i|} \qquad (2\text{-}46)$$

as

$$\frac{(\alpha - 2\beta)\lambda_{B^-} + 2\beta \; \lambda_{n^{2-}}}{\alpha\lambda_{H^+} + (\alpha - 2\beta)\lambda_{B^-} + 2\beta \; \lambda_{D^{2-}}} \qquad (4\text{-}1)$$

or

$$T_B = 1 - T_{H^+} \quad = \quad 1 - \frac{\alpha\lambda_{H^+}}{H^+ + (\alpha - 2\beta)\lambda_{B^-} + 2\beta \; \lambda_{D^{2-}}}$$

which gives a working relationship between $T_{B^-(calc)}$ and $T_{B^-(expt)}$ in terms of equilibrium ionic concentrations. This equation has been used to explain the anomalous concentration dependence of tranference numbers in aqueous Barbituric Acid solutions.

The fundamental argument in using equation (4-1) is that the R.H.S of equation (4-1) should give the same value of transference number, $T_{B^-(calc)}$ at each concentration as obtained experimentally if the equilibrium equations (2-7) and (2-8), involving dimeric anions are correct.

To carry out the calculations, α and β were obtained using equations (2-13), (2-15) and (2-16a), assuming a value for K_D: and λ_i of the species involved, at each concentration, were worked out using the equation:

$$\lambda_i = \frac{(B_1 \lambda^o + 0.5B_2)\,[m(\alpha - 2\beta)]^{1/2}}{1 + B_3 a^o\,[m(\alpha - 2\beta)]^{1/2}}$$

Essentially the calculations are similar to those done for freezing point depression results. The $T_{B^-(calc)}$ so obtained are compared with $T_{B^-_{(expt)}}$ in Table (4-2-3) where the two values differ only in the third and fourth places of decimal.

It is evident from the analysis that the dimerization hypothesis satisfactorly explains the deviation of the transference number data from the theory. Similar measurements in citric acid(87) solutions extend corroboration to the existence of dimeric anion in these solutions

Table (4-2-3): COMPARISSON OF $T_{B^-_{(calc.)}}$ and $T_{B^-_{(expt.)}}$

HB M	$T_{B^-_{(calc.)}}$	$T_{B^-_{(expt.)}}$	$T_{B^-_{(calc.)}} - T_{B^-_{(expt.)}}$
0.00197	0.060	0.591	+0.0009
0.00299	0.0580	0.0589	-0.0009
0.004106	0.0583	0.0587	-0.0004
0.00598	0.0571	0.0586	-0.0015
0.007994	0.058	0.0584	-0.0004
0.009978	0.0582	0.0583	-0.0001
0.01988	0.0588	0.0579	+0.0011

Parameters: $K_D = 3.0$ dm^3 mol^{-1}

$D = 40$ S cm^2 equiv.$^{-1}$

$B^- = 22.51$ cm^2 equiv.$^{-1}$

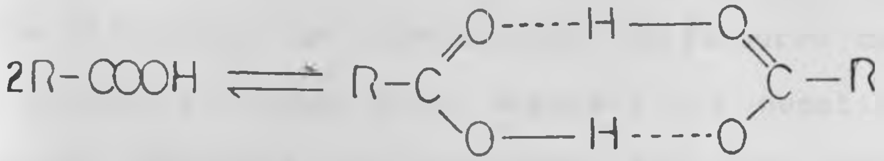
$H^+ = 349.8$ cm^2 equiv.$^{-1}$

Units:M,mol l^{-1}

4.2.2 SOME STRUCTURAL ASPECTS OF DIMERIC ANIONS

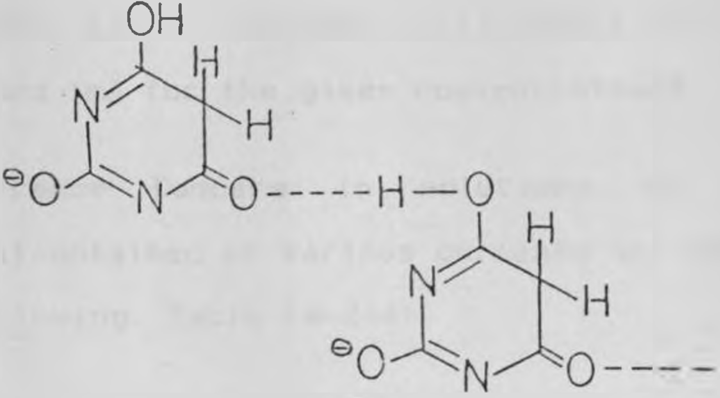
Several groups of investigators(89,90) have found that the carboxylic acids and salts dimerize in aqueous solutions. Rossotti and Co-workers(91) have carried out the most extensive series of measurements and have shown that, while higher oligomers form in solution of the acids, dimerization in the major process occuring in the low concentration range.

A well-known manifestation of the strong hydrogen-bonding ability of carboxylic acids(92) is the formation of cyclic dimers (shown below) in the gas phase or in non-polar solvents, such as benzene or carbon tetrachloride(92)



In protic and dipolar aprotic solvents at low acid concentrations the dimers are broken up to form 1:1 or 1:2 hydrogen-bonded complexes with the solvent. However, it is important to note that the formation of carboxylic dimers and homoconjugated anions cannot always be neglected even in aqueous solutions at high concentrations of acid and salt(93). Farrer and Rossotti(91) described the hydrolytic equilibrium in sodium acetate and suggested the formation of $(CH_3COOH)_2$ and $(CHCOO)_2H^-$ to explain their experimental results. Recently transference number measurements and analysis of the literature conductance data in aqueous citric acid(87) have indicated the presence of dimeric anions.

The dimerization of B- ions in aqueous solutions of Barbituric acid can be visualized to have the above structure. The dimerization is favoured due to the cyclic rings which separate the negative charges. Therefore we can assume that the above dimer is cyclic as shown by Schrier, Pottle and Scheraga(94) for carboxlic acid dimers in water.



4-2-3 TRANSFERENCE NUMBERS IN SODIUM BARBITAL

Transference numbers of Sodium Barbital were also determined using the Hittorf's method. The solution in the cathode compartment was titrated against oxalic acid and the transference number of sodium ion was obtained using equation (2-47), the transference numbers, of Barbital ions, B^* were obtained. The electrolysis in these experiments were done for a minimum of 12 hours at 0.3mA, 0.5mA and 1mA for the given concentrations.

Transference Numbers in solutions of Sodium Barbital obtained at various currents are shown in the following Table (4-2-4)

TABLE (4-2-4): TRANSFERENCE NUMBERS OF SODIUM BARBITAL AT VARIOUS CONCENTRATIONS AND CURRENTS

NaB* M	Current I	T_{Na}	T_B
0.0222815	0.3	0.5603	0.4397
0.022815	0.5	0.5605	0.4395
0.022815	1.0	0.5610	0.4390
At Zero Current		0.5600	0.4400
0.050086	0.3	0.5605	0.4395
0.050086	0.5	0.5608	0.4392
0.050086	1.0	0.5615	0.4385
At Zero Current		0.5601	0.4399
0.072346	0.3	0.5606	0.4394
0.072346	0.5	0.5610	0.4390
0.072346	1.0	0.5619	0.4381
At Zero Current		0.5600	0.4400
0.10519	0.3	0.5608	0.4392
0.10519	0.5	0.5612	0.4388
0.10519	1.0	0.5623	0.4377
At Zero Current		0.5602	0.4398
0.20079	0.3	0.5609	0.4391
0.20079	0.5	0.5615	0.4385
0.20079	1.0	0.5627	0.4373
At Zero Current		0.5602	0.4398

Units:M,mol l-1; I,mA

FIG (4-2-9)

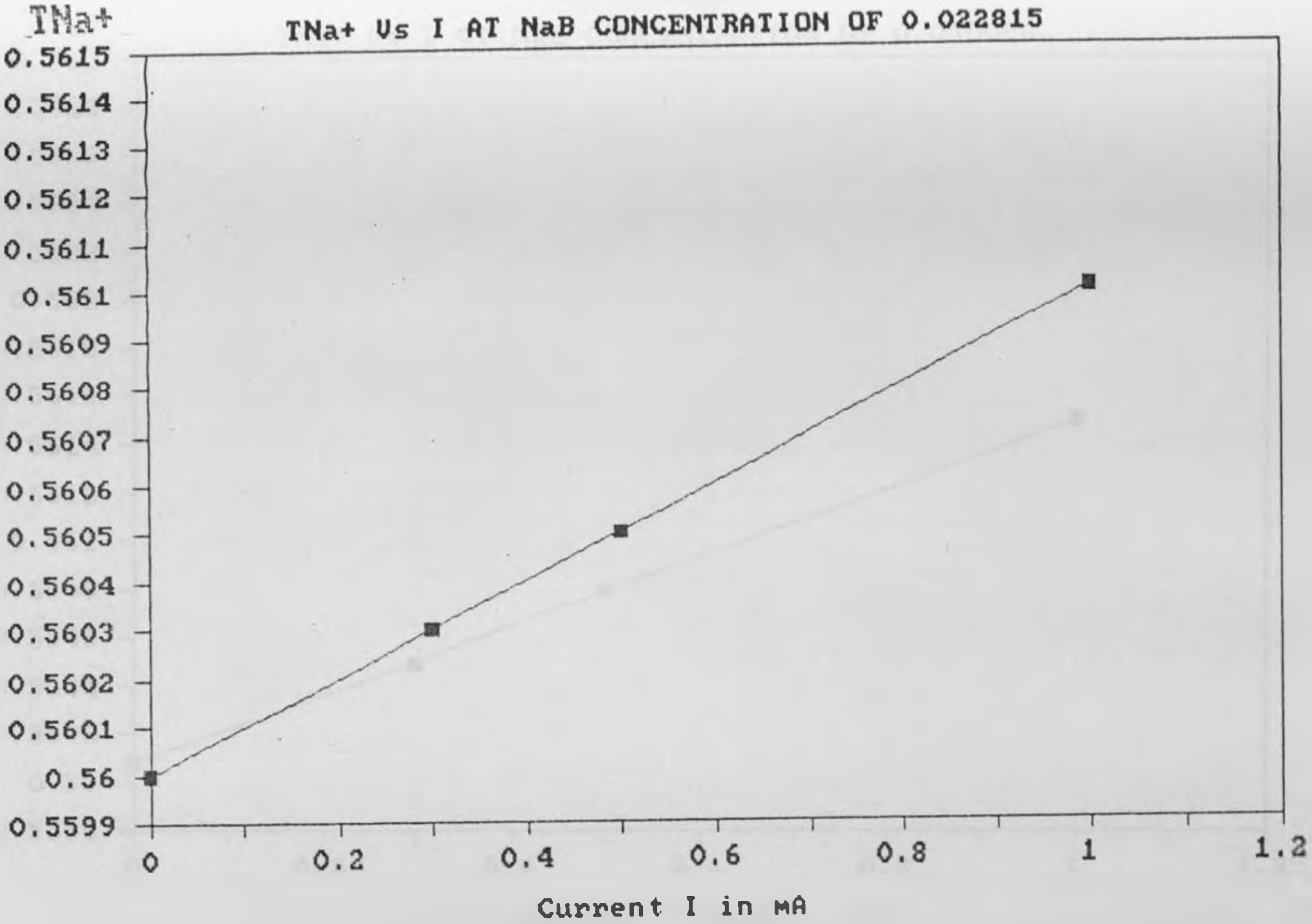
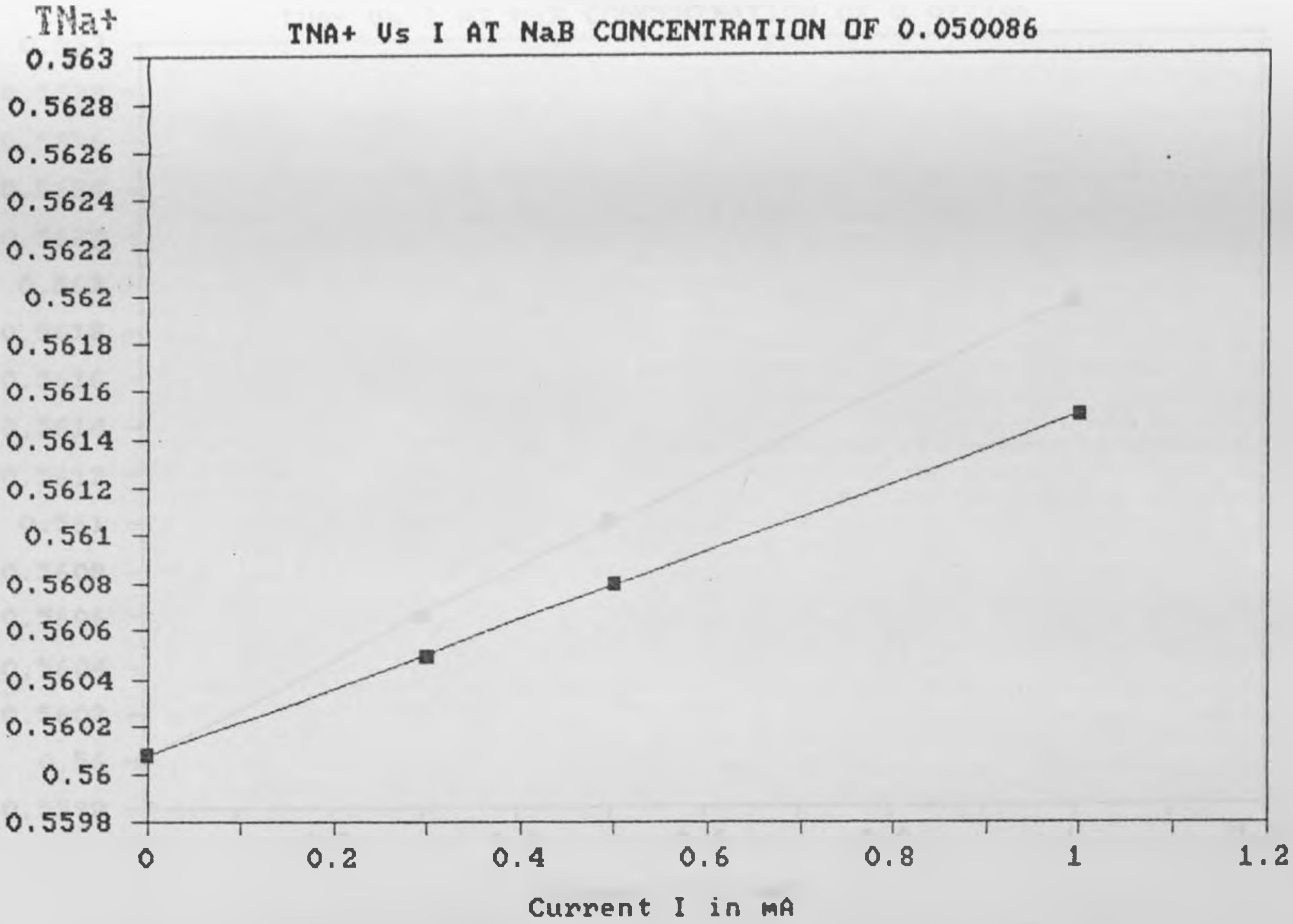

TNa+
TNa+ Vs I AT NaB CONCENTRATION OF 0.022815
0.5615
0.5614
0.5613
0.5612
0.5611
0.561
0.5609
0.5608
0.5607
0.5606
0.5605
0.5604
0.5603
0.5602
0.5601
0.56
0.5599
0
0.2
0.4
0.6
0.8
1
1.2
Current I in mA

FIG (4-2-10)



TNa+
TNA+ Vs I AT NaB CONCENTRATION OF 0.050086
0.563
0.5628
0.5626
0.5624
0.5622
0.562
0.5618
0.5616
0.5614
0.5612
0.561
0.5608
0.5606
0.5604
0.5602
0.56
0.5598
0
0.2
0.4
0.6
0.8
1
1.2
Current I in mA

FIG (4-2-11)

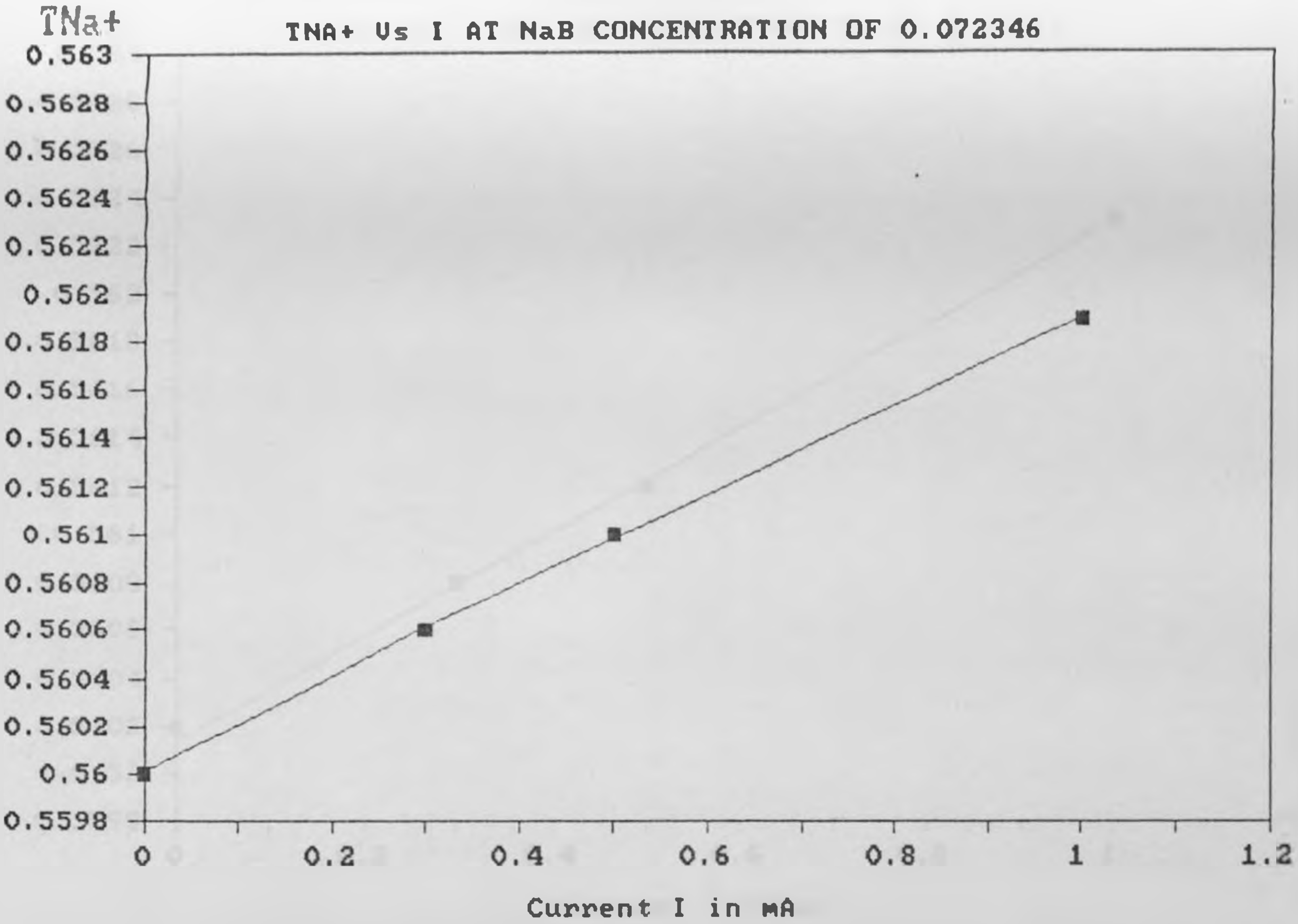

TNa+
TNA+ Vs I AT NaB CONCENTRATION OF 0.072346
0.563
0.5628
0.5626
0.5624
0.5622
0.562
0.5618
0.5616
0.5614
0.5612
0.561
0.5608
0.5606
0.5604
0.5602
0.56
0.5598
0
0.2
0.4
0.6
0.8
1
1.2
Current I in mA

FIG (4-2-12)

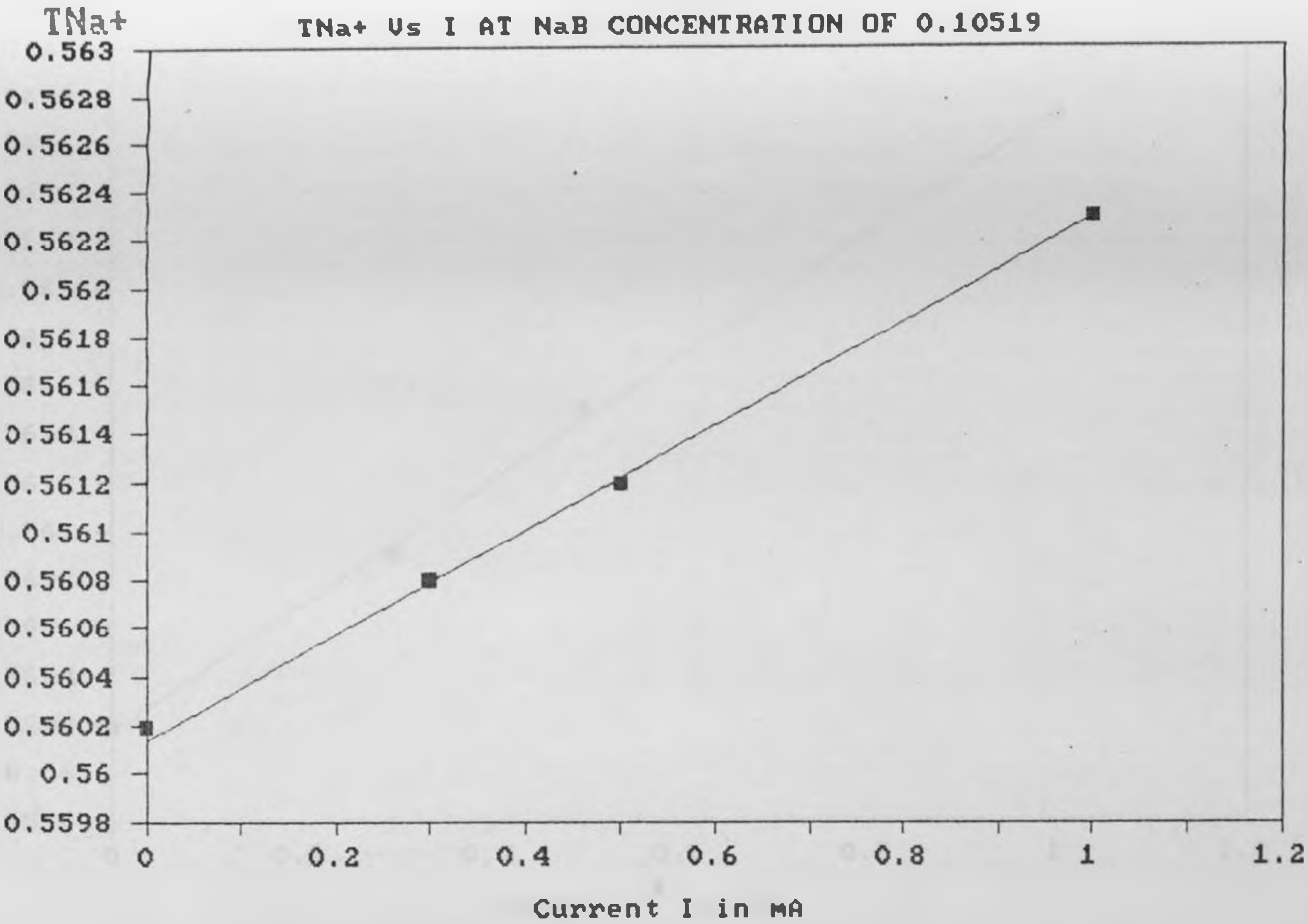

TNa+
TNa+ Vs I AT NaB CONCENTRATION OF 0.10519
0.563
0.5628
0.5626
0.5624
0.5622
0.562
0.5618
0.5616
0.5614
0.5612
0.561
0.5608
0.5606
0.5604
0.5602
0.56
0.5598
0
0.2
0.4
0.6
0.8
1
1.2
Current I in mA

FIG (4-2-13)

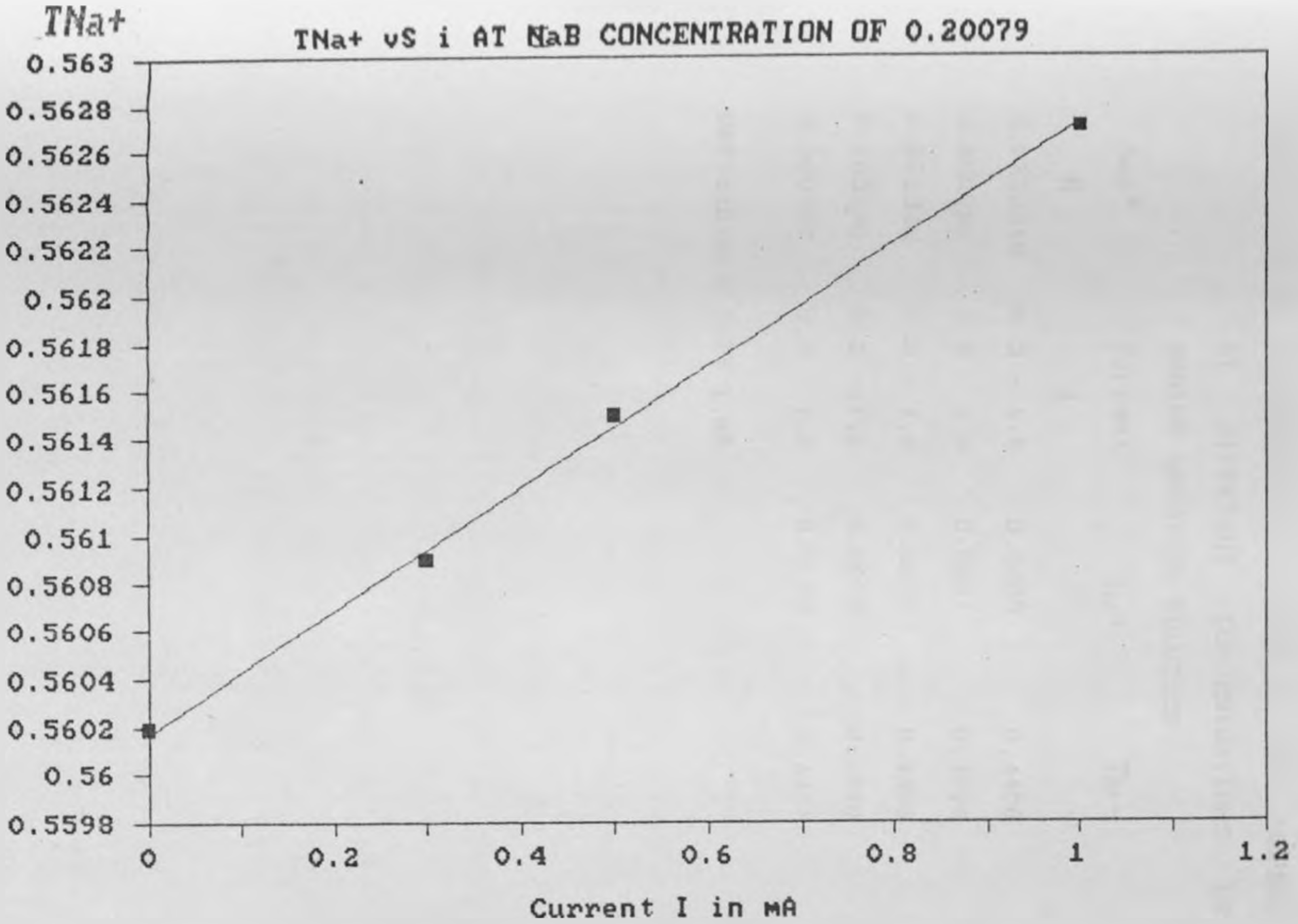

TNa+
TNa+ vS i AT NaB CONCENTRATION OF 0.20079
0.563
0.5628
0.5626
0.5624
0.5622
0.562
0.5618
0.5616
0.5614
0.5612
0.561
0.5608
0.5606
0.5604
0.5602
0.56
0.5598
0
0.2
0.4
0.6
0.8
1
1.2
Current I in mA

Table (4-2-5) TRANSFERENCE NUMBERS AT ZERO CURRENT AT DIFFERENT CONCENTRATIONS OF SODIUM BARBITAL SOLUTION

NaB*	Current	T_{Na^+}	$T_{B^{*-}}$
M	I		
0.0222315	0.3 - 1.0	0.5600	0.4400
0.050086	0.3 - 1.0	0.5601	0.4399
0.072346	0.3 - 1.0	0.5600	0.4400
0.105190	0.3 - 1.0	0.5602	0.4398
0.200790	0.3 - 1.0	0.5602	0.4398

Units:M,mol l-1; I,mA

For Sodium Barbital, the theoretical (or calculated) transference numbers can be calculated for each molality using the equation below

$$T_{B^{*-}} = \frac{B^{*-}}{Na^{+} + B^{*-}}$$

For Na^{+} and B^{*-} ions the λ^{o} values were taken as 50.1 and 39.8 S cm^{2} equiv.$^{-1}$ respectively. The numerical constants B_1, B_2, B_3 and a^{o} are the same as employed for Barbituric acid.

λ values can be found using the equation

$$\lambda_i = \lambda_i^{o} - \frac{(B_1 \lambda_i + 0.5B_2)\ m^{1/2}}{1 + B_3\ a^{o}\ m^{1/2}}$$

Table (4-2-6) shows a comparison between $T_{B(expt)}$ and $T_{B(calc)}$ and it is obvious that the values are in good agreement.

The two independent experimental studies namely freezing point and transference numbers meaurements in aqueous Barbituric acid and Sodium Barbital reveals that Barbituric acid undergoes dimerization while Sodium Barbital behaves as a normal 1:1 electrolyte.

Table (4-2-6): COMPARISSON OF $^{T}B(expt)$ and $^{T}B(calc)$ IN SODIUM BARBITAL SOLUTIONS

NaB* M	$^{T}B(expt)$	$^{T}B(calc)$	.T
0.022815	0.4420	0.4427	-0.0027
0.050086	0.4399	0.4410	-0.0011
0.072346	0.4400	0.4400	0.0000
0.105190	0.4398	0.4389	+0.0009
0.200790	0.4398	0.4360	+0.0038

Parameters $Na = 50.1\ S\ cm^2\ equiv.^{-1}$

$B^- = 39.8\ S\ cm^2\ equiv.^{-1}$

4-2-4 CONCLUSIONS

Cryoscopic and transference numbers data has been presented and discussed in chapter 4. It is obvious from what has been said that Barbituric Acid does not behave as a simple 1:1 weak electrolyte. Both cryoscopic and transference number measurments show a pronounced deviation from the theory. The postulate that a dimeric anionic species, $(B_2)^{2-}$, is present in the entire concentration range studied, explains very well the discrepancy between theory and experiment. The calculations of activity coefficients - a thermodynamic property- further substantiates the existance of these complex ionic species.

It can therfore be concluded that the formation constant, equivalent conductance of Barbiturate ion B^- and the complex ionic species $(B_2)^{2-}$ are

$K_D = 3.0 \pm 0.1$ kg Mol^{-1}

$\lambda^{\circ}_{B^-} = 22.51 \pm 0.15$ S cm^2 eqiv^{-1}

$\lambda^{\circ}_{(B_2^{2-})} = 40.0 \pm 0.1$ S cm^2 equiv^{-1}

$T_{B^-} = 0.584 \pm 0.01$

As for Sodium Barbital, the experimental data find a good correspondence with the theory. Hence the salt retains it's 1:1 strong electrolyte behavior in the entire concentration range. The expected hydrolysis, however, cannot be ignored. Unfortunately the effect of hydrolysis is much more manifested in the very low concentration range. The effect of hydrolysis, therefore, could not be detected and at least did not affect the measured values to the extent that it showed any departure from the 1:1 electrolyte nature.

Thus NaB^* remains effectively a 1:1 electrolyte with

$$\lambda^{o}_{B*-} = 39.8 \pm 0.2 \ \text{S cm}^2 \ \text{eqiv}^{-1}$$

$$T_{B*-} = 0.4390 \pm 0.01$$

APPENDIX 1

```
   5  REM BBC BASIC
   10 ON ERROR GOTO 560
   20 AERROR   ERL
   30 DATA
1.973E-3,.004,2.999E-3,.007,4.119E-3,.009,4.143E-3
,.009,5.999E-3,.013
   40 DATA
6.109E-3,.013,8.021E-3,.017,8.076E-3,.017,1.0012E-
2,.02,1.0522E-2,.021
   50 DATA 1.9961E-2,.038,2.029E-2,.04
   55 *DEL. ALBE2
   60 LL = OPENOUT "ALBE2"
   70 A=0.4918
   80 Z1=1
   90 Z2=1
  100 B3=0.3248E8
  110 A0=5E-8
  120 KA=1.01E-4
  130 REM INITIAL APPX VALUES OF ALPHA AND BETA
  140 INPUT "INPUT VALUE OF KD" KD
  150 PRINT
TAB(2);"MOLALITY";TAB(20);"ALPHA";TAB(35);"BETA";T
AB(55);"KF"
  160 FOR N=1 TO 12  STEP 1
  170   READ M,DT
  180   ALPHA = 1
  190   TEST1 =1
  200   TEST2 =0
  210   BETA=0
  220   REM CALC LOG GAMMA
  230   J=SQR(( ALPHA + BETA)*M)
  240   LGAMMA1=(-A)*Z1*Z2*J/(1+(B3*A0*J))
  250   GAMMA1=10^LGAMMA1
  260   REM CALC ALPHA
  270   QA=M*GAMMA1
  280   QB=KA-(2*M*BETA*GAMMA1)
  290   QC=-KA
  300   GOSUB 590
  310   ALPHA=SOLN1
  320   REM CALC BETA
  330   LGAMMAD=(-A)*4*J/(1+(B3*A0*J))
  340   GAMMAD=10^LGAMMAD
  350   REM CALC BETA VALUE FROM QUOD
  360   QA=4*M*KD*GAMMAD
  370   QB=-((4*ALPHA*M*KD*GAMMAD)+GAMMAD)
  380   QC=M*(ALPHA^2)*KD*GAMMAD
  390   GOSUB 590
  400   BETA=SOLN1
  410   IF ABS(TEST1-ALPHA) < 0.00001 AND
ABS(TEST2-BETA) < 0.000000001 THEN 440
  420   TEST1 = ALPHA :TEST2=BETA
  430   GOTO 230
```

```
  440   REM SOLVE FOR KF
  450   L=DT*(1+(5.4E-4*DT))
  460   S=(1+ALPHA-BETA)*M
  470   KF=L/S
  480   PRINT
TAB(4);M;TAB(20);ALPHA;TAB(35);BETA;TAB(50);KF
  490 PRINT£LL, ALPHA,BETA
  500 NEXT
  510 INPUT "WOULD YOU LIKE ANOTHER RUN ? Y/N";
ANS$
  520 GOSUB 750
  530 IF ANS$ = "N" THEN PRINT "END OF
PROGRAM":GOTO 575 ELSE 540
  540 RESTORE
  550 GOTO 130
  560 PRINT "ERROR FOUND IN LINE "AERROR
  562 PRINT
  565 PRINT "TYPE OF ERROR FOUND IS GIVEN IN LINE
BELOW "
  570 REPORT
  575 CLOSE£0
  580 END
  590 REM SUBROUTINE TO SOLVE QUADRATIC EQN
  600 D=QB*QB-4*QA*QC
  610 IF D <> 0 THEN 650
  620 PRINT "BOTH ROOTS ARE EQUAL, AND HAVE THE
SAME VALUE:";-QB/(2*QA)
  630 GOTO 740
  640 PRINT
  650 IF D > 0 THEN 680
  660 PRINT "THIS EQN DOES NOT HAVE REAL ROOTS"
  670 GOTO 740
  680 D1= SQR(D)
  690 IF QB >= 0 THEN 720
  700 R1 = (-QB+D1)/(2*QA)
  710 GOTO 730
  720 R1 = (-QB - D1)/(2*QA)
  730 SOLN1=QC/(QA*R1)
  740 RETURN
  750 REM ANSWER CHECK SUBROUTINE
  760 IF ANS$ =  "N" OR ANS$ = "Y" THEN 780
  770 PRINT  "  RESPOND Y OR N": GOTO 510
  780 GOTO 530
  790 RETURN
```

>

APPENDIX 2

```
    5  REM BBC BASIC
   10 MODE0
   20 DATA
1.967E-3,.0044,2.99E-3,.0065,4.106E-3,.0088
   30  DATA
4.13E-3,.0088,5.98E-3,.0125,6.089E-3,.0128
   40  DATA
7.994E-3,.0165,8.05E-3,.0166,9.977E-3,.0204
   50 DATA
1.0485E-2,.0214,1.98766E-2,.0397,2.0205E-2,.0404
   60 DIM TEST(3), ACCUR(3)
   70 LAMDAD20=40
   80 PRINT
   90 PRINT "LAMDAD20 = ";LAMDAD20
  100 PRINT TAB(10);"MOLARITIES";TAB(25);"TRANSPORT
No"
  110 XX=OPENIN "ALPBETA"
  120   FOR N=1 TO 12
  130      READ M,DT
  140      INPUT£XX,ALPHA,BETA
  150      REM
  160      A=0.4918
  170      Z1=1
  180      Z2=1
  190      B3=.3248E8
  200      A0=5E-8
  210      KA=9.83E-5
  220      LAMDAH0=349.8
  230      LAMDAB0 = 22.51
  240      B1 = 0.23
  250      B2 =60.65
  260      LAMDA0 = 372.31
  270      REM CALC LOG GAMMA
  280      J=SQR(( ALPHA + BETA)*M)
  290      LGAMMA1=(-A)*Z1*Z2*J/(1+(B3*A0*J))
  300      GAMMA1=10^LGAMMA1
  310      ROOTI = SQR((ALPHA+BETA)*M)
  320      CONST1 =((B1*LAMDAB0)+(B2/2))* ROOTI
  330      CONST2 = 1+(B3*A0*ROOTI)
  340      LAMDAB = LAMDAB0 - (CONST1/CONST2)
```

```
  350      REM OPTIMISATION OF LAMDADO
  360      REM OPTIMISATION LOOP
  370      CONST3 = ((B1*LAMDAD20) + (B2/2)) * ROOTI

  380      LAMDAD2 = LAMDAD20-(CONST3/CONST2)
  390      CONST4 = (B1*LAMDAH0+(B2/2))*ROOTI
  400      LAMDAH = LAMDAH0-(CONST4/CONST2)
  410      CONST5 = ALPHA*LAMDAH
  420      CONST6 = (ALPHA-2*BETA)*LAMDAB
  430      TH =
CONST5/(CONST5+CONST6+(BETA*LAMDAD2))
  440      PRINT TAB(10);M;TAB(27);TH
  450    NEXT
  460    RESTORE
  470 CLOSE£0
  480 END
>
```

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