ANALYTICAL APPLICATIONS

OF

LIQUID JUNCTION POTENTIAL

BY

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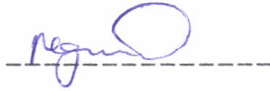
A thesis submitted in partial fulfilment of the degree of master of Science of the University of Nairobi.
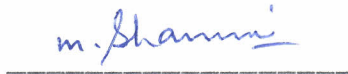
DECLARATION

This thesis is my original work and has not been presented for a degree in any other University.

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This thesis has been submitted for examination with our approval as University supervisors.

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Dedicated to friends

Analytical applications of the liquid junction potential.

Abstract

The results presented in this thesis reveal a marked improvement in the use of liquid junction potential which in most occasions is a bother in our electrochemical measurement. The liquid junction potential is encountered in many living and non-living systems. In all concentration cells there is a component arising from liquid junction. The concept of liquid junction is as old as the electrochemistry and in this research we have used the liquid junction as an analytical tool.

The main work has been to develop a convenient method of setting up a cell that offers a straight forward liquid junction measurement.

This cell is then used to study the variation of ϵ_j (liquid

junction potential) with concentration and hence used this as an analytical probe by adopting the usual calibration curve method. The liquid junction potential was found to have a linear relationship with concentration. This enabled the use of the plot to obtain the concentration of unknown solution. The theoretical liquid junction was compared with observed one and they were found to be almost the same. An attempt was also made to make a cheaper F^- responsive electrode. The result was positive as the electrode was more responsive towards the fluoride solutions.

Acknowledgement

I wish to express my sincere gratitude to my supervisors , Prof. M. Shamim and Dr. N. Desai for their supervision, advice and encouragement during the course of this work. I am particularly thankful to Prof. Shamim , my first supervisor for his inspiration throughout the course of investigation and compilation of this work. Prof. Shamim tirelessly read many drafts of this thesis, and his innumerable comments and suggestions helped to clarify many of the ideas.

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CHAPTER 1

INTRODUCTION

In the field of electrochemistry in physical chemistry one of the areas of interest for study is the liquid junction and the potential that arises from it. In this research it is the central theme of interest and therefore it is important to have a close look at it first.

1.1 Liquid junction potential

When two solutions either of different concentrations or of different ions are brought into contact a potential comes into being. This potential is known as liquid junction potential. The liquid junction is a function of diffusion which is an irreversible process that causes a spontaneous flow of matter from higher concentration to the lower concentration and continues till the matter attains uniform concentration throughout the body of the system.

In concentration cells, electrical energy is a result of free energy of dilution in which two solutions of different concentrations tend to mix at constant temperature and consequently increase the entropy of the system [1].

In a solution containing a single solute, the solute moves from a region of higher concentration to that of lower concentration while the solvent moves in the opposite direction. From the point of view of molecular kinetics no individual solute particle shows preference for motion in any particular direction, but a definite fraction of the particles in an elementary unit

volume may be considered moving, say in the positive x-direction. In an adjacent volume element the same fraction may be considered moving in the negative x-direction. If the concentration in the first volume element is greater than in the second, this means that more particles will be leaving the first element for the second than will be entering from the second to the first. So there will be a resultant flow of solute in the direction of lower concentration [2].

The concentration gradient is the driving force for diffusion which leads to a spread of the boundary. The flow of matter through a unit surface driven by concentration gradient is equal to the concentration gradient multiplied by the diffusion coefficient [3]. Diffusion, in everyday practical application, is often two or three dimensional process, however nothing essential is lost in understanding by confining attention to the one dimensional case. It is implied above that an ion in solution is acted on by at least two physical forces. One arising from the chemical potential gradient and the other from the electrical potential difference. The chemical potential is related to the concentration of the ion and the electrical potential is as a result of the net positive and negative charges carried by the ions. When a salt is added to the water, it diffuses throughout the solution from the region of high concentration to that of lower concentration until a uniform concentration is achieved.

One of the ions may have a higher mobility than the other and will tend to diffuse faster than its oppositely charged partner causing slight separation of charge. This sets up an electrical potential gradient leading to a diffusion potential.

As a result the faster ion is slowed down and the slower one is speeded up until they both move at the same rate.

According to the Fick's law

$$\frac{dV}{dt} = -DA \frac{\partial c}{\partial x}$$ 1.1

where

$$\frac{dV}{dt}$$ = rate of diffusion,

D= diffusion coefficient proportionality constant,

A= area across which diffusion occurs,

$$\frac{\partial c}{\partial x}$$ = concentration gradient.

The region most affected by the phenomenon above is that next to the electrodes. The electrodes function as sites for the transfer of charge (electrons or ions) across phase boundary. In one of the separate phases, charge moves by electronic conductive processes whereas in the other it moves by electrolytic mechanisms, through transport of ions [4].

It is worth pointing out that differences in the diffusion rates can influence rates of electro-chemical reactions during polarisation to maintain the steady state concentration. This is the usual assumption if the bulk of the respective ion is high and diffusion can replace discharged ions sufficiently fast so

that no appreciable concentration overpotential develops [5].

1.2 Role of liquid junction potential

Liquid junction potential is encountered in many living and non-living systems. For example in concentration cells, the potential observed arises from liquid junction. The fluids in plants have got different concentrations at different regions and hence solutions lying alongside each other generate liquid junction potential. The concept of liquid junction is as old as the electrochemistry, which is a well developed area of chemistry with a complete set of theories and quantitative relationships. In many respects it is one of the oldest concepts of classical physics and chemistry and traces its origin to the mid-nineteenth century. During the past two decades the dynamics and mechanisms of electron transfer process have been studied by numerous groups throughout the world. This has been made possible by applying transition state theory to the electrochemical kinetics occurring at the electrodes. As a result both the kinetics of electron transfer process (from solid to solution) as well as pre and post chemical homogenous process can be characterized quantitatively. Electrochemistry has found extensive new application for the study of electrochemical reactions and adsorption phenomena [6].

Liquid junction finds its application in interfacial phenomena which deals with equilibria established when two phases like metal electrode and an aqueous solution are brought into contact with each other in liquid-liquid junction. In these

cases a transition region develops in which the properties of each compound deviate from its properties in the bulk of either phase [7].

1.3 Objective

The objective of this research is to use the liquid junction as an analytical tool. The general equation for the liquid junction potential, ε_1, is,

$$\varepsilon_1 = 2t_{\pm} \frac{RT}{nF} \ln\frac{C_2}{C_1} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 1.2$$

It is obvious that the ε_1 is a function of the two concentrations C_1 and C_2, forming the junction. If one of the two concentrations is known, the other can be determined from the measured value of ε_1.

Cells have been investigated in detail and equation for ε_1 have been arrived at. The general cell of the type involving liquid junctions can be written as

$$M/MX_{(s)}/AX_{(1)}/AX_{(2)}/MX_{(s)}/M.$$

Where M/MX(s) is an electrode and AX(1) and AX(2) represent two solutions at concentrations 1 and 2 respectively. The emphasis was either to take ε_1 into account in the computation of the total emf of the cell or to get rid of it or at least to minimize it to a negligible extent. However, no attempt has been made to make use of ε_1 in the determination of the concentration of a given solution. The cell shown above offers a straight-forward method to determine the concentration. Perhaps it was the

inconvenience and difficulties in setting up new cells each time which deterred the workers to use it for analytical purposes.

The main purpose of the work was to develop a convenient method of setting up such cells and use it to study the variation of ϵ_1 with concentration and hence to use it as an analytical probe by adopting the usual calibration curve methods.

1.4 Types of liquid junction

There are three different types of liquid junctions which one can usually encounter. These include:

(a) solutions of the same ions but at different concentrations,

(b) solutions of the same concentration but having different ions,

(c) solutions of different ions at different concentrations.

The movement of the ions in the three categories of junction above are represented pictorially in figure 1.

(a)

HCl (0.01M) | HCl (0.1M)

← H^+

← Cl^-

⊕ | ⊖

(b)

HCl (0.1M) | KCl (0.1M)

H^+ →

← K^+

⊖ | ⊕

(c)

HCl (0.1M) | KNO_3 (0.05M)

H^+ →

Cl^- →

← K^+

← NO_3^-
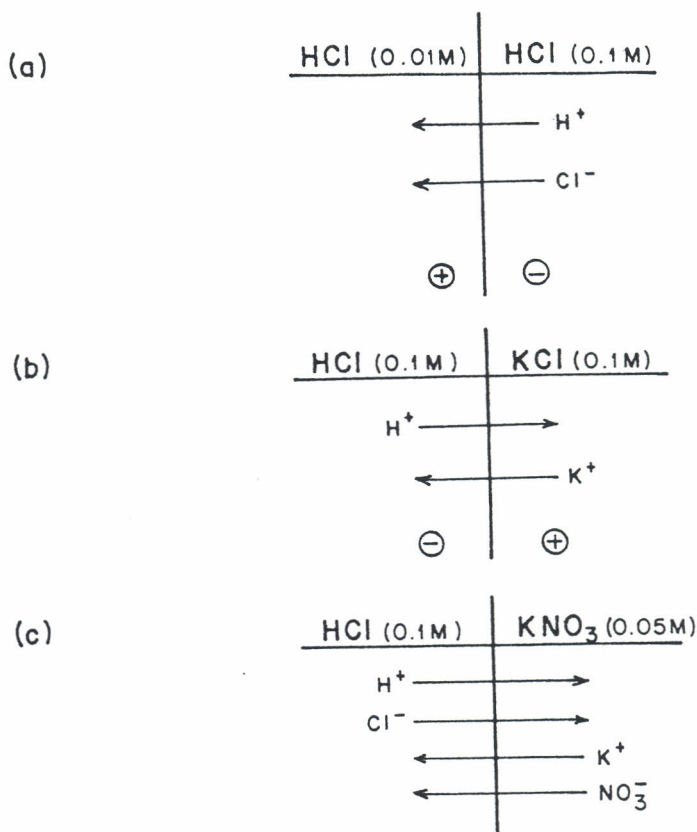
Figure 1 Pictorial representation of junctions

The junction types also differ in the resistance to block the rate of attainment of steady state diffusion and in the electrical resistance. Most liquid junctions of commercial reference electrodes are a compromise between the requirement for an ideal junction and mechanical strength and practical usefulness [9].

The above types suggest that the measured liquid-junction potential can be used no matter what kind of cell eventually it is. It is not out of place to compare the technique under investigation with those commonly in use e.g polarographic and conductance techniques.

The utility of polarographic techniques depends upon

existence of some definite relation between limiting current i_d and the rate of diffusion D of the electro-active species and the characteristics of the electrode. The equation relating the quantities derived by Ilkovic and Heyrovsky is

$$I_D = knD^{1/2} \, m^{2/3} t^{1/6} C \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 1.3$$

where

I_D = diffusion current, μ amp

n = number of electrons transfered in electrode reaction

k = constant = 607 when I_D is mean diffussion current

D = diffusion coefficient of reducible species $cm^2 \, s^{-1}$

t = drop time, sec

C = concentration of reactant, millimoles /liter

m = rate of flow of mercury from tip, mg/sec

Polarographic method is applied to determine the concentrations of a variety of inorganic anions and metallic cations. The apparatus for polarographic analysis consists essentially of an electrolytic cell in which the cathode is mercury which is being continuously renewed by falling drops from the end of a capillary tube. The anode is relatively large pool of mercury at the bottom of the vessel. A dilute solution containing one or more salt is placed in the cell and an emf is increased gradually from 0.0 to -2.0V and the corresponding values of the current is recorded [10]. A polarogram obtained in this way of a solution containing, say, four cations, each at a concentration of $10^{-3}M$ is shown in fig. 1.2.
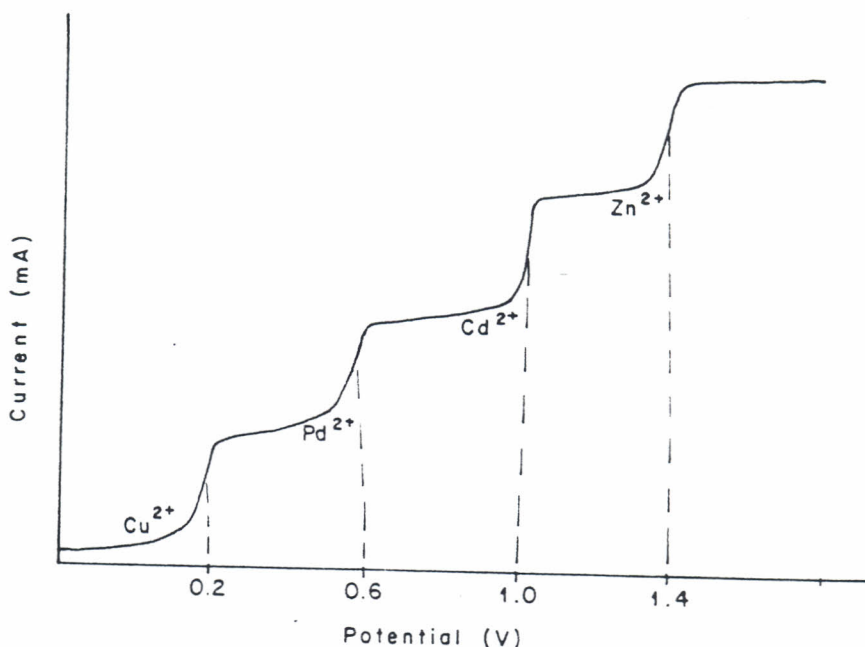
Figure 1.2: Polarogram

In the electrolysis of this solution copper deposits first on the cathode as this has the lowest oxidation potential. As the current increases a point is reached at which diffusion of copper ions to the dropping mercury cathode is no longer able to satisfy the requirements of the current; another process that is the discharge of lead ions must occur in addition.

The discharge of each ion is represented by a 'wave' represented by an increase of current followed by an increase of potential at almost constant current to the next wave. The height of a wave in units of current is called the diffusion current and it is proportional to the concentration of the solution of the ion being discharged. The potential at the centre of the rising part of the wave referred to as half-wave potential serves to

identify the ion. [11] [12]

In conductivity measurements, both the specific and equivalent conductances of a solution vary with concentration. For strong electrolytes, at concentrations up to several equivalents per litre, the conductances change sharply and linearly with increase in concentration. In contrast, the conductances of weak electrolytes initially drop sharply then tend to become steady with concentration. The equivalent conductances of substances such as strong acids, alkalis and their sodium salts change linearly with concentration. This is evident from the figure below [13] [14].
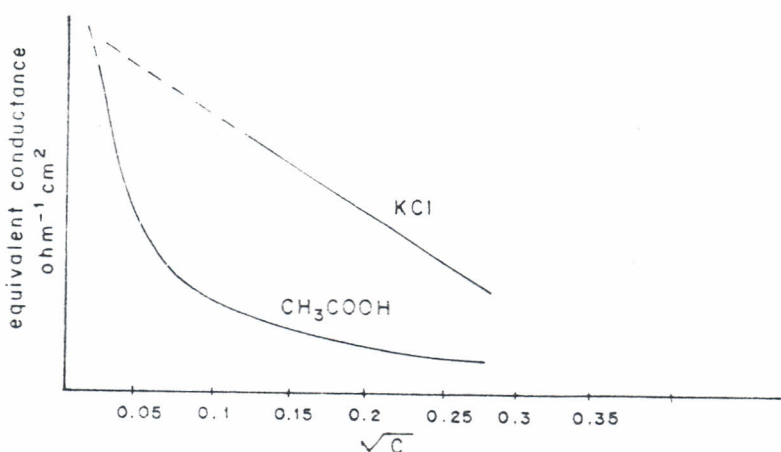
Figure 1.3 Equivalent conductance versus concentration

In the case of a liquid junction, it does not require elaborate equipment for analytical purposes provided the setting up of the cell is not a problem as it will be shown in the experimental section. It is very easy to determine the concentration of a substance in any solution by measuring emf of a series of known solutions.

1.5 Ion responsive electrodes

These are, in many respects, ideal sensors for use in analysis of industrial sample or in the control of particular constituent in a flowing system. Thus in recent years, the advantages which they offer have led to their adoption in a wide range of applications. There are several characteristics in performance of ion-responsive electrodes which give them important advantages over other techniques in the field of process control. However, the final choice for a particular application will be the result of a careful consideration of the relative merits of the techniques available. Taking into account such factors as maintenance, the degree of skill needed to run them, the necessary accuracy and precision and equipment cost etc.It is not an expensive technique.

The prime advantage of ion-responsive electrodes is their insensitivity to the presence of other ionic species. They offer rapid response to change in concentration of a particular ion. They are used in wide range of concentrations and are simple to use though are relatively expensive [15].

1.6 Fluoride responsive electrode

In the commercially produced fluoride ion responsive electrode LaF_3 is used wherein fluoride ion conducts the current. The ion F^- is smaller than La^{3+} and is more mobile and virtually all charge transfer is due to F^- ion. When the equilibrium between $F^-(aq)$, and $F(s)$ has been established at each interface, the activity of the F- at the inner surface is likely to be different from that of the outer surface i.e.

a(F⁻ inner surface) ≠ a(F outer surface)

The result is a diffusion potential which sets up between the two surfaces in a similar fashion to liquid junction potential. As the former is a constant value, the diffusion potential is thus dependent on the activity of F^- in the test solution. Only ions of similar size, shape and charge to F^- ions can occupy these sites. The combinations of these three characteristics are unique for F^- ion electrode [16]. There are two types of F^- responsive electrodes with heterogeneous or homogeneous membrane. In the latter the active material is reasonably conducting single crystal whose conductance, if it is low, is increased by doping it with other compatible material such as lanthanum tri-fluoride whose conductance is increased by doping it with europium. In the case of heterogeneous membrane, AgF is used as the active material and it is held in an inactive matrix such as paraffin, thermoplastics, polymer material or silicone rubber. AgF behaves like solid electrolyte and the silver ion acts as the charge carrier moving

through the crystal lattice. The crystal lattice could be highly selective since its conduction occurs by a lattice defect mechanism.

Any interference can only arise from chemical reaction at membrane surface. Thus no diffusion potential is generated within the surface because fluorides of lanthanides crystallize with hexagonal lattice with orthorhombic structure. In hexagonal lattice each metal ion is surrounded by five F^- ions [17]

The problem of specificity and mechanism of ion transfer in ion exchange membrane has been considered by Stuffs [18]. In a number of studies, simple membrane electrodes made from organic or inorganic ion exchangers and showing little selectivity to a particular ion has been used in the estimation of ion activities. Ion exchange membranes have been used to concentrate ions in analysis of certain trace elements.

A big problem with the commercially available F^- responsive electrodes is that, apart from being very expensive, a buffer solution has to be used to ensure a minimal response from the H^+ or OH^- ions. Scarcity of buffers is quite common and in most cases a buffer solution at an undesirable range is used. It is desirable to have cheaper way to prepare F^- responsive electrode that will be stable over a wide range of pH and is easy to use [18] [19].

THEORETICAL ASPECTS

2.1 Types of junction

Liquid junction can be classified into four types:

(a) Continuous mixture junction

It consists of a solution layer of any thickness whose composition varies continuously from pure sample on one side to pure bridge salt solution on the other. It is somewhat unstable and difficult to achieve. It is therefore not commonly used.

(b) Constrained diffusion junction

The constrained junction utilizes a membrane or any other permeable material to separate two solutions and diffusion occurs across this constant-thickness transition layer. The solution on either side of the membrane are maintained at a constant composition so that mixing occurs in a transition phase.

(c) Flowing junction

This type of junction is obtained when two solutions move towards each other to meet and thus forming a sharp boundary. It can be achieved by allowing solution to enter in opposite arms of a tube meeting and leaving through the third limb as shown in the following figure (Fig.2.1).

Diagram
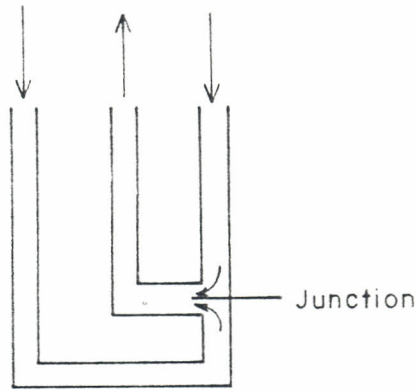
Figure 2.1   Flowing junction

(d) Free diffusion junction.

This type of junction is easy to produce and is most widely used. When solutions are caused to meet initially a sharp boundary is formed which subsequently undergoes free diffusion [20].

2.2 Junction potential and reference electrode

The reference electrode is electrically connected to the working electrode by a salt bridge or by a Lugging's capillary.There can be one or more junctions in a cell. A potential difference will arise between two different ionic solutions in contact because of different mobility of the ions across the junction. The liquid junction and the resulting potential arises from the contact between dissimilar ionic

solutions. This constitutes one of the most important and difficult part of electrochemical measurements both from theoretical and practical standpoints [21],[22].

Let us consider a junction of two electrolytes where

```
|            |              |              |
|            | +        -   |              |
|            | +        -   |              |
|            | +        -   |              |
|            | +        -   |              |
|            | +        -   |              |
|            | +        -   |              |
|            | +        -   |              |
|            | +        -   |              |
|            | +        -   |              |
|            | +        -   |              |
|            | +        -   |              |
|            | +        -   |              |
```

$C_{KCl} = C_1$ $C_{HCl} = C_2$
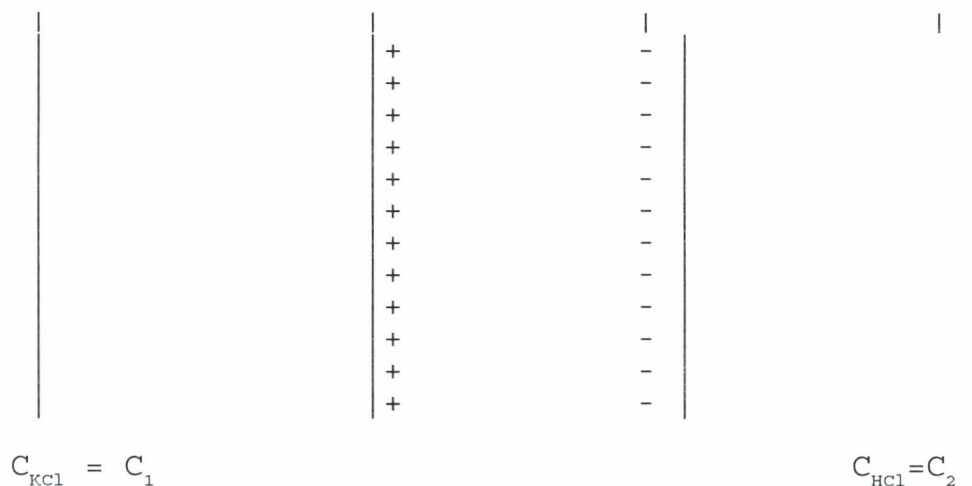
C_{HCl} of concentration C_2 and C_{KCl} of concentration C_1 form a junction. They diffuse in opposite directions across the junction from region of greater activity to one of lower activity. The H^+ ions have greater mobility than K^+ or Cl^- ions. They therefore, diffuse more rapidly across the junction. This causes separation of charge which retards the velocity of faster ions and accelerates the ions of low mobility until their velocities becomes equal and a steady junction is produced. Potential measurements in two different solvents cannot be related although the same reference electrode is used. If thermodynamic assumptions are made then the dilemma can be resolved. This can be realised if we recall that chemical potential for each solvent is different from each other and this will affect the potential obtained [23] [24].

2.3 Calculation and direct measurement

The fraction of the total cell potential due to the junction potential cannot be unambiguously assigned. It is possible, however, to estimate junction potential indirectly or to make

calculations based on assumptions about the distribution of the ions in the region of the junction. For a junction between the dilute solutions of the same univalent electrolyte, the calculated values appear to be quite exact and independent of the way in which the junction is formed.

Attempts have been made to calculate the liquid junction potentials by solving diffusion equation for the ions in solution. Semi-quantitative estimates based on the above picture have led to junction potentials of 5 - 30 mV-not as large as compared to the usual cell emf. [25,26]

2.4 Derivation of the general differential equation for liquid junction potential

If two solutions of electrolytes are brought into contact there will be a region in which the composition varies from that of one solution to that of the other. The region of concentration will depend on the extent of the diffusion, convection and mixing. Consider a thin layer AB.

```
       A           B
 C₁  |        | C₁  ±  dC₁
     |        |
     |        |
 C₂  |        | C₂  ±  dC₂
     |        |
 C₃  |        | C₃  ±  dC₃
     |        |
     |        |
 Cₙ  |        | Cₙ  ±  dCₙ
     A       B
```

Where

1, 2, i ....and n are ions at concentration C_1, C_2 C_i...and C_n and Z_1, Z_2 Z_i......and Z_n are the valencies of ions 1,2 i.......and n and t_1, t_2 t_i..........and t_n are the transference numbers of the ions.

If a faraday of current is passed reversibly from side A to

side B; $\dfrac{t_i}{z_i}$ mole of each ion will pass through the layer.

The total change of Gibbs free energy d_z will be

$$d_z = \sum_n \frac{t_i}{z_i} d\mu_i \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 2.4.1$$

here

μ_i = chemical potential and

$t_1 + t_2 + t_3 \dots\dots\dots + t_i \dots\dots\dots + t_n = 1$

$$-d\varepsilon_1 = \frac{RT}{F} \sum \frac{t_i}{z_i} \, d \ln a_i \quad \dots\dots\dots\dots\dots\dots\dots 2.4.2$$

This follows from,

$$d_z = -nF\varepsilon_L \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 2.4.3$$

and

$$\mu_i = \mu_0 + RT \ln a_i \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots 2.4.4$$

Integrating both sides we obtain.

$$\varepsilon_1 = \frac{RT}{F} \int_I^{II} \sum_n \frac{t_i}{z_i} \, d \ln a_i \quad \dots\dots\dots\dots\dots\dots\dots\dots 2.4.5$$

For the junction of the cell

$Ag/AgCl_{(s)}/NaCl(C_1)/NaCl(C_2)/AgCl_{(s)}/Ag$
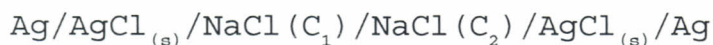
$$\varepsilon_1 = \frac{RT}{F} \left[t_+ Na^+ \ln \frac{a_{Na^+}^1}{a_{Na^+}^{II}} - (1 - t_+ Na^+) \ln \frac{a_{Cl^-}^1}{a_{Cl^-}^{II}} \right] \quad \dots\dots\dots\dots 2.4.6$$

If the transference number is not constant in the range C_1 to C_2 equation 2.4.5 becomes

$$-\epsilon_1 = \frac{RT}{F} \int_1^{11} t_+ Na^+ d\ln a_{Na^+} - \frac{RT}{F} \int_1^{11} (1 - t_+ Na^+) \, d\ln a_{Cl^-} \quad \dots\dots\dots\dots 2.4.7$$

or

$$\epsilon = \epsilon_1 + \epsilon_2 + \epsilon_3 = \frac{RT}{F}\int_1^{11} t_+ Na^+ d\ln a_{Na^+} a_{Cl^-} \quad \dots\dots\dots\dots\dots 2.4.8$$

We have no means of evaluating individual ionic activities such as a_{Na^+} and a_{Cl^-} but can be connected with mean ion activities obtained thermodynamically.

Cells of the type

$$NaCl(C_1)/NaCl(C_1')$$

have potentials that are independent of the manner in which the liquid juntion is formed i.e

$$-\epsilon = \frac{RT}{F}\int_1^{11} \sum_n \frac{t_i}{Z_i} d\ln a_i \quad \dots\dots\dots\dots\dots\dots 2.4.9$$

There is no proof as to the validity of the computations for any single potential .If the tranference number is constant and the ion activities of positive and negative ions are both equal to the mean ion activity then equation (2.4.6) becomes ,

$$\mathbf{g}_1 = (2t_m - 1)\ \frac{RT}{F}\ \ln\ \frac{a_{Cl^-}^{I}}{a_{Cl^-}^{II}} \quad \dots\dots\dots\dots\dots\dots 2.4.10$$

Where m is either Na$^+$ or Cl$^-$

2.5 The Henderson's integration of "mixture boundary".

For integration of equation (2.4.9) to obtain a simple equation, an assumption is made that the function consists of a continuous series of solutions produced by mixing two solutions initially brought into contact. If x is the mixing fraction in the proportion of solution (11) at a particular point in the boundary then proportion of solution I will be (1-x) .

Let $C_1\ C_2\dots\dots\dots C_i\dots\dots\dots C_n$ be the concentrations expressed in equivalents of ions in solution I and $C_1'C_2'\dots\dots C_i'\dots\dots C_n'$ be the corresponding concentrations in II and $Z_1, Z_2,\dots\dots Z_i\dots\dots Z_n$ the valencies retaining the signs. At a position in the boundary where mixing fraction is X the

concentration C_i of ion i will obviously be,

$$C_i = C_i + (C'_i \ C_i) x \dots\dots\dots\dots\dots\dots\dots 2.5.1$$

The transference number t_i of the ion i will be

$$t_i = \frac{C_i \mu_i}{(1-x) \sum_n C_i \mu_i + x \sum_n C'_i \mu_i} \dots\dots\dots\dots\dots\dots 2.5.2$$

where

μ_i = mobility of the ion i and

$\sum_n$ = summation of all terms indicated .

Assuming that the activities a_i are equal to the concentrations C_i and that mobilities are constants in concentration range then the equation (2.4.9) becomes

$$\epsilon_1 = \frac{RT}{F} \int_0^1 \sum \frac{\mu_i / Z_i (C_i - C'_i) \, d_x}{\sum_n C_i \mu_i + x \sum \mu_i (C_i - C'_i)} \dots\dots\dots\dots\dots\dots 2.5.3$$

The above equation on integration within the limits, becomes

$$\epsilon_1 = \frac{RT}{F} \frac{\sum_n \mu_i / Z_i (C_i^{11} - C_i^1)}{\sum_n \mu_i (C_i^{11} - C_i^1)} \ln \frac{\sum_n C_i^1 \mu_i}{\sum_n C_i^{11} \mu_i} \dots\dots\dots\dots\dots\dots 2.5.4$$

which is the Henderson equation [26], [27].

2.6 Calculation of ϵ_1 values

The experimental arrangement for the measuring emf of cells resulted by interposing solution of concentrations ranging from 10^{-1} M to 10^{-6} M . From the measured emf value of cell and the emf contributions of Ag/AgCl/HCl and calomel electrode, the value of ϵ_1 for each cell can be calculated by subtracting one from the

other.To establish the validity of the device it was found

necessary and desirable to cross-check the experimental ϵ_1 with

those given by the Henderson equation (2.5.4).

It is obvious from the Henderson equation that computation of ε_1 requires precise and accurate μ_i values for the anions and cations at specified concentrations. This was done following the steps below

(a) The limiting conductance value for the anion in

question λ°_i was taken from the literature [28] and

substituted in the conductance equation

$$\lambda_i = \lambda^{\circ}_i - (B_1 \lambda^{\circ}_i + x B_2) \sqrt{I} \ \dots\dots\dots\dots\dots\dots\dots\dots 2.5.5$$

to calculate the λ_i value at the desired concentration

of the solution having ionic strength, I.
Here the ionic strength was calculated using
the equation

$$I = 1/2 \ \Sigma C_i \ z_i^2 \ \dots\dots\dots\dots\dots\dots\dots\dots\dots 2.5.6$$

and the values of B_1 =0.23 and that of B_2= 60.65. The value of x for a univalent ion was taken as 0.5 and corresponding values for ions of higher valence.

(b) Once λ_i at desired concentrations was

calculated it was used in the equation

$$\mu_i = \frac{\lambda_i}{|Z_i|F} \ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 2.5.7$$

and appropriate value of μ_i at required concentration

was worked out.

(c) Steps (a) and (b) were carried out for anions

and cations of the electrolyte under investigation and were substituted in Henderson

equation and the ϵ_l values were determined.

(d) The ϵ_l values so obtained were compared with

the experimental values. In most cases the agreement was good and was found to be within expected experimental errors (Table 3.3).

The computation carried out alone ensured that the double junction contraption produced stable and reproducible junction and behaved as expected from the theory. Comparison of theoretical and

experimental ϵ_l were carried out with few systems of different

valence type solutions and it was made certain that it will behave as expected. The determination of the concentration of different kinds of solutions later proved that the assumptions were true (see chapter on results and discussions).

CHAPTER 3

EXPERIMENTAL

3.1 Preparation of solution

(1) All solutions were prepared using distilled water obtained from a commercially available distilling water plant. The conductivity of this water was found to be 1×10^{-5} ohm^{-1} cm^{-1}. This water was used in the final rinsing of the washed glassware. It was stored in a 5 litre capacity measuring flask and was used in preparation of all the solutions of one particular electrolyte for measurements when necessary.

(ii) Chemicals

KCl, $MgSO_4$, KH_2PO_4, $NaCl$, Na_2SO_4, NH_4Cl, were analytical grade chemicals supplied by the α-Chemical Company. Na_2CO_3, HNO_3, HCl, $NaOH$, KNO_3, K_2SO_4 were of reagent grade and were obtained from Kobian Chemical Company.

(iii) All solutions were prepared by weighing a required quantity of the substance and transferring them into a measuring flask and making it up to the mark at room temperature.

The lower concentrations were prepared by sequential dilutions. In some cases, however, all the six solutions were prepared by weighing a substance for each solution.

3.2 Setting up of the cells

Usually a concentration cell is set up using two solutions of the same substance and at different concentrations or of different electrolytes at the same or different concentrations and the two half cells are connected together either by a salt-bridge or through a porous diaphragm in a H-type cell as shown in fig. 3.1 and fig 3.2.
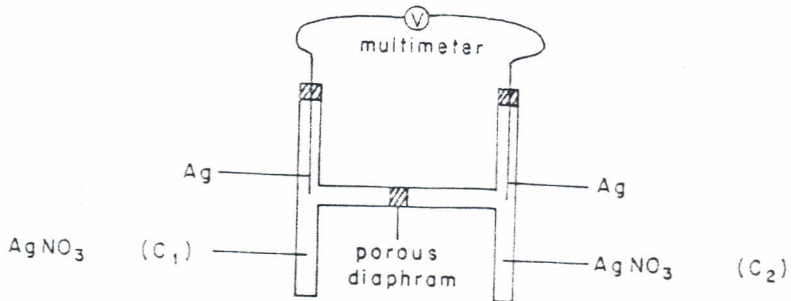
Figure 3.1 : Two half cells connected through a porous membrane
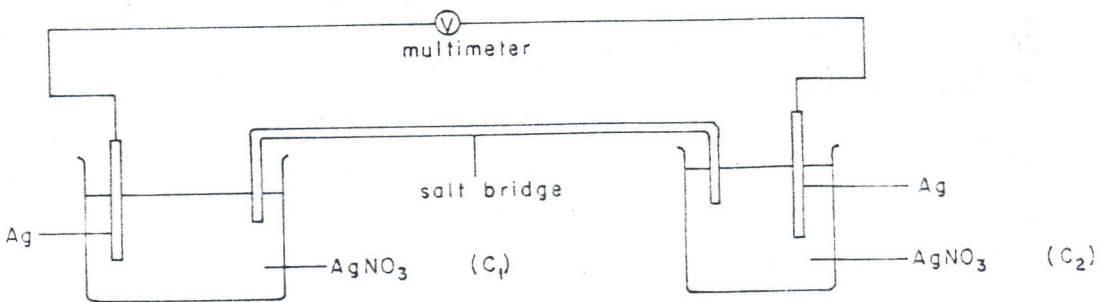
Figure 3.2 Two half cells connected through a salt bridge

The author has used a very different method to set up a concentration cell by using standard sockets and cones and G4 sintered glass (100 microns) as porous diaphragm. The details of the set up are explained with reference to the following diagram

Figure 3.3 Component parts for producing half-cell of a concentration cell

(iv) = (i) + (ii) + (iii) = assembly of the half cell

Concentration half cell with two fixed junctions.

The final assembly (iv) is as a result of the sequential fitting of (i) into (ii) and (i) + (ii) into (iii).

3.3 Details of the three component parts

Component (i)

A B-5 extended cone with an extended part of around 15 cm was tapered at the far end. The tapered end carried one inch long piece of silver wire which had previously been welded to a copper wire.

The Ag wire end was fixed into the tapered part of the glass tubing with araldite and left to set for 24 hours.
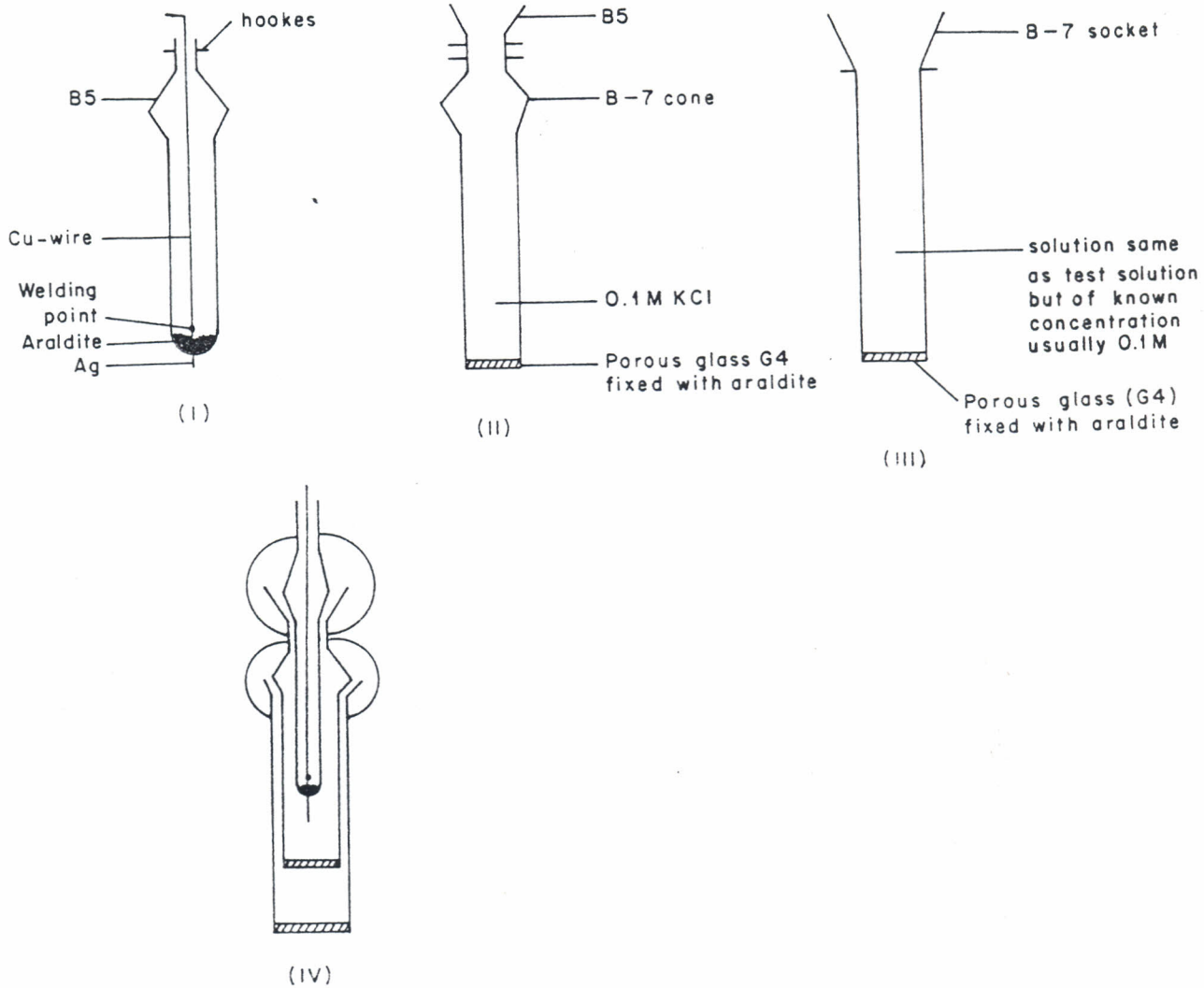
Component (ii)

This part of the assembly was made of a B-7 cone, B-5 socket and G4 (100 microns) porous glass. A B-5 socket was blown on top of a B-7 extended cone. The far end of the cone carried an appropriate size of G4 glass disc which was glued into the tube at the far end with araldite. The construction is shown in figure above.

Component (iii)

This part was essentially a B-7 extended socket and carried a G4 porous glass piece in the far end.

Assembly: The length of the three components were such that (i) fitted well into (ii) and (ii) into (iii). Component (ii) was filled with 0.1M KCl solution and likewise the component (iii) was filled with a solution of the electrolyte, the concentration of which was to be determined i.e. the test solution. This standard socket and the two cones produced a leak-free arrangement preventing the flow of the bulk solution and hence assured the stability of the junction. The whole assembly was used to determine the concentrations of unknown solutions. The assembly, henceforth, would be referred to as double-junction electrode.

3.4 Agar-agar bridge

The arrangement as shown in Fig 3.3 was connected to the saturated calomel reference electrode through a KNO_3-agar-agar bridge which was prepared as follows.

1.01g of potassium nitrate were dissolved in enough distilled water to give 100 ml of 0.01M KNO_3 solution. 1g of agar-agar was mixed with 100 ml of 0.01M KNO_3 and heated with continous stirring till a slurry was formed. The slurry was poured in a U-tube and left to cool to set.

The experimental arrangement

The experimental arrangement shown in figure 3.4 was employed by the author. Some salient features of the set up are being described below.

(i) The double junction electrode had the fixed and variable fixture. The Ag electrode in 0.1M KCl remained fixed and consisted of component (i) and (ii) whereas component (iii) always held the 0.1M solution of that electrolyte whose unknown concentration was to be determined.

(ii) The agar-agar bridge containing potassium nitrate and the saturated KCl solution and calomel electrode also remained fixed in all the measurements.

(iii) The e.m.f measuring instrument was electronic digital multimeter model Y 122 AJ MX 190, manufactured by Altai company.

(iv) A series of solutions ranging from 10^{-1}M to 10^{-7}M were prepared and used one by one as the test solution measuring the voltage of each set up .

(v) The measured e.m.f values thus depended only upon the junction potential arising at the 0.1M solution in component (iv) and the test solution.

(vi) From the measured e.m.f values of the known solution the concentration of the unknown was determined by the calibration curve method . The author worked out an analytical expression for each electrolytic solution as discussed in the chapter of results and discussions.
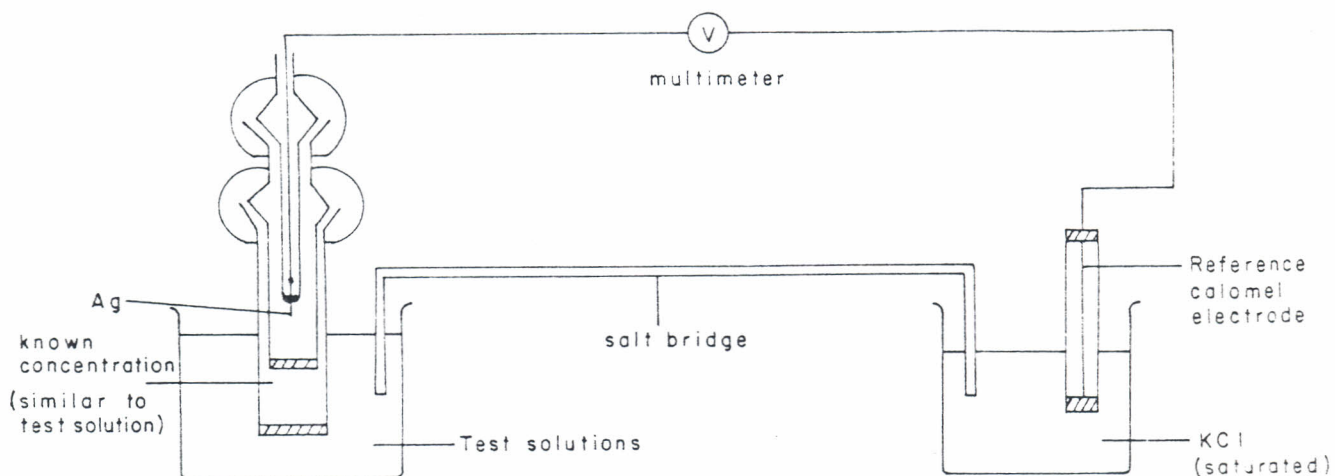
Figure 3.4 The set-up of the cell

3.5 Fluoride ion responsive electrode

An attempt has been made to produce a fluoride ion responsive electrode in the laboratory by a simple method. The electrode was prepared in the following way.

(i) A small disc of G4 porous sintered glass was made from a bigger piece of glass and was ground to 0.05 cm thickness. The disc was then fixed at the end of a pyrex glass tubing with araldite and was allowed to cure overnight.

(ii) Approximately 1g of NaF was thoroughly mixed with silicon-rubber sealant and a thin layer of the paste was spread

over the porous disc previously fixed into a glass tube. Care was taken to spread the paste as uniformly as possible and that it remained fairly thin. The spreading was done with the help of a plastic spatula.

The mixture was allowed to cure for 24 hours after which it adhered to the disc firmly. After curing of the film, it was tested for any leak by filling the tube with distilled water and testing by blowing-in some solution under pressure. Those pieces were rejected in which the water started flowing through the porous disc with coated film.

It was thus assumed that NaF is trapped into the lattice of the silicone-sealant layer and it was expected that the film will exchange F$^-$ ions when dipped into a fluoride solution as a commercially produced F$^-$ ion electrode does. It is shown in Fig 3.5

(iii) The tube was then filled with 0.1M HCl solution and Ag/AgCl$_{(s)}$ electrode was dipped into the solution. The whole assembly is shown in figure 3.6.

0.1M HCl

Ag/AgCl

F$^-$ trapped on silicone sealant placed on G4 porous glass
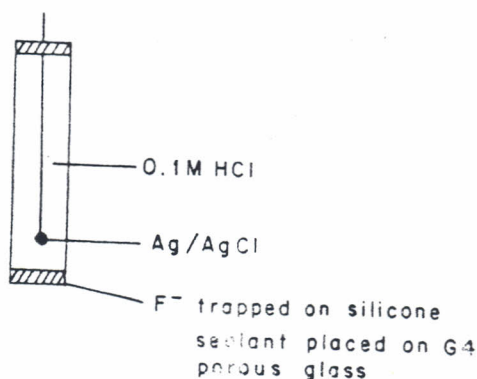
Figure 3.5 Fluoride-ion responsive electrode
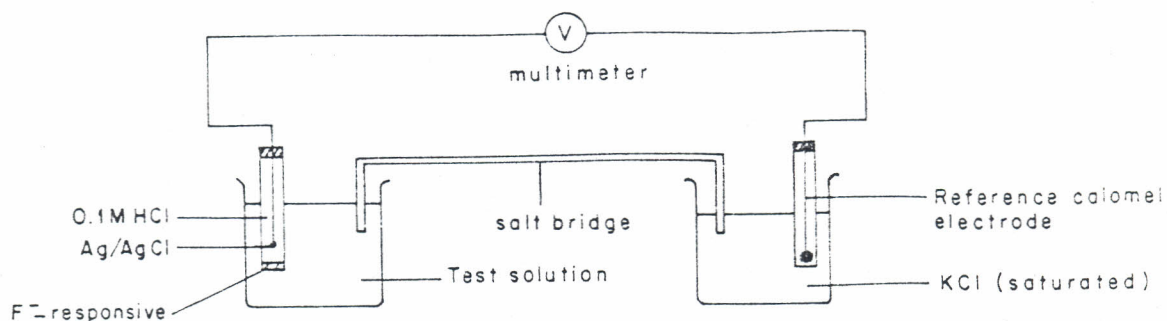
Figure. 3.6 Arrangement for measuring the potential of the cell using F⁻ responsive electrode

Known masses of KBr, KI, NaF and NaCl were weighed and dissolved in distilled water and later made to the mark in a volumetric flask. The subsequent solutions were made by dilutions. These solutions were used in the e.m.f measurements against the standard calomel electrode.

The e.m.f resulting from different F⁻ concentration were recorded using the digital multimeter. The potential as a result of addition of NaCl, KI and KBr were also recorded sequentially and the voltage change was observed. A graph of potential versus the concentration was drawn.

The experiment above was then carefully repeated using the commercially available fluoride selective electrode. Comparison was then made between the performance and data obtained from the two electrodes.

3.6 A run

The details of a run are given below which was carried out to determine the concentration of NaCl solution of unkown concentration. The cell used for the purpose was

Ag/KCl(0.1M)/NaCl(0.16347M)/test solutions/saturated KCl- calomel electrode

Six solutions ranging from 1.6347×10^{-1} M to 1.6347×10^{-6} M were prepared by dilution and one of them was assumed to be unkown .A solution of NaCl of concentration 1.0×10^{-2} M gave a potential of 155mV which corresponded to the 0.96036×10^{-2} M concentration.

Starting with the solution that is least concentrated , the solutions were put in the cell sequentially recording the potential and rinsing the electrode each time with distilled water.The potentials obtained with the respective concentrations are shown in the table 3.1

Concentration Molarity	Potential (mV)
1.6347×10^{-2}	160
1.6347×10^{-3}	144
1.6347×10^{-4}	129.5
1.6347×10^{-5}	115.5
1.6347×10^{-6}	102

Table 3.1 Concentration versus potential

The difference between the emf of the two cells having sequentially decreasing concentrations of the test solution gave the value of the liquid junction potential ε_1.

The author found it desirable to compare these experimental values with those produced by the theory. To achieve this the following procedure was adopted to calculate the theoretical value of ε_1 in each case.

Essentially, Henderson equation was employed to calculate the ε_1 values. The equation derived and reported in the literature gives ε_1 in terms of mobilities of the ions in the two solutions. Since the mobilities of the ions are concentration dependent the author first calculated the equivalent conductance of the ion at a given concentration using Onsager's equation

$$\lambda_1 = \lambda_\cdot - [\frac{2.801x10^{-6}Z_1Z_2}{(\in T)^{2/3}(1+q^{1/2})} + \frac{41.25Z_1}{\int(\in T)^{1/2}}] I^{1/2}$$

where

$$q = \frac{Z_1Z_2(\lambda_1^\circ + \lambda_2^\circ)}{(Z_1 + Z_2)(Z_2\lambda_1^\circ + Z_1\lambda_2^\circ)}$$

λ_1 =mobility of the ion considered in cm^2 Ω^{-1} equi^{-1}

λ_1° =mobility at infinite dilution in cm^2 Ω^{-1} equi^{-1}

$\in$ =dielectric constant (for water =78.55)

$\int$ =viscosity of solvent (for water =0.008949 poise) at 298°

I= ionic strength

The above equation with numerical values of the constant simplifies to

$$\lambda = \lambda^\circ - (B_1 \lambda^\circ + B_2) \sqrt{I} \quad \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots 3.6.1$$

For aqueous solution of NaCl which is a 1:1 electrolyte

$$B_1 = \frac{2.801 \times 10^{-6} q}{(78.55 \times 298)^{2/3} (1 + q^{1/2})}$$

$$= \frac{0.7821128 q}{1 + q^{1/2}}$$

$$q = \frac{\Lambda_1^\circ + \Lambda_2^\circ}{2 (\Lambda_1^\circ + \Lambda_2^\circ)} = 1/2$$

$$B_1 = \frac{0.7821128 \times 0.5}{1 + (0.5)^{1/2}} = 0.2290755$$

and for B_2

$$B_2 = \frac{41.25 Z_1}{I (\in T)^{1/2}}$$

$$= \frac{41.25 \times 2}{0.008949 (298 \times 78.55)^{1/2}}$$

$$= 60.255711$$

Having calculated the variables B1 and B2 the ionic mobilities of

Cl⁻ and Na⁺ were obtained from the equation

$$\mu_i = \frac{\lambda_i}{|Z|F}$$

Since λ_i was calculated from equation (3.6.1) above.

The two solutions forming the junction have different ionic strengths and hence the ionic conductances and therefore the corresponding ionic mobilities for each ion were calculated.

$$\lambda_{Na}^° = 50.1 cm^2 \Omega^{-1} equi^{-1}$$

$$\lambda_{Cl}^° = 76.35 cm^2 \Omega^{-1} equi^{-1}$$

The ionic strength of the NaCl solution was calculated using equation

$$I = 1/2 \Sigma C_i Z_i$$

$$I = 1/2 \{ 1.6347 \times 10^{-1} \times 1^2 + 1.6347 \times 10^{-1} \times 1^2 \}$$

$$= 1.6347 \times 10^{-1} \ mol^2 \ l^{-2}$$

The ionic conductance of Na⁺ was then calculated using equation (3.6.1).

$$\lambda_{Na}^1 = 50.1 - (50.1 \times .2290755 + 30.1279) \sqrt{1.6347 \times 10^{-1}}$$

which worked out to be

$$= 33.21166 cm^2 \ \Omega^{-1} \ equi^{-1}$$

The ionic mobility was then calculated using the relation

$$\mu_{Na}^{1} = \frac{\lambda_{Na}}{|Z|F} = \frac{32.21166}{96500} = 3.4416228 \times 10^{4} \, cm^{2} \, sec^{-1}$$

The mobility of Na^+ in the second solution in contact with the first one is different since the concentrations were different. The ionic strength of the second solution was $1.6347 \times 10^{-2} \, mol^2 l^2$ and the corresponding ionic conductance

$$\lambda_{Na}^{11} = 50.1 - (50.1 \times 0.2290755 + 30.1279)\sqrt{1.6347 \times 10^{-2}}$$

$$= 48.41786 \, cm^2 \, \Omega^{-1} \, equi^{-1}$$

$$\mu_{Na}^{11} = 4.6415607 \times 10^{-4} \, cm \, sec^{-1}$$

In order to be able to calculate the ε_1 the author assumed that the mobility of the Na^+ and Cl^- is constant over the range of two concentrations. To be a bit more precise the average of the two mobilities were used.

i.e. $\dfrac{3.4416228 \times 10^{-4} + 4.6415607 \times 10^{-4}}{2} = 4.0415918 \times 10^{-4} \, cm \, sec^{-1}$

The same procedure was then repeated to calculate the mobility of Cl^- ion. For Cl ion we have

$$\lambda_{Cl}^{1} = \lambda_{Cl}^{'} - (\lambda_{Cl}^{'} B_1 + B_2)\sqrt{I}$$

where I= $1.6347 \times 10^{-1} mol^2 l^{-2}$

which gives

$$\lambda^1_{Cl}=76.35-(76.35 \times 0.2290755+30.1279)\sqrt{1.6347 \times 10^{-1}}$$

$$=57.12061 cm^2 \; \Omega^{-1} \; equiv^{-1}$$

The mobility was then worked out as before which gave

$$\mu^1_{Cl}=\frac{57.12061}{96500}=5.91923 \times 10^{-4} \; cm \; sec^{-1}$$

The ionic strength of the second solution of concentration 1.6347×10^{-2} M is 1.6347×10^{-2}

hence

$$\lambda^{11}_{Cl}=76.35-(76.35 \times 0.2290755+30.1279)\sqrt{1.6347 \times 10^{-2}}$$

$$=70.2618 cm^2 \; \Omega^{-1} \; equi^{-1}$$

and

$$\mu^{11}_{Cl}=7.28177 \times 10^{-4}$$

The mean mobility of Cl^- ion in the two solutions was

$$\frac{5.91923 \times 10^{-4}+7.28177 \times 10^{-4}}{2}=6.6005 \times 10^{-4} \; cm^2 \; sec^{-1}$$

Having the ionic mobilities of the two ions of Na^+ and Cl^-,

the liquid junction potential was calculated using the Henderson equation .

i.e.

$$\epsilon_1 = \frac{RT}{F} \frac{\sum_n \mu_i / Z_i (C_i'' - C_i')}{\sum_n \mu_i (C_i'' - C_i')} \ln \frac{\sum_n C_i' \mu_i}{\sum_n C_i'' \mu_i}$$

C_i' and C_i'' are known however

$$\epsilon_1 = \frac{RT}{F} \frac{4.041 x 10^{-4} (1.6347 x 10^{-1} - 1.6347 x 10 - 2) - 6.601 x 10^{-4}}{4.041 x 10^{-4} (1.6347 x 10^{(-1)} - 1.6347 x 10^{-2}) + 6.0601 x 10^{-4}}$$

$$\frac{(1.634 x 10^{-1} - 1.634 x 10^{-2})}{(1.634 x 10^{-1} - 1.634 x 10^{-2})} \ln \frac{1.634 x 10^{-1} (4.041 x 10^{-4} + 6.601 X 10^{-4})}{1.634 X 10^{-2} (4.041 x 10^{-4} + 6.601 x 10^{-4})}$$

$$\epsilon_{l_1} = \frac{5.946111 x 10^{-5} - 8.8348097 x 10^{-5}}{5.946111 x 10^{-5} + 8.8348097 x 10^{-5}} \frac{RT}{F} \ln 10$$

$$= \frac{2.8886986 x 10^{-5}}{1.4780921 x 10^{-4}} \frac{RT}{F} \ln 10$$

$$= 0.1954342 \frac{RT}{F} \ln 10$$

$$= 0.19543 x 59.1$$

=11.55mV

This was the calculated value of the liquid junction potential between solutions of concentration 1.6347×10^{-1}M and 1.6347×10^{-2}M

The procedure above was used to obtain the ionic mobilities of Na^+ and Cl^- ions at different concentrations and are shown in table 3.2

C	μ_{Na^+}	μ_{Cl^-}
1.6347×10^{-1}	3.4416228×10^{-4}	5.9192345×10^{-4}
1.6347×10^{-2}	4.6415607×10^{-4}	7.2817755×10^{-4}
1.6347×10^{-3}	5.0177374×10^{-4}	7.7126488×10^{-4}
1.6347×10^{-4}	5.1366949×10^{-4}	7.8489029×10^{-4}
1.6347×10^{-5}	5.1743126×10^{-4}	7.8919903×10^{-4}
1.6347×10^{-6}	5.1862084×10^{-4}	7.9056157×10^{-4}

C=Conc: $moll^{-1}$ μ =mobilities : $cm\ sec^{-1}$

Table 3.2 Mobilities of Na^+ and Cl^- ions in NaCl solution.

The junction potentials between two such solutions were calculated and are shown in table 3.3 below.

ϵ_l calculated	ϵ_l experimental
16.0	16
13.5	14.5
13.58	14
13.64	12.5

Table 3.3 ϵ_l values between two NaCl solutions

The theoretical values are slightly different from the experimental ones which are within the expected range due to the temperature variations and the accuracy of the multimeter.

CHAPTER 4

RESULTS AND DISCUSSIONS

It has been described in the previous chapters that the emf of the cells resulting from the combination of the double-junction electrode and the reference electrode by sequentially changing the test solutions of varying concentrations registered a change in the emf of each cell. The observed change solely depended on the ϵ_1 value of the junction between the solution of fixed concentration inside the double-junction electrode and the solutions. The change of the cell emf was found to be linearly dependent on the concentration of the test solutions.

As there is a linear relationship between the cell emf and the concentration, the calibration curve method was used to determine the concentrations of the solutions of unknown concentrations. Thus the usefulness and the limitation of the double-junction electrode as an analytical tool was tested on a variety of electrolytic solutions. Since higher concentrations are easy to determine by the conventional methods the electrode was tested in the concentration range of $10^{-2}M$ to $10^{-6}M$ molar solutions. The result obtained using this electrode in 1:1, 2:1, 2:2, etc type of electrolyte solutions at room temperature are described in the following sections.

The 1:1 electrolytic solutions

Among this class of electrolytes the selected systems were NaCl, NH_4Cl, KIO_3, HCl, HNO_3. The results obtained for each system are presented in the sections below.

NaCl-water system

The results of the NaCl system are shown in table 4.1 and the corresponding plot between the emfs and the logarithm of concentrations is depicted in figure 4.1.

It is apparent from the figure 4.1 that a perfect linear relationship between the emf and the concentration is obtained. The linear regression computer program yielded

y = -15.6x +189.8

allowing to determine the concentration of any unknown solution lying between 10^{-2} M and 10^{-6} M provided the temperature is kept constant. The intercept of 189.8 lies within the expected value and the slope is steep enough to expect fairly accurate results.

Table 4.1   NaCl-water system

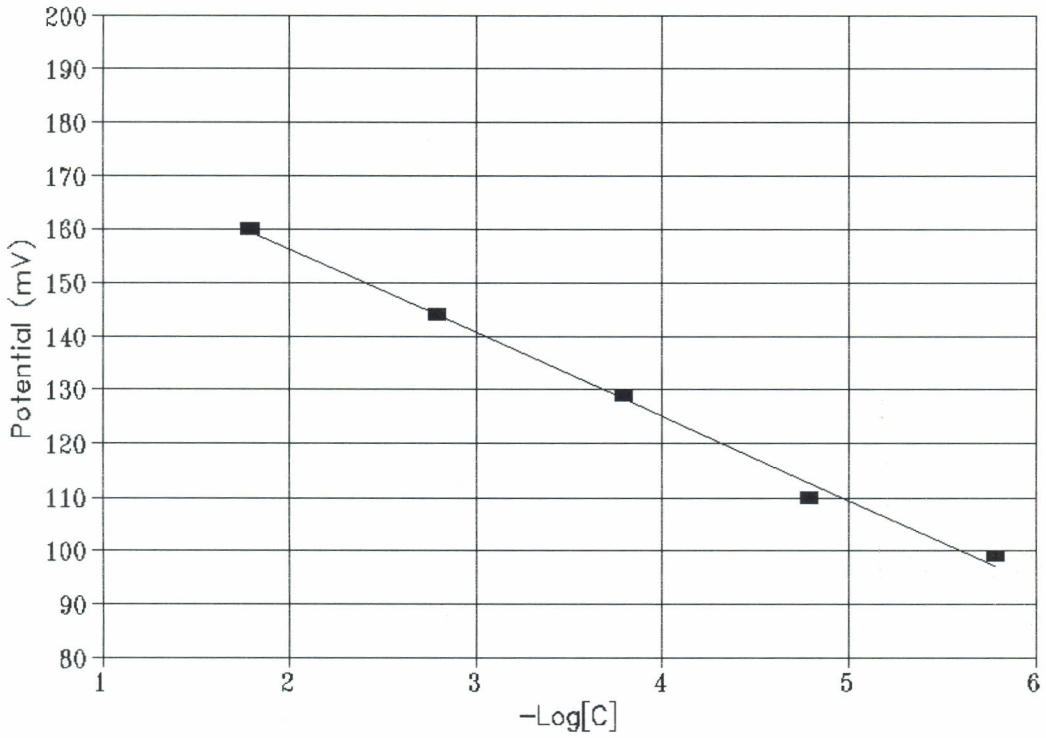| C	E
mol/l	(mV)
1.6347×10^{-2}	160
1.6347×10^{-3}	144
1.6347×10^{-4}	129.5
1.6347×10^{-5}	115.5
1.6347×10^{-6}	102

Fig 4.1   Concentration dependence of emf on NaCl solution

NH$_4$Cl-water system

The results for this system are displayed in table 4.2 and the figure 4.2 shows the corresponding relationship.

The table shows that the difference in the emf is approximately 10mV when the concentration is changed by a factor of 10.The corresponding plot shows a steeper slope than in NaCl solutions ensuring better accuracy.

Here the point lies slightly up or down of the best line drawn by the computer.The cause of these fluctuation seems to be due to errors incurred during dilution, variation of room temperature during the course of experiment and the performance of the multimeter used for the measurement of the emf. However the temperature variations affected all the measurements and therefore the trend was not affected.

If an estimated overall error of 1% is taken into consideration the observation falls within expectations.Thus the electrode behaved very well in the system under consideration as it did in case of NaCl and lends confidence in its application in solutions of other 1:1 electrolyte solutions. Accordingly KIO$_3$ was chosen as another electrolyte to test the performance of the electrode.

Table 4.2   NH$_4$Cl-water system

C	E
mol/l	(mV)
8.591x10^{-3}	143
8.591x10^{-4}	136
8.591x10^{-5}	128
8.591x10^{-6}	115
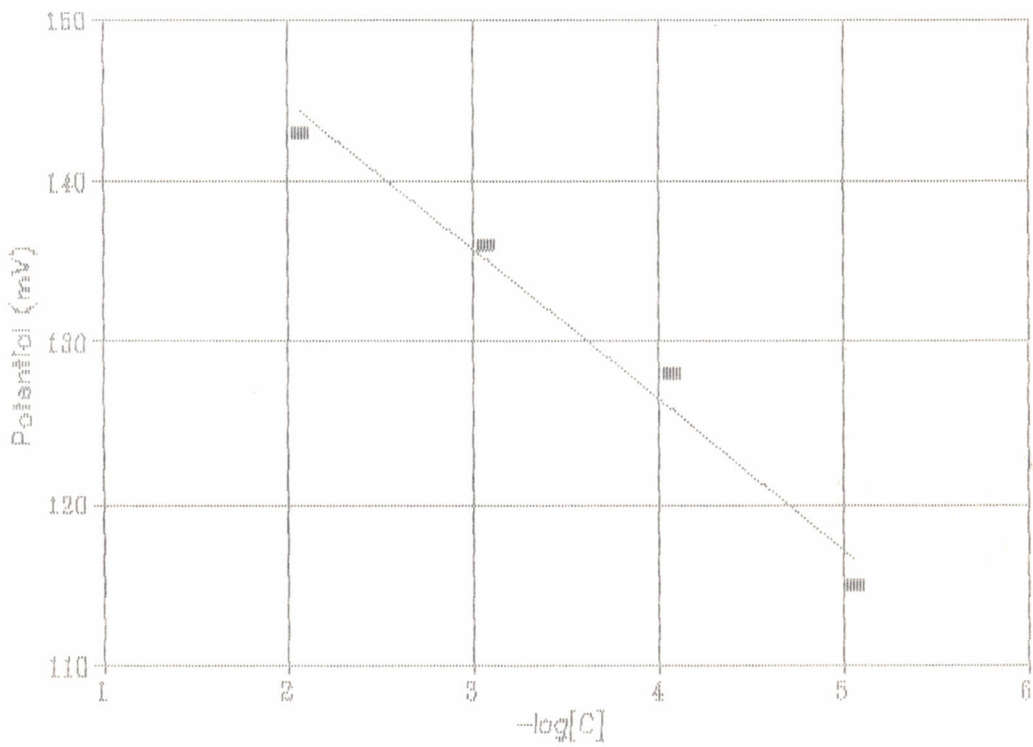
Fig 4.2   Concentration dependence of emf in NH$_4$Cl solution

KIO$_3$ -water system

The system was investigated in the concentration range of 10^{-3} M to 10^{-7} M Table 4.3 contains the experimental data and the figure 4.3 portrays the linear relationship.

A notable difference in this system is the positive slope. The previous two slopes registered a decreasing trend whereas in KIO$_3$ solution the emf increases with concentration .This is perhaps due to a common K$^+$ ion in the double-junction electrode and the tendency of IO$_3^-$ ion to form a dimeric anion $[IO_3]^{2-}$. The dimerization affected the transference number of ion and hence the numerical value of the junction potential ε_f . In this case

it adds on to the emf due to the two electrodes and thus increases the total measured emf of this cell with change in the concentration.

The slope is not that steep either indicating that the precision in this case would not be very good. It was therefore found desirable to calculate concentration using the linear equation

$y = 4.3x + 22.49$

and compare it with those employed in this experiment.Table 4.3(a) compares the two concentrations and the last column gives the difference between the two as Δ C.

The agreement inspite of small slope is excellent between these two concentrations. Thus as long as the experimental conditions are constant the estimation of the unknown concentration will be fairly reliable.

Table 4.3   KIO$_3$-water system

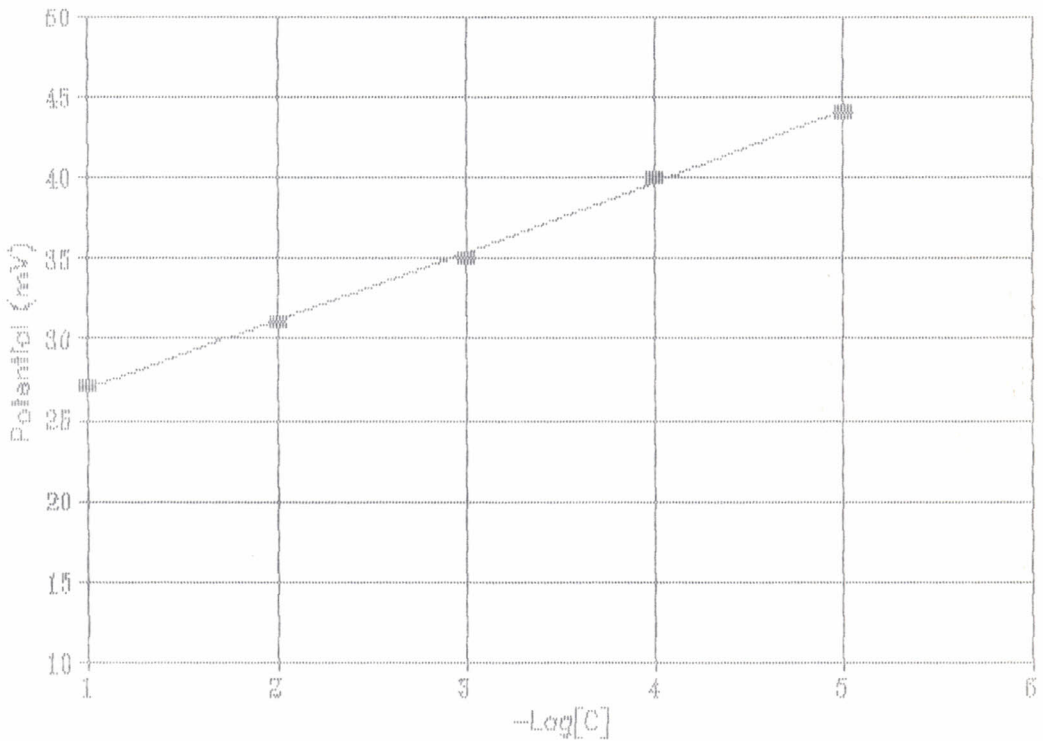| C	E
mol/l	(mV)
9.9486x10^{-3}	27
9.9486x10^{-4}	31
9.9486x10^{-5}	35
9.9486x10^{-6}	40
9.9486x10^{-7}	44

y=4.3X+22.49

Fig 4.3 Concentration dependence of emf in KIO$_3$ solution

Table 4.3(a) comparison of concentration of KIO_3 to the calculated concentration from the equation, $Y=4.3x + 22.49$.

C	$C^\ddagger$	Δ C
mol/l	mol/l	mol/l
0.099486	0.08936	0.0101219
0.0099486	0.01049	0.00005451
0.00099486	0.0012322	0.0002374
0.00009948	0.0000847	0.00001478
0.000009948	0.00000995	0.000000009

$C^\ddagger$:Calculated C

Δ C:Difference in C and $C^\ddagger$ using the equation

The next system of 1:1 electrolyte, HCl-water, wherein one of the ions is hydrogen was studied. The results are shown in table 4.4 and the corresponding plot of the emfs versus logarithm of the concentrations is given in figure 4.4

It is clear from the figure that at a high concentration the emf deviates from the line as compared to that at lower concentrations. Nevertheless a linear regression computer program yielded the equation

$$y = -16.9x + 238.2$$

which could allow its use to estimate the concentration of unknown solutions between 10^{-2} M to 10^{-6} M solutions.

HNO_3 -water system

Lastly, the 1:1 electrolytic system studied was HNO_3-water system. The results of this system are shown in table 4.5 and the figure 4.5 shows the corresponding relationship.

As in the HCl system, at higher concentration the emf falls off the line. There is something common in HCl and HNO_3 systems such as the hydrogen bonding or the behaviour of H^+ ions themselves and hence the values obtained. The H^+ ion which is common in the junction contributes more in terms of mobility than the other ions i.e. NO_3^- and Cl^-. This is the cause of the fluctuation of the emf at higher concentrations.

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Table 4.4 HCl-water system

C	E
mol/l	(mV)
1.0×10^{-2}	195
1.0×10^{-3}	199
1.0×10^{-4}	172
1.0×10^{-5}	154
1.0×10^{-6}	133

y= -16.9X + 238.2
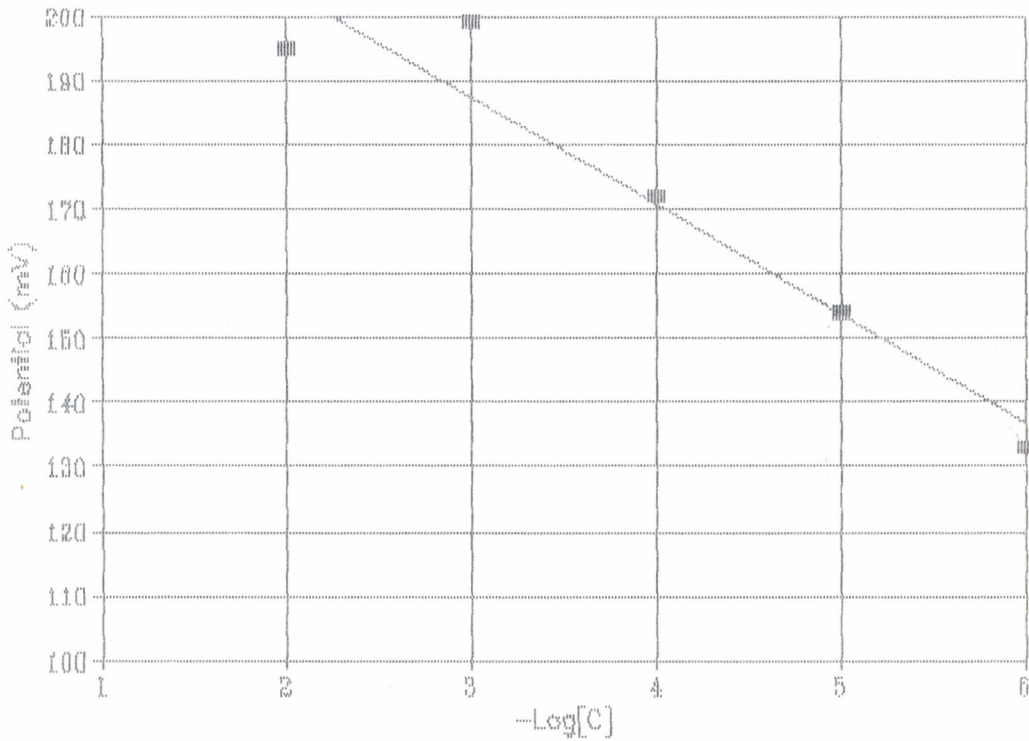
Fig 4.4 Concentration depedence of emf in HCl solution

494949
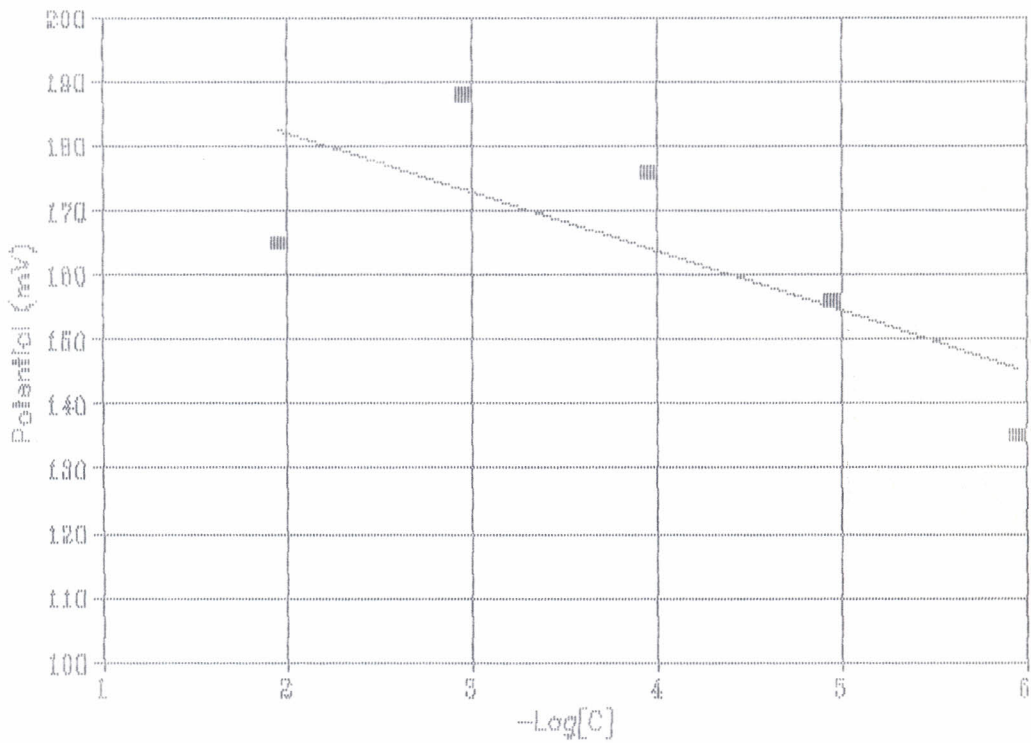
$(NH4)_2SO_4$ -water system

This is a 1:2 electrolytic system. The results of the system are shown in table 4.6 and the corresponding relationship on figure 4.6. The relationship between the concentration and the emf of this system was also linear. The line had a gradient of 3.3 and the y-intercept of 128.164. The plot obtained had most of the points lying above the line. The linearity observed allowed the use of the plot to determine the concentration of unknown solutions.

Na_2SO_4-water system

This is also 1:2 type electrolytic system. The results of the system are shown on the table 4.7 and the corresponding plot on figure 4.7. A linear relationship is portrayed on the plot. The plot which was obtained from a regression computer program had a slope of -13 and the y-intercept was 194. The concentration of Na_2SO_4 of any unknown solutions between 10^{-2} M and 10^6 M can easily be determined from the linear plot.

K_2SO_4-water system

Among the 1:2 type of electrolyte system studied was also K_2SO_4 The results of this system are shown in table 4.8 and the corresponding relationship in figure 4.8. Just like other systems the relationship is linear with a positive slope of gradient 3.5 and y-intercept 19.23 . These were obtained from the linear regression computer program. The linearity obtained allowed estimation of the concentration in range 10^{-2} M to 10^{-5} M

Table 4.6   (NH4)$_2$SQ$_4$-water system

C	E
mol/l	(mV)
1.48219^{-2}	133
1.48219^{-3}	138
1.48219^{-4}	142
1.48219^{-5}	145
1.48219^{-6}	146

Y=3.3X +127.6
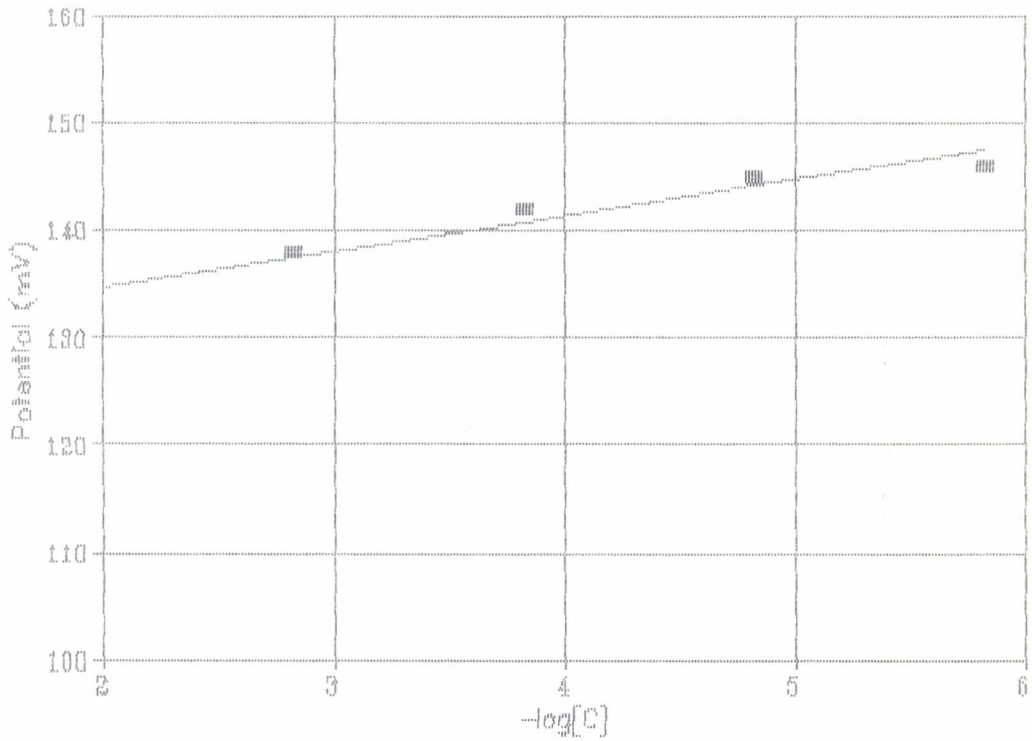
Fig 4.6   Concentration dependence of (NH4)$_2$ SO$_4$ solution.

Table 4.7   Concentration dependence of emf in Na_2SO_4 solution.

C	E
mol/l	(mV)
1.7214×10^{-2}	170
1.7214×10^{-3}	160
1.7214×10^{-4}	150
1.7214×10^{-5}	130
1.7214×10^{-6}	120

$y = -13x + 194$
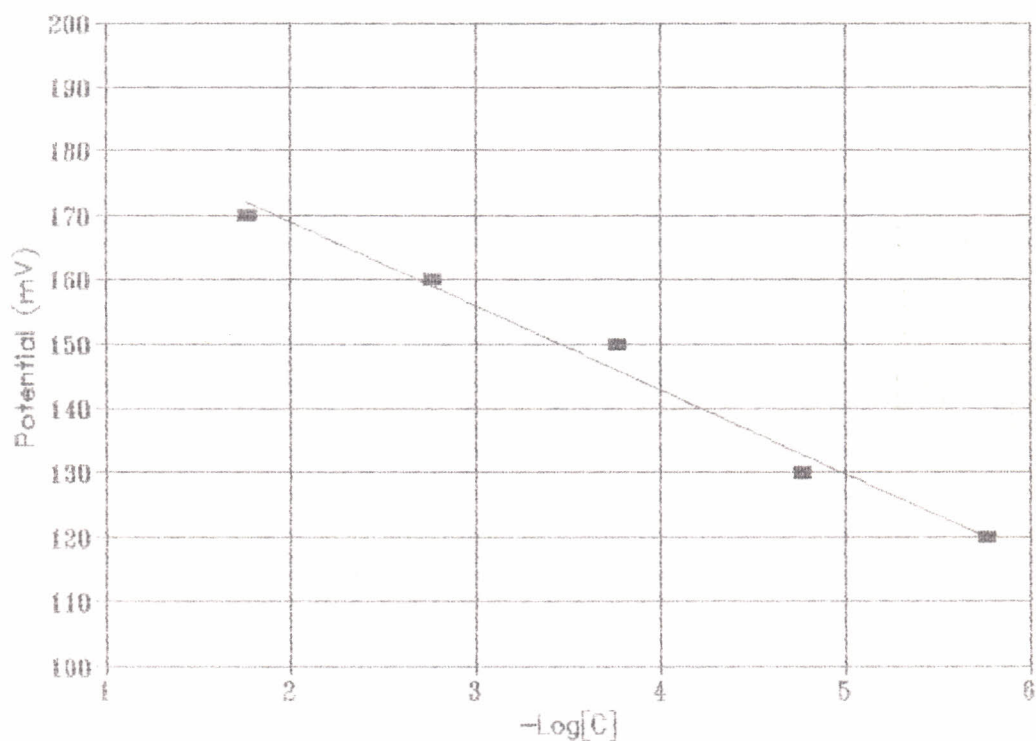
Fig 4.7   Concentration dependence of emf in Na_2SO_4 solution

Table 4.8 K₂SO₄-water system

Table 4.8 K_2SO_4-water system

C	E
mol/l	(mV)
3.3316×10^{-2}	25
3.3316×10^{-3}	27
3.3316×10^{-4}	32
3.3316×10^{-5}	34
3.3316×10^{-6}	39

$y = 3.5X + 19.23$
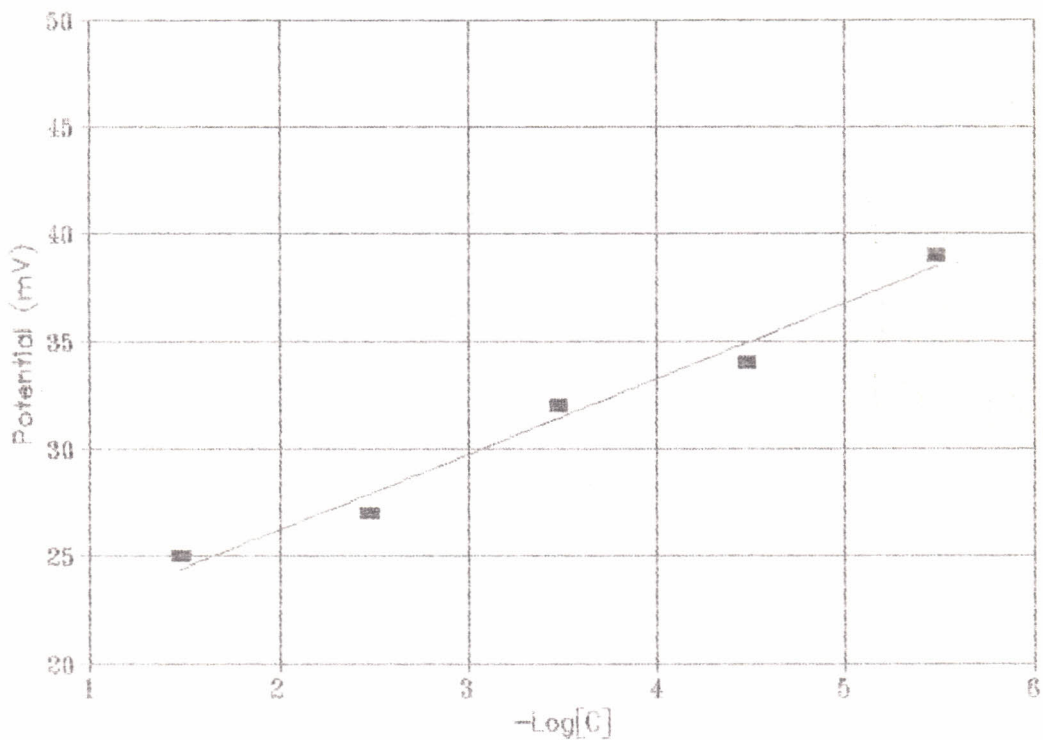
Fig 4.8 Concentration dependence of emf in K_2SO_4 solution.

KH_2PO_4-water system

This is a 1:1:3 electrolytic system and it is known to associate extensively with other ions to produce ion such as $H_2PO_4^-$. The results of this system are shown on table 4.9 and the corresponding relationship in figure 4.8. From the figure it is apparent that the slope is positive unlike quite a number of systems considered perhaps due to its high degree of association the system exhibits. However just like other systems the system is linear and therefore can be used to estimate the concentration of unknown solution with the stipulated range.

Table 4.9 : KH_2PO_4-water system.

C	E
mol/l	(mV)
1.02492×10^{-2}	155
1.02492×10^{-3}	162
1.02492×10^{-4}	**166**
1.02492×10^{-5}	169
1.02492×10^{-6}	170

$y = 3.7X + 149.6$
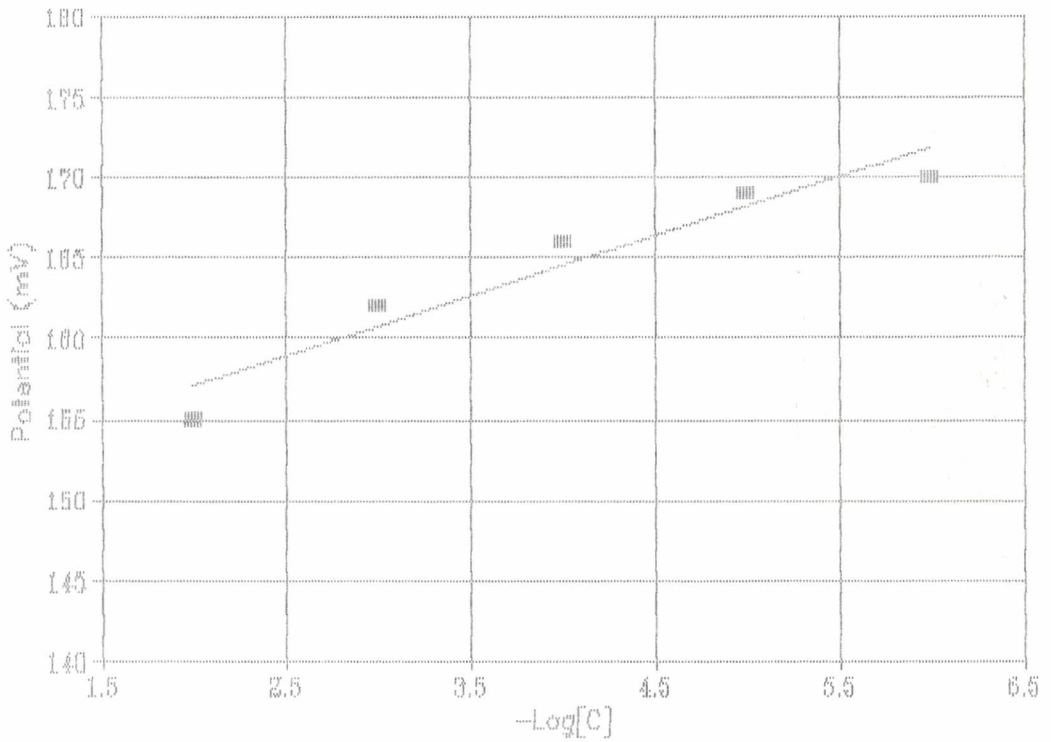
Fig 4.9 Concentration dependence of emf in KH_2PO_4 solution.

$MgSO_4$-water system

Unlike the previous systems this is a 2:2 electrolytic system. The results of this system are shown in table 4.10 and the corresponding relationship in figure 4.10

Just like other systems the relationship of the emf with the concentration was found to be linear and the linear regression computer program yielded the equation

$$y = -14x + 173$$

If 1% error which is given in the multimeter specification is taken into consideration the observations falls within expectations.

Table 4.10 MgSO$_4$-water system

C	E
mol/l	(mV)
8.88867×10^{-3}	143
8.88867×10^{-4}	129
8.88867×10^{-5}	118
8.88867×10^{-6}	99

$y = -14.3X + 173.0$
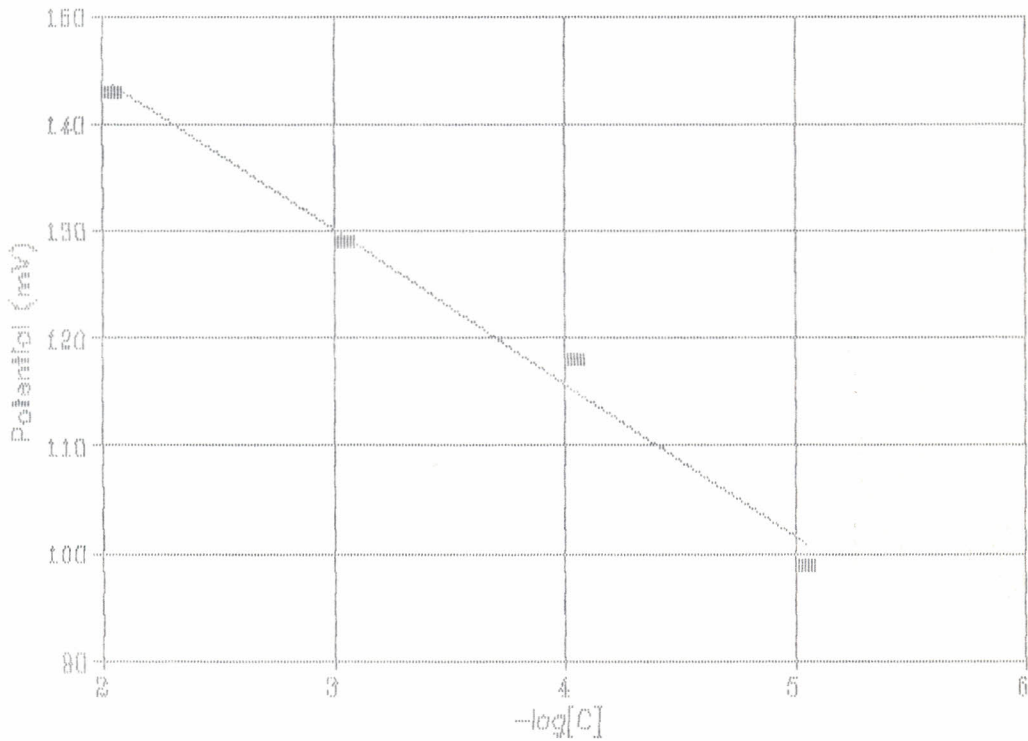
Fig 4.10 Concentration dependence of emf in MgSO$_4$ solution

Apart from the applications of liquid junction potential to determine the concentration of 1:1, 1:2, 1:1:3, and 2:2 types of electrolytes, the attempt was made to design the fluoride-responsive electrode to determine the concentration of F⁻ ions alone and also in presence of other halide ions. The work is described below

Fluoride-responsive electrode

Attempts were made to produce a fluoride responsive electrode by trapping fluoride salt in silicon rubber sealant by the method described earlier in the experimental section, (pp.28-29).

The electrode so prepared was put to test in fluoride solutions of varying concentrations. Its performance was compared with such a commercially available electrode.

The electrode was tested in aqueous solutions of single fluoride salt and in aqueous solutions of fluoride ion in presence of other halides.In presence of fluoride ions alone the electrode responded fairly well but in presence of other halide ions such as Cl⁻, Br⁻, I⁻ the behaviour became erratic.In the following lines the results obtained from lab-made fluoride electrode are described.

F⁻ ion concentration alone

The electrode was used in aqueous solutions of NaF in the concentration range 10⁻M to 10⁻M at room temperature with calomel as the reference electrode.Table 4.11 shows the emf obtained at each concentration of fluoride solution. The figure 4.11 shows the corresponding plot of emf and logarithm of concentrations.

Table 4.11 Emf of the cell with lab made electrode in aqueous NaF solution at room temperature.

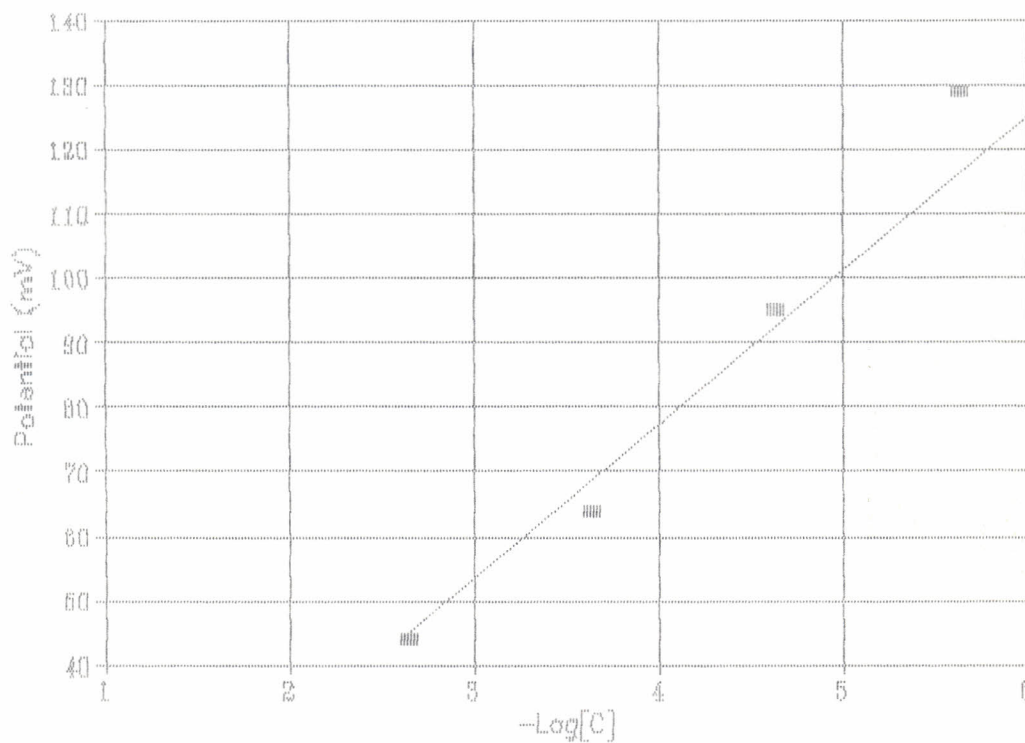| C	E
mol/l	(mV)
2.31×10^{-3}	44
2.31×10^{-4}	64
2.31×10^{-5}	95
2.31×10^{-6}	129
2.31×10^{-7}	130

Fig 4.11 Variation of emf with concentration in aqueous NaF solution at room temperature

It is seen from the table that the change in concentration between successive concentration is fairly large and consequently the shape of the plot is steep. The data points do not fall on a straight line nevertheless the average line represents fairly well a linear behaviour.

It is therefore expected with fair degree of confidence, that such an electrode can be used for routine work in a lab for fluoride concentrations.Table 4.12 depicts the results obtained using commercially produced fluoride ion selective electrode.Likewise figure 4.12 potrays the plot of emf and logarithm of concentrations. It is apparent that the change in emf between two successive concentrations is not as large and as consistent as in the case of lab-made electrode.Moreover the plot shows a bigger scatter in this case.

The smaller slope in this case and the scatter suggest that the lab made electrode would yield much better results than the commercial electrode.

Table 4.12 Emf of the cell with commercial   electrode of aqueous
NaF solution at room temperature.

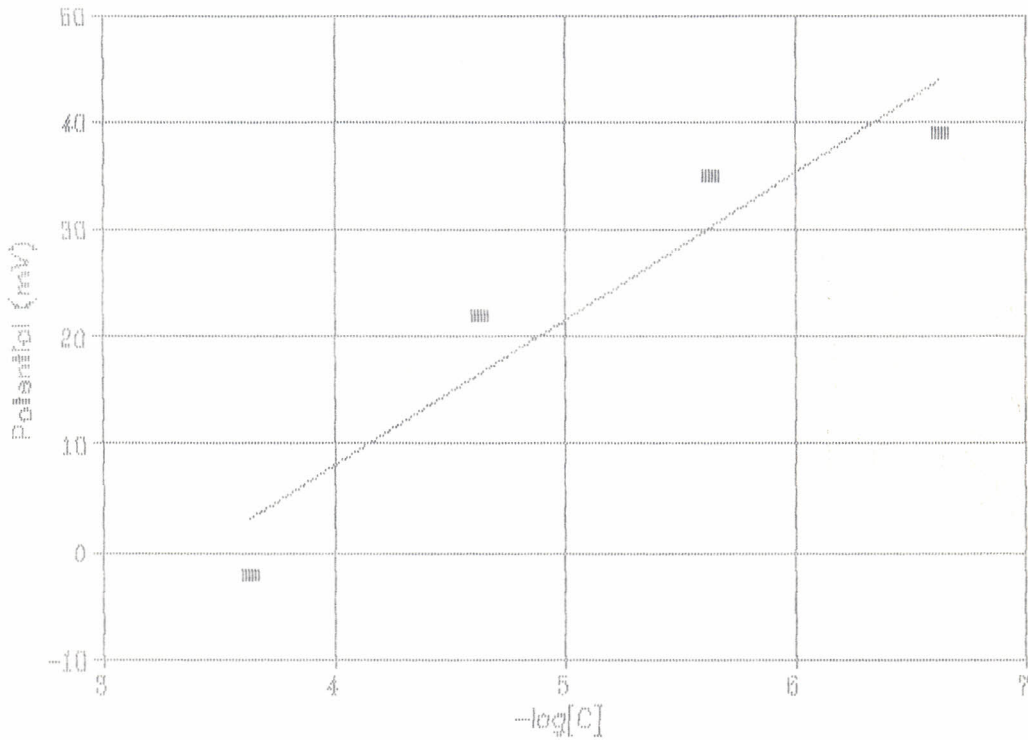| C	E
mol/l	(mV)
2.31×10^{-3}	-2
2.31×10^{-4}	22
2.31×10^{-5}	35
2.31×10^{-6}	39

Fig 4.12 Variation of emf of cell with concentrations with
commercial electrode of aqueous NaF solutions at room temperature

F-ion concentration in presence of other halide ions

In this experiment NaF solutions were prepared in presence of $1.5674 \times 10^{-3} M$ KBr solution. Thus the resulting solution contained both the F^- and Br^- ions at known concentrations. The results are depicted in table 4.13 and figure 4.13 displays the corresponding plot. It is obvious from the table as well as from the plot the differential of emf is approximately 10mV and likewise the linearity is fairly good. Under the circumstances it is expected that the lab-made electrode would produce meaningful results.

The corresponding situation with commercial electrode is shown in table 4.14 and figure 4.14 It is surprising to note that the emf does not show any sensible change and the scatter is much too wide. In this case, as well, it is clear that lab made electrode behaves better than the commercial electrode.

Table 4.13   Emf of the cell with lab-made electrode in aqueous
NaF solutions in presence of KBr at room temperature

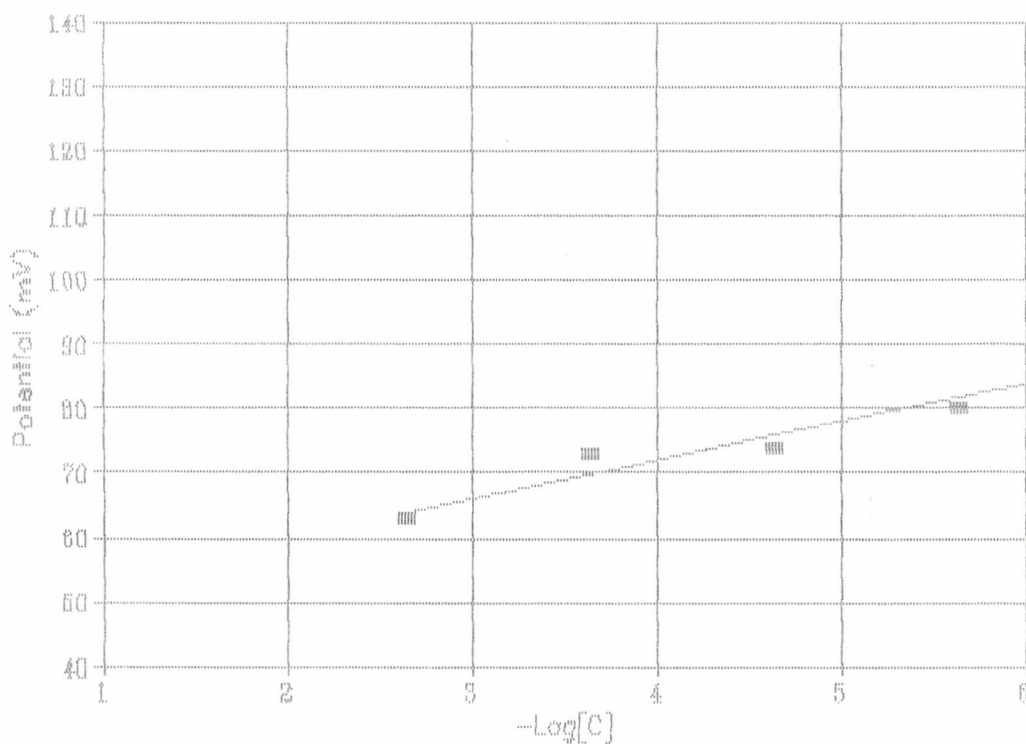| C	E
mol/l	(mV)
2.31×10^{-3}	63
2.31×10^{-4}	73
2.31×10^{-5}	74
2.31×10^{-6}	80
2.31×10^{-7}	89

Fig 4.13 Variation of emf of the cell lab-made electrode with
various concentrations of aqueous NaF solutions in presence of
KBr at room temperature

Table 4.14 Emf of the cell with commercial electrode
of aqueous NaF solutions in presence of KBr at room
temperature

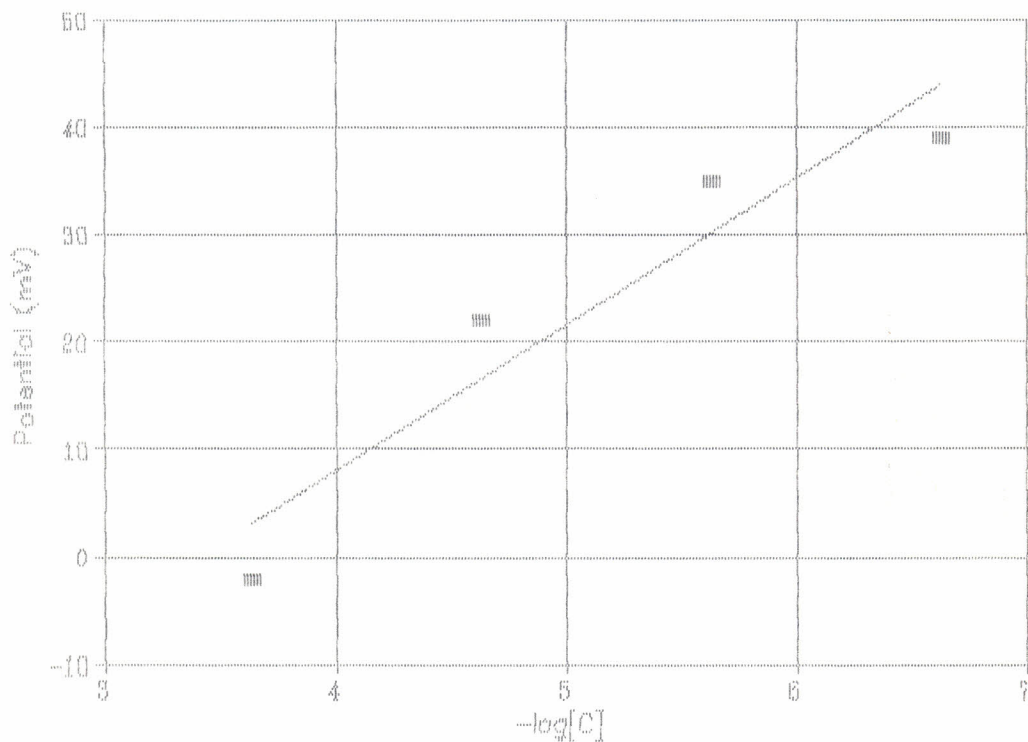| C	E
mol/l	(mV)
2.31×10^{-3}	0
2.31×10^{-4}	25
2.31×10^{-5}	37
2.31×10^{-6}	38

Fig. 4.14 Variation of emf of the cell with commercial electrode
with various concentrations of aqueous NaF solutions in presence
of KBr at room temperature

F-ion concentration in presence of Br$^-$ and Cl$^-$ ions.

In this experiment NaF solutions were prepared using equal volumes of 2.397×10^{-3}M KCl and 1.5674×10^{-3}M KBr solutions. The resulting solution therefore contained F$^-$, Br, Cl$^-$ ions at known concentrations. The results of this experiment are shown in the table 4.15 and the corresponding relationship in the figure 4.15. It is apparent from the table as well as from the plot that the emf that resulted was almost constant. Although the linear relationship is still pronounced, there is no doubt of some interference from other ions.

The corresponding results from the commercial electrode are shown in the table 4.16 and figure 4.16. As had been observed earlier there is hardly any change and still the scatter is still significant. In conclusion it is clear that the lab-made F$^-$ -responsive electrode gives similar results when there is minimal interference from other ions.

Table 4.15   Emf of the cell with lab-made electrode of aqueous
NaF solutions in presence KBr and KCl at room temperature

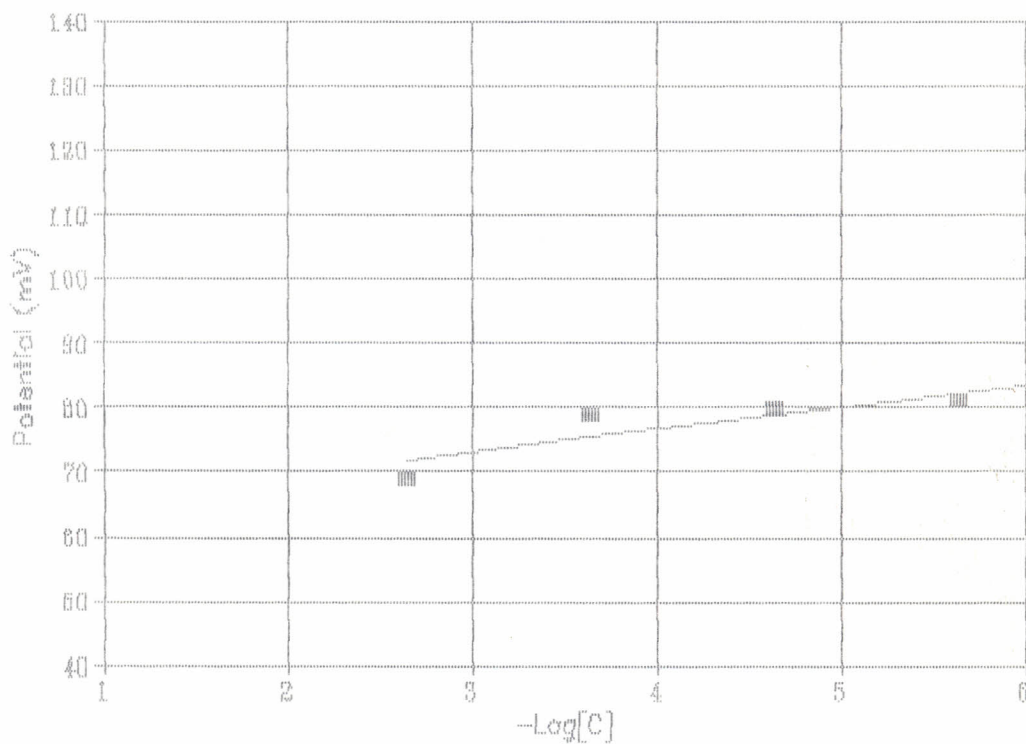| C	E
mol/l	(mV)
2.31×10^{-3}	69
2.31×10^{-4}	79
2.31×10^{-5}	80
2.31×10^{-6}	81
2.31×10^{-7}	85

Fig 4.15 Variation of emf of the cell with lab-made electrode
with various concentrations of NaF solutions in presence of KBr
and KCl at room temperature

Table 4.16 Emf of the cell with commercial electrode
of aqueous NaF solutions in presence of KBr and KCl at
room temperature

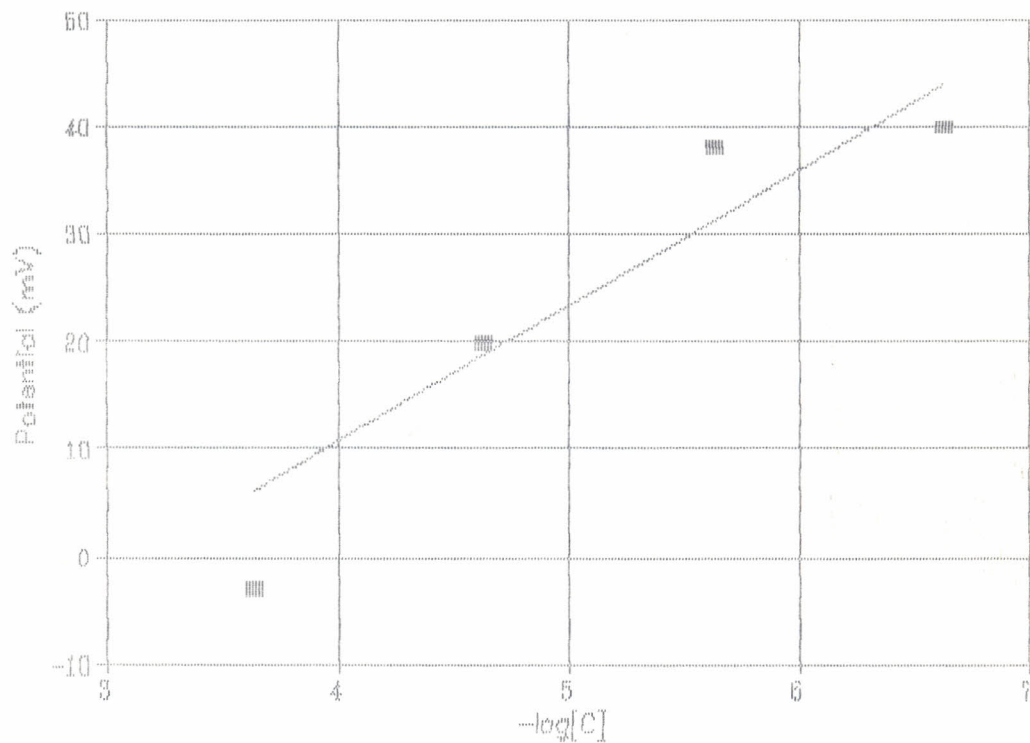| C	E
mol/l	(mV)
2.31×10^{-3}	-3
2.31×10^{-4}	20
2.31×10^{-5}	38
2.31×10^{-6}	40

Fig 4.16 Variation of emf of the cell with commercial electrode
with various concentrations of NaF solutions in presence of KBr
and KCl at room temperature

CONCLUSIONS

Although metal-metal insoluble salt electrodes can be used to determine the concentration of certain ionic species conventionally such salts are very few. It was therefore desired to have a universal electrode which can be used in any kind of solutions. Double-junction electrode therefore fills this gap remarkably. No matter what kind of electrolyte it is, the electrode finds its effective application.

It needs to be suggested, also that the cones and sockets must have a perfect fit so that the junction is free of hydrostatic flow. The author at times suspected the fit of these sockets and cones.

The double-junction electrode has demonstrated its applicability in all electrolytic solutions. Nevertheless it cannot be used for fluoride ions as the glass gets attacked by F^- ions. Therefore the need of an electrode responsive to fluoride ions was felt. Accordingly attempts were made to make a film which can act selectively to F^- ions.

The use of such an electrode has shown that the electrode works well in fluoride solutions alone over a wide range of concentrations. The presence of other halide ions mars its effective performance and therefore extensive work in terms of better design of electrode and also as to the fundamental reasons for the interference of other halide ions need to be carefully pursued.

The author also feels that LaF_3 would have been a better salt to use for making F^- ion more mobile. Much work in this direction is also necessary.

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