TRANSPORT NUMBER DETERMINATION BY ANALYSIS OF TRANSPORT OF AQUEOUS ELECTROLYTES THROUGH CEMENTITIOUS MATERIALS USING EMF METHOD.

BY

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

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ABSTRACT

The main aspect of this study was to determine the transport number of cations through membranes made out of mortar. Two types of membranes were used, namely :

(i) The 1.0:3.0:0.6 membrane and

(ii) The 2.0:4.0:1.0 membrane

Both comprised of the components;

Cement:Sand:Water respectively.

To determine transport number analysis, two types of cells were used:

(i) One for measuring emf with transference. This cell had a mortar membrane incorporated in it. On one side of the membrane the concentration - independence (reference) side, the concentration of the electrolyte was fixed at 0.01M. The compartment on the other side of the membrane contained a solution of the same electrolyte but whose concentration was varied from 0.05M to 0.40M in steps of 0.05M .

(ii) The second cell measured emf without transference. This assembly did not have a membrane incorporated in it. It comprised of two H-shaped cells connected back - to - back, one containing an electrolyte having a constant concentration fixed at 0.01M and the other unit containing the same electrolyte but with a concentration that was varied from 0.05M to 0.40M as explained in (i) above.

Readings of emf were taken in both cases for each of the concentrations between 0.05M to 0.40M of the electrolyte. The

ratio of emf values with and without transference was taken to be the transport number of the cations using the right type of electrode for each electrolyte used.

The following chloride electrolytes were used:

(a) Monovalent cations: NaCl and HCl .

(b) Divalent cations: $CdCl_2$, $CuCl_2$ and $ZnCl_2$.

As a further extension of the project, a miniature reinforced-concrete-cement steel support used in building industry was prepared (the RCC model).

Experiments were carried out to try monitor the movement of cations within the structure by use of electrodes (emf measurements) and analysis of chloride ion concentration in the ambient solution.

The results obtained in both for cells type (i) and (ii) were useful and provided a platform from which fairly adequate explanations could be made about the behaviour of cations within a mortar matrix. Some of these results indicated that movement of cations through membranes of this nature was dependent on:

(i) Size of ion

(ii) Valency and

(iii) Concentration of the electrolyte.

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CHAPTER ONE

1.0 INTRODUCTION

Transport through membranes is of increasing importance in technology and industry. Microfiltration (sterilization), ultrafiltration (pollution Control), reverse osmosis and electrodialysis (desalination) and dialysis (artificial kidney) are examples of well known membrane processes. The transport of ions through membranes has become an essential exercise. Examples of these include, the transformation from the mercury process for producing the basic chemicals NaOH and Cl_2 to a membrane process contributes to a reduction of the mercury pollution problem. Electrodialysis which is an important industrial operation is employed very much in the desalting of brackish waters and also used in the other operations involving the recovery or removal of salts or other colloidal substances from industrial waste liquid. In analytical chemistry ion selective membranes have become an important tool. Some of the most important biological processes are based on selective transport through membranes. Thus many different fields of science and technology may benefit from the understanding and quantitative description of transport processes in membranes.

When a membrane separates two solutions the number of forces that may normally operate in the absence of external magnetic and gravitational forces to cause a flow or flux of molecular or ionic species through it are[2]:

(a) Difference of chemical potential, $\triangle\mu$ e.g diffusion.

(b) Difference of electrical potential $\triangle E$ e.g electrodialysis.

(c) Difference of pressure, $\triangle P$ e.g streaming potential.

(d) Difference of temperature, $\triangle T$ e.g thermoosmosis.

Interest is hereby confined to (b). The presence of ionogenic groups and pores (space occupied by water) in the membrane confers certain functionality to the membrane, namely; permselectivity and/or semipermeability. The former is controlled by the phenomenological transport property called transport number, t_i. As the presence of narrow pores and high fixed charge density of the ionogenic groups give high values of t_i, membranes, characterized by this value i.e ion exchange membranes prove useful and industrially important. The efficiency with which a membrane transports selectively any particular ionic species may be infered by measuring the transport number of the species in the membrane. Two methods are normally used to determine the membrane transport number[3].

(a) The Hittorf's method which was developed by the German Physicist Johann Wilheim (1824-1914) in 1853.

(b) The emf method.

Membrane potentials are measured using suitable electrodes immersed in suitable electrolyte solutions.

Average tranport number $\bar{t}_+$ is derived from [4].

$$E = +\bar{t}_{+(app)} \frac{VRT}{V_+ Z_+ F} \ln \frac{a^I}{a^{II}}$$

Where;

a^I is the salt activity in the electrolyte of concentration I.

a^{II} is the salt activity in the electrolyte of concentration II

V_+ is a positive integer that denotes the valency of either the Cation or anion i.e V_+ and V_- respectively and V is sum of V_+ and V_- i.e $V=V_+ + V_-$

The derived transport number value has been called the apparent transport number because in this type of measurement water transport has not been taken into account.

This apparent value will be close to the true value when very dilute solutions are used. Lakshminarayanaiah[5] indicates that the determination of meaningful transport numbers for any membrane-electrolyte system calls for careful control of a number of factors. The important factors besides the control of the concentration of the donating or receiving side are:

(a) External concentration

(b) Current density

(c) Difference in concentration on either side of the membrane.

Kressman[6] recommended preliminary tests for determining which side controlled the E values. By keeping the concentration of the concentration dependent side constant, the transport number may be determined by the analysis of the solution on the other side after electrolysis. By this technique, values for t_i have been determined at various external concentration.

Owing to forces of interionic attraction, the transport numbers, and hence the ionic mobilities, vary with concentration. At high concentrations, the transport number of some ions change markedly in value and often in sign. This is generally due to complex ion formation, for example CdI^{2-}. The transport number also depends on the extent of solvation of the ion. This accounts for the series Li^+, Na^+, K^+ where, at the same concentration E increases with increasing atomic weight and size of unsolvated ion.

1.1 A review on previous work done in this field:

The moving boundary method for the determination of transference numbers was very popular in the early years of the 20th Century. MacInnes,D.A and T.B Brighton[7] came up with what they described as a novel form of apparatus. Transference number of K^+ ions were obtained from the ratio.

$$T_k = V_k/(V_k + V_{Cl})$$

in which V_k and V_{Cl} were the columns swept through by the boundaries in which the K^+ and Cl^- ions respectively are leading and are shown to agree for 0.1M and 0.2M KCl at 25°C. MacInnes later on, with the collaboration of I.A. Cowperthwaite and K.C.Blonchard[8], used the same method to determine the transference numbers with a constant current apparatus.

A modification of the moving-boundary method for determining transference numbers was later made by Cady and Longsworth[9]. Rising boundaries were used and in this new method the boundary started at the surface of the metal electrodes, which furnished the indicator ions by electrochemical solution of the metal.

Longsworth later on inspired by the previous success worked alone and measured the transference numbers at 25°C of aqueous solution of KCl, NaCl, LiCl and HCl still using the moving-boundary method. He formulated an equation connecting the transport numbers with the concentrations which was useful for interpolation and which gave a correct extrapolation to infinite dilution.

The emf method was also not to be outdone. Pearce and Mortimer[10] determined the emf of concentration cells for solutions of LiCl in water, methyl, ethyl, n-propyl, n-butyl and isoamyl alcohols.

All of the cells measured contained solutions having anormality ratio of 10:1. The emf with transference increased with increasing dilution for all of the solvents used, except butyl and isoamyl in which it decreased. The emf without transference decreased with increase in dilution in all of the solvents.

Jones and Bole[11] made improvements in the details of washburns analytical method for the determination of transference numbers of chlorides which made it more precise especially with dilute solutions. Transference number of Barium ion was measured (in $BaCl_2$ at 25°C). They discussed the computation of transference numbers from emf with and without liquid junction. Measurements of emf of concentration cells with liquid junction containing Barium Chloride were made covering the range from 0.001M to 1.0M.

A small but real migration of Barium ion in Barium bisulphate solutions in the solvent Sulphuric acid was demonstrated by Hammet and Lowenheim[12]. The process of conduction in these solutions was found not to depend upon a simple ionic migration.

This conclusion supported the theory of conduction by intermolecular proton jumps which was much discussed as an explanation of the anomalous mobilities of Hydroxyl and hydrogen ions in aqueous solutions..

Harned and Dreby[13] investigated the phenomenon of transference for hydrochloric acid in water and dioxane-water mixtures (i.e 0, 20, 45, 70 and 82% dioxane solutions) at 5° intervals from 0-50° and from 0.005 to 3.0M acid concentration. They measured emf of the following cells:

Ag-AgCl/HCl(m),dioxane(x),H_2O(y)/HCl(r),dioxane(x),H_2O(y)/AgCl-Ag

The cation transference was calculated over these ranges of concentration and temperature, by the thermodynamic relation.

$$t_+ = \frac{dE_t}{dE}$$

Where the tranference number of the cation at any given concentration is the ratio of the emf of the cell with transference (E_t) to that emf of the cell without transference (E). The limiting tranference number was determined by extrapolation for all solutions over the entire temperature range. Agreement with the limiting law of average conductance theory was observed in the water; 20, 45 and 70% dioxane-water mixtures. Results obtained with the mixtures containing 82% dioxane were less accurate.

Taylor and Sawyer[14] examined the transference of water with special emphasis on its dependance on concentration in the electrolysis of Sodium Chloride solutions. They observed that water moved from the anode to the cathode, and the quantity of water transported per Faraday of electricity decreased with increase in temperature and with increase in

concentration. Urea was used as the inert reference substance. Taylor later on worked with Wilcox[15] using Barium Chloride solutions. The transference numbers of Barium ion showed large increase with increasing dilution. The cathodic water transport did not increase with increasing dilution. It was therefore suggested that the double charge on the Barium ion produced a hydration shell which was more firmly bound and less sensitive to change in concentration than that around the chloride or Sodium ion.

The cation transport number (t_+) of aqueous solutions of nitric acid (C = 0.001 to 0.2 $moll^{-1}$) were determined by Stonehill, H.I[16] who combined the activity coefficient data with measurement of the emf of concentration cell with transport using quinhydrone electrodes. The results were compatible with the theoretical limiting value and the limiting scope of the t_+ Vs $\sqrt{C}$ curve agreed with the Jones-Dole and Longsworth equation but not with the Owen equation and indications were that upto 0.2 $moll^{-1}$ the hydrogen ion mobility in nitric acid and hydrochloric acid at the same concentration were equal. The nitrate mobility of Potassium nitrate (upto C = 0.1 $moll^{-1}$) were however lower than those of nitric acid.

Smits and Duyvis [17] obtained by measuring the emf of galvanic cells with transference, the transport numbers of Sodium in Sodium Chloride solutions at 25°C from 0.024N upto saturation (6.144M). The values were higher than those obtained by caramazza (up to 5M using the emf method) and those of Currie and Gordon (upto 2.5M using the adjusted indicator Technique); the latter observations being corrected for volume changes. For this correction an equation was derived that differs from an approximate equation obtained by Bearman, Hearse and Spiro. Their results were in excellent agreement with Stokes theory over the entire concentration.

In a more recent approach applying the Hittorf's method[18,19] a known quantity of electricity was passed through the membrane cell containing two chambers filled with the same electrolyte solution and seperated by a membrane.

Cations migrate to the cathode and anions migrate to the anode. The concentration change brought about in the two chambers, which was not more than about 10% was estimated by the usual analytical methods. The transport number t_i was calculated from

$$\bar{t}_i = J_i/I$$

Where J_i is the flux of the ion when the current density is I.

Previous work has been done by B O Ogolla[1] who investigated transport numbers of Sodium Ions through mortar membranes of varying thickness. Ogolla's investigations revealed that a mortar membrane behaved like an anion exchange membrane due to the high quantity of hydroxyl (OH) ions leached from the membrane into the cell solutions and chloride ions being retained in the membrane matrix. This retention of the chloride ions increased with increased membrane thickness, but both the chloride ion-constituent transference number, t_{Cl^-} and Sodium ion-consituent transference number, t_{Na^+} were found to be independent of the thickness for a constant set of the external electrolyte concentration.

The chloride ion-constituent transference number decreased with increase in electrolyte concentration variations ($\triangle C$) between the two half-cells for a certain membrane thickness. This observation he reasoned out to be a further confirmation of the anion exchange nature of the mortar membrane.

The present work highlights the transference properties of cations through mortar membranes at fixed thickness but with a variation in concentration of the ambient electrolyte solution.

1.2 Electrodes

Electrodes are the prima donnas of emf Opera, their performance makes or mars their results and they are apt to be temperamental unless they are carefully handled, Suitable electrodes should be, not only reversible to one of the ion constituents in solution, but also insoluble, stable and reproducible.

Two electrodes are normally chosen whose potential difference is small, and this small bit is then eliminated either by correcting for it directly [20] or by interchanging the electrodes (or the solutions) in the two compartments of the cell with transference and recording the mean emf[20,21,22]

Electrodes may be divided into two main classes:

(i) Indicating, and
(ii) Reference electrodes

1.2.1 Indicating Electrodes:

Example: The hydrogen electrode:

When platinum coated with platinum black (i.e metal in finely divided form to increase its surface area) is saturated with hydrogen gas, it behaves like a metallic electrode:

$$1/2H_{2(g)} \rightleftharpoons H^{+}_{(aq)} + e^{-}$$

The electrode potential is given by

$$E_H = E_H^o + \frac{RT}{F} \ln \frac{a_{H^+}}{P_{H_2}(g)^{1/2}}$$

It is the recognized convention to take standard hydrogen electrode, in which P_{H_2} = 1atm and a_{H^+} = 1, as the arbitrary zero of electrode potential. Thus $E_H o$ = 0, and hence.

$$E_H = \frac{RT}{F} \ln \frac{aH^+}{P_{H_2(g)}^{1/2}}$$

Cylinders of hydrogen provide the most convenient source of gas which must be passed through wash bottles containing a solution of alkaline pyrogallol (2g of pyrogallol in 40ml of 4N NaOH solution); dilute Sulphuric acid, water and a sample of the solution under test in the cell (this latter prevents alteration of the concentration of the solution in the cell).

Advantages of the hydrogen electrode

The electrode is capable of a high degree of accuracy, giving reproducible results over the complete pH range 0-14. There is no salt error, i.e no apparent shift of pH caused by variation of the ionic strength. The electrical resistance of the electrode is small, it can therefore be used with a normal potentiometer.

Limitations of the hydrogen electrode

It cannot be used in the presence of air, Oxygen, Oxidising and reducing agents. The platinum black deteriorates and must be frequently reviewed. The platinized surface is readily poisoned by alkanoids, cyanides, arsenic and antimony compounds and by colloids which are absorbed on the surface.

1.2.2 Reference electrodes

Any cell system involving the use of an indicator electrode must be completed by a reference electrode, the potential of which is not affected by the ion of the indicating electrode.

Example: Silver - Silver chloride Electrode

This electrode consists of a strip or disc of silver on which is deposited a film of silver chloride. It behaves as a reversible chlorine electrode with a potential given by:-

$$E = E^{\circ} - \frac{RT}{F} \ln a_{Cl^-}$$

Other electrodes can also be used like the Sodium amalgam electrode, The only mishap with this electrode is that, just like any other amalgam - electrode, it introduces some experimental errors. In the Sodium amalgam electrode, the dissolution reaction:

$$Na_{(s)} + H_{2(l)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)} + 1/2H_{2(g)}$$

may still take place at the amalgam - electolyte interface(23,24,25). Dissolution of the amalgam shifts the

zero-current potential from the reversible value because of hydrogen evolution and it increases the concentration of Sodium ions in the diffusion layer immediately adjacent to the electrode surface.

Besides hydrogen evolution, a reaction can also take place between the amalgam and another solute. It has been shown that in NaCl-KCl electrolytes, the reaction.

$$Na(Hg)_{(l)} + K^{+}(aq) \rightleftharpoons K(Hg)_{(l)} + Na^{+}(aq)$$

Can shift the potential of a Sodium amalgam electrode by several millivolts[26].

Platinum electrodes on the other hand can be used either as a reference electrode or for making contact in Oxidation -reduction systems. Platinum, the more commonly used metal, may be used either in the shiny form (oxidation - reduction electrodes), black form (hydrogen electrode and conductance measurements) or grey form (conductance measurements). But for conductance measurements it is advisable to use grey platinum electrodes. These are prepared by heating blacked electrodes to dull redness in a flame.

1.3 The liquid Junction:

In our study concentration cells with transference had "electrodes reversible to one ion present in the electrolyte" For example the AgCl/Ag electrode is reversible to Cl^{-} ion, and the H^{+}/H_2 electrode is reversible to H^{+} ion. The two electrolytes of different concentration are connected by a liquid junction, where the concentrations are changing gradually from the constant concentrations of electrolyte I to the constant concentrations of electrolyte II.

A liquid junction can be obtained in different ways:-

(a) By means of a salt bridge

(b) A porous wall or plug

(c) Or any other device that prevents convective mixing of the two solutions, without hindering diffusion and electric transport.

The liquid junction therefore represents a boundary between two dissimilar solutions across which ions migrate. The ionic movement generally takes place by a diffusional process; or it may involve a flow depending on the way the liquid-liquid boundary is constructed. The liquid junction potential arises from the differences in the mobilities of positive and negative ion. If the cation has a higher mobility than the anion, the former will move ahead of the latter into the dilute solution which will become positively charged with respect to the concentration solution. If the anion moves faster, then the dilute solution will be negatively charged. In either case a "double Layer" on a microscopic scale is produced at the junction of the two solutions.

In other words a gradient of electric potential exists. This will in effect increase the speed of the slower ion and decrease the speed of the faster ion, so that in the steady state both ions, positive and negative, will move at the same speed.

1.4 Common types of Ion-exchange membrane

A membrane can easily be described as a phase that acts as a barrier to the flow of molecular and ionic species present in the liquids and/or vapours contacting the two surfaces.

Membranes may be divided into two categories; natural and artificial. The ones that fall into the natural category are of particular interest in relation to the study of biological processes. These membranes are formed from lipids; large molecules having a polar group on one end and the rest of the molecle being a long tail consisting of non-polar hydrocarbons. In the membrane the lipids form a double layer. The polar groups are oriented towards the two aqueous phases. The non-polar tails in the interior of the membrane are attracted to one another by weak Van der Waals forces and act as a blockage to the transfer of ions. Ions may be transported through charged channels, however, or they may pass through the membrane in the form of complexes. Artificial membranes are polymer networks which possess positive and negative fixed charged particles embedded in the membrane matrix.

Artificial membranes can be classified on the basis of their structures. This kind of classification is depicted by Lakshminarayanaiah[5]. Two very clear classes given are: Homogeneous and Heterogeneous.

Homogeneous membranes are coherent gels and are often translucent or even transparent, an apparent indication of the non-existence of inhomogeinity.

These membranes are accorded a special preference in Scientific investigations because they possess special properties.

They are strong-acid or strong-base membranes, and have a uniform structure with a high electric conductivity. They impart an extremely low permeability for electrolytes.

Heterogeneous membranes consist of colloidal particles embedded in an inert binder like polystyrene. Their permeability for electrolytes is higher and the electric conductivity is lower. But they do possess a superior mechanical stability. This type of membranes are being replaced by the homogeneous type.

In the simplest type of membrane large solute particles are prevented from permeating because of size. However, the pore or channels are sufficiently wide to allow solvent particles (and other small particles) to pass through. Such a membrane is called a "semipermeable membrane". Grossly porous membranes (wide pores) are neither permselective[27,28] nor semipermeable, whereas membranes with narrow pores are semipermeable but may not be permselective if the number of fixed ionogenic groups are too few in number.

Ion exchange membranes contain ionogenic groups and show selectivity with regards to the transport of charged particles, ions. Due to this they are often said to be permselective membranes and while in contact with external electrolyte solutions, they take up electrolytes in a way different from non-ion exchange membranes. Ion-exchange membranes have the following groups of ionogenic species embedded in the resin matrix:

(i) Negative groups such as; $-SO_3^-$, $-COO^-$, etc in the case of cation exchangers, and

(ii) Positive groups such as $-NH_{3+}$, $>NH_{2-}$ etc in the case of anion exchangers.

Because of the presence of these ionogenic groups the membrane excludes the co-ions (ions of the same sign; either positive or negative, as the fixed group) by electrostatic repulsion. The amount of exclusion is fully controlled by the concentration of the external electrolyte. At very low concentration, the amount of co-ion is almost zero in the membrane phase, but as the external concentration is increased, the co-ion content in the membrane increases.

1.5 Transport Processes in Concentration Cells

1.5.1 Electromotive Force of Cells

All cells consist of a series of conducting phases in contact, i.e electrodes and one or more liquid electrolytes. Phase potentials exist at any boundary between phases of different composition; thus, the emf of a cell is the algebraic sum of all the phase boundary potentials, including any metal-metal contact potentials which may be present.

In contrast to simple cells, in which a definite chemical reaction occurs, no overall chemical reaction occurs in concentration cells. The process resulting in the production of an emf is merely the transfer of some substance from one concentration to another. If two electrodes can be found, each reversible to one of the ions of an electrolyte, then a concentration cell without transport can be constructed:

$$\overset{-}{A} \;/\; \underset{m_1}{AX_{(aq)}} \;/\; \underset{\text{Solid}}{BX} \;/\; B - B \;/\; \underset{\text{Solid}}{BX} \;/\; \underset{m_2}{AX_{(aq)}} \;/\; \overset{+}{A} \quad \ldots\ldots(1.5.1.a)$$

where molality $m_2 > m_1$

The net result for the passage of one Faraday through the cell is the transfer of 1 mole of AX from m_2. The emf of such a cell, when AX is a 1:1 electrolyte, is:

$$E = \pm \frac{vRT}{V_+ Z_+ F} \ln \frac{a_2}{a_1} = \pm \frac{vRT}{V_+ Z_+ F} \ln \left[\frac{m_2^{v} \gamma_{\pm}^{v} \left(V_+^{V_+} V_-^{V_-} \right)}{m_1^{v} \gamma_{\pm}^{v} \left(V_+^{V_+} V_-^{V_-} \right)} \right] \quad \text{.....(1.5.1.b)}$$

Where m, a and γ (with the appropriate subscripts) are the mean ionic molality, activity and activity coefficient respectively, defined as:

$$m = m_{\pm} = (m_+ \, m_-)^{1/2}$$

$$a = a_{\pm} = (a_+ \, a_-)^{1/2}, \text{ etc}$$

for 1:1 electrolytes.

This concentration is simply a combination of two seperate cells connected back-to-back i.e

$$B \,/\, BX \,/\, AX_{(aq)} \,/\, A \text{ of emf } E_1$$
$$\text{Solid} \quad m_1$$

$$B \,/\, BX \,/\, AX_{(aq)} \,/\, A \text{ of emf } E_2$$
$$\text{Solid} \quad m_2$$

Hence; $E = E_1 - E_2$. E_1 and E_2 can obviously be measured seperately.

In equation (1.5.1.b), E, m_1 and m_2 can be measured. It is thus possible to calculate the ratio of the mean ionic activity coefficients (γ_2/γ_1) at the two concentrations. If m_1 could be made so dilute that $\gamma_1 = 1$, then γ_2 at any molality m_2 could be determined from a single emf measurement. This is not possible experimentally and instead the emf values of a series of cells are measured in which m_2 is kept constant and m_1 varied. An extrapolation to zero ionic strength using the Debye-Huckel theory permits the calculation of activity coefficient.

It is not always possible to construct such a concentration cell as electrodes reversible to both ions are not available. If only one is available, a concentration cell with transport can be constructed.

$$A \;/\; AX_{(aq)}\,(m_1) \;|\; AX_{(aq)}\,(m_2) \;/\; A \qquad \ldots\ldots\ldots\ldots\ldots (1.5.1.c)$$

In this cell a direct transfer of AX from the more concentrated side (m_2) to the more dilute side (m_1) takes place. An example of such a cell is,

$$Pt\text{-}H_2 \;/\; HCl_{(m_1)} \;|\; HCl_{(m_2)} \;/\; H_2 - Pt$$

The emf of which is given by:

$$E = -t_a \frac{\nu RT}{\nu_- Z_- F} \ln \frac{a_2}{a_1} = -t_a \frac{\nu RT}{\nu_- Z_- F} \ln \left[\frac{m_2^{\nu} \gamma_{\pm}^{\nu} \left(\nu_+^{\nu_+} \nu_-^{\nu_-} \right)}{m_1^{\nu} \gamma_{\pm}^{\nu} \left(\nu_+^{\nu_+} \nu_-^{\nu_-} \right)} \right] \ldots (1.5.1.d)$$

In the derivation of which it is assumed that the transport number of the anion (t_a) does not vary between m_1 and m_2.

If the electrodes are reversible to the anion then,

$$E = tc \frac{vRT}{v_+ Z_+ F} \ln \frac{a_2}{a_1} \qquad \text{.....(1.5.1.e)}$$

When the transport number is known, extrapolation by a similar method to that for concentration cells without transport provides another method for the determination of activity coefficients.

Comparison of emfs of cells with and without transport, from equations (1.5.1.b) and (1.5.1.d) gives:

$$t_a = \frac{E_{transport}}{E} \quad ;$$

The transport number of the anion.

1.5.2 Water Transport Effect

In ion-exchange membranes, measured membrane potentials deviate from ideal potentials due to both chloride ion diffusion and water diffusion by electroosmotic effect. These effects reduce the measured emf[29].

In poor membranes there is certainly some doubt that the reversible emf values are the ones measured for the cell without liquid junctions. The degradation of cells of these type may be considered as the establishment of significant concentration gradients in the liquid layers at the membrane interfaces as a result of chloride ion diffusion.

Hence, if the whole electrochemical process of the cell:

$$Ag\text{-}AgCl/NaCl(m^{I})/Membrane/NaCl(m^{II})/AgCl\text{-}Ag$$

is considered to be the reversible transport of Sodium Chloride and water and assuming no change in the composition of the membrane during an emf measurement, we may write (30,31).

$$E_c = E_i - t_{Cl}\frac{2RT}{F}\ln\frac{a_{\pm}(NaCl)^{I}}{a_{\pm}(NaCl)^{II}} + t_w\frac{RT}{F}\ln\frac{a(H_2O)^{I}}{a(H_2O)^{II}} \qquad .....(1.5.1.b)$$

Where E_c is the measured cell emf, E_i is the ideal potential for a hypothetical membrane permeable only to cations; t_{Cl} and t_w represent the moles of chloride and water transfered per Faraday (tansport number values).

The ideal potential (E_i) for a hypothetical membrane permeable only to cations can be calculated by the equation,

$$E_i = \pm\left(\frac{vRT}{V^{\pm}\,Z^{\pm}\,F}\right)\ln\left[\frac{a_{\pm}(NaCl)^{I}}{a_{\pm}(NaCl)^{II}}\right]^{v}$$

These electrical potentials arising across permselective membranes of high fixed charge density are based on several theories, the most satisfactory being the theory of Scatchard[32]. This theory is based on the application of well - established principles of classical thermodynamics used in the consideration of liquid-liquid junction potentials generated across membranes, and is quite successful in describing the emfs of the membrane cells of the type shown above.

Membranes that are not very permselective, are not able to keep the co-ions out of the membrane phase even in very low salt external environment to the same extent as ion exchange membranes of high fixed charge density. The Scatchard theory has taken the factors causing the decrease in selectivity with the mean external activity, viz transport of co-ion and solvent taken into account. Thus the Scatchard theory describes satisfactorily the emf's of the cells of the given type containing membranes of low fixed charge density[33].

Water transport by electroosmosis is a function of the internal ion concentration of the membrane pore solution and the membrane ionic form i.e electroosmotic water transport depends on membrane properties such as[34];

(i) Exchange capacity
(ii) Moisture content
(iii) Internal ion concentration of the membrane pore solution and
(iv) Membrane ionic form

Water transport normally decreases with increasing external electrolyte solution concentration and also varies with the variation in the effective radii of the cation e.g Li^+, Na^+, K^+ and H^+, in their hydrated forms.

A very "tight" (compact) membrane of e.g phenolsulphonic Acid (PSA) requires many weeks to hydrolyse and represents very nearly the limiting condition of membrane internal solution concentration. This consequently reduces drastically water transport.

In general water transport for any one ion appears to follow the moisture content[29,35] of the membrane in that ionic form. Although the moisture content of a membrane differs only slightly only with ionic form, a large difference in water transport between for example Lithium, Sodium, Potassium and hydrogen ions is observed. The moving ion exerts the major control over the magnitude of water transport.

The major determining parameters in water transport for a given ion appear to be the membrane moisture content and exchange capacity of the ion i.e the internal concentration of the membrane pore solution. Water transport increases almost linearly with increasing membrane moisture content.

One might consider that interactions within a membrane during water transport, between the moving ion and water, and between the water and membrane pore wall may be represented by a simple viscious force balance.

A moving ion under the influence of an applied electric potential will exert a force on the water which will be balanced by the friction force between the water and the stationary membrane pore wall.

It must be noted that membrane cell potentials are not reversible potentials unless the membrane used are impermeable to water. If the osmotic flow of water is negligibly small, water may still be transfered reversibly by electroosmosis and contribute to the cell reaction[31]. In addition there is the possibility of an anion transfer in a cation exchange membrane. Hence we assume that the membrane cell reaction is:

$$a_1 \xrightarrow{(1-t_{Cl}) \text{ moles NaCl}} a_2$$

$$a_{w1} \xrightarrow{t_w \text{ moles } H_2O} a_{w2}$$

$$\xrightarrow[\text{positive electricity}]{1 \text{ Faraday of}}$$

and assuming that osmotic degradation is negligible, the measured cell potential is written as in equation (1.5.1.b)

It has been customary to neglect water transfer in the consideration of membrane potentials[36] and to refer to the ratio of measured to ideal potential as the cation transport number[37].

A number of authors have noted that this procedure gives erroneous values[32,38]. From values that have been calculated using polystyrenesulhponic Acid membrane[31], indicate that in some circumstances the water transfer term is greater than the anion transfer term in equation (1.5.1.b)

The value to be assigned to the anion transfer term in this equation may be estimated using the assumptions of Mayer-Sievers[36] and Toerell[38].

Hence, it can summarily be said that transport of water which accompanies the passage of ions through the membrane, is caused partly by ionic hydration and partly by electroosmotic transfer.

1.6 Flux Equations

1.6.1 Concentration Cells without membranes:

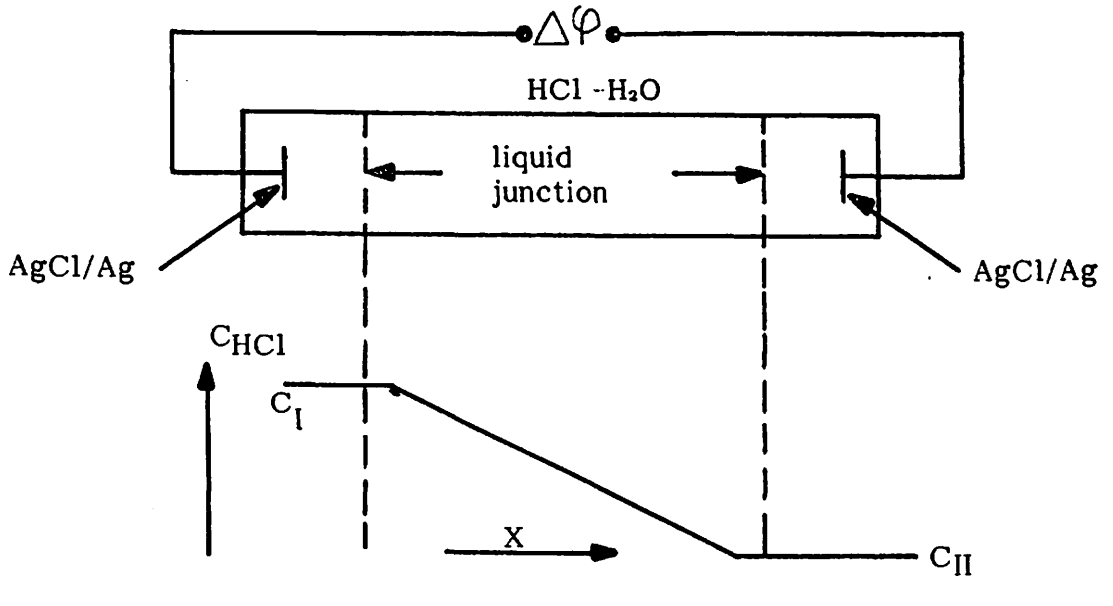
a) An HCl - H_2O concentration cell AgCl/Ag electrodes

As a simple example we shall consider the following concentration cell at constant temperature and pressure;

$$Ag(s)/AgCl(s)/HCl(aq,c_I) \;||\; HCl(aq,c_{II})/AgCl(s)/Ag(s)$$

The two electrodes are both AgCl/Ag electrodes. The two aqueous solutions of HCl, separated by a liquid junction are of different conncentration.

Diagram (a)



With a closed circuit, an electric current will pass through the cell, chemical reactions take place at the electrodes, and a transport of matter takes place in the electrolyte. When one mole electrons pass through the outer circuit from left to right, the following changes will take place.

At the electrodes the chemical reactions are;
left hand side electrode : $Ag_{(s)} + Cl^- \longrightarrow AgCl_{(s)} + e^-$
righthand side electrode: $AgCl_{(s)} + e^- \longrightarrow Ag_{(s)} + Cl^-$

One mole Ag is transfered from the left hand side electrode to the right hand side one, while one mole AgCl is transfered in the opposite direction. One mole Cl^- is removed from the electrolyte at the electrode on the left hand side, while one mole Cl^- is added to the electrolyte at the electrode on the right hand side.

The aqueous solution is always electrically neutral, and the transfer of one mole Cl^- from left to right is compensated for by the migration of Cl^- to the left and of the H^+ to the right in the electrolyte. The fraction of the current carried by Cl^- is t_{Cl^-}, the transference number of Cl^-, while the fraction of the current carried by H^+ is t_{H^+}, the transference number of H^+ the transference number vary slightly with the concentration of HCl, but Cl^- and H^+ being the only current carriers, their sum is always equal to unity;

$$t_{Cl^-} + t_{H^+} = 1$$

The total changes caused by the transfer of charge in electrolyte I on the left hand side are thus: one mole Cl^- removed at the electrode, t_{Cl^-},I mole Cl^- gained by migration and t_{H^+},I mole H^+ moved by migration[39],

$(-1+t_{Cl^-},I)$ mole Cl^- - t_{H^+},I mole H^+ = $-t_{H^+}$,I mole HCl
$-t_{H^+}$,I

Similarly the total changes in the electrolyte II on the right hand side are:

One mole Cl^- gained at the electrodes, $t_{Cl^-,II}$ mole H^+ gained by migration.

$(1-t_{Cl^-,II})$ mole Cl^- + $t_{H^+,II}$ mole H^+ = + $t_{H^+,II}$ mole HCl

$t_{H^+,II}$

The difference $(t_{H^+,I} - t_{H^+,II})$ mole HCl, is retained in the liquid junction.

The electrolytes consist of the two components HCl and H_2O. We may choose water as the frame of reference. For an irreversible process we may thus express the changes taking place locally, anywhere in the electrolytes, by the two fluxes J_{HCl} and J_I. The forces bringing about the changes are:

$$X_{HCl} = - \nabla U_{HCl} \text{ and}$$

$$X_I = - \nabla \varphi$$

This is an isothermal system, where the force.

$$X_{q'} = - \nabla \ln T = 0,$$

and heat flux is not included in a complete set of flux equations. The transfer of Ag and AgCl between the electrodes does not represent any change in chemical potential, the force is equal to ZERO. The flux equations expressing the changes are;

$$J_{HCl} = - L_{11} \nabla U_{HCl} - L_{12}$$

$$I = - L_{21} \nabla U_{HCl} - L_{22}$$

The Onsager relations require that $L_{12} = L_{21}$. Further, L_{11} and L_{22} have positive values and

$$L_{11}\, L_{22} \; > \; L_{12}^2$$

The phenomenological coefficients are dependent on local concentrations, but they are independent of gradients.

We can arrange the cell such that gradients occur only in the direction of the X-axis between the electrodes. Then we have

$$X_{HCl} = - dU_{HCl}/dx \quad \text{and}$$

$$X_I = - d\varphi/dx$$

Both gradients are well defined anywhere in the cell as the limiting value of observable quantities;

$$\text{e.g} \quad dU_{HCl}/dx = \lim_{\triangle x \longrightarrow 0} \triangle U_{HCl} / \triangle x$$

We avoid the concepts of the unmeasurable electric potential difference between electrode and solution. The two forces may be varied independently, X_{HCl} by changing concentrations, and X_I by changing the applied potential.

b) <u>An HCl-H_2O Concentration Cell with H^+/H_2 electrodes</u>:

The cell is similar to the cell envisaged in diagram (a), except for the electrodes;

$(Pt)H_{2(g)}/HCl_{(aq,C_I)} \;||\; HCl_{(aq,C_{II})}/H_{2(g)}(Pt)$

Both electrodes are H^+/H_2 electrodes. The two aqueous solutions of HCl connected by a liquid junction are of different concentration.

The following is an analysis of the changes taking place when one mole electron passed through the outer circuit from left to right.

<u>At the electrodes</u> the chemical reactions are;

left hand side electrode : $1/2H_{2(g)} \longrightarrow H^+ + e^-$
right hand side electrode: $H^+ + e^- \longrightarrow 1/2H_{2(g)}$

One half mole H_2 is transfered from the left hand side electrode to the right hand side one, while one mole H^+ is removed from the electrolyte at the electrode on the right hand side and added to the electrolyte at the electrode on the left hand side.

<u>The aqueous solution</u> stays electrically neutral, and the transfer of one mole H^+ from right to left is compensated for by the migration of Cl^- to the left and of H^+ to the right in the electrolyte, Cl^- and H^+ being the current carriers in the electrolyte. The sum of the transference numbers being equal to one, $t_{H^+} + t_{Cl^-} = 1$.

The total changes caused by the transfer of charge in electrolyte I on the left hand side may be written;

$(1-t_{H^+,I})$ mole $H^+ + t_{Cl^-,I}$ mole $Cl^- = + t_{Cl^-,I}$ mole HCl $-t_{Cl^-,II}$

and the total changes in electrolyte II on the right hand side is correspondingly,

$(-1+t_{H^+,II})$ mole $H^+ - t_{Cl^-,II}$ mole $Cl^- = -t_{Cl^-,II}$ mole HCl $-t_{Cl^-,II}$

The flux equations for this cell may be written;

$$J'_{HCl} = - L'\nabla U_{HCl} - L'_{12}\nabla\varphi'$$

$$I' = - L'_{12} U_{HCl} - L'_{22}\nabla\varphi'$$

The transfer of $H_{2(g)}$ between the electrodes does not enter the flux equations as it does not represent any change in chemical potential.

We shall compare the phenomenological coefficients for two cells that differ only in electrodes, their electrolytes having identical compositions.

The conductivity of the electrolyte is independent of the electrodes, and thus we have;

$$L'_{22} = L_{22}$$

with H^+/H_2 electrodes, the net transport of HCl will be right to left, the opposite direction of the net transport of HCl when using AgCl/Ag electrodes. Thus we have;

$$J'_{HCl}/I = L'_{12} / L'_{22} = t_{HCl}$$

With H^+/H_2 electrodes, the transference coefficient is negative and equal to minus the transference number of Cl^-

$$t_{HCl} = - t_{Cl^-}$$

to determine L' we can study the pure diffusion,

$J'_{HCl} = l'_{11} \nabla U_{HCl}$. Pure diffusion is electrode independent, and thus we have;

$$l'_{11} = l_{11}$$ where l_{11} is called a "diffusion Coefficient".

Therefore; $l'_{11} = L'_{11} - L'_{21}/L22$ and we can find L'_{11} from the diffusion values of l'_{11} and L'_{21}.

In a similar way as discussed previously, we can study the short circuited cell with ZERO electric potential difference, and we find;

$$(J'_{HCl}/I)_{\nabla\varphi=0} = 1$$

which gives $L'_{11} = - L'_{21}$

c) A concentration cell containing the chloride of a divalent cation, AgCl/Ag electrodes:

Let us consider the following cell at constant temperature and pressure;

$$Ag_{(s)}/AgCl_{(s)}/CaCl_{2(aq,C_I)}||CaCl_{2(aq,C_{II})}/AgCl_{(s)}/Ag_{(s)}$$

The changes taking place when one mole electrons passes from left to right in the outer circuit, may be studied in the same way as for the previous cells. Total changes on the left handside.

$$(-1 + tCl^-,I) \text{ mole } Cl^- + 1/2\ t_{Ca^{2+},II} \text{ mole } Ca^{2+}$$
$$= +1/2t_{Ca^{2+},II} \text{ mole } CaCl_2$$

The transference number for Ca^{2+} ions is defined as the fraction of electric charges transfered by means of the Ca^{2+} ions, it refers to the number of equivalents Ca^{2+} transfered. Since transference numbers refer to equivalents, the sum of the transference numbers is equal to unity,

$$\sum t_+ + \sum t_- = 1$$

The transference coefficients, however, refer to the number of moles of neutral salts.

In this cell we have;

$$t_{CaCl_2} = 1/2t_{Ca^{2+}}$$

The flux equation expressing the changes are;

$$J_{CaCl_2} = -L_{11}\nabla U_{CaCl_2} - L_{12}\nabla\varphi$$

$$I = -L_{21}\nabla U_{CaCl_2} - L_{22}\nabla\varphi$$

As we did previously, we arrange our experiments such that gradients occur only in the direction of the X-axis, when studying the phenomenological coefficients.

Again we find L_{22} from conductivity measurements when $dU_{CaCl_2}/dx = 0$. The coefficient L_{22} can be interpretted in terms of mobilities of the ions, $U_{Ca^{2+}}$

$$L_{22} = \frac{2C}{F}(U_{Ca^{2+}} + U_{Cl^-})$$

Further t_{CaCl_2} can be determined from the Hittorf method, thus;

$$J_{CaCl_2}/I = L_{12}/L_{22} = t_{CaCl_2} = 1/2t_{Ca^{2+}} = 1/2\,\frac{U_{Ca^{2+}}}{U_{Ca^{2+}} + U_{Cl^-}}$$

When short - circuiting the cell, such that

$$d\varphi = /dx = 0$$

We obtain

$$J_{CaCl_2}/I = 1/2 = L_{11}/L_{12}$$

For pure diffusion we have;

$$J_{CaCl_2} = - L_{11} \nabla U_{CaCl_2}$$

Where;

$$L_{11} = L_{11} - L_{12}\, L_{21}/L_{22}$$

Keeping in mind that $t_{Cl^-} = 1 - t_{Ca^{2+}}$ and $L_{12} = L_{21}$ we obtain.

$$L_{11} = 1/4\, L_{22}\, t_{Ca^{2+}}\, t_{Cl^-}$$

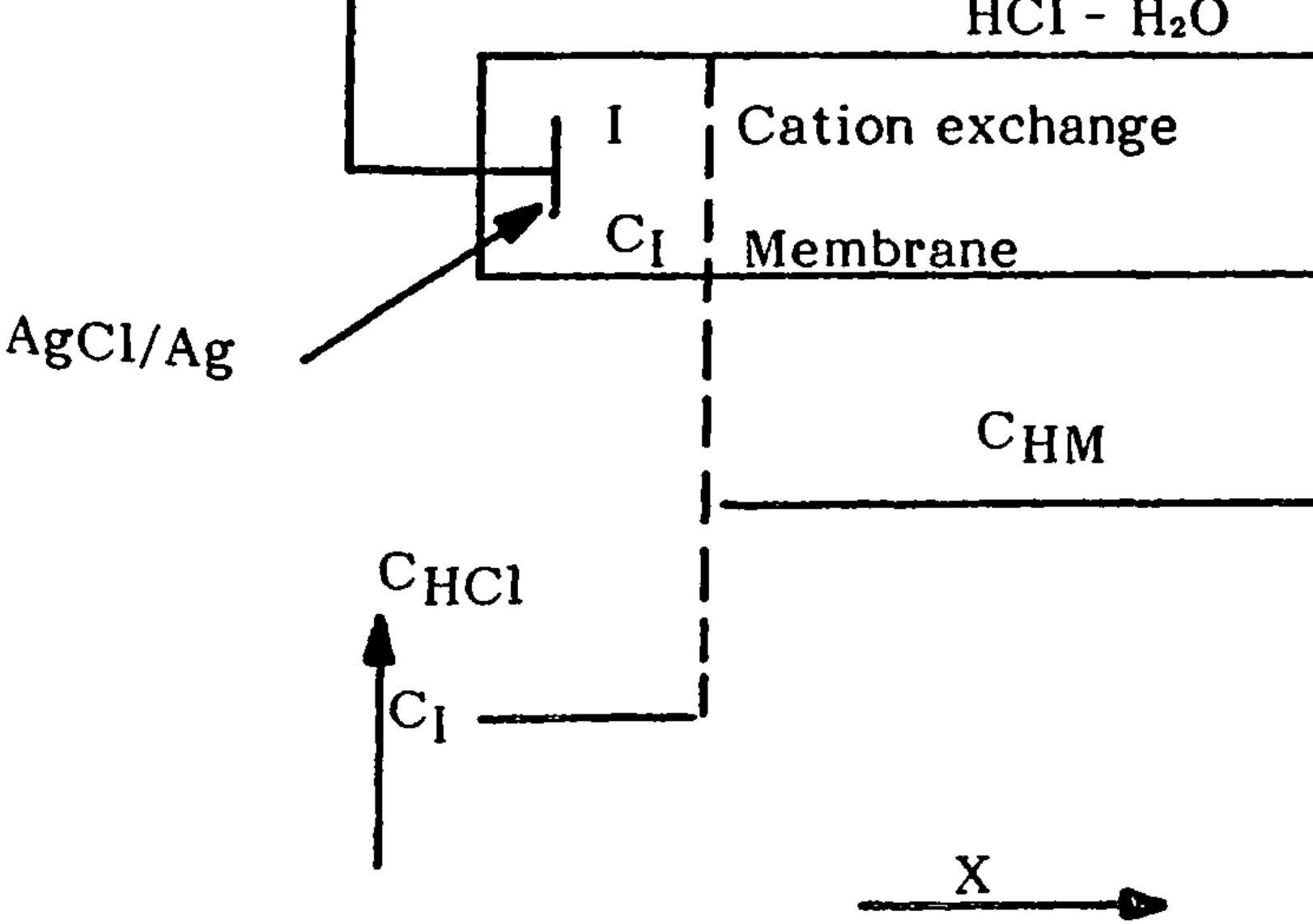
The coefficients L_{12} can also be expressed by concentration and mobility;

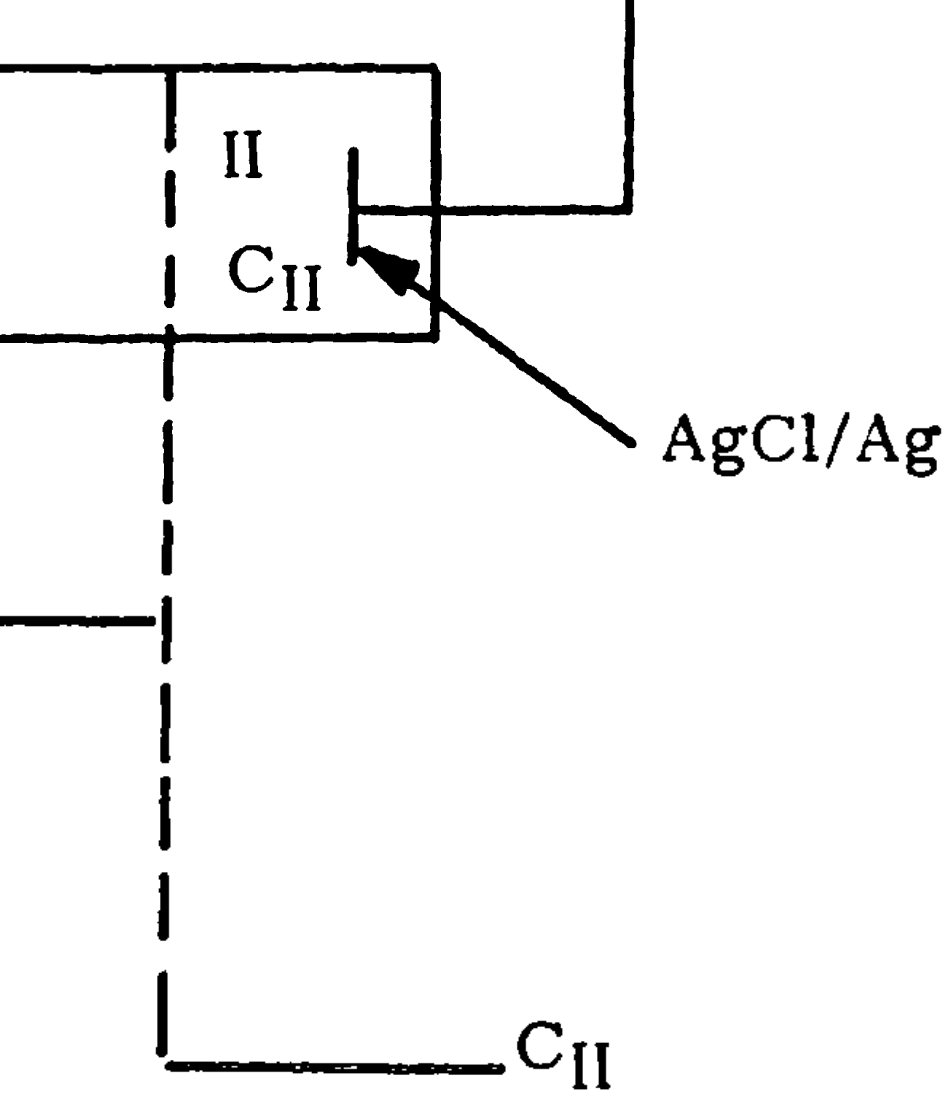
$$L_{12} = \frac{C}{F} U_{Ca^{2+}}$$

1.6.2 Concentration cells with membranes:

e.g An HCl - H_2O concentration cell with cation exchange membrane and AgCl/Ag electrodes:

As a simple example we shall consider the following concentration cell at constant temperature and pressure.


HCl - H2O
I
Cation exchange
CI
Membrane
AgCl/Ag
CHM
CHCl
CI
X


II
C_{II}
AgCl/Ag
C_{II}

In this case, as opposed to the previous cases, the liquid junction is replaced by a cation exchange membrane.

In the liquid junction the concentration gradient of HCl is determined by the concentrations of HCl in the two adjacent electrolytes. In the cation exchange membrane the cation sites, M^- are filled with H^+ to keep the membrane electrically neutral, and the concentration of HM anywhere in the membrane is determined by the concentration of cation sites. Such a membrane usually contains a large amount of water (sometimes more than half the weight).

If the membrane is not a perfect cation exchanger, it will contain a small amount of the neutral species HCl. The concentration of HCl decreases from electrolyte I to electrolyte II.

The present cell consists of three components, HCl, H_2O and HM (Ag and AgCl at the electrodes). We shall choose HM, the membrane as the frame of reference for the movements, Since the content of HCl in the membrane is very low (or nil), very little HCl can diffuse through the membrane. In a closed circuit, however, HCl can be transported from one side to the other with the electric current, H^+ via the membrane and Cl^- by the electrode reactions. The net observable result is a transfer of neautral HCl from one side to the other. Water is transported through the membrane by diffusion and together with H^+.

With the membrane as a frame of reference, we have the three fluxes J_{HCl}, J_{H_2O} and I. The three corresponding forces are given the symbols $-\nabla U_{HCl}$, $-\nabla U_{H_2O}$, and $-\nabla\varphi$. We have a set of three flux equations (compared to only two for the cell with the liquid-junction);

$$J_1 = J_{HCl} = -L_{11}\nabla U_{HCl} - L_{12}\nabla U_{H_2O} - L_{13}\nabla\varphi$$

$$J_2 = J_{H_2O} = - L_{21}\nabla U_{HCl} - L_{22}\nabla U_{H_2O} - L_{23}\nabla\varphi$$

$$I = - L_{31}\nabla U_{HCl} - L_{32}\nabla U_{H_2O} - L_{33}\nabla\varphi$$

For emf calculations we give the conditions I = 0 and obtain;

$$\nabla\varphi = -t_{HCl}\nabla U_{HCl} - t_{H_2O}\nabla U_{H_2O}$$

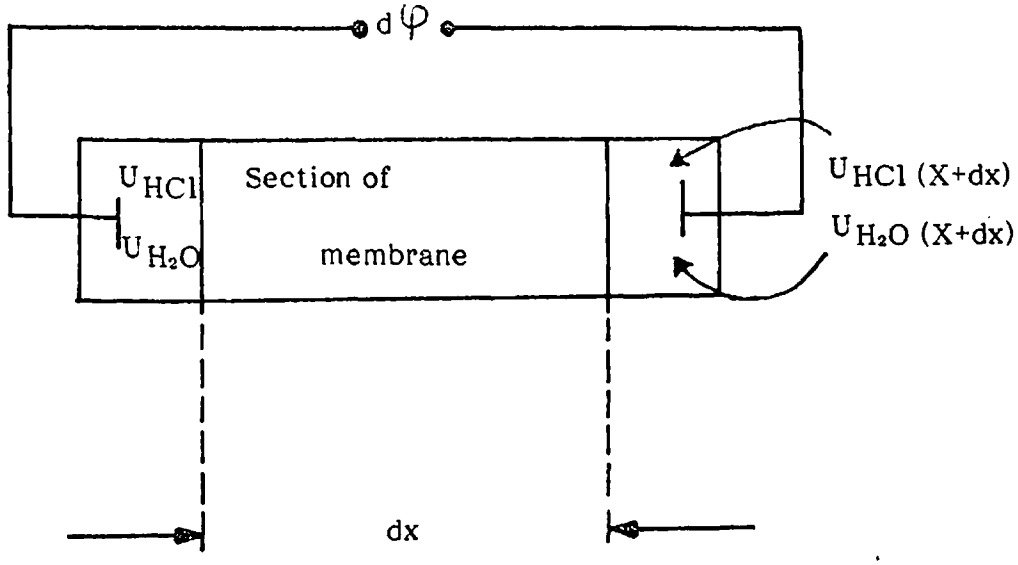
Where $t_{HCl} = L_{31}/L_{33}$, the transference coefficient of HCl, and $tH_2O = L_{32}/L_{33}$, the transference coefficient of H_2O. With gradients in one direction only, we may write;

$$d\varphi = -t_{HCl}\, dU_{HCl} - t_{H_2O}\, dU_{H_2O} \text{ -------(1.5.1.a)}$$

In order to define the forces $-\nabla\varphi$, $-\nabla U_{HCl}$ and $-\nabla U_{H_2O}$, or the changes $d\varphi$, dU_{HCl} and dU_{H_2O}, over a distance dx inside the membrane, we may visualize a section of thickness dx cut out of the membrane.

The section is placed between two electrolyte solutions, each one of a composition that is in local equilibrium with the membrane section at the phase boundary. Thus the gradients in the section are kept undisturbed. We place an AgCl/Ag electrode in each solution and measure the potential across this cell when $I \simeq 0$.

Diagram (c)



The gradient in electric potential, $d\varphi/dx$, across any section of the membrane is defined as the potential of a cell such as the one shown in diagram(c). The gradients in chemical potential in the membrane are defined by the differences in chemical potentials.

$$dU_{HCl}/dx = \{U_{HCl}(x+dx) - U_{HCl}(x)\}/dx \text{ and}$$

$$dU_{H_2O}/dx = \{U_{H_2O}(x+dx) - U_{H_2O}(x)\}/dx$$

In this way the gradients and forces inside the membrane are defined by external quantities, the membrane is treated as a "black box".

A basis for the above definitions is the assumption [2] that the composition anywhere in the membrane has a corresponding equilibrium composition of the $HCl-H_2O$ solution at the external pressure.

We can eliminate dU_{H_2O} from equation 1.6.1(a) by using the Gibbs-Duhem equation in the solution,

$$C_{HCl} \cdot dU_{HCl} + C_{H_2O} \cdot dU_{H_2O} = 0$$

and we obtain,

$$d\varphi = FdE = -\left(t_{HCl} - t_{H_2O} \frac{C_{HCl}}{C_{H_2O}}\right) dU_{HCl} \qquad \text{.....(1.6.1.b)}$$

The equation may be rearranged and integrated over the membrane from electrolyte I to electrolyte II;

$$\Delta U_{HCl} = U_{HCl,II} - U_{HCl,I} = -F \int_{(I)}^{(II)} dE/\left(t_{HCl} - t_{H_2O} \frac{C_{HCl}}{C_{H_2O}}\right)$$

.....1.6.1(c)

The value of the integral on the right hand side of equation 1.6.1(c) can be found by a numerical integration from known values of t_{HCl}, $^{t}H_2O$ and E for different values of C_{HCl}. Thus one can find the chemical potential of HCl in an HCl-H_2O mixture as a function of composition, using the left hand side electrolyte as reference state.

Conversely, if $\triangle U_{HCl}$, ^{t}HCl and $^{t}H_2O$ are known as functions of composition, the emf of the cell can be found by integrating equation 1.6.1(b).

$$F.E = \int_{(I)}^{(II)} (t_{HCl} - t_{H_2O} \frac{C_{HCl}}{C_{H_2O}}) \, dU_{HCl} \qquad \text{----------1.6.1(d)}$$

The transference coeffiecient, tHCl, is equal to the transference number, t_{H^+}. The transference coefficient, $^{t}H_2O$, is the number of moles H_2O transfered from left to right per Faraday transfered. Water molecules are transported to the right with cations and to the left with anions. For the cation exchange membrane t_{H^+} is very close to unity and therefore $^{t}H_2O \simeq \alpha_{H^+} t_{H^+}$, where α_{H^+} is the number of water molecules transported with a proton.

The contribution to the emf of the present cell, however, from the transport of water is very small, as can be seen from equation 1.6.1(d). For HCl concentrations of the order of magnitude 0.1 mole litre and with $t_{H_2O} \simeq 1$ (a common value) we have:

$$t_{H_2O}\ C_{HCl}/C_{H_2O} \simeq 1.100/(56 \times 10^3) = 0.0018$$

1.7 Sand and Cement

1.7.1 Sand

Sands and gravels are derived from the weathering of rocks and are composed of the more resistant minerals which have withstood the destructive effects of weather and transport for a long period. Sand passes through a 3/16 inch mesh and larger particles are classified as gravel[40]

Quartz is the most important mineral in sand[41]. Fieldspars, micaceous, carbonate, sulphate, iron sulphide, ferromagnesium and clay, Zeolites and iron oxides are other minerals which may be present in small quantities.

River and glacial deposits are a source of most sands used in mortar and concrete. Other sources are crushed friable sandstones and sea sands but the latter must be well washed on account of the presence of soluble salts.

Quartz is an unreactive crystalline form of silica having an orderly arrangement of the silicon oxygen tetrahedra (d-SiO_2). It has minor oxides of titanium, magnesium, iron, manganese, Sodium and potassium. The proportion of the minor components varies from sample to sample depending on the origin of the sand. Other reactive forms of silica such as opal are different and are characterized by a random network of tetrahedra with irregular spaces between the groups of molecules[42].

Particle size distribution of sand affects workability and strength of a fully compacted mortar with a given w/c ratio. The distribution leads to grading which is a foremost important factor in obtaining a dense concrete. Sand and coarse aggregates are thus graded to ensure that voids left unfilled between the particles shall be as low as possible. This requires a progressively lower sand content in the concrete mix as the sand becomes finer[43].

Four permissible grading zones for sand varying from coarse (zone 1) to fine (Zone 4) are given in British standard 882 and British Standard 1201 of 1965[45]. The specification allows sand to contain 5-50% of material passing number 52 sieve, whereas American Standard for testing materials C33-67 places the maximum at 30%. The main bulk of the sand which lies between a number 52 sieve and a 3/16 inch mesh should contain particles of varying sizes and not consist predominantly of any one size.

1.7.2 Cements

Cements are defined as "adhesive substances capable of uniting fragments or masses of solid matter to a compact whole "[44]. There are basically two types of cements, the most common, will set and harden on addition of water and examples include portland cements. Non-hydraulic cements will neither set nor harden in water, but will do so on exposure to other substances, an example is "fat lime" which hardens on exposure to carbon dioxide.

Further classification of cements shows a gradual evolution whereby some cements which are very important at certain times have fallen partly or entirely into disuse as more sophisticated varieties were made.

Presently, research is still being directed towards production of better varieties which can withstand specific or general corrosive environments. The various classes of cements are: Limes, natural cements, portland cements, high alumina cements, cements containing granulated blastfurnace slag, pozzolanus and pozzolanic cements, Sorel cements and gypsum[45]. Each class may have a number of varieties under it. Portland cement, for example has ordinary, sulphate resisting, rapid hardening and many others. The properties of the cements are determined by the properties of the individual constituents as well as their percentages. The percentage of tricalcium aluminate ($3CaO.Al_2O_3$) in a cement, for example, determines the sulphate resisting ability of the cement[46].

Chemical and Mineralogical Composition of Portland Cement:

Portland cement is a hydraulic cement produced by clinkering a mixture of raw materials containing, lime, silica, alumina and iron Oxide[47]

The approximate limits of chemical and mineralogical compostion of Portland cement are given in table 1[48]. The values vary as a result of the developments of the cements over the years so as to meet different challenges. The different areas also contribute to the divergent compositions.

Table 1

Approximate Oxide and Mineralogical Composition limits of Portland Cements

Oxide	Percent	Constituent	Percent
CaO	60-67	C_3S(alite)	35-55
SiO_2	17-25	C_2S(belite)	15-35
Al_2O_3	3-8	C_3A	7-15
Fe_2O_3	0.5-6.0	C_4AF(celite)	5-15
MgO	0.1-5.5	$CaSO_4.2H_2O$ (gypsum)	3-12.5
Na_2O+K_2O	0.5-1.3	CaO(free lime)	0.66-1.02
SO_3	1-3	MgO, K_2O, Na_2O etc	$\simeq 3$

The constituents given in the table are classified as minor and major components of the cement.The major constituents are : Tricalcium Silicate $3CaO.SiO_2$ (C_3S);dicalcium Silicate $2CaO.SiO_2$ (C_2S); Tricalcium Aluminate $3CaO.Al_2O_3$ (C_3A); and tetracalcium aluminoferrite $4CaO.Al_2O_3.Fe_2O_3$ (C_4AF).

The constituents do not exist in their pure form but contain small amounts of other Oxides in solid solution. Alite (C_3S), for example, contains traces of Al_2O_3, Fe_2O_3, MgO, Na_2O.

Chemical attack on Cement and Concrete

Deterioration or corrosion of concrete due to chemical agencies is a well known phenomena. The agencies may either be natural like sea water, rain water, and some soils; or man made in the form of effluents from industries.

It is this same concrete that provides a high degree of protection against corrosion to embedded steel, because the high alkalinity in concrete cause a thin protective film of γ-Fe_2O_3 to form on the steel surface. However, this protective film can be disrupted either by lowering of pH of the water phase in concrete (e.g by carbonation) or by a penetration of aggressive ions (e.g chloride ions) to the steel surface.

In high chloride environments, such as the ocean, investigations indicate that it is just a question of time before detrimental amounts of chlordie reach embedded steel[49].

Once the passivating film on the surface of the embedded steel is disrupted, the electrical resistivity of the concrete and the availability of oxygen at the steel surface will be the main controlling factors for further steel corrosion[50]. The degree of water saturation for concrete structures in the oceans will generally be very high and the electrical resistivity will be very low[51]. For such structures, therefore, it appears that the rate of steel corrosion is primarily controlled by diffusion of dissolved oxygen through the concrete cover. A.H.S. El-Busaidy, O E Gjorv and O. Vennesland have analysed the effect of dissolved oxygen through concrete[52].

The cement mortar has been shown to be the point of attack by most destructive agencies and the one which forms the channel by which waters can permeate into the concrete[53]. Research has been done over the years to identify the agencies and to come up with appropriate remedies. In some cases, change of cement type, use of admixtures and surface treatments have been found necessary, while in others complete change of materials, for example plastic, for the concrete systems has been recommended.

Only one agency that is relevant to our work is considered.

Chloride Solutions

Chloride Solutions are deleterious because they form soluble salts that leach out of the concrete. The chloride ions also penetrate the concrete systems endangering any reactive enforcement especially steel. In an investigation of the effect of chlorides on concrete in hot and arid regions, Ben Yair[54] studied the effect of chlorides on the physicochemical properties of cement and concrete exposed to chloride solutions.

He found that the penetration and absorption of the ions into Portland cements was much higher than that of Sulphate ions, and that climatic factors had a decisive influence on the character and magnitude of corrosion.

Gjorv and Vennesland[55] in a study of the diffusion of chloride ions from sea water into concrete found out that "the diffusion of chloride ion into concrete is not just dependent on permeability and the capacity of chloride binding but also on the ion-exchange capacity of the system. For blended cements like pozzolanic, the pore solution has a lower concentration of hydroxyl ions hence the capacity for exchanging anions with the permeating solution is lower."

Calcium Chloride's aggressiveness against portland cement has been attributed by Chatterji[56] to

(i) Crystallisation of complex salts containing hydroxide and/or carbonate.
(ii) Leaching of Calcium hydroxide from the cement paste thereby making the paste porous and susceptible to subsequent intrusions.

Other work by Ono et al[57] has shown that chloride ions in the early stages quickly penetrate deeply into a specimen as compared to sulphate ions, react with calcium hydroxide, and convert calcium ions into extractible species in the acqueous phase thereby, making the specimens very porous, although some chloride is retained as Friedels' Salt, $3CaO.Al_2O_3(CL,SO_4)12H_2O$.

CHAPTER TWO:

2.0 EXPERIMENTAL:

2.1 The Materials used

In this project, the following materials were used.

1. A water bath which contained water that was at a thermostatted temperature of $25\pm0.1^{O}C$ with the cell submerged in it.

2. The cell contained electrodes, the electrolyte solutions and mortar membranes.

3. Cement, sand and water were used to prepare the mortar specimens.

4. The electrolyte solutions were prepared from the chemicals shown below (the purity levels are indicated alongside the Chemical formula and are bracketted):

a)	$ZnCl_2$	(97.5%)
b)	$CuCl_2.2H_2O$	(98%)
c)	NaCl	(99.9%)
d)	HCl	(35.5-37.5%)
e)	$CaCl_2$	(99.5%)

These chemicals when dissolved in de-ionized water provided the desired cation under study at the given concentration. In addition to these; concentrated nitric acid and carbon tetracloride were used for the cleansing of copper electrodes and the prepared sodium amalgam respectively.

2.2 Solutions:

The salts used in making solutions were all general pupose reagents (GPR). Zinc chloride, Sodium Chloride and Copper chloride were BDH Chemical Ltd, Poole England general reagents. Hydrochloric acid was koch-light Ltd general reagent; and cadmium chloride was Hopkin and Williams Ltd general reagent.

A calibrated 1 litre flask was used to make 1M bulk solutions of NaCl, $CuCl_2.2H_2O$, $CaCl_2$ and $ZnCl_2$, and pipettes were used in diluting the bulk solutions to the required concentrations (e.g 0.01M, 0.05M, 0.10M etc). De-ionized water was used to make bulk and dilute salt solutions.

2.3 Preparation of Electrodes

Advice on the preparation, mounting and care of specific electrodes was sought in papers devoted to the determination of the appropriate standard electrode potentials[58] or the kindred matters, and some details regarding such useful and popular types such as the silver-silver halide[59,60], calomel[61,62,63] hydrogen[64,65] quinhydrone and two-phase amalgam[66,67,68,69,70].

Diffculties were sometimes encountered until the technique of making and using the electrodes was perfected. Some of the difficulties were:

a) Electrodes prepared by plating tended to behave erratically if the whole surface was covered, but they often responded sluggishly if the deposit was too thick. This was overcome by giving a fairly thick coat on the required area of the surface.

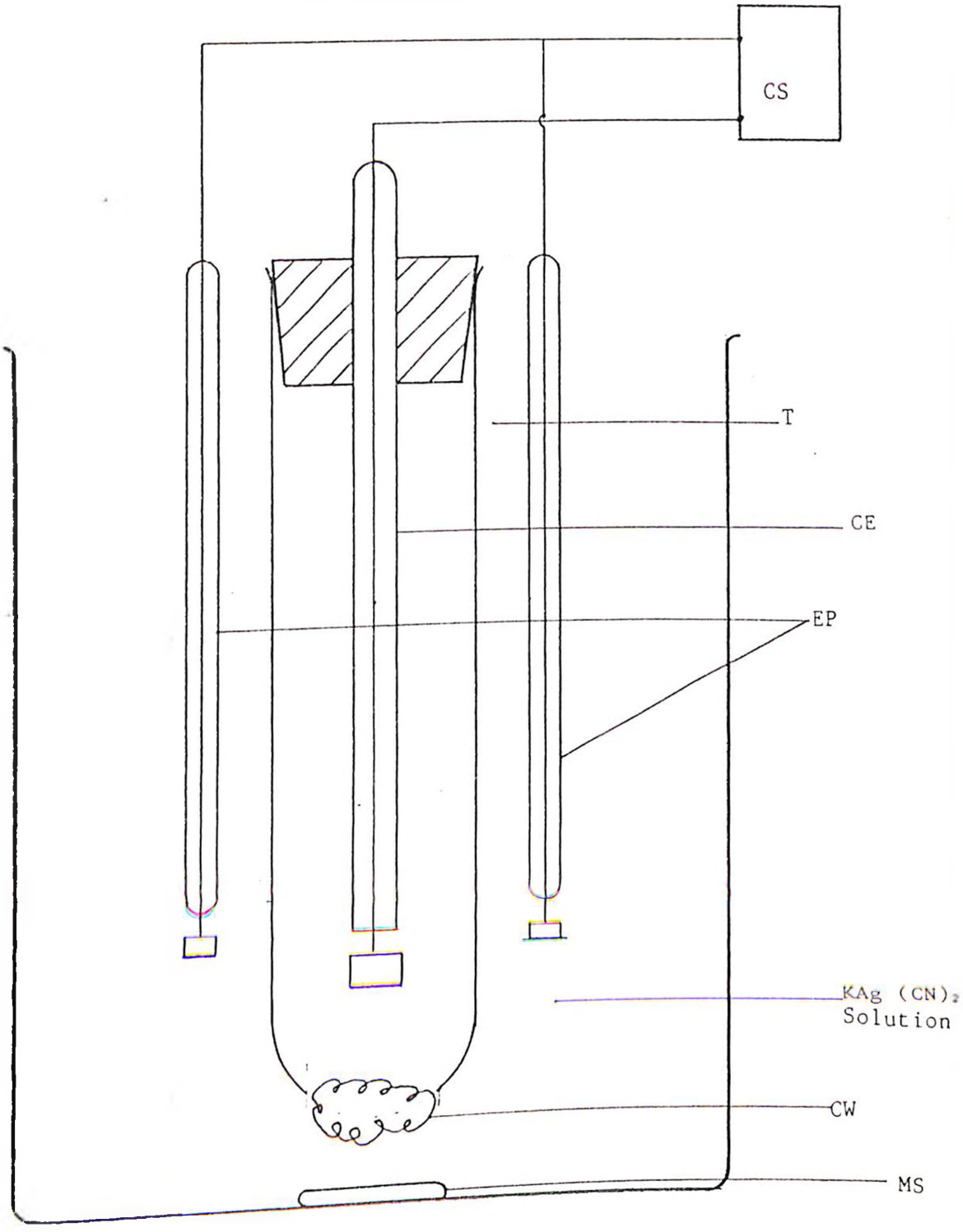
b) Some electrodes were adversely affected by:

i) Shock, hence the electrodes were mounted firmly.
ii) by traces of grease therefore cleanliness was ensured before use.
iii) by oxygen, which was eradicated by bubbling purified H_2 or N_2 through a saturator filled with solution or solvent and then through the solutions.

2.3.1 Preparation of Ag/AgCl electrodes

The Ag/AgCl electrode consisted of a round platinum disc which was used as the electrode base. On this disc a layer of silver was electro-deposited and chlorodised in a dilute solution of 0.1MHCl. The method used for this preparation followed to a larger extent what is given by Ives and Janz[71].

The electrodes used were to be re-prepared. First the electrodes were washed in 25% ammonia solution to remove the AgCl layer. They were rinsed with distilled water to remove the ammonia and then washed in boiling concentrated HNO_3 acid for atleast one hour to remove the silver layer and any other metallic impurity from the surface of the discs. The electrodes were then cleaned in stirred distilled water for atleast 12 hours to remove all the acid on the discs. They were then ready for silver-plating. The $KAg(CN)_2$, used in making the silver plating solution, was prepared by the addition of 41g of silver cyanide to an aqueous solution of Potassium cyanide (20g) as recommended by Basett and corbett[72]. 1% solution of $KAg(CN)_2$ in distilled water was used for silver-plating. The silver-plating solution may be used upto about five times. Figure 2.3.1 shows the arrangement for silver plating.



CS - Current Source
T - Test-tube with cotton wool
CE - Counter electrode
EP - Electrode under preparation
CW - Cotton Wool
MS - Magnetic Stirrer

Fig. 2.3.1. The arrangement for Silver-plating of electrodes

Initially dilute $AgNO_3$ solution was added dropwise to remove free cyanide by precipitation while stirring until a faint cloudiness was produced.

A pair of electrodes was prepared simultaneously. The electrodes under preparation were short circuited and connected to the cathode while a simple platinum foil was used as the anode. The latter was encased in a test-tube with a cotton plug to act as a scintered diaphragm. The cotton plug ensured that products of the anode were not released into the bulk of the solution. This prevented poisoning of the electrodes as dark marks left on the electrode disc resist Chlorodisation.

Next, a current of $1mA/cm^2$ from a constant current source (Associated Electrical Industries Limited, England) was used for silver-plating for a period of 5 hrs. The solution was constantly stirred magnetically. The electrodes were rinsed with distilled water followed by washing them in 25% ammonia solution for atleast 12 hours to remove the ammonia. The chlorodisation in 0.1M HCl was performed in a similar arrangement as in figure 2.3.1 but without incooporating the test-tube with the cotton plug. The electrodes under preparation were connected to the anode and the counter electrode was the cathode. A current density of $0.5mA/cm^2$ from a constant current source was used for a period of 1.5 hours.

Finally the short-circuited electrodes were washed in stirred distilled water for at least 36 hrs but washing for a longer period produced more stable electrodes. They were then equilibrated in the test solutions for at least 12 hours before testing.

2.3.2 Preparation of H_2- electrodes:

In this type of electrodes, hydrogen gas was bubbled over platinum black electrode.

The platinum black or platinized platinum was deposited as follows[73]:

First two platinum electrodes were cleaned in an acid cleaning mixture (a boiling mixture of 12NHCl, 16NHNO_3 and H_2O mixed in the ratio 3:1:4 by volume respectively). The electrodes were then washed with distilled water and then kept in AR concentrated HNO_3 acid for atleast 30 minutes. To ensure that the electrodes were clean, dilute H_2SO_4 acid (0.35N) was electrolysed with both platinum electrodes for approximately 10 minutes at 10mA until clean small bubbles of H_2 gas were evolved; if not then cleaning was repeated.

The platinizing solution consisted of 1g chloroplatinic acid in 50ml of water and 400g lead acetate added to this solution. The electrodes were supported in this solution and connected through a reversing switch to a rheostat and 4V accumulator. Current was passed through the solution and adjusted so that there was only a moderate evolution of gas, for 10 to 15 minutes reversing the polarity every 30 seconds. This procedure was used to ensure that a moderately thick coating of platinum black was obtained. A moderately thick coat is prefered to a thin coat because it gives a more compact and stable coating.

The deposit now contained occluded gas (chlorine) and liquid. This was removed by immersing the electrodes in 0.5N sulphuric acid and connecting them through a reversible switch to the 4V accumulator. The solution was electrolysed for 30 minutes with reversal of polarity every 30 seconds so that gas bubbles were evolved vigorously from both electrodes. The electrodes were then thoroughly washed with distilled water and stored in distilled water.

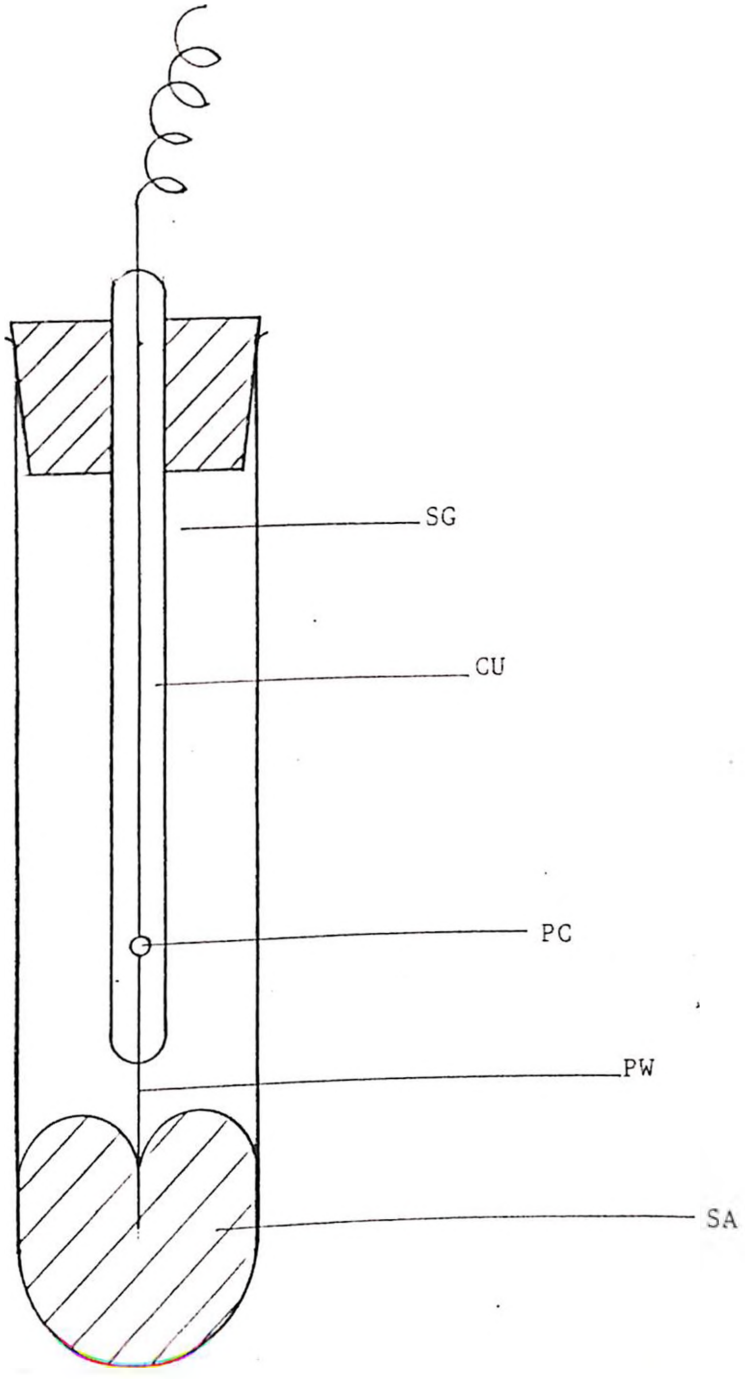
2.33 **Preparation of Sodium - Amalgam electrodes:**

Mercury metal was thoroughly cleaned by filtering it through a conical filter paper arrangement that had a pierced bottom (narrow pore). The mercury was collected in a beaker and was stirred using a rolled filter paper thus facilitating further cleansing. It was then transferred into a test-tube.

A piece of Sodium metal was washed in Carbon tetrachloride. This washed away the paraffin (Kerosine) oil. The clean and dry Sodium metal piece was then dropped in the mercury contained in the test-tube (the reaction is highly exothermic). This amalgam was then cleansed by use of a filter paper.

No measurements and weighings of Sodium and mercury were done since in the set-up of a cell without transference; Ag/AgCl/NaCl(0.01M)/Na(Hg)/NaCl(x)/AgCl/Ag the oxidation - reduction effect occuring at the Na(Hg) electrodes that are joined together cancel and nullify any net effect.

A small piece of platinum wire was Soldered onto a piece of Copper wire. This was sealed in a piece of glass-tubing so that the platinum wire protruded through one end of the tubing. Care was taken such that no solution came into contact with the platinum - Copper junction.



SG - Sealed glass tubing
CU - Copper Wire
PC - Platinum - Copper junction
PW - Platinum Wire
SA - Soduim - Amalgam

Fig.2.3.2: The Sodium-Amalgam electrode assembly

This was then dipped in the Sodium - amalgam as is illustrated in figure 2.3.2. The Sodium amalgam electrode was incoorporated in the galvanic cell and left in a water-bath overnight in order to acquire the required constant temperature.

This kind of arrangement gave an electrode having a low resistance and hence could be used with a simple potentiometer circuit.

2.3.4 Preparation of metal electrodes

The appropriate metal (Copper, Zinc and Cadmium) was melted in a crucible. This was transfered into a test-tube and care was taken to ensure that no gas was trapped within this molten metal. One end of a piece of copper wire was dipped in this melt and held in place until the melt solidified fusing the Copper wire onto the metal solid. The test-tube was broken and the electrode shaped into a fine rod by filing the surface. This assembly was sealed in a piece of glass tubing so that the metal rod protruded through one end of the tubing.

It is essential to remove impurities from the Copper electrode. This was done by dipping the Copper electrode in dilute H_2SO_4 acid and thoroughly rinsing it with distilled water.

2.4 Mortar Specimens:

The casting process for the mortar specimens is of paramount importance. The process included the proper mixing of cement, sand, and water in the required proportions i.e 1.0:3.0:0.6 and 2.0:4.0:1.0 by volume respectively. This was accomplished by mixing the first two components first before adding water to this mixture. The mortar specimen was then placed in a curing room that provided ideal conditions for the setting of cement, i.e a temperature of 21-22°C and a humidity level of 80%. This enabled a minimised rate of dehydration and subsequently providing ideal surroundings for the hydration process. This eliminated any distorted features on the mortar specimen, like cracks.

Compacting of the mortar is also essential to device a thoroughly mixed and compact product. Two models were built from mortar: the membrane and the steel reinforced concrete cement (RCC) model. Ordinary Portland cement (OPC) and British Standard sand (STD) were used in both cases and their details are given in section (1.7).

2.4.1 MEMBRANE:

Preparation:

Ordinary Portland Cement (OPC) and British Standard Sand (STD) were thoroughly mixed in the appropriate ratios by volume i.e 1.0:3.0 and 2.0:4.0 respectively; to give a homogeneous mix. An appropriate volume of water was then added in each case and the mortar mixture swirled for about five minutes giving a "mortar paste" of the required ratio (either 1.0:3.0:0.6 or 2.0:4.0:1.0).

The mortar paste was embedded in a PVC pipe which was half-a-foot long and compacted by firmly placing the pipe on a machine shaker.

The pipe containing the compact mortar paste was Transferred to a curing room (at 80% humidity) and the pipe was further covered with a polythene cover.

This slowed down the dehydration process enormously, hence prohibiting cracking of the mortar cylinder. The dehydration process should be complete after 28 days but the PVC pipe was removed after 30 days to ensure proper hydration.

The membranes were derived by cutting right across the mortar cylinder which subsequently provided membrane discs that had a constant diameter of 3cm. They were then placed in distilled water. During the experiments, specimens were kept wet.

2.4.2 Membrane thickness

The thickness of the membranes used were measured on the surface dried membrane using vernier callipers.

The average thickness used was 3mm.

2.4.3 Fixing of the Liquid-junction on the membrane

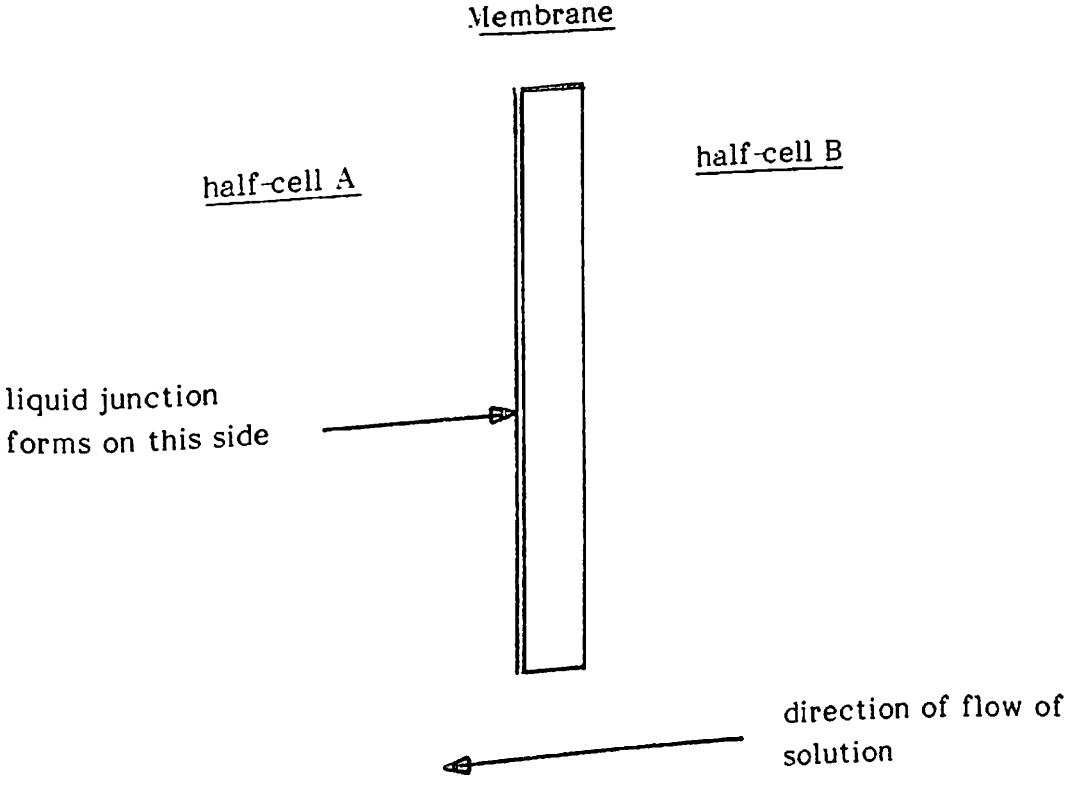
A liquid-junction can be fixed either within the membrane or on either surface of the membrane. In either case, it has to remain fixed in a particular position throughout the experiment for the sake of ensuring the reproducibility of the results.

In this particular context the liquid-junction was fixed on one surface of the membrane.

The membrane was part of the galvanic cell used in this experiment. The reference solution of concentration 0.01M was placed in half-cell A and the same electrolyte solution with an arbitrary concentration higher than 0.01M was placed in half-cell B. The solution level of half-cell B was higher than that of half-cell A. This set-up was left overnight.

Due to hydraulic Pressure, direction of flow of the solution was from B to A. This stopped when equilibrium was achieved, enabling the liquid-junction to form on the surface of the membrane facing half-cell A.

Fixing of the liquid-junction on the face of the membrane was an important exercise because it provided a stable and steady interface between the two different concentrations. Otherwise the emfs measured would be erratic.



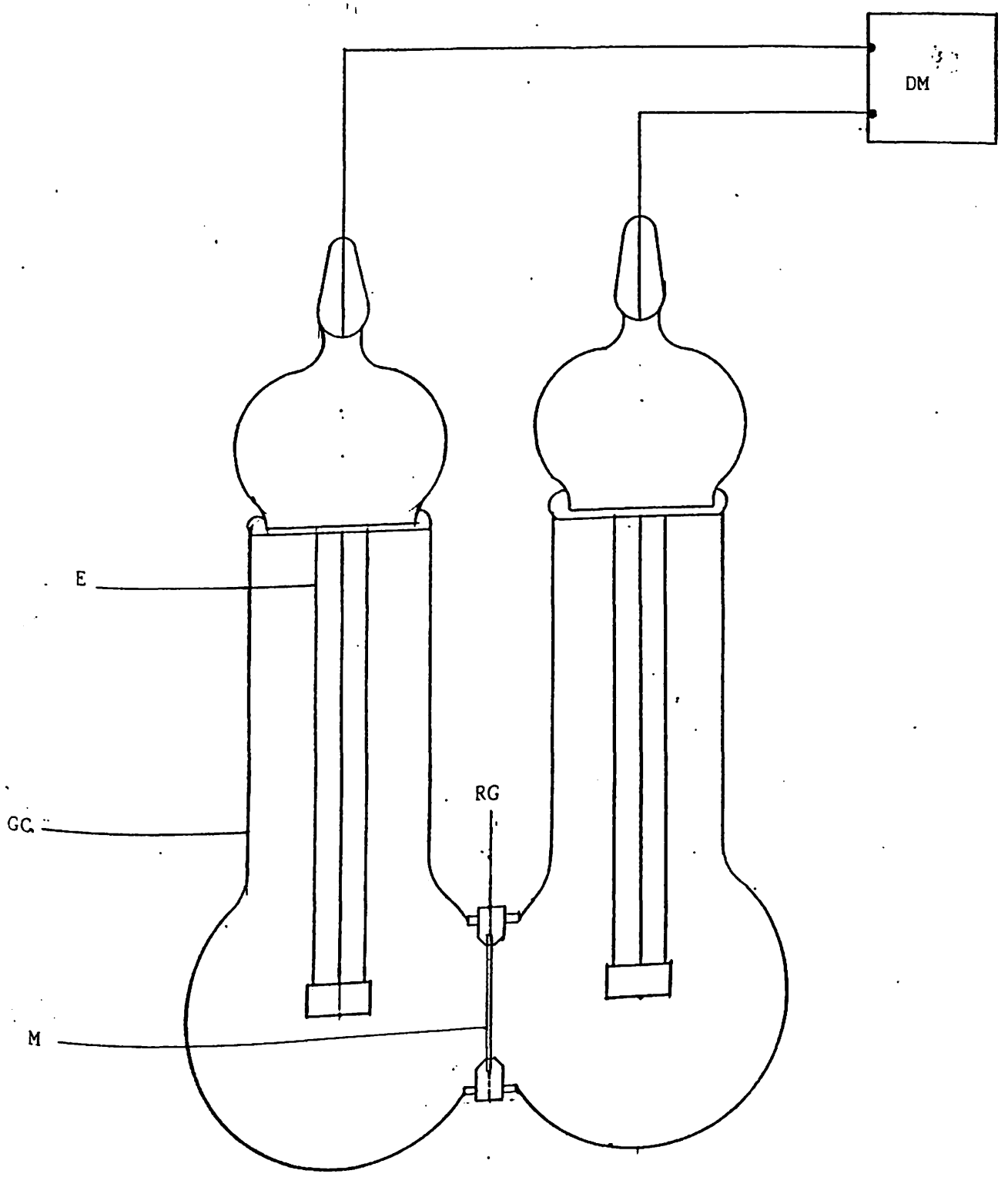
2.5 The Cell:

The galvanic cell used in the present work for emf measurement is shown in figure 2.5.1. It comprised of two pyrex glass flasks each with a capacity of approximately 850ml.

A piece of mortar membrane mounted between two circular rubber gaskets with central circular holes of diameter 3cm seperated the two half-cells. Electrical contact between the two half-cells was through this exposed piece of membrane. High vacuum grease was applied in-between the rubber gaskets holding the membrane. The half-cells were bolted together tightly with six screws to make them water tight. This prevented any leakage of water from the water bath into the piece of membrane.

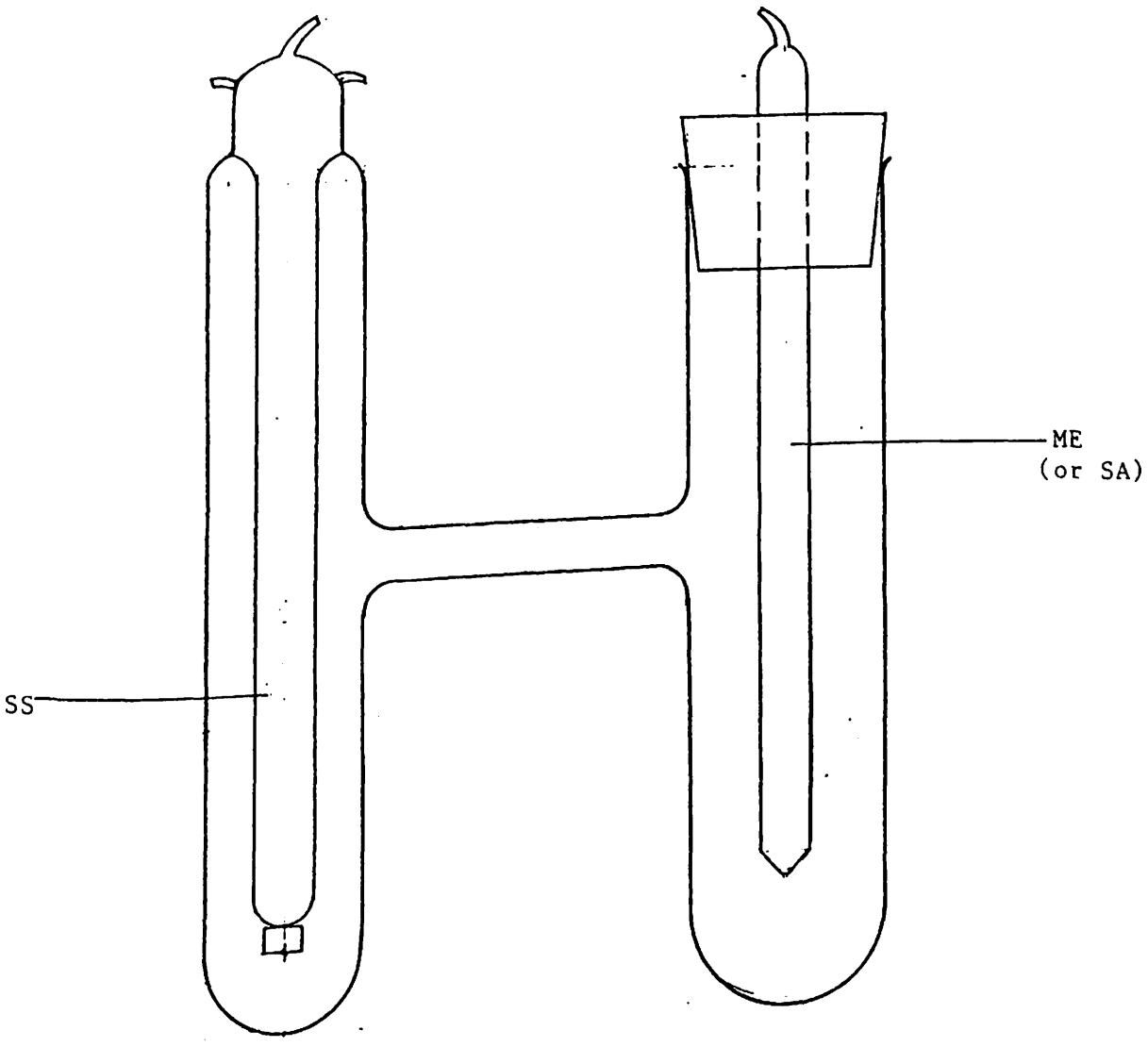
Each half-cell was fitted with a Ag/AgCl electrode, and each was half filled with the appropriate electrolyte from the reserviors. The solution concentration on one side of the membrane was maintained at a fixed value of 0.01M (this was the reference solution), while the concentration of the solution on the other side was varied from 0.05M to 0.4M in steps of 0.05M and in each case a measurement was taken after stabilization.

The electrodes were connected to a data precision digital Multimeter, 4.5 digit (model 945 s/n, data precision coorporation) for emf measurement. The cell was immersed in a water-bath kept at a constant temperature of $25\pm0.1^{o}C$.



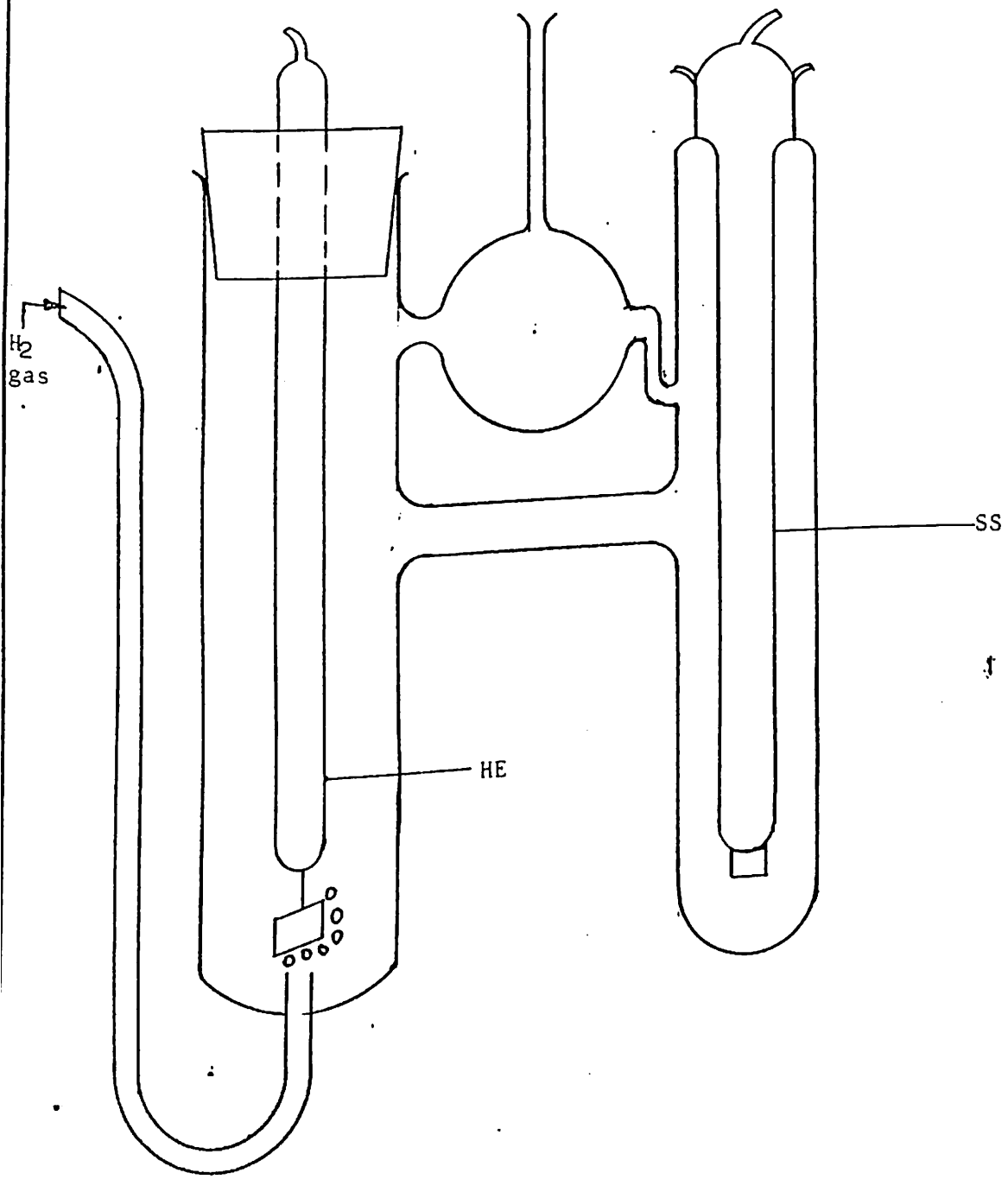
E - Electrode
GC - Glass Cell
M - Membrane
RG - Rubber gasket
DM - Digital Multimeter

Fig.2.5.1: The cell used for emf measurements.



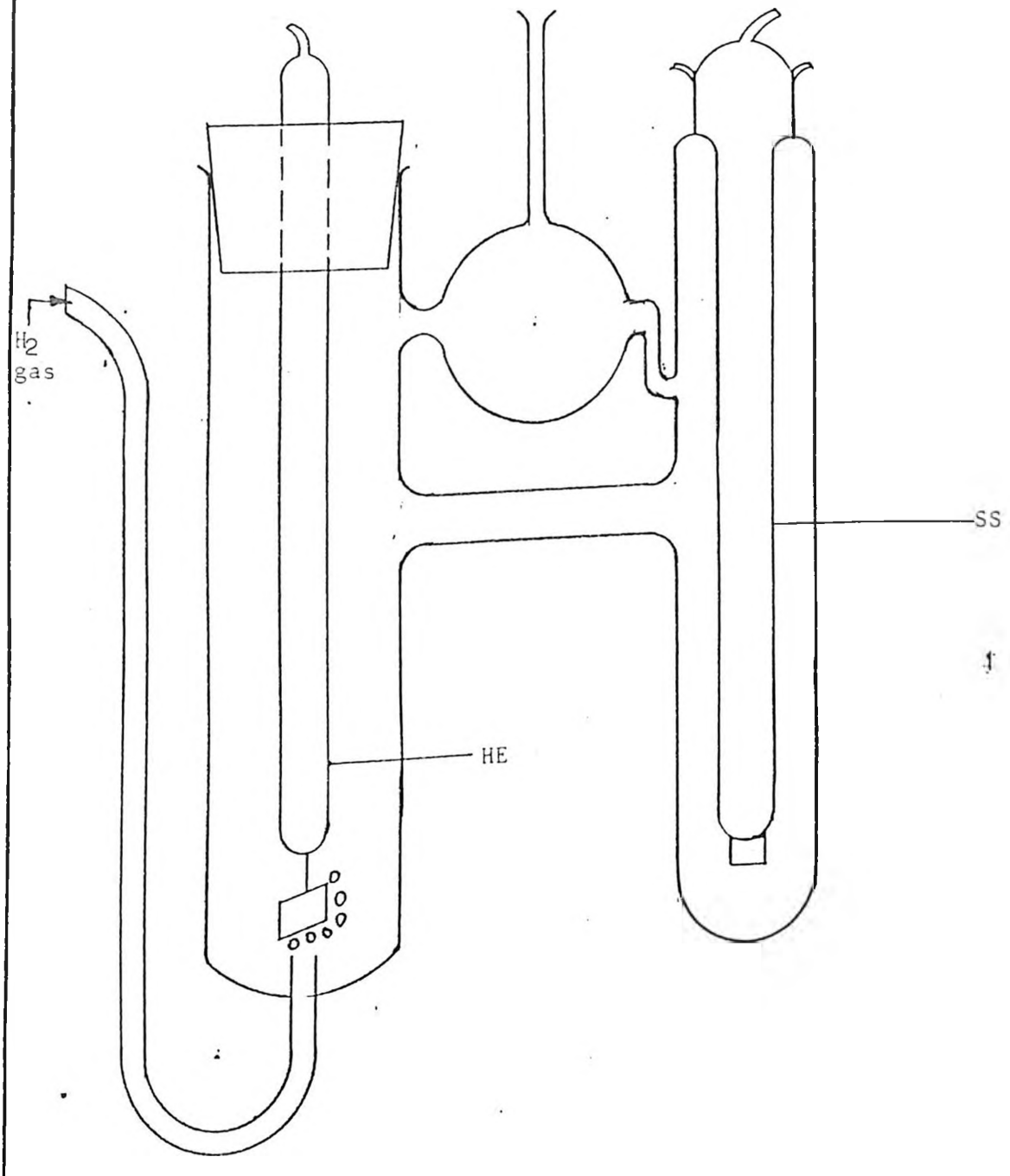
ME - Metal electrode
SA - Sodium - Amalgam electrode
SS - Silver - Silver Chloride electrode

Fig.2.5.2: The cell used for measuring emf without transference (excluding Hydrogen electrode)



HE- Hydrogen electrode
SS- Silver - Silver Chloride electrode

Fig.2.5.3 The cell used for measuring emf without transference appropriate only for the hydrogen electrode.



HE- Hydrogen electrode
SS- Silver – Silver Chloride electrode

Fig.2.5.3 The cell used for measuring emf without transference appropriate only for the hydrogen electrode.

This set-up gave an emf of the cell with transference. A different set-up was used to determine emf without transference, with no membrane incoorporated within the cell. These were fundamentally H-shaped cells joined back-to-back, and consisted of Ag/AgCl electrodes connected to the multimeter together with appropriate electrodes, reversible with the cations in the electrolyte solution, connected to each other. This cell is shown in figure 2.5.2. The only modification was in the hydrogen electrode cell which was constructed in such a way as to allow for the entry and exit of the gas enabling a suitable access to the platinum metal piece (coated black) as indicated in figure 2.5.3.

The cells were also immersed in a water-bath kept at a constant temperature of $25 \pm 0.1^{o}C$.

2.6 Potential Measurements:

In measurement of the emf of a cell, the following details were rigidly followed:

(1) The circuit was only closed momentarily, to avoid polarizing the cell under test or the standard cell.

(2) Since the potentiometer used was a commercial one it was used in the most sensitive range appropriate to the emf under measurement. In this case 0-0.2V was more appropriate.

(3) The emf was not measured immediately. This applied particularly to cells that were using gas electrodes (H_2 - electrodes) as some time was necessary for equilibrium to be established. A series of measurements were made until three concordant results were obtained.

(4) The temperature of the cells was thermostatted at 25±0.1^{o}C otherwise varying values of 2.303RT/F at different temperatures would have been obtained.

2.6.1 Measurement of emf with transference:

All potential measurements were made with the solutions at rest in the cell. None were made with solutions flowing. For each renewal of solutions, a time interval of five minutes was sufficient to establish the concentration gradient in the membrane and thus maintain the liquid-junction. In this case the potential remained unchanged (±0.2mV) over a period of at least 10 minutes.

The potentials were measured using a digital multimeter, model 945 with a current input of 5.184mA.

No assymmetry for membranes and Ag/AgCl electrodes used was observed. The data recorded here were average values of three concordant measurements.

2.6.2 Measuremets of emf without transference:

In this measurement, two sets of electrodes were used. One pair was reversible to cations present in the electrolyte solution and the other was Ag/AgCl electrode which was reversible to the chloride anion since chloride solutions were used in all cases.

Two H-shaped cells illustrated in figures 2.5.2 and 2.5.3 were used where appropriate. Each H-shaped cell contained a Ag/AgCl electrode and a relevant electrode e.g H_2- electrode for HCl solution. The two cells were joined back-to-back by connecting the Ag/AgCl electrodes to the potentiometer and joining the other respective electrodes together.

The complete cell was then placed in a water-bath maintained at a constant temperature of $25\pm0.1^{o}C$. It was left in the water bath for a duration of about 30 minutes to let the electrodes stabilize, before measurements were made.

One H-shaped cell contained the reference solution (0.01M) which was not varied while the solution in the other H-shaped cell was varied from 0.05M to 0.4M in steps of 0.05M. In each case a measurement was taken using a digital multimeter, model 945 as the potentiometer.

2.7 The steel reinforced concrete cement (RCC) model

This model was constructed on the basis of viewing it as an epitome of the steel reinforced concrete structures used for building purposes. An analysis based on the RCC model was used to monitor the movement of chloride ions, an agent of corrosion of steel.

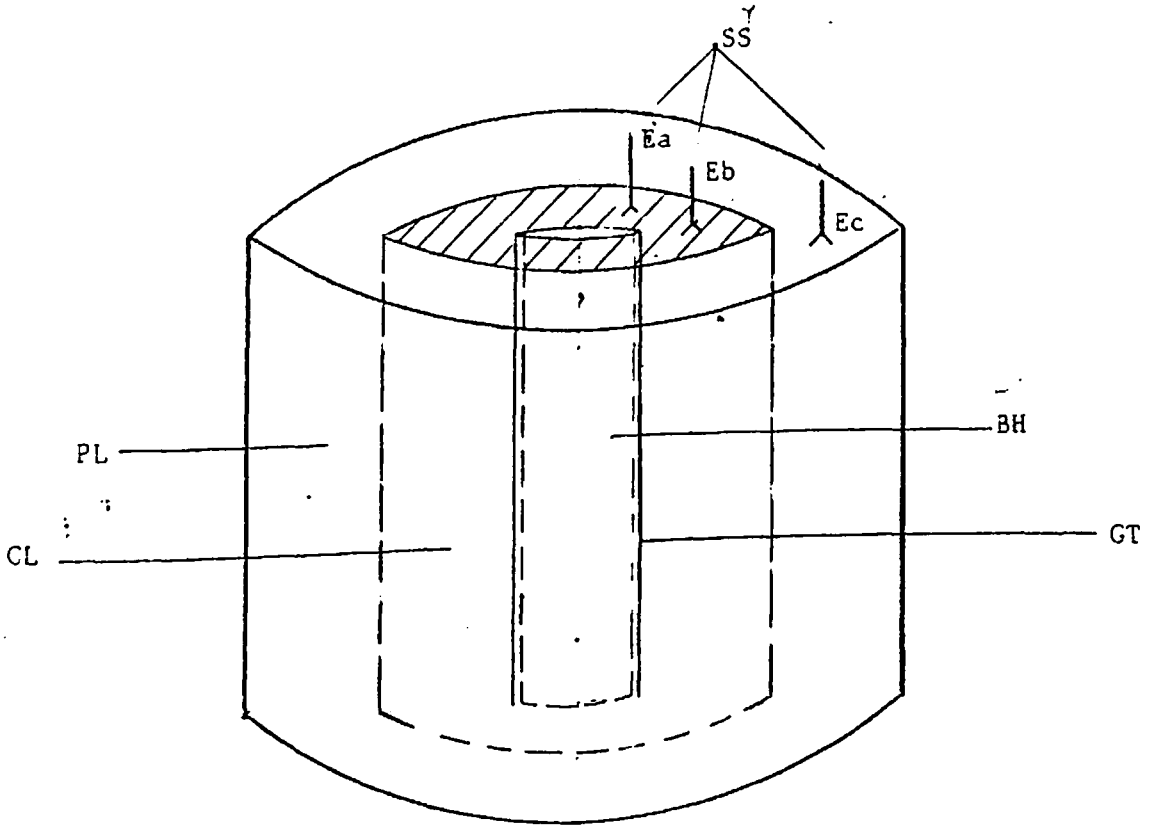
2.7.1 Construction of the RCC model

The mortar ratio used here was 1.0:3.0:0.6 for cement, sand and water respectively. The first two components were mixed first before adding water in the required ratio by volume.

Two concentric PVC pipes were used, each half-a-foot long, to provide a two layer model. The inner (core) layer had the cement, sand and water mixed in the ratio of 1.0:3.0:0.6 by volume, but the water used in this case contained 2.5M NaCl. This was embedded in a PVC pipe of diameter 3cm with a glass tubing running right through the middle providing a bore-hole. It was then compacted and two "model Ag/AgCl" electrodes were inserted on the upper surface of the compact mortar model 1cm apart. This sample was transfered to the curing room for hydration. The setting/curing process was left for 30 days.

After this curing/setting period, the PVC pipe was removed. This cylindrical mortar sample was then placed in the middle of the second PVC pipe of diameter 5cm giving a concentric arrangement. A mortar paste mixed in the ratio 1.0:3.0:0.6 using NaCl - free water was then placed all round the mortar cylinder. This ensured that the peripheral layer was 1cm thick from the core layer all round. The peripheral layer was compacted and a model - Ag/AgCl electrode inserted in it, providing a 1cm seperation between all three electrodes (two of which were in the core layer and one in the peripheral layer). This sample was then transfered to the curing room and removed after 30 days setting/curing period.

The PVC pipe was removed. Two RCC models were extracted from the complete mortar cylinder. These were similar in all aspects but only that one accommodated the model - Ag/AgCl electrodes and the other had none. They were 5cm high, 5cm in diameter; with a core layer (that contained a bore-hole 1cm in diameter) of diameter 3cm. The peripheral layer was 1cm thick all round the core layer.



SS- Silver-SilverChloride electrode
BH- Bore-hole
GT- Glass tubing covering the bore-hole
CL- Core layer
PL- Peripheral layer

Ea,Eb,Ec - "Model Ag/Ag Cl" electrodes

Fig.2.7.1 The RCC model

The top and bottom surfaces were then covered with an epoxy adhesive coating and left overnight to dry. The only exposed parts of the samples were therefore the sides. The design of this sample (bearing electrodes) is illustrated in figure 2.7.1.

The samples were then placed in different containers that were partially filled with de-ionized water. The levels of the water were slightly below the top surface of both samples. These containers were always covered on the exposed top with flat glass covers after use, to avoid any external interference and contaminations.

The sample bearing the electrodes was used for emf measurements and the other sample with no electrodes was used for chloride ion analysis.

The glass tubing covering the bore-hole and the epoxy coatings on the top and the bottom prevented contact between the sample and the surrounding water except through the sides of the sample. Hence, any diffusion of chloride ions could only occur through the sides of the sample. The bore-hole, BH, was also filled with the ambient solution that had permeated through.

2.7.2 Model - Ag/AgCl Electrodes

These electrodes, unlike the Ag/AgCl electrodes encountered previously, were made from thin platinum wires.

AgCl solid was melted in a crucible. Three platinum wires, each 15 mm long, were covered with this AgCl leaving half the wire exposed.

Only the coated half was inserted in the mortar sample. The exposed half protruded out of the sample.

In an attempt to use stainless steel instead of platinum wire, an interesting observation was made: corrosion occured at the junction of the exposed and coated parts. A brown solution (of $FeCl_3$) was formed at the contact point and the wire split into two, subsequently separating the exposed and coated parts. After about 24 hours, the coating on the steel turned to a silver colour. This observation falls in line with the principle of the "local cell theory of corrosion". The silver was left depositted on the coating.

2.7.3 Emf measurement of the RCC model:

For emf measurement, two sets of electrodes were used; Ag/AgCl and sodium-amalgam, Na(Hg), electrodes. These were reversible to chloride and sodium ions respectively, thus are ideal in monitoring the chloride ion movement.

To prepare the Na(Hg) electrode; the amalgam was placed at the bottom of the bore-hole. A sealed glass-tubing with a platinum wire protruding from one end was then dipped in the amalgam.

A fourth Ag/AgCl electrode (Es), of the type mentioned previously in the cells used for determining emf with and without transference, was immersed in the solution surrounding the RCC sample. This set-up was left for 1 hour for these two electrodes to adjust to the new environment. This was ascertained after preliminary work showed 1 hour to be fairly ideal for stable readings.

By connecting the Na(Hg) electrode to a potentiometer (digital multimeter, model 945) and alternately connecting the three model - Ag/AgCl electrodes (Ea, Eb and Ec) and Es to this potentiometer, potentials between the various regions (namely; the core layer, the peripheral layer and the solution) and the surrounding solution, were measured.

After use the sealed glass tubing containing the protruding platinum wire and Es were removed and left dipping in distilled water. The container of the sample was always covered after the measurement had been made.

2.7.4 Chloride and pH analysis

For these analyses, the sample bearing no electrodes was used. Samples were extracted from the surrounding solution of this sample every 24 hours by pipetting out 1ml of the solution and storing in sample bottles.

Chloride and pH analyses were then carried out on these solutions by use of the potentiometric analysis.

2.7.5 Potentiometric analysis

Potentiometric technique is an easily adaptable method to different circumstances. It can be used to determine a wide range of concentrations, with only a minimum of procedural variations. The technique uses ion selective electrodes.

Species commonly detected by such electrodes are: Sodium in water; sulphide and cyanide in industrial effluents; potassium, calcium, and carbon dioxide in biological fluids; and chloride and ammonia in a variety of media[74].

The technique depends on the relationship between the concentration of the determinand and the emf of an electrochemical cell in which the determinand is one of the components of the equilibrium system[75]. The ideal system is the one which utilizes the Nernst equation expressed as:

$$E = E^{O} + K \log C$$

where E is the measured potential, E^{O} the standard reduction potential for the particular species; C the concentration of the determinand and K a constant.

$$(K = \frac{RT}{nF} \log 10)$$

Digital meters can read to 0.1 mV or 0.0001pH units over a range of 999.9 mV or 0-14 pH units. Most of these meters display the polarity sign automatically on the millivolt scale.

Specific ion membrane electrodes are used and complexing substances affect the accuracy of the ion in question. Such effects are removed from the solution by buffering, and addition of chemicals which free the ions in question. When compared to other available methods, potentiometric analysis of chlorides and fluorides has been found to be far much superior[76].

2.7.6 Chloride Analysis:

Apparatus:

(a) Orion ionalyser model 801
(b) Orion chloride electrode 94-17B
(c) Double junction reference electrode with accompanying filling solutions.
(d) 100ml plastic beakers.

Reagents:

a) Stock chloride solution (1000 ppm):

The electrodes were dipped into the S1 solution. 5ml buffer was added and stirred. After stabilization, the read out (mV) was recorded as E1. The procedure was repeated with 500ppm (S2) solution and the potential recorded as E2.

The calibration slope K(-57± 2mV) and the concentration of the chloride were calculated using equations 2.7.1 and 2.7.2 shown below:

$$K = \frac{E1 - E2}{\log S1 - \log S2} \quad \text{----------2.7.1}$$

$$C = S1 \text{ antilog } (E/K) \quad \text{-------2.7.2}$$

Where E is the difference between Ex (potential of a sample solution) and E1. C is the concentration of the chloride ion calculated.

2.7.7 pH determinations

Apparatus

a) pH - meter model 22S ,Pye Unicam
b) Glass electrode type G200
c) Calomel electrode type K100
d) Shield of stainless steel

(1) Preparation:

Switch 1 was turned to position 0. The meter needle adjustment was verified at 7.00. A type G200 glass electrode was rinsed with distilled water and the water was carefully removed from the glass surface between the bulb and the socket by means of a clean, dry rag. The electrode was then inserted in the glass electrode holder of the pH meter.

A type K100 calomel electrode was filled with saturated potassium chloride and inserted in the electrode holder marked calomel electrode.

The beaker support and the stop collar were adjusted so that the beaker could not touch the electrodes. The shield of stainless steel was mounted.

(2) Buffer check:

A beaker containing the buffer solution was placed in position. Switch 2 was set to the temperature closest to that of the buffer solution. Switch 1 was turned to the proper pH range and the buffer adjustment knob rotated until the meter needle indicated the exact buffer pH (the series of figures corresponding to the position of switch 1 were read).

Switch 1 was returned to position 0.

(3) Measurements:

The electrodes were rinsed and wiped. A beaker containing the sample was placed in position. Switch 1 was turned to the proper range and the pH read from the series of figures corresponding to the setting of switch 1. Occasionally the buffer adjustment was repeated during an extended series of measurements.

CHAPTER 3

3. RESULTS AND CALCULATIONS:

3.1 Average emf measured:

The average results of emf measured for both monovalent and divalent cations for the two membrane systems viz 1.0:3.0:0.6 and 2.0:4.0:1.0 are presented in tables 3.1.1, 3.1.2, 3.1.3, 3.1.4 and 3.1.5 and graphically in figures; 3.1.1, 3.1.2, 3.1.3 and 3.1.4.

The standard electrode used was Ag/Agcl electrode.

Table 3.1.1- Average emf values measured for Na^+ cation system (NaCl) at 25°C.

Concentration of electrolyte(M)	EMF VALUES (VSCE) With Transference 1.0:3.0:0.6	With Transference 2.0:4.0:1.0	Without Transference
0.05	0.0193	0.0005	0.2602
0.10	0.0250	0.0055	0.2590
0.15	0.0337	0.0132	0.2579
0.20	0.0416	0.0195	0.2570
0.25	0.0474	0.0252	0.2554
0.30	0.0516	0.0310	0.2543
0.35	0.0624	0.0350	0.2534
0.40	0.0773	0.0433	0.2522
Standard Deviation	0.0180	0.0138	0.00263

TABLE 3.1.2 Average emf values measured for H^+ cation system (HCl) at 25°C.

Concentration of electrolyte (M)	EMF VALUES (V_{SCE}) With Transference 1.0:3.0:0.6	With Transference 2.0:4.0:1.0	Without Tranference
0.05	0.0023	0.0110	0.1280
0.10	0.0092	0.0146	0.1380
0.15	0.0167	0.0194	0.1456
0.20	0.0226	0.0222	0.1576
0.25	0.0313	0.0275	0.1685
0.30	0.0405	0.0322	0.1772
0.35	0.0451	0.0368	0.1830
0.40	0.0562	0.0408	0.1952
Standard Deviation	0.0174	0.00992	0.0219

ABLE 3.1.3 - Average emf values measured for Zn^{2+}
ation system ($ZnCl_2$) at 25°C.

Concentration of electrolyte (M)	EMF VALUES (V_{SCE}) With Transference 1.0:3.0:0.6	With Transference 2.0:4.0:1.0	Without Transference
0.05	0.0318	0.0385	0.0368
0.10	0.0333	0.0330	0.0425
0.15	0.0344	0.0310	0.0464
0.20	0.0365	0.0273	0.0535
0.25	0.0380	0.0226	0.0600
0.30	0.0392	0.0196	0.0645
0.35	0.0403	0.0173	0.0699
0.40	0.0419	0.0118	0.0754
Standard Deviation	0.00332	0.00834	0.0128

TABLE 3.1.4 Average emf values measured for Cd^{2+} cation system ($CdCl_2$) at 25°C.

Concentration of electrolyte (M)	EMF VALUES (VSCE) With Transference 1.0:3.0:0.6	With Transference 2.0:4.0:1.0	Without Transference
0.05	0.054	0.0530	0.0523
0.10	0.0559	0.0498	0.0583
0.15	0.0579	0.0470	0.0674
0.20	0.0595	0.0443	0.0766
0.25	0.0616	0.0414	0.0827
0.30	0.0635	0.0380	0.0900
0.35	0.0658	0.0352	0.0975
0.40	0.0674	0.0328	0.1050
Standard Deviation	0.00443	0.00667	0.0174

TABLE 3.1.5 Average emf values measured for Cu^{2+} Cation system ($CuCl_2.2H_2O$) at 25°C

Concentration of electrolyte (M)	EMF VALUES (VSCE) With Transference 1.0:3.0:0.6	With Transference 2.0:4.0:1.0	Without Transference
0.05	0.0266	0.0661	0.0559
0.10	0.0281	0.0545	0.0607
0.15	0.0290	0.0468	0.0646
0.20	0.0312	0.0398	0.0682
0.25	0.0326	0.0325	0.0735
0.30	0.0343	0.0253	0.0778
0.35	0.0358	0.0177	0.0820
0.40	0.0374	0.0124	0.0865
STANDARD DEVIATION	0.00359	0.0173	0.00998

3.2 CALCULATION OF TRANSFERENCE NUMBER OF THE CATION IN THE AQUEOUS ELECTROLYTE MCl OR MCl_2

In section 1.5.1, a clear illustration was given of a cell with and without transport.

In general the emf of any cell with transference is given in equation (1.5.1.e):

$$E = 2tc \frac{RT}{F} \ln \frac{a2}{a1}$$

Since Ag/AgCl electrodes, reversible to Cl ions, were used in this particular project then the transport number derived was for cations.

Similarly, the general equation of a cell without transport is given in equation (1.5.1.b):

$$E = \frac{2RT}{F} \ln \frac{a2}{a1}$$

If equation (1.5.1.e) is divided by equation (1.5.1.b), a value of t+(or tc) is obtained. So by measuring the emf's of identical cells but with and without transference, the transference number of ions can be determined.

The calculated values of transference numbers for the various cation systems are presented in tables 3.2.1, 3.2.2, 3.2.3, 3.2.4, and 3.2.5 and graphically in figures 3.2.1, 3.2.2, and 3.2.3.

There values were derived from the corresponding emf values presented in the tables 3.1.1, 3.1.2, 3.1.3, 3.1.4 and 3.1.5.

TABLE 3.2.1: The calculated values of transference number of the Na^+ cation in the membrane system, 1.0:3.0:0.6 and 2.0:4.0:1.0 at 25°C.

Concentration of electrolyte (M)	Transference Number Values	
	1.0:3.0:0.6	2.0:4.0:1.0
0.05	0.0742	0.0019
0.10	0.0965	0.0212
0.15	0.1307	0.0512
0.20	0.1619	0.0759
0.25	0.1856	0.0987
0.30	0.2029	0.1219
0.35	0.2463	0.1381
0.40	0.3065	0.1717
STANDARD DEVIATION	0.0722	0.0549

TABLE 3.2.2: The calculated values of transference number of H^+ cation in the membrane system, 1.0:3.0:0.6 and 2.0:4.0:1.0 at 25°C.

Concentration of electrolyte (M)	Transference Number of Values	
	1.0:3.0:0.6	2.0:4.0:1.0
0.05	0.0359	0.0859
0.10	0.0667	0.1058
0.15	0.1147	0.1332
0.20	0.1434	0.1409
0.25	0.1858	0.1632
0.30	0.2286	0.1817
0.35	0.2465	0.2011
0.40	0.2879	0.2090
STANDARD DEVIATION	0.0833	0.0413

TABLE 3.2.3 The calculated values of transference number of Zn^{2+} cation in the membrane.

System; 1.0:3.0:0.6 and 2.0:4.0:1.0 at 25°C.

Concentration of electrolyte (M)	Transference Number Values	
	1.0:3.0:0.6	2.0:4.0:1.0
0.05	0.8641	0.8424
0.10	0.7835	0.7765
0.15	0.7414	0.6681
0.20	0.6822	0.5103
0.25	0.6333	0.3767
0.30	0.6076	0.3039
0.35	0.5765	0.2475
0.40	0.5557	0.1565
STANDARD DEVIATION	0.1012	0.2387

TABLE 3.2.4 The calculated values of transference number of Cd^{2+} Cation in the membrane

System: 1.0:3.0:0.6 and 2.0:4.0:1.0 at 25°C.

Concentration of electrolyte (M)	Transference Number Values	
	1.0:3.0:0.6	2.0:4.0:1.0
0.05	-	-
0.10	0.9588	0.8542
0.15	0.8591	0.6973
0.20	0.7768	0.5783
0.25	0.7449	0.5006
0.30	0.7056	0.4222
0.35	0.6749	0.3610
0.40	0.6419	0.3124
STANDARD DEVIATION	0.2443	0.1788

NB: For a concentration of 0.05M, an unacceptable transference number value greater than 1 is derived.

TABLE 3.2.5 The calculated values of transference number of Cu^{2+} cation in the membrane system; 1.0:3.0:0.6 and 2.0:4.0:1.0 at 25°.C.

Concentration of electrolyte (M)	Transference Number Value	
	1.0:3.0:0.6	2.0:4.0:1.0
0.05	0.4758	-
0.10	0.4629	0.8979
0.15	0.4598	0.7245
0.20	0.4574	0.5836
0.25	0.4435	0.4422
0.30	0.4409	0.3252
0.35	0.4366	0.2159
0.40	0.4324	0.1434
STANDARD DEVIATION	0.0141	0.2545

NB: An unacceptable transport no value greater than 1 is obtained for a concentration of 0.05M in the system in the membrane system; 2.0:4.0:1.0.

3.3 The Steel Reinforced - Concrete - Cement (RCC) model results

The RCC model was viewed as an epitome of the steel support used in the building industry.

Two sets of results were obtained.

a) Emf analysis which was used as a tool to trace the movement behaviour of the Cl ion within the membrane matrix.

b) Cl^- ion analysis which was done to find out the amount of ion that had leached from the model matrix into the surrounding solution.

The results of (a) and (b) are clearly illustrated in tables 3.3.1 and 3.3.2 and presented graphically in figures 3.3.1.

With reference to figure (2.6.1), electrode Ec was the Ag/AgCl electrode closest to the sodium-amalgam electrode, followed by E_b and finally by E_a, within the RCC matrix. E_a and E_b were in the core-layer while Ec was in the peripheral layer.

Es was the Ag/Agcl electrode when placed in the surrounding solution. The extraction of a sample of this solution for chloride ion analysis and the reading of emf values were done at the same time on a daily basis. The pH. of this extracted sample solution ranged from 7.1 to 8.7 but not in any given order.

TABLE 3.3.1 Variation of emf values after every 24 hours.

Day after starting the experiment	EMF Values (V_{SCE})			
	E_A	E_B	E_C	E_D
0	0.1537	0.0795	0.1004	0.1962
1	0.0869	0.0931	0.1142	0.1786
2	0.0902	0.1002	0.1013	0.1773
3	0.0903	0.0989	0.0980	0.1708
4	0.0870	0.0918	0.0931	0.1558
5	0.0866	0.0855	0.0938	0.1608
6	0.0856	0.0851	0.1007	0.1569
7	0.0855	0.0836	0.0989	0.1535
8	0.0855	0.0835	0.0948	0.1487
9	0.0855	0.0840	0.0942	0.1476
10	0.0854	0.0840	0.0941	0.1460
11	0.0853	0.0843	0.0940	0.01457

TABLE 3.3.2 Variation of PH and Cl ion after every 24 hours

Day after starting the experiment	Concentration of Cl ion (ppm)	PH
0	2.8612	5.7
1	1196.32	8.7
2	2576.15	8.7
3	3958.12	7.7
4	4923.20	8.6
5	4042.02	8.0
6	4183.34	7.5
7	4341.49	8.7
8	3749.11	7.7
9	4015.18	8.2
10	3963.14	7.6
11	4202.55	8.6
12	3924.54	7.1
13	4076.78	7.7
14	3969.94	8.3
15	4067.88	7.1

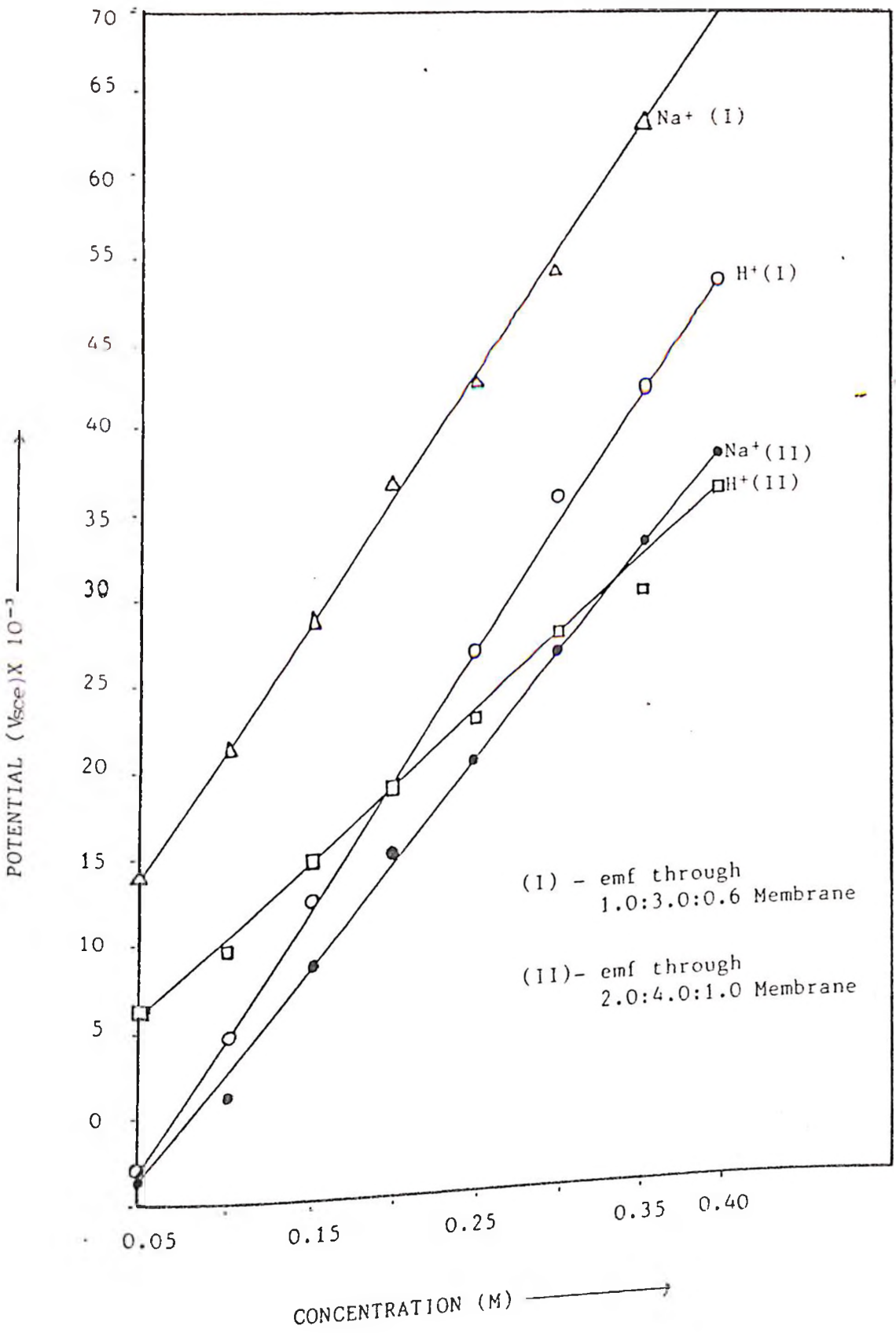


Fig.3.1.1: Graph of emf with transference for monovalent cations against concentration.

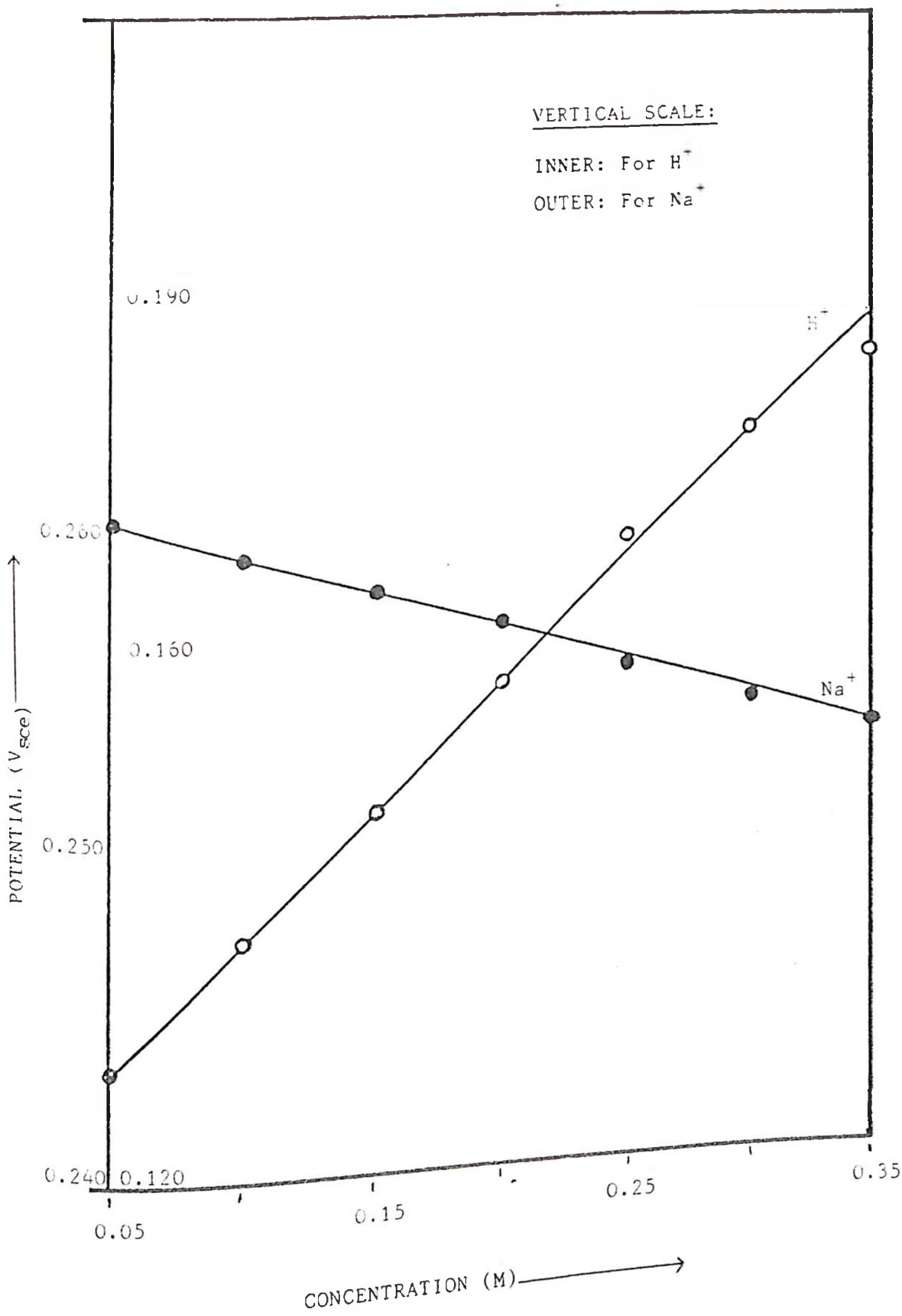


Fig.3.1.2 Graph of Emf without transference for monovalent cations as a function of concentration.

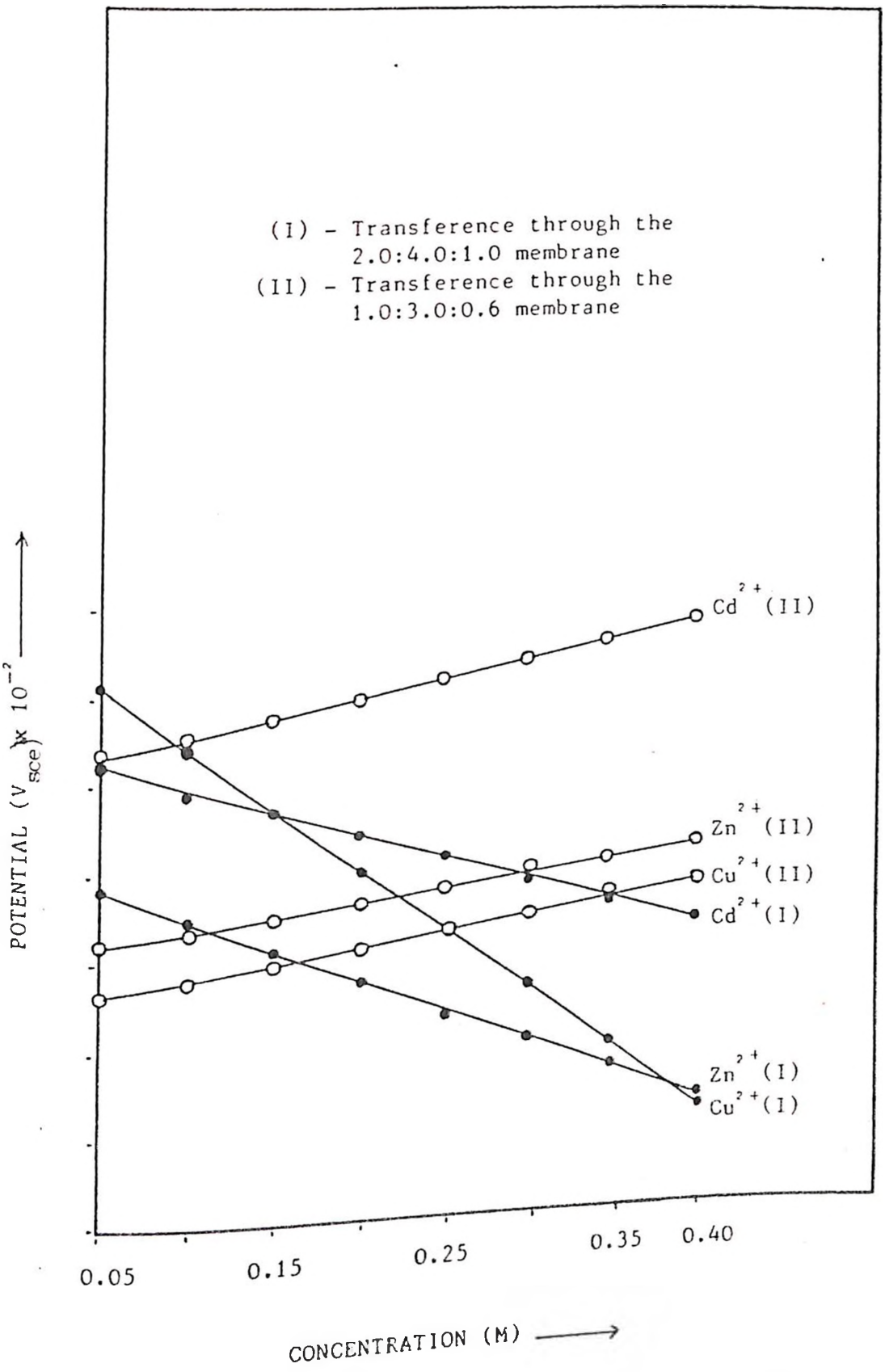


Fig.3.1.3 Graph of emf with transference for divalent cations as a function of concentration.

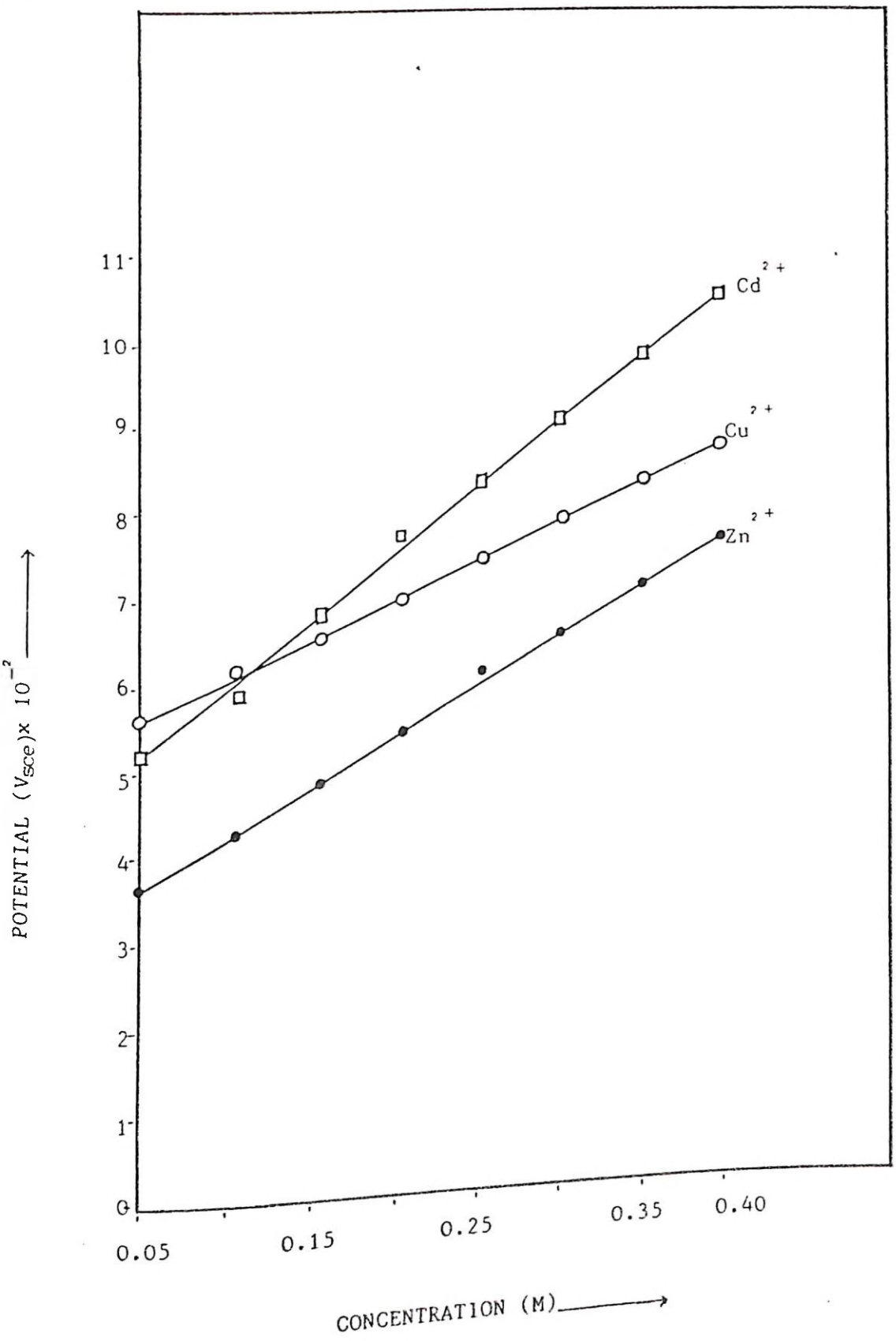


Fig. 3.1.4 Graph of emf without transference for divalent cations as a function of concentration.

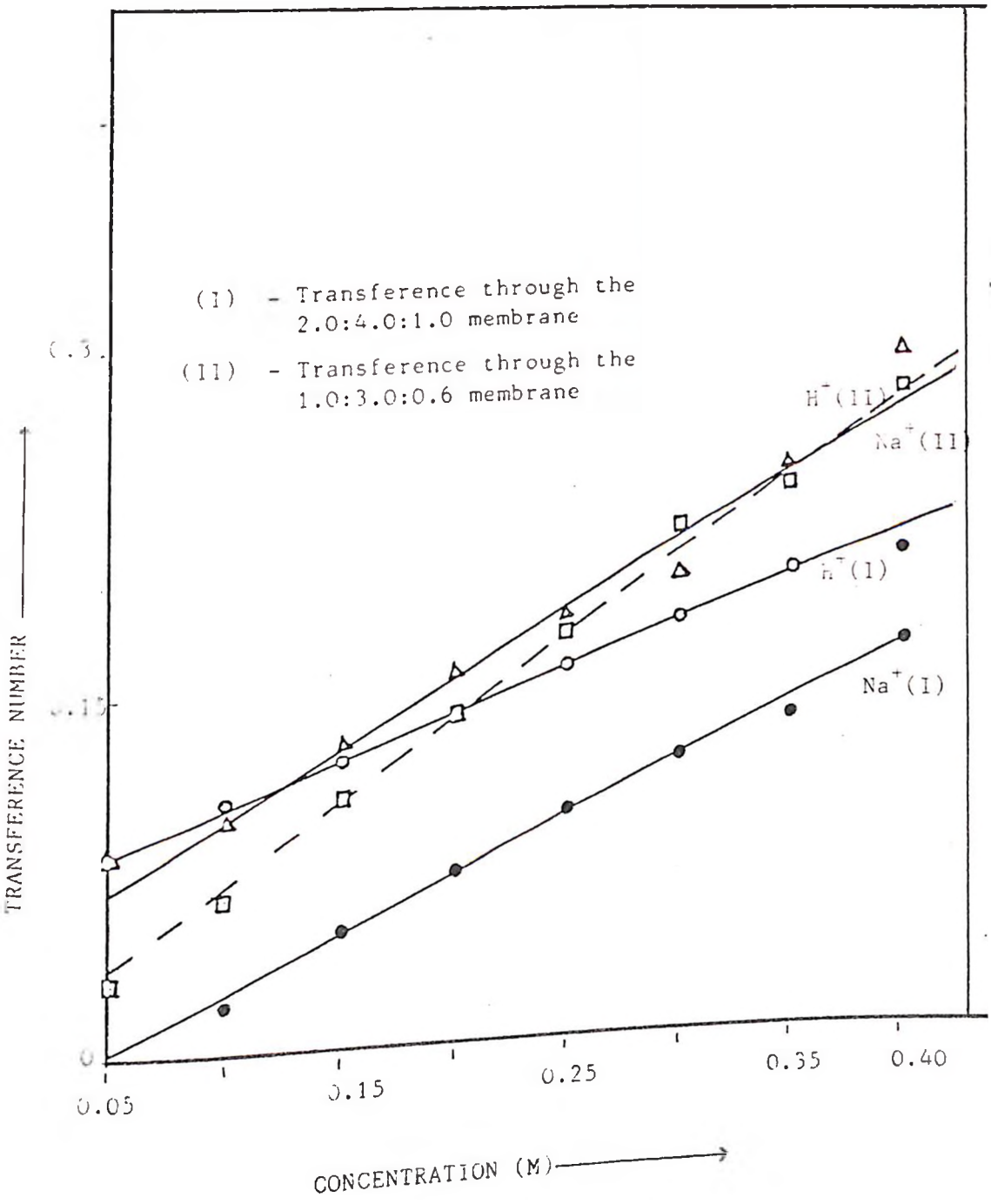


Fig.3.2.1 Graph of transference number for monovalent cations as a function of concentration.

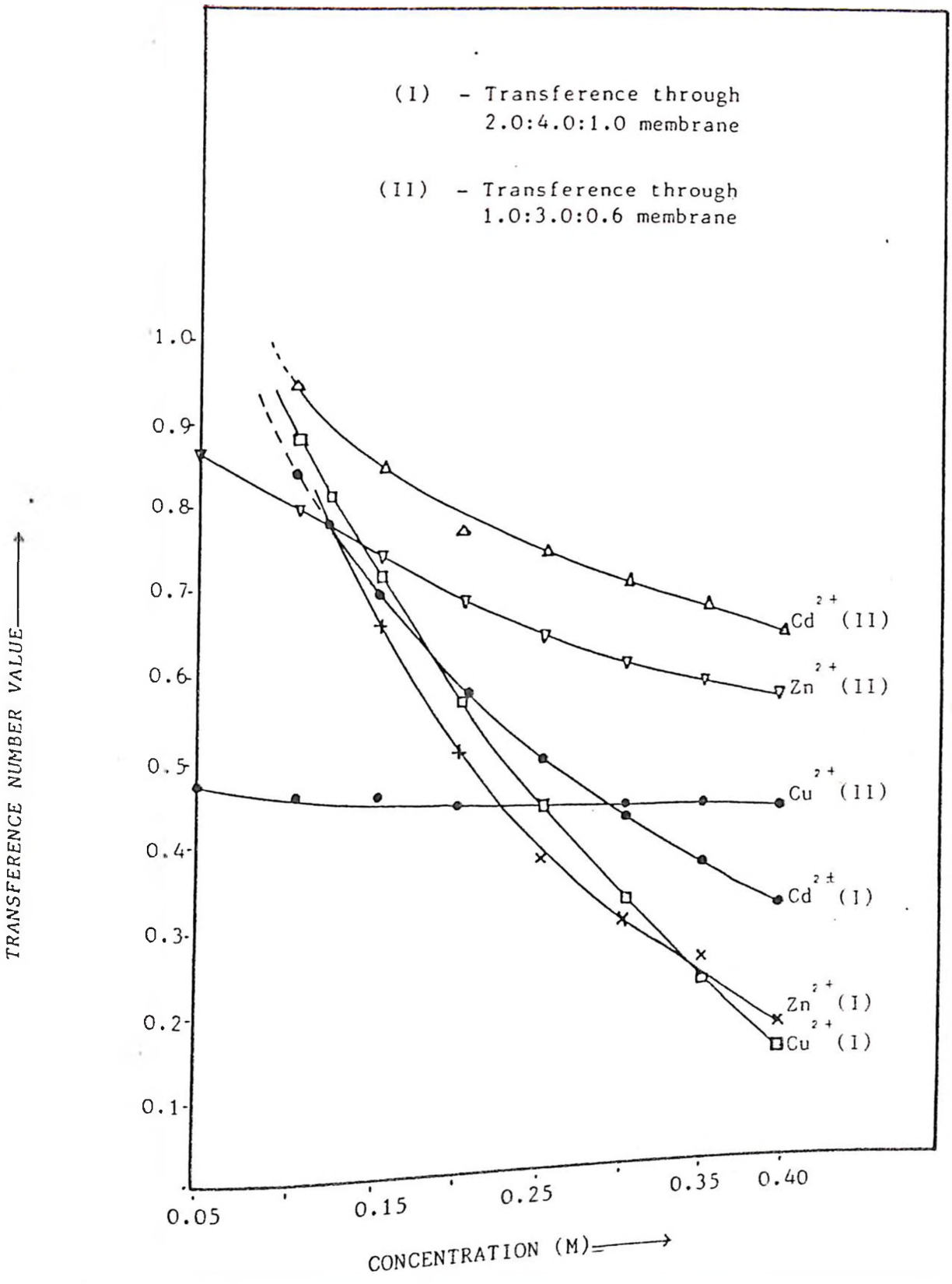


Fig.3.2.2 Graph of transference numbers of divalent cations as a function of concentration

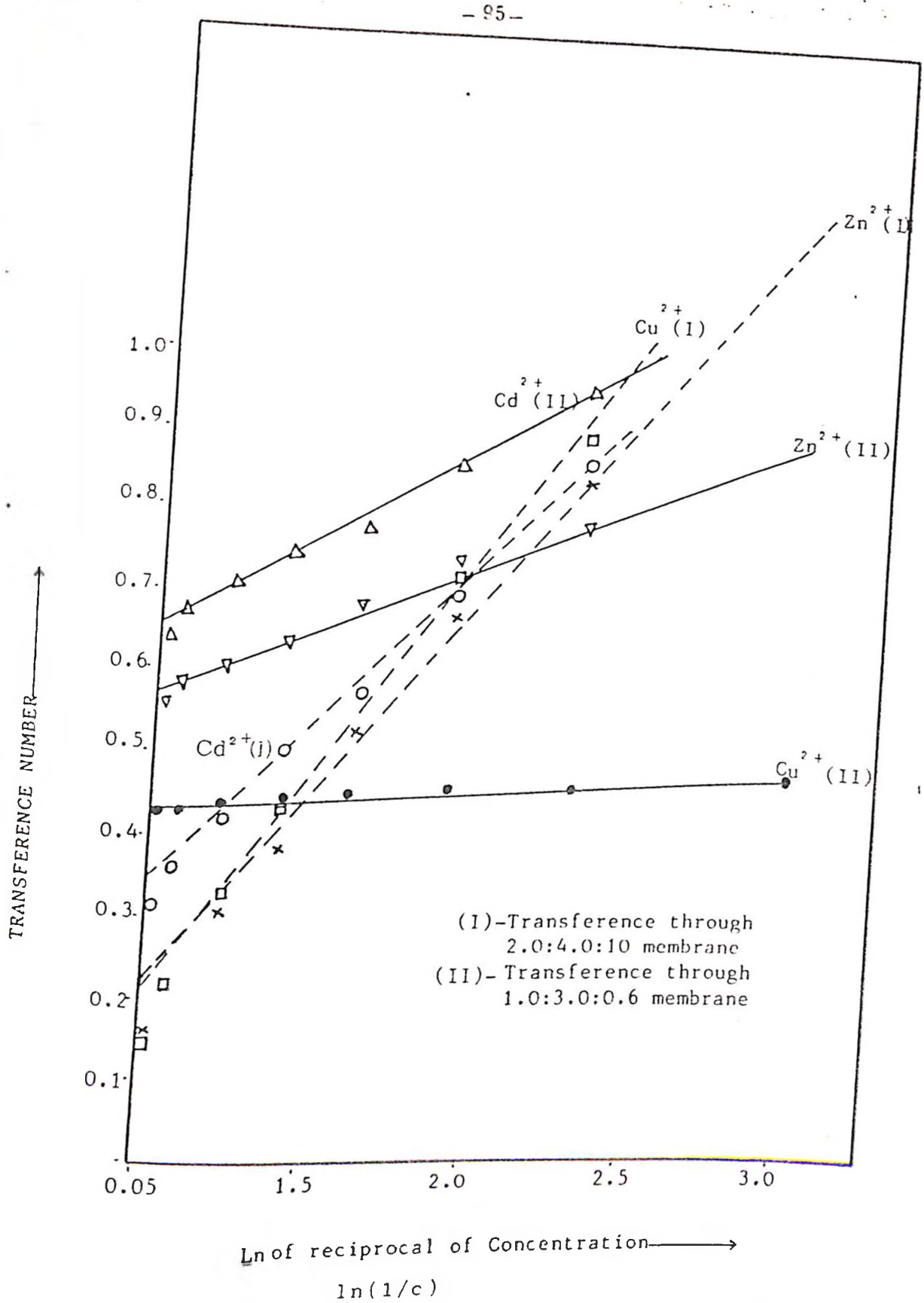


Fig: 3.2.3 Graph of transference number of divalent cations against natural logarithm of the reciprocal of concentration.

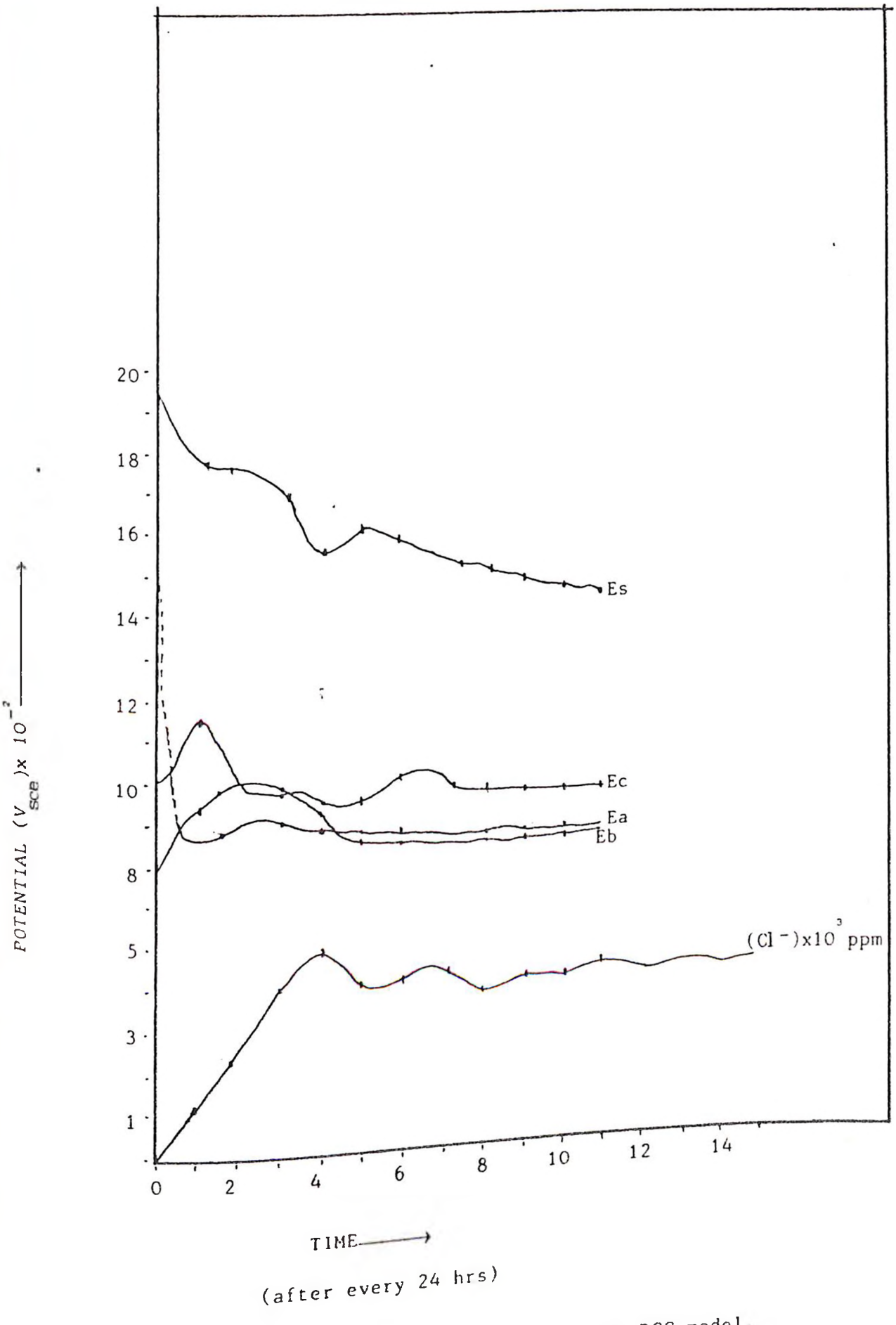


Fig.3.3.1. Graph of the results obtained from the RCC model.

CHAPTER 4

4.0 Discussion of Results and Conclusion

4.1 Factors affecting measured emf

4.1.1 Structure of the membrane matrix

Sollner (76,77,78) in his work concluded that pore systems in real membranes could be visualized as consisting of narrow channels and wider cavities which, interconnected at random, traversed the membrane. The electrical behaviour of these pore systems was governed by two factors:

(a) The ability or inability of ions of an eletrolyte to enter purely on a basis of size, and

(b) An electrical factor, the repelling forces emanating from fixed dissociable groups on the pore walls.

If the combination of structural and electrical factors was perfect and one ion of a binary electrolyte was wholly excluded, the membrane action would be perfect and the membrane would behave as an electrode reversible with respect to the other ion. If the membrane is not perfect there would be an ionic leak and the membrane would not function as a reversible electrode.

4.1.2 Faulty Membrane Systems

Work done by Willie and Patnode[27] shows that the effect

of cracked or faulty shale membrane specimens, even if the cracks are microscopic, will be to give rise to anionic leaks between the two solutions seperated by the shale membrane and thus impair the electrochemical performance. A similar effect is possible in a shale if the electrically conducting paths through the membrane do not all involve passage through materials which possess the necessary structural and electrical factors to reduce to zero the transport number of the anions of the solutions separated by the membrane.

If it is assumed that the materials in shales which possess the necessary fixed dissociable groups to repel anions are the clay minerals which exhibit Cation exchange, then the overall electrochemical efficiency of a shale membrane may be affected both by the chemical structure of the clay particles, and by the nature and arrangement of the electrochemically inactive materials which comprise what may be termed as the matrix of the shale.

4.1.3 Thickness of Membrane

If the shale matrix considered in section (4.1.2), has some electrical permeability to anions whereas the clay minerals imbedded in it possess none, the shale might be expected to show improved electrochemical performance with increase in thickness. This case is analogous to

one considered by Sollner (76) and involves the conclusion that all shales would tend to give the theoretical reversible electrode potentials if sufficiently thick. It is probable that this view is an oversimplification, while it appears unlikely that the clay minerals present in the shale have the perfect structural and electrical factors necessary to prevent completely any anion conduction. However, even if the clay minerals are not electrochemically perfect in the sense described, the conclusion that a sufficiently thick shale sample would tend to give the theoretical potential would still be valid. This conclusion seems to be supported by observations of shale potentials in the earth (79,80).

4.1.4 Water Transfer Contribution to Emf

Water transport by electroosmosis is a function of the internal ion concentration of the membrane pore solution and the membrane ionic form.

Water transport normally decreases with increasing external electrolyte solution concentration and also varies with the variation in the effective radii of the cations e.g Li^+ , Na^+ , K^+ and H^+, in their hydrated forms. A very compact (tight) membrane represents very nearly the limitting conditions of membrane internal solution concentration. This consequently reduces drastically water transport.

In general, water transfer for any one ion appears to follow the moisture content[29,35] of the membrane in that ionic form. Although the moisture content of a membrane differs only slightly with ionic form, a large difference in water transport between for example Li+, Na+, K+ and H+ ions is observed. The moving ion exerts the major control over the magnitude of water transport.

It must be noted that membrane cell potentials are not reversible potentials unless the membranes used are impermeable to water. If the osmotic flow of water is negligibly small, water may still be transfered reversibly by electrosmosis and contribute to the cell reaction.[31] In addition there is the possibility of anion transfer in a cation exchange membrane. In a membrane in which interactions between different membrane components, viz counterion, co-ion, water and membrane matrix, are absent, one may assume that the fixed water in the membrane is negligible and that all mobile water moves with the same velocity and in the same direction as the counterion[3] . As a result, counter-ions move faster and co-ions move slower than they would otherwise if water stood still.

4.1.5 Temperature Effect

The emf measured using the cell shown in figure 2.1.1 was temperature dependent. This is evident from equation (3.2.1). The water-bath was maintained at a constant temperature of 25±0.1° C. To ensure that there were no temperature gradients in the water-bath, it was stirred uniformly.

4.2 Interpretation of results from the membrane analysis

The two membrane systems, 1.0:3.0:0.6 and 2.0:4.0:1.0, both have the same electrical factors i.e the repelling forces emanating from fixed dissociable groups on the pore walls. The only difference is the structural factor which controls the entry of ions of an electrolyte purely on a basis of size[76,77,78] Of the two membrane systems, the former is the more compact one therefore water transport is more reduced. Subsequently from equation (1.5.2) the measured emf with transference for the membrane, 1.0:3.0:0.6 will generally be higher than for membrane 2.0:4.0:1.0 which thus implies that the transference number for any particular ion will be higher. This can clearly be observed in the emf and transference number graphs. The Cu^{2+} ion shows a remarkable difference maybe because of the behaviour of the copper electrodes.

These electrodes if left in the open, a coating of copper oxide and copper sulphide will form. This will necessitate dipping them in dilute HNO_3 acid to eliminate these impurities, and rinsing with distilled water. Storage always has to be done under distilled water. However, this does not imply the yield of good and dependable results. The phenomena arising across a membrane separating two aqueous solutions of different concentration is an interesting aspect of membrane science. In this context the diffusing species are ions and diffusion occurs in the direction of their gradients.

Whatever the nature of the diffusing species, a feature common to all these diffusing processes is the role the liquid films adhering to the membrane faces play in controlling the overall rates of permeation of the species across the membrane. Usually, in studies involving diffusion, the bulk solutions on either side of the membrane are kept very well stirred. Despite this, a zone of finite thickness without any convection will exist on either side. Under these conditions, the diffusional flux may be controlled either by the membrane or by the liquid layer; the layer across which the slowest rate of flow across determines the overall rate of diffusion. Besides these extremes, the coupled

membrane-film diffusion mechanism might also operate to control the rate of permeation across the membrane[81].

In general:

a) Lower values of membrane thickness.

b) Higher values of films (thicker film) as a result of little stirring or force convection.

c) Higher diffusion coefficients in the membrane (greater porosity and little permselectivity).

favour film diffusion control.

Irrespective of how thin the membrane is, if diffusion through the membrane is very low, as it is with some of the membranes (charged or uncharged) of very low water contents (<20%), the rate of diffusion, provided good stirring is employed, will be controlled by the membrane.

The principal factor determining the diffusion control in membranes with water contents greater than 50% is the ratio $c/\bar{c}$ i.e the ratio of concentration of species in bulk solution to the concentration of the same species within the membrane matrix[82]. In uncharged membranes, both electrolytes and non-electrolytes are likely to have $c/\bar{c} \simeq 1$; as such membrane Control of diffusion is expected. In the case of charged membranes, because of their ability to be permselective, the conditions will be entirely different. For co-ions $\bar{c}$ is always less than c. Therefore $c/\bar{c}$ is always greater than unity and will become very large if the membrane is used with dilute solutions due to the Donnan Principle operating to prevent Co-ions from entering the membrane

phase. Film diffusion control, therefore, is likely to be very rare. In the case of counter-ions, $c/\bar{c}$ is less than unity and will become very small at high dilutions and hence diffusion will be controlled by the film. As c is increased, $\bar{c}$ will approach c and when it does, membrane diffusion control will set in. So in the case of counter ions, flux rate will change from film control to membrane control as the external concentration is increased. In between, the coupled film-membrane mechanism will prevail for the case of non-electrolyte, $c/\bar{c}$ will be nearly unity and so, as the flux of co-ions, the flux will be controlled by the membrane. In these considerations, it was assumed that the concentration profile in the diffusion layer was linear. This would be so if the rates of stirring employed were high enough to give only a thin diffusion layer.

In this project monocations showed direct proportionality between transference number and concentration of the electrolyte solution as shown in figure 3.2.1. This was for both membranes, i.e

1.0:3.0:0.6 and 2.0:4.0:1.0.

But direct proportionality for Dications is only envisaged when natural logarithm of the reciprocal of the concentration is considered. Otherwise, with increase in concentration the transference number decreases along a curved line; figures 3.2.3 and 3.2.2 respectively.

This can be explained in the same lines as the findings by Planck whose approach, is based on a Kinetic treatment which gave a dif-

ferential approach, the derivation of which is based on thermodynamic reasoning:-

The rate of diffusion or flux J_i (mole cm^{-2} sec^{-1}) of a molecular or ionic species across a membrane is given by the product of three terms, namely, a proportionality constant, concentration C_i, and force. The flux due to diffusion $J_i(d)$ caused by the force represented by the gradients of chemical potential $(-dU_i/dx)$ is given by:-

$$J(d) = \frac{D_i}{RT} C_i \left(-\frac{dU_i}{dx}\right)$$

$$= -D_i C_i \frac{d\ln a_i}{dx}$$

where D_i is the diffusion coefficient.

substituting for a_i $(a_i = C_i \gamma_i)$

$$J_i(d) = -D_i C_i \left[\frac{d\ln C_i}{dx} + \frac{d\ln \gamma_i}{dx}\right]$$

$$= -D_i \left[\frac{dC_i}{dx} + C_i \frac{d\ln \gamma_i}{dx}\right]$$

when γ_i is constant (ideal solution), the flux equation reduces to Fick's first Law.

$$J_i\,(d) = -D_i\, dC_i/dx$$

The diffusion of charged species (ie.ions) generates an electric field (diffusion potential) which acts as another driving force. Thus flux due to an electric field -dE/dx is given by

$$J_i(e) - U_i Z_i C_i\, dE/dx$$

Di is related to mobility Ui by the Nernst - Einstein relation.

$$D_i = (RT/F)U_i$$

The total flux J_i is given by

$$J_i = J_i(d) + J_i(e)$$

$$= -\frac{RT}{F} U_i \left[\frac{dC_i}{dx} + C_i \frac{d\ln\gamma_i}{dx} + Z_i \frac{F}{RT} C_i \frac{dE}{dx} \right]$$

This is the Nernst - Planck flux equation with activity factor included, and applies to all mobile species.

Hence, apart from the concentration gradient across a membrane, the following factors contribute to the behaviour of ionic species (i.e. monocations and dications in this context) and their Transference members with increase in concentration:

(i) Mobility, U_i

(ii) Valency, Z_i

(iii) Activity, a_i

Therefore for a divalent cation system, transference number against concentration exhibit a non-linear behaviour which probably can be adequatly explained by the valency of the ions and is an exponential dependence of transference number on concentration of electrolyte.
This indicates a strong interaction between the divalent ion and the membrane system.

4.3 interpretation of results from the RCC model-

With reference to figure 3.3.1, results showed minute leaching of Cl^- ions, from the sample into the surrounding solution in the first 8 days. The leaching was due to reverse diffusion of the chloride ions towards the solution as indicated by the emf Vs days graph (page 96). A steady state was finally achieved after the 8th day in which flow characteristics in either direction were noted. Day zero on the graph denotes the day the model was submerged in de-ionized water. The figure 2.8612 for chloride ion concentration(ppm) was derived when sampling of ambient solution was done about half an hour later and analysed. Hence, after the 8th day the graph steadied itself and showed no leaching indications. The behaviour within the

sample matrix could also be easily monitored by considering the emf values;Ea, Eb and Ec. These parameters, together with Es, supplement the results obtained from the chloride analysis i.e. leaching of chloride ions tends to stop after 8th day. This illustration is an important industrial phenomenon. The results clearly show that after 8 days some kind of equilibrium is attained which probably can sustain itself for a very long time. Hence, ions from the surrounding solution may not reach the center of the sample.

4.4 Conclusion

1) A clear analysis of two sets of cations: divalent and monovalent; has been given considering their transporting properties and factors that affect them with parameters that determine these transport properties.

Example:

(a) Electrical factors: This is due to repelling forces emanating from fixed dissociable groups on the pore wall.

(b) Structural factor: Controls entry of ions purely on the basis of size.

(c) The coupled membrane - film diffusion mechanism might also operate to control the rate of permeation across a membrane. Film diffusion control is favoured by:-

i) Thicker film as a result of little stirring.

ii) Lower values of membrane thickness.

iii) Greater porosity and little permselectivity.

(d) Concentration gradient across the membrane also affects transport properties and lastly

(e) Behaviour of ions with respect to the following inherent properties.

i) Mobility

ii) Valency

iii) Activity

2) With some modification, it is possible to stop a one way flow of Cl^- ions towards steel that is imbedded in concrete.

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