PERMEABILITY OF IONS THROUGH INORGANIC GELS AND A STUDY OF THEIR ELECTRODES SYSTEM

Thesis submitted for the award of the
Degree of Doctor of Philosophy
in Chemistry

by

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DEPARTMENT OF CHEMISTRY

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CERTIFICATE

Certified that the Thesis entitled "PERMEABILITY OF IONS THROUGH INORGANIC GELS AND A STUDY OF THEIR ELECTRODES SYSTEM" which is being submitted by Mr. Mohammad Shamim Anwar for the award of the degree of Doctor of Philosophy in Chemistry of the University of Roorkee, is a record of his own work under my supervision and guidance. The matter embodied in this thesis has not been submitted for the award of any other degree of any University.

This is further to certify that he has worked for a period of two years and two months from May 15, 1964 to July 15, 1966 at this University to prepare this thesis.

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GENERAL INTRODUCTION

GENERAL INTRODUCTION

The importance of transport phenomenon in engineering, technology, biology and medicine is well recognised. Chemists and chemical engineers fabricate membranes for fundamental studies on permeability and diffusion of solutions, for exchange studies and for many unit operations when a membrane of any desired property or properties is to be employed for a particular chemical process. Basic research in the field of physiology and medicine involves the use of simple models to understand the behaviour of complex cell membranes.

It is difficult to give a precise definition of the word "membrane" (1). Any complete definition given to cover all the facts of membrane behaviour will be inexact and precise statement will be incomplete. However, the characteristic feature of membrane in their selective permeability, in other words, their function as barriers irrespective of the name given to the membrane system. Thus membranes considered from the physico-chemical standpoint are given the name "physico-chemical membranes" (2). Other terminologies associated with membranes are 'Semipermeable'; 'homogeneous phase membranes' (oil membranes); 'membranes of porous character's; 'ion-exchange membranes' etc.

From the physico-chemical point of view; ' a membrane is a phase or structure interposed between two phases or compartments which obstracts or completely prevents gross mass movement between the latter, but permits passage, with various degrees of restriction, of one or several species of particles from the one to the other or between the two adjacent phases or compartments, and which thereby acting as a physico-chemical machine transforms with various degrees of efficiency according to its nature and the nature and composition of the two adjacent phases or compartments the free energy of the adjacent phases or compartment, or energy applied from the outside to the latter into other forms of energy (3). Similar views were held by Krogh (4). The thermodynamics of transport of ordinary solutions, though as such not simple, becomes all the more complex in the case of electrolytes where numerous additional effects may be observed, such as static or dynamic membrane potentials, anomalous osmosis, movement of ions against concentration gradient, electro-osmosis etc.

It is necessary to distinguish two basic classes of membranes "homogenous phase membranes" (oil membranes) and 'membranes of porous character'. Homogenous phase membranes exert their typical membrane function by means of selective differential solubility (5). Membranes of porous character act as sieves that screen out the various species of solute particles according to their different size and to some extent according to their different adsorbabilities and in the case of ions, also according to the sign and magnitude of their charge.

The question of membrane structure becomes of great importance when a membrane is not completely inactive (in fact a complete inactive membrane is difficult to realise in practice). The ionogenic groups fixed to the membrane matrix, as seen in well characterised ion exchange membranes, or adsorbed as found in some colloidal systems (6) greatly influence the transport phenomenon. The presence of ionogenic groups and pores in the membrane confers certain functionality to the membrane which is described in the literature by the words permselectivity (7) and/or semipermeability. The phenomenological transport property which controls the former is the 'transport number' $\bar{t}_i$ whereas the latter is determined by the reflection coefficient σ (ratio of the actual hydrostatic pressure required to give zero net volume flow to that which is required if the membrane were truly semipermeable) introduced by Staverman (8-14).

Grossly porous membranes (wide pores) are neither permselective nor semipermeable; whereas "ion sieve" membranes with narrow pores are semipermeable but may not be permselective if the number of fixed ionogenic groups are too few in number. As the presence of narrow pores and high fixed charge density of ionogenic groups gives high values for $\bar{t}_i$ and σ , membranes characterised by these values i.e. ion-exchange membrane prove useful and industrially important. As a result, the bulk of the membrane literature abounds in papers describing the work on ion-exchange membranes.

Ion-exchange membranes in contact with external electrolyte solutions take up electrolytes in a way different from nonion-exchange membranes. Because of the presence of ionogenic groups fixed to the resin matrix-negative groups like $-SO_3^-$, $-COO^-$ et seq., in case of cation exchangers, and positive groups like $-NH_3^+$, $>NH_2^+$, $>N^+-$ et seq. in case of anion exchangers- the membrane excludes the co-ions (ions of same sign - or + charge as the fixed groups) by electrostatic repulsion. The amount of exclusion is governed by the concentration of the external electrolyte. At very low concentration, the amount of co-ion in the membrane is almost zero, but as the external concentration is increased, the co-ion content of the membrane phase increases. There will be less number of co-ions than counterions (ions of opposite charge to fixed groups) by an amount equal to the number of fixed groups; whereas in the nonion-exchange membrane, the distinction between co-ion and counterion being non existent because of the absence of fixed groups there will be equal numbers of positive and negative ions. In the case of non electrolytes, both types of membranes will behave alike.

The theoretical aspect of membrane phenomenon was first of all considered by Donnan (15) some fifty years back. In a series of papers published, the distribution of ions across a copper ferrocyanide membrane (semi-permeable in character) was discussed from different angles. He also for the first time pointed towards the importance of distribution of ions in biological studies and showed that if two solutions are separated by a membrane which is impermeable to atleast one of the ionic species (usually a colloidal component) present in one of the solutions, an unequal distribution for the other ionic species to which the membrane is permeable results. At equilibrium the two solutions show a difference in pressure and if the two calomel electrodes are connected to the solution by means of salt bridges, an E.M.F. is found to be present. Verification of Donnan's theory was made by studying the distribution of sodium ferrocyanide and potassium ferrocyanide across copper ferrocyanide and amyl alcohol membranes. Analysis of the two solutions in the two compartments proved that the equation

$(Na)_I x (K)_I = (Na)_{II} \times (K)_{II}$ holds good.

Donnan's theory has found many applications in biological processes. Loeb (16) and collaborators investigated the effects of acids, alkalis, and salt, on the osmotic pressure and membrane potential of amphoteric proteins. Loeb has shown that the simple theory of membrane equilibria was capable of accounting fairly quantitatively many of his experimental results. On the basis of his studies on protein ampholytes he was able to show that the diffusion phenomenon with proteins is due to simple chemical reaction and not to the adsorption of ions by colloid aggregates or micelles. Here the simple ionised molecules or the ionic micelles are subjected to the same constraint, namely, inability to diffuse freely through the membrane. This constraint - then imposes a restraint on equal distribution on both sides of the membrane of otherwise freely diffusible ions, thus giving rise to the concentration, osmotic and electrical effects with which the theory deals.

Proctor (17) and collaborators had used the Donnan's theory to account for the effects of acids and salts on the swelling of gelatin. The hydrogen ions of the acid react chemically with the gelatin molecule thereby becoming ionised. Although no membrane exists, the necessary constraint is provided by the inability of the gelatin ions to leave the structural network owing to the forces of cohesion which hold it together. A restraint on the free diffusibility of ions thus sets in leading to an unequal distribution of hydrogen ions and anions of the acid between the jelly phase and the surrounding aqueous solution. On the basis of this theory Proctor and Wilson (loc.cit) were able to account quantitatively for the remarkable effects of acids in low concentration in first increasing and then diminishing the swelling of gelatin jelly. The difference of ionic concentration gives rise to excess of osmotic pressure of the jelly accompanied by entrance of water in it and consequently swelling. Loeb (loc.cit) adopted Proctor's theory of the effects of acid in support of his experimental results.

The case of biological membrane, the fundamental unit of transport in human body is much more complicated one. It is the membrane which regulate the transport in the body, elg., the passage of food stuffs of various kinds from the stomach and intestines to the blood, from

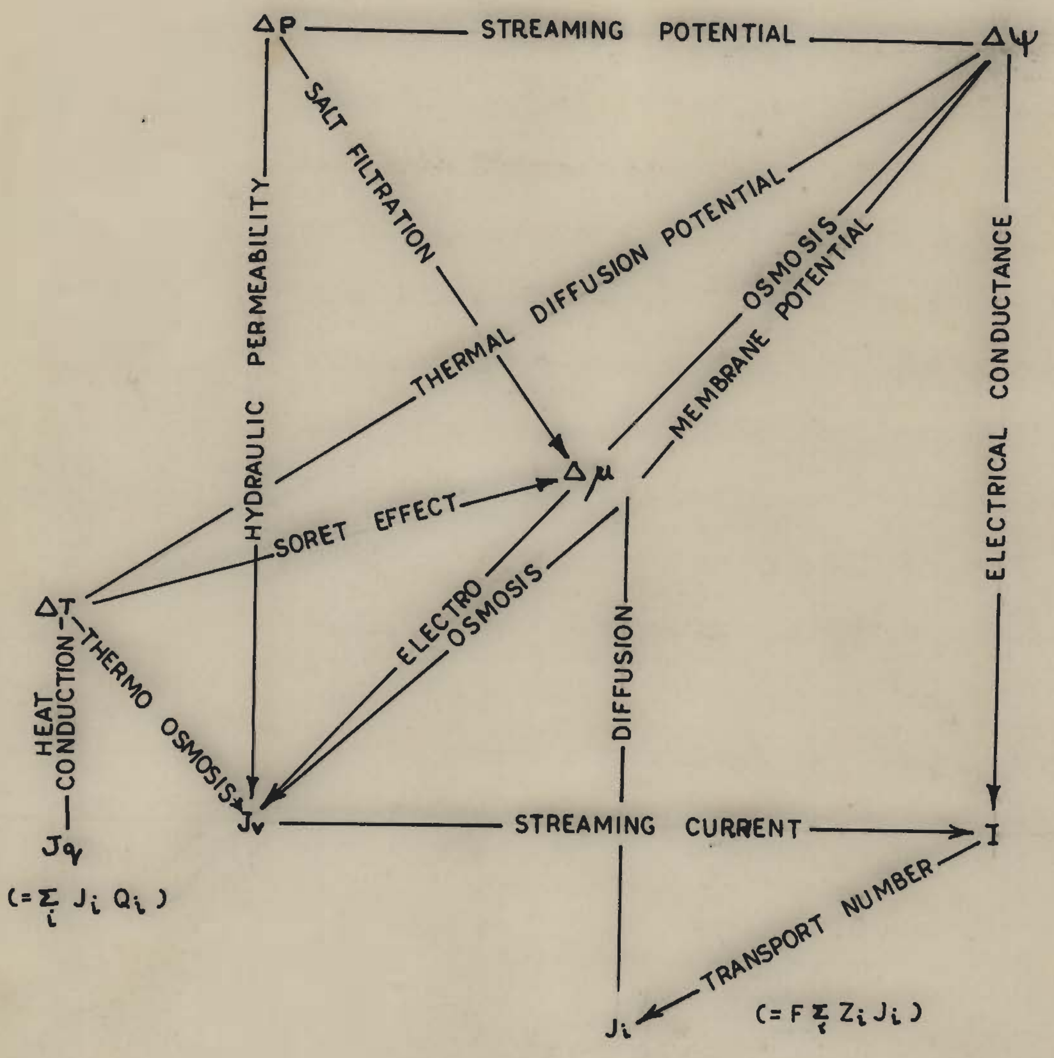

FIG.1. SCHEME OF DIFFERENT TRANSPORT PHENOMENA ACROSS MEMBRANE

the blood to extra cellular fluids and the tissue cells. The cell membranes are responsible for the transport forces. Polarization microscopes have explained the well oriented structures of proteins and lipoids. The electrical activity in the nerve- the nerve signal is as well known an electrical event with frequency modulated signals. The secret of the electrical nerve communication signal is in fact a permeability process and thus a membrane phenomenon. It is a question of ionic transport process. The phenomenon have been most ingeniously characterized, analysed and partly synthesised by Hodgkin, Katz, Keynes and Hauxly.

When a membrane separates two solutions, the number of forces that may normally operate to cause a flow or flux of molecular or ionic species through it are: (a) difference of chemical potential $\Delta\mu$, (b) difference of electric potential $\Delta\psi$, (c) difference of pressure ΔP, and (d) difference of temperature ΔT.

These forces when they operate severally or in combination may generate a number of phenomena and these are indicated in Fig.1 (18, 19).

The current membrane theories may be divided roughly into three groups based on the nature of the flux equation used in the treatment (Schlogl (20)). In the first group fall many of the theories based on the Nernst-Planck flux equations for their refinements. In the second group are included all the theories using the principle of irreversible thermodynamics. In the third group is included the theory which utilizes the concepts of the theory of rate processes. In general, the theories of group one are based on the ideas of classical thermodynamics or quasi-thermodynamics which is restricted to isolated systems. The theories of group two, apart from being more rigorous and realistic, allow a better understanding of transport phenomena in membranes and is useful in dealing with non-isothermal systems. The theories of group three contain parameters which are still unknown for the membrane and hence have restricted applicability.

The relationships based on the three different groups are mathematically represented in the following manner:

(a) Nernst-Plenck Flux equations:

The diffusional flux caused by chemical potential is given by the equation:

$$Ji(d) = - D_i \frac{dc_i}{dx} \qquad (i)$$

where $J_i(d)$ is diffusional flux, D_i is the diffusion coefficient and C_i is concentration.

The flux due to an electrical field is given by the equation:

$$J_i(e) = - D_i \frac{F}{RT} Z_i C_i \frac{d\Psi}{dx} \qquad (ii)$$

where $J_i(e)$ is flux due to electric field, Z_i is the valence, D_i is diffusional coefficient.

and the total flux in an ideal system is given by:

$$J_i = J_i(d) + J_i(e) = - D_i \frac{dc_i}{dx} + Z_i C_i \frac{F}{RT} \frac{d\Psi}{dx}. \qquad (iii)$$

and on introducing the activity coefficient term:

$$J_i = -D_i \frac{dc_i}{dx} + Z_i C_i \frac{d\psi}{dx} + C_i \frac{d\ln\gamma_i}{dx} \qquad \text{(iv)}$$

The flux of the counter ions due to convection of pore liquid may be given as:

$$J_i(c)\ \bar{C}_i\ V^* \qquad \text{(v)}$$

where $\bar{C}_i$ is the concentration of counterions in the membrane phase (barred terms refer always to membrane phase) and V^* is the velocity of movement of the center of gravity of the pore liquid. V

While the convection velocity is given by

$$V^* = \frac{wXF}{\rho_o v_o} \frac{d\psi}{dx} = w\ \bar{u}_o \frac{d\psi}{dx} \qquad \text{(vi)}$$

where is the specific flow resistance of the membrane, v_o is the fractional pore volume, X is the concentration of fixed charge and w is the sign of the fixed charge (-for negatively charged membrane and + for positively charged membrane) and $\bar{u}_o = \frac{XF}{\rho_o v_o}$ is the 'mobility' of pore liquid.

Equation (vi) when added to equation (iii) would give the total flux J_i.

(b) <u>Thermodynamics of Irreversible Processes:</u>

A membrane acting as a restrictive barrier to the flow of various chemical species between two subsystems (′) and (″) contacting the two membrane faces is considered to maintain differences in concentration ($\Delta\mu$), temperature (ΔT), pressure (ΔP) and electric potential ($\Delta\psi$) across it. The subsystems are kept so well stirred as to obtain uniform values of these variables throughout each subsystem and to have the whole difference occurring only across the membrane. The fundamental theorem of the thermodynamics of irreversible process is (21, 22) that the forces and the fluxes are so chosen as to conform to the equation:

$$T = \sum_i J_i X_i \qquad \text{(i)}$$

where X_i ($i=1, 2, 3 \ldots n$) incorporate , T, P, and J_i ($i=1, 2, 3 \ldots n$) the fluxes. The phenomenological cofficient L_{ik} ($i,k=1,2\ldots n$) in the equations:

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \qquad \text{(ii)}$$

satisfy the Onsagar reciprocal relations $L_{ik} = L_{ki}$ (iii)

A recent review of the existing data by Miller (23) gives the experimental justification for regarding the Onsagar law as a law of nature (24). The description of transport processes in a system of n components therefore requires the measurement of only $n\,(n+1)/2$ coefficients and not all n^2 coefficients. $\Theta = \frac{d_i s}{dt}$ is the rate of entropy production due to irreversible processes within the system. The evaluation of Θ requires the use of the law of conservation of mass and energy and Gibb's relationship for the second law of thermodynamics.

Based on the above considerations the final general expression for the material fluxes is given by:

$$J_i = \sum_k L_{ik} \left(-\bar{V}_k dP - RT\, d\ln a_k - Z_k F d\psi - Q_k^* \frac{dT}{T}\right)$$

where J_i is total flux, L_{ik} phenomenological coefficients L_{ik} ($i,k = 1,2..n$), $\bar{V}_k$ valence of sign of species k, Q_k^* is heat transport, Z_k is the valence sign including sign of species k.

Moreover the observable electrical parameters may be written in terms of the phenomenological coefficients (23, 24, 25, 26).

(1) Current density $I = F \sum_i Z_i J_i$ and substituting for J_i from equation (iii).

$$I = \sum_i \sum_k Z_i F L_{ik} (-\bar{V}_k \, dP - RTd \ln a_k - Q_k^* \, d\ln T)$$
$$- \sum_i \sum_k Z_i Z_k L_{ik} F^2 d\psi \quad \text{(iv)}$$

(2) Electrical conductance

$$\bar{k} = -(I/d\psi) \; (dP=0,\ dT=0,\ d \ln a_k=0)$$
$$\bar{k} = \sum_i \sum_k Z_i Z_k F^2 L_{ik} \quad \text{(v)}$$

where $\bar{k}$ is Electrical conductance, I is current density.

(3) Transport number

$$\bar{t}_k = (F Z_k J_k/I) \; (dP = 0,\ dT = 0,\ d \ln a_k = 0)$$
$$\bar{t}_k = \frac{F \sum_i Z_i Z_k F L_{ik} d}{\sum_i \sum_k Z_i Z_k L_{ik} F^2 d} = \frac{F^2 \sum_i Z_k Z_i L_{ik}}{\bar{k}} \quad \text{(vi)}$$

where $\bar{t}_k$ is transport number, J_k is matter flux.

Staverman (26) has defined a useful quantity the reduced electrical transport number $\bar{t}_k{}^r$ which has also been called mass transport number (27).

Thus $\bar{t}_k{}^r = (\bar{t}_k/Z_k) = F^2 \sum_i Z_i L_{ik}/\bar{k}$ (vii)

The flow of uncharged molecules e.g. water, may be expressed in terms of their reduced transport number where $\sum_k Z_k \bar{t}_k{}^r = 1$. Rearranging equation (iv) for d and substituting from equation (v) and (vii), the potential gradient at any point in the membrane may be obtained. Thus $d\psi = -(I/\bar{k}) - (1/F) \sum_k \bar{t}_k{}^r (\bar{V}_k dP + RTd \ln a_k + Q^* \, d \ln T_k)$ (viii)

The first term is given by the purely electrical part and the second term is due to the chemical part .

Various special cases follow directly from equation (viii).

(a) Isothermal diffusion potential is obtained at uniform temperature and pressure:

$$d\psi = -\frac{RT}{F} \sum_k \bar{t}_k{}^r \, d \ln a_k \qquad \text{(ix)}$$

This has been derived many years ago by Nernst using Thomson's method and more recently by Staverman (26) and Kirkwood (27).

(b) Streaming potential is obtained at uniform temperature and chemical potential:

$$d\psi = -\frac{1}{F} \sum_k \bar{t}_k{}^r \, \bar{V}_k \, dP \qquad \text{(x)}$$

(c) Thermal diffusion potential is obtained at uniform pressure and activity,

$$d\psi = -\frac{1}{F} \sum_k \bar{t}_k{}^r \, Q_k^* \, d \ln T \qquad \text{(xi)}$$

In the considerations given above nothing has been said explicitly about the reference frame work to which the fluxes are referred. It is implied that the reference frame was the membrane (28). Some choices about the frame of reference are possible. For example the solvent in the membrane phase may be considered stationary and therefore taken as one of the frames of reference. Hills, Jacobs and Lakshiminaryanaiah (24) have given a treatment choosing for reference frame work, the plane normal to the direction of fluxes and passing through the center of mass of the system.

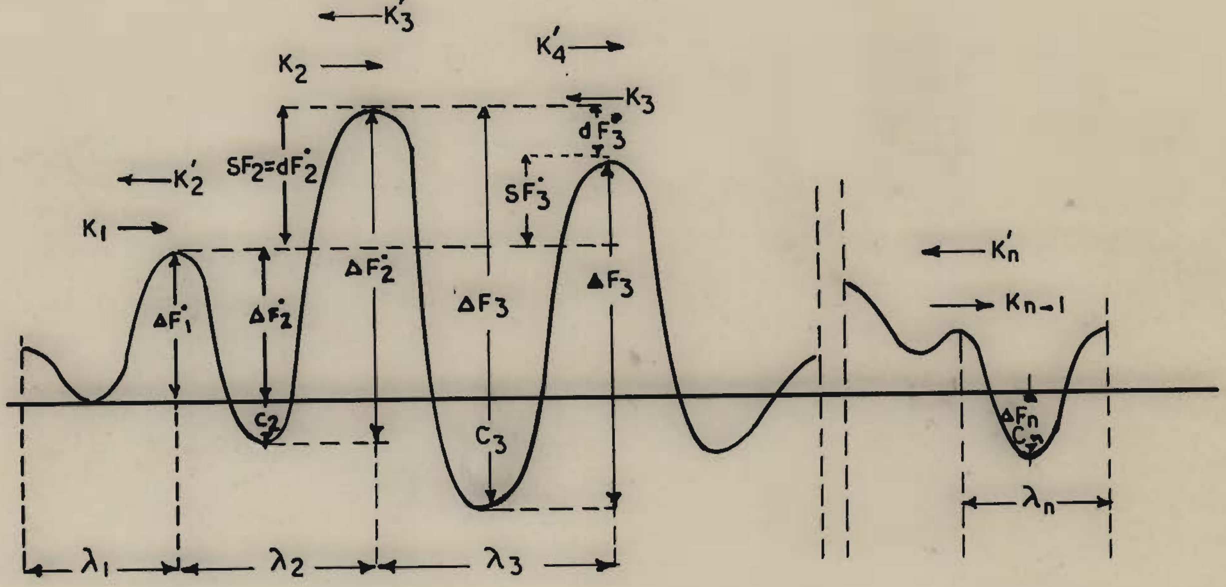

FIG. 2. POTENTIAL ENERGY DIAGRAM REPRESENTING PERMEATION IN A MEMBRANE

The values of the phenomenological coefficients in this type of treatment depend on the reference framework chosen. This being very unsatisfactory attempts have been made to translate these coefficients into parameters (frictional coefficients) which are independent of the motion of the reference frame and thus give a clearer picture of the membrane processes. The classical work of Lord Rayleigh (29) and the investigations of Klemn (30) and Laity (31) have laid the foundations for the successful applications of these principles to membrane processes (32, 33, 34) pioneered by Spiegler (35) and illustrated by Spiegler (35) and Meares (34) and expounded by Kedem and Katchalsky (36, 37, 38, 39, 40, 41, 42) taking different membrane systems into consideration.

(c) Theory of Absolute Reaction Rates:

A membrane is considered as a series of potential energy barriers existing one behind the other, across which material must pass to cross membrane (43, 44, 45, 46). To do so, the permeating species must have certain minimum energy. A typical potential energy diagram is shown in Fig.2 (47), where λ indicates the mean jump distance. If c_1 is the initial concentration of the substance (molecules per c.c.) the velocity of forward diffusion is

$$q_f = K_1\, C_1\, \lambda_1 \text{ (molecules/cm}^2\text{)} \qquad \text{(xii)}$$

where K_1 is the specific velocity for crossing the barrier 1 and $k_1 = \dot{k}\,\frac{kT}{h}\,e^{-\Delta \dot{F}_1/RT}$ (xiii) where $\dot{k}$ is the transmission coefficient for which a value of unity is assumed. K is the Boltzmann constant, h is the Planck constant and $\Delta \dot{F}_1$ is the free energy of activation necessary for crossing the barrier 1.

Similarly the velocity of the backward diffusion over the barrier 1 is $q_b = K_2' C_2 \lambda_2$ (xiv)

The net rate of diffusion or flux is

$$J = K_1 C_1 \lambda_1 - K_2' C_2 \lambda_2 \qquad \text{(xv)}$$

In the steady state

The diffusional flux is the same over every barrier

$J = K_2 C_2 \lambda_2 - K_3' C_3 \lambda_3$ for second barrier

$J = K_3 C_3 \lambda_3 - K_4' C_4 \lambda_4$ for third barrier

$J = K_{n-1} C_{n-1} \lambda_{n-1} - K_n' C_n \lambda_n$ for (n-1)

equations give upon rearrangement

$$J = \frac{K_1 C_1 \lambda_1 - \dfrac{K_2' \cdot K_3' \cdots\cdots K_{n-1}'}{K_2 \cdot K_3 \cdots\cdots K_{n-1}} K_n' C_n \lambda_n}{1 + \dfrac{K_2'}{K_2} + \dfrac{K_2' \cdot K_3'}{K_2 \cdot K_3} + \cdots\cdots + \dfrac{K_2' \cdots\cdots K_{n-1}'}{K_2 \cdots\cdots K_{n-1}}} \qquad \text{(xvi)}$$

But according to equation (xiii)

$$\frac{K_2'}{K_2} = e^{(\Delta \dot{F}_2 - \Delta \dot{F}_2')/RT} = e^{\delta F_2^*/RT} \qquad \text{(xvii)}$$

where δF_2^* is the difference in energy barriers 1 and 2

$$\frac{K_2' K_3'}{K_2 K_3} = e^{(\Delta F_i - \Delta \dot{F}_2') + (\Delta \dot{F}_3 - \Delta \dot{F}_3')/RT} = e^{\delta F_3^*/RT} \qquad \text{(xviii)}$$

where δF_3^* is the algebric sum of dF_2 and dF_3 and is the difference in height of barriers 1 and 3. Similarly

$$\frac{K_2' K_3' --- K_{n-1}'}{K_2 K_3 --- K_{n-1}} = e^{\delta F_{n-1}^*/RT} \qquad (xix)$$

and

$$\frac{K_2' K_3' --- K_{n-1}' K_n'}{K_1 K_2 K_3 --- K_{n-1}} = e^{(\Delta F_1 + \delta F_{n-1}^* - \Delta F_n')/RT} \qquad (xx)$$

But $\Delta F_1 + \delta F_{n-1}^* - \Delta F_n' = \Delta F_n$, is the difference in free energy between position 1 and n. Substituting equations (xviii)-(xx) into equation (xvi)

$$J = \frac{\lambda_1 K_1 \left(c_1 - \frac{\lambda_n}{\lambda_1} e^{\Delta F_n/RT} c_n \right)}{1 + e^{\delta F_2^*/RT} + e^{\delta F_3^*/RT} + \cdots\cdots + e^{\delta F_{n-1}^*/RT}} \qquad (xxi)$$

A number of special cases have been considered by Parlin and Eyring (48). In all these considerations considerable skill to manipulate equation (xxi) is called for. An analogous type of kinetic approach to membrane processes has been presented by Laidler and Schuler (49) and applied to experimental Osmotic results by Schuler, Dames and Laidler (50). Similar ideas prevail in the theory of membrane potential discussed by Nagasawa and Kobatake (51).

MEMBRANE ELECTRODES

The potentiometric determination of activities of the alkali and alkaline earth metal ions in solution by means of conventional electrodes is beset with experimental difficulties and so far has been successful for practical purposes only with more concentrated solutions. The potentiometric determination of the activities of anions is at present restricted to a limited number of ionic species, because of the lack of suitable electrodes; the activity of many, even some of the most common anions cannot be determined electrometrically. Many of these difficulties can be overcome readily by the use of permselective membranes as "membrane electrodes". The term "membrane electrode" is applied to a system in which a selective membrane separates two electrolyte solutions and at which an electrical potential difference is established characteristic of the difference in activity of a common ion constituent on either side. This membrane potential responds in a reproducible manner to changes in the activity difference of one kind of ion so that if one of the two solutions is of fixed and known composition, then the observed membrane potential is indicative of the composition of the other. For various membranes used under suitably restricted conditions this result can be acheived for almost any ionic species.

The potential usefulness of membrane electrodes was first recognized by Haber (52) after Nernst and

. Riesenfeld (53) had shown that any interphase (membrane) which in a concentration cell selectively allows the reversible transfer of only a single ionic species from the one solution to the other gives rise to a potential and acts electromotively in a manner strictly analogous to a conventional reversible electrode for this ion.

The experimental work on the use of glass membrane electrodes for the determination of hydrogen ions is well known (54, 55, 56). The attempts of Horowitz (57) and Schiller (58) to use glasses of various compositions as membrane electrodes for several cations did not meet with success.

Marshall and Collaborators (59, 60) and later Wyllie (61) have prepared membranes from various zeolitic minerals and have shown that they can serve as reversible electrodes for alkali and alkaline earth cations. These membranes have certain practical drawbacks: they possess high ohmic resistances (1-10 megohms), require several hours or days to attain equilibrium and are stable for limited periods of time only.

Membranes prepared from clays or from natural or synthetic polymer materials and much of their development has been carried out by colloid chemists, polymer chemists and biochemists. The analytical uses of membranes, e.g., as membrane electrodes represents only one of the several aims of this development work and certainly the principal goal has been the imitation and understanding of the controlled selectivity of the natural membranes of biological systems.

The practical application of membrane electrodes to analytical purposes requires not only directions for the preparation and use of the membranes but very practically an appreciation of the theory of membrane potentials. A knowledge of factors governing the selectivities and degree of non-ideality of membranes is essential both the development and use of membrane electrodes and to the interpretation of the emf values of cells containing them.

The development of membrane electrodes has followed the steady refinement of the measurement of membrane potentials. The theory of membrane potentials was developed by Donnan (62), by Horovitz (63, 64) by Teorell (65, 66) by Meyer and Sievers (67), by Tendeloo (68) by Marshall (69) and by Scatchard (70)-the last two authors dealing especially with membrane electrodes.

The most significant advance was the practical realization of the systems idealized in these theoretical treatments. Michaelis (71, 72) was the first to describe, the successful application of membranes of high ionic selectivity but the two most important developments were due to Marshall (69, 73, 79) who was responsible for developing zeolite and clay membranes, and especially to Sollner and Gregor (80-87) whose collodian-based membranes remain the simplest and often the most suitable membrane electrodes for the potentiometric determination of ionic activities.

The selectivity of ion-exchange resins towards different ionic species is governed by the same factors which control the ionic permeability of membranes and several research workers, notably Kressman (88, 89) and Wyllie and Patnode (90) showed how membranes of ion exchange materials also functioned reproducibly and selectively as membrane electrodes over a wide range of concentrations of individual ionic species. This type of membrane can be prepared in two ways (i) as a homogenous sheet or film of porous cross-linked polymer material, the pores of which are charged with fixed carboxylic or sulfonic acid groups (cation-selective membranes) or aminogroups in the-onium form (anion selective membranes) (88, 89, 91-103) and which are accessible to all but the largest ions, or (ii) as a heterogenous membrane which can be made by impregnating a porous polymer material with adsorbable polyelectrolyte (104-106) or more usually by incorporating particles or beads of ion exchange resin into an inert plastic matrix by molding the beads and plastic binder in a suitable process (90, 106, 107). This last type of membrane is tough and flexible and is available in large sheets (e.g. of several square feet) from the manufacturers of ion exchange materials.

THE THEORY OF MEMBRANE ELECTRODES

The simplest concept of an ion selective membrane is that due to Teorell (65, 66, 107-109) and to Meyer and Sievers (110). The membrane is regarded as a porous diapharam throughout which there is an even distribution, along the pore walls of one particular species of fixed ionized or ionizable groups which is permeated by the solution in which it is immersed. Assuming that the pH of the imbibed solution is such that all of the groups are ionized, their concentration ($\bar{X}$ gm equivalent per thousand gm water) is virtually constant being subject only to the relative minor changes in the degree of swelling of the membrane. This concentration is the most important characteristic of the membrane and, provided that there are no large or uncharged pores through which electrolyte can "leak" it will determine the efficiency or selectivity of the membrane.

The unequal distribution of diffusible ions at the interface is accompanied by a potential difference, the Donnan potential , given by the general equation for counter ions of any valency z_i (including sign).

$$\pi = \frac{RT}{z_i F} \ln \frac{a_i}{\bar{a}_i} \qquad \text{(i)}$$

where a_i is the mean molal activity of electrolyte and $\bar{a}_i$ is the mean molal activity in the membrane phase.

This phase boundary potential is indeterminate but if the membrane separates two solutions of different composition there will be two unequal Donnan potential give rise to a potential (volts) difference across the membrane which is approximately atleast easily measurable. The sum of the Donnan potential differences is given by

$$\pi_I + \pi_{II} = \frac{RT}{z_i F} \ln \left[\left(\frac{a_i}{\bar{a}_i}\right)_I \Big/ \left(\frac{a_i}{\bar{a}_i}\right)_{II} \right] \qquad \text{(ii)}$$

since $a_i = m_i \bar{\gamma}_i$ and m_i is given by

$$\bar{m}_i = \frac{\bar{X}}{2} + \left\{ \frac{\bar{X}^2}{4} + \frac{m_\pm^2 \gamma_\pm^2}{\bar{\gamma}_\pm^2} \right\}^{\frac{1}{2}} \qquad \text{(iii)}$$

where X = concentration of fixed charges

$m_\pm \gamma_\pm$ = mean molal activity

$\gamma_\pm$ = mean molal activity coefficient inside the membrane phase and

The sum of equations (ii) and (iii) for (1:1) electrolytes is

$$\pi_I + \pi_{II} = \frac{RT}{z_i F} \cdot \ln \frac{(a_i)_I \left[\bar{X}_{II} (\bar{\gamma}_i)_{II}^2 + 4 (a_\pm)^2 (\bar{\gamma}_i / \bar{\gamma}_j)_{II} \right]^{\frac{1}{2}} + \bar{X}_{II} (\bar{\gamma}_i)_{II}}{(a_i)_{II} \left[\bar{X}_I (\bar{\gamma}_i)_I^2 + 4 (a_\pm)^2 (\bar{\gamma}_i / \bar{\gamma}_j)_I \right]^{\frac{1}{2}} + \bar{X}_I (\bar{\gamma}_i)_I} \quad \ldots \text{(iv)}$$

which it may be noted, takes into account the separate values of $\bar{X}$, $\bar{\gamma}_i$ and $\bar{\gamma}_j$ approaches to each interface.

DIFFUSION POTENTIAL

Total potential difference across the membrane includes a diffusion potential arising from the spontaneous transfer of dissociable entities across it from one solution to the other. In all the theories of membrane potentials it is equated to that of a "contained liquid junction" i.e.

$$\phi_{diffusion} = -\frac{RT}{F}\int_{I}^{II}\sum\frac{\bar{t}_i}{z_i}\,d\ln\bar{a}_i \qquad \text{(v)}$$

where t_i, t_j etc. are the transport numbers of the diffusible species in the membrane phase. This equation is not integrable unless certain assumptions are made about the appropriate ionic distributions and about single ionic activity coefficients. Planck assumed that the total ionic concentration varied linearly through the diffusion zone and this assumption together with-equation of the relevant activity coefficients to unity, is the usual basis for evaluating membrane diffusion potential. No integration of the flux equations in terms of the activities has yet been given although the difficulties involved have been emphasised by Schlogl and Helfferich (111) and a general integration for ions of different valencies (but again restricted to ideal systems) has been performed by Schlogl (112). The Planck assumption used by Teorell, leads to the expression for diffusion for a single (1:1) electrolyte.

$$\phi_{diffusion} = \frac{RT}{z_iF}\cdot\frac{\bar{u}_i-\bar{u}_j}{\bar{u}_i+\bar{u}_j}\cdot\ln\left[\frac{\bar{u}_i(\bar{m}_i)_I+\bar{u}_j(\bar{m}_j)_I}{\bar{u}_i(\bar{m}_i)_{II}+\bar{u}_j(\bar{m}_j)_{II}}\right] \qquad \text{(vi)}$$

where u_i and u_g are the counter-ion and co-ion mobilities (assumed to be constant) within the membrane phase. The total membrane potential is therefore given by

$$\Delta_E = \Pi_I + \Pi_{II} + \phi .\text{diffusion}$$

$$\Delta E = \frac{RT}{z_i F} \ln \frac{(a_i)_I}{(a_i)_{II}} . \left[\frac{\bar{X}_{II} (\bar{\nu}_i)_{II} \{ 1 + (1 + \xi^2_{II})^{1/2} \}}{\bar{X}_I (\bar{\nu}_i)_I \{ 1 + (1 + \xi^2_I)^{1/2} \}} \right.$$

$$\left. + \frac{\bar{u} . R . T}{z_i F} . \ln \left[\frac{\bar{X}_{II} \{ \bar{u} + (1 + \xi^2_{II})^{1/2} \}}{\bar{X}_I \{ \bar{u} + (1 + \xi^2_I)^{1/2} \}} \right] \right. \qquad \text{(vii)}$$

where $\bar{u} = \frac{\bar{u}_i - \bar{u}_j}{\bar{u}_i + \bar{u}_j}$ and $\xi = 2a_\pm / \bar{X} \bar{\nu}_\pm$

This equation for membrane potential is still deficient in two respects. Firstly it takes no account of differential swelling across the membrane, i.e. the effect on $\bar{\nu}_\pm$ of a swelling-pressure gradient. This however is not likely to be a large factor and can be avoided by a suitable design of membrane. This could lead to an appreciable error and although the transport of water can also be minimized by suitable choice of membrane, its effects can seldom be neglected it is considered further below. The equation as it stands can take two extreme forms

(1) When external concentrations are large compared with the fixed ion concentration i.e. $a_\pm \gg \bar{X}$ it reduces to that for a normal diffusion potential

$$E_J = -\frac{RT}{F} \left[\left(\frac{\bar{u}_+}{\bar{u}_+ + \bar{u}_-} \right) \ln \frac{(a_+)_{II}}{(a_+)_I} - \left(\frac{\bar{u}_-}{\bar{u}_+ + \bar{u}_-} \right) \ln \frac{(a_-)_{II}}{(a_-)_I} \right] \qquad \text{(viii)}$$

(2) When $a_{\pm} \ll \bar{X}$ the equation reduces even further to

$$E = -\frac{RT}{z_i F} \ln \frac{(a_i)_{II}}{(a_i)_I} \qquad \text{(ix)}$$

which is true for counter-ions of any valency. The last condition is the one most closely approached in practice. It is equivalent to the total exclusion of the co-ion species when the membrane is perfectly permselective towards the counter ions. Under these conditions, the membrane potential has its maximum value and is frequently designated $\Delta E_{max.}$ It is this equation which is most commonly used to express membrane potentials and to evaluate the results from membrane electrode measurements.

The extent to which equation (ix) can be used to study ionic activities depends of course on the precision required from the measurments.

It is applicable within experimental error to many of the membranes described below in contact with solutions of molality upto 0.05 mole per thousand gm and in two instances upto 1 mole per thousand gm. Above 0.05 m and very often even above 0.01 m many membranes show significant deviations from the ideality expressed by equation (ix) and then a more complete equation e.g. equation (vii) must be used.

A more general method of measuring potentials and one most frequently used employs two standard half cells as reference electrodes e.g.

Saturated calomel electrode	salt bridge	standard solution of counter	membrane	test solution	salt bridge	saturated calomel electrode

Neglecting any asymmetry potential difference between the two liquid junctions the emf of this membrane cell is equal to the volta potential difference across the membrane as described by equation (ix). On either basis the ratio $(a_i)_{II}/(a_i)_I$ is directly obtainable. Further the single ion activity $(a_i)_{II}$ in the test solution can be evaluated in terms of whatever assumption is made in resolving the known $(a_i)_I$ value of the standard solution.

Membranes which present interesting permeability characteristics has been empirically investigated by Malik and Coworkers. The membranes used were mostly metal ferrocyanogen and metal tungstates parchment supported membranes. Ferricyanide membranes of Co, Ni and Ag (113) were found permeable to electrolytes KCl, K_2SO_4 and $K_3Fe(CN)_6$ following the order $KCl > K_2SO_4 > K_3Fe(CN)_6$. This order was reverse of the order of adsorption of these anions on the freshly precipitated compounds. In their earlier studies they employed the isotonic sucrose method of Weiser (114) to measure electrolyte transfer across the membranes. This method was later replaced by a constant flow technique (115-117) and using thorium tungstate membranes, the permeability of a number of electrolytes were measured (118). The order of permeability was $KCl > NaCl > K_2SO_4 > Na_2SO_4 > Na_2WO_4$. The membranes were also used after a pretreatment with either Na_2WO_4 or thorium nitrate. Pretreatment with the former did not show any change, whereas with the latter, the rates of diffusion of the electrolytes increased although the order of permeability remained the same. The increase was attributed to the peptising action of thorium nitrate on the thorium tungstate gel membrane. The order of electrolyte adsorption was again in the reverse order. These studies were extended to cobalt and manganese ferrocyanide membranes (119) and to chromic ferro and ferricyanide membranes (120). Later studies were also made on cadmium, silver ferro and ferricyanide membranes.

Membrane potentials arising across these membranes were also measured and related to permeability parameters by a Freundlich adsorption type equation $E = a\ P^{1/n}$ where E is the membrane potential, P is the permeability and a and n are constants characterising the membrane and were evaluated graphically.

Statement of the problem

The investigations described in the thesis deal with the following aspects of the problem:

(i) Preparation of parchment supported and unsupported membranes of ferric oxide, alumina, silica, ferric silicate, aluminium silicate.

(ii) A review of the methods employed for measuring permeability of electrolytes through membranes with special reference to the advantages and disadvantages of Hartung's constant flow method.

(iii) Permeability of metal hydrous oxide membranes to various electrolytes employing both treated (Fe^{+++}, Al^{+++}, soap solutions) and untreated membranes.

(iv) Studies on the permeability of silica and metal silicate membranes (both treated and untreated) to various electrolytes:

(v) Membranes electrodes, their preparation and performance including measurements of activity of anions, coagulation phenomenon etc.

Appendix:

The appendix deals with the studies on aluminium ferrocyanide sol, incorporating the following aspects (i) preparation of aluminium ferrocyanide and verification of Bhattacharya's equation (ii) viscosity of the sol with progressive dialysis (iii) behaviour of parchment supported aluminium ferrocyanide membrane.

CHAPTER I

PREPARATION OF MEMBRANES

Artificial membranes, apart from their importance as models for physiological studies, have found use in many fields connected with the study of colloidal phenomenon. More recently its use has been successfully extended to industry and technology incorporating chemical operations like using demineria lization by electrolysis, salt filtration etc. employing suitable membranes.

Inorganic gel forming systems which may provide useful membrane material for fundamental studies, have not been fully exploited and except copper ferro-and ferricyanides other compounds have not been seriously considered for investigation.

Classification of Membranes

Unlike the classification based usually on either the nature of the product, i.e., coherent gel or otherwise, or the nature of the chemical reaction, i.e., addition or condensation reaction producing the product, a different mode of classification based on this ultimate use has been followed.

The efforts of various workers have been directed towards (i) preparing or manufacturing membranes, mostly ion exchangers, with good chemical and mechanical stability and favourable electrical performance, suitable for fundamental transport studies and for applications in some industrial operations like treatment of brackish waters, saline water conversion etc. (ii) building suitable model systems to mimic the properties of natural membranes and (iii) preparing composite membranes containing cationic and anionic groups in suitable arrangement to demonstrate and to study the physico-chemical phenomenon associated with rectification of alternating current and other special membranes for specific purposes.

A large amount of work is primarily concerned with the preparation of operationally useful membranes and so a variety of methods have been used to prepare them. A rational classification of these many procedures is difficult to present. They are, therefore, treated under the following heads:

(a) Homogeneous membranes

(b) Heterogeneous membranes

which are subdivided into (i) non reinforced membranes (ii) woven fabric-backed membranes (iii) membranes formed by chemical treatment (iv) membranes formed by mechanical treatment of membrane forming monomers or polymers and (v) membranes formed by photochemical treatment.

Homogeneous membranes:

In this respect polymethacrylic acid (PMA), phenolsulfonic acid (PSA) and polystyrene sulfonic acid (PSA) and polystyrene sulphonated sulfonic acid (PSSA) have proved very useful (1-7). Loeb and Sourirajan (8-10) described a procedure for the preparation of cellulose acetate membrane suitable for demineralization saline waters. Cellulose acetate was dissolved in acetone and made up with water to which magnesium perchlorate had been added. The materials were taken in the proportion 22.2: 66.7: 10: 1.1. Uniformity of thickness was obtained by passing an inclined knife across the top of the plate. Solvent was allowed to evaporate.

Harper (11) has prepared ethyl cellulose membrane by spreading a solution of it in chloroform and drying.

Oil films also constitute the same class of artificial membranes, and as models for biological membranes their permeability behaviour has been studied by Overton, Osterhout and Others (12). The wide variety of 'oils' used are usually classed as 'neutral' (e.g. benzene, long-chain paraffins such as higher alcohal like amyl alcohal or octyl, esters such as octyl acetate etc.) 'acid' (e.g. phenols, oleic acid) or 'basic' (e.g. aniline, long-chain amines).

Heterogeneous Membranes:

(i) Non-reinforced membranes:

These are prepared by employing suitable casting techniques for solutions of membrane forming substances. Membranes may be cast on metal, glass or mercury surface.

A membrane was prepared by drying at 70° a solution of polyethylenimine (1000 gms) and polyvinyl alcohal (1 gm) in hot water (15 gms) poured on a glass plate. It was converted into an anion-exchange membrane

A

(12) by drying and acetalizing in bath containing H_2SO_4, Na_2SO_4 and HCHO at 70-80°. Membranes suitable for dialysis have been made from block copolymers based on polyoxyethylene glycol and polyethylene terphthalate (13).

(ii) Woven-Fabric-Backed membranes:

The steps involved in the preparation of these membranes are (a) solubilization of monomers in suitable solvents or preparation of partially polymerized gels (b) impregnation of cloth with the solution of the monomer or partially polymerized gel (c) curing to complete polymerization with or without pressure and (d) introduction of ionogenic groups if necessary by conventional procedures like sulfonation or chloromethylation followed by amination.

PVC or polyvinylidene chloride cloth impregnated with resins from anthranilic or salicylic acid and resorcinol and cured in a moist atmosphere showed selectivity to Fe, Co, Ni, Cu and Zn (14).

Anion-exchange membrane suitable for physicochemical research were prepared (15) using polyacrylonitrile fabric supports.

(iii) Membranes formed by chemical Treatment:

A parchment film was impregnated with a benzene solution of polymer from styrene, ethylvinylbenzene and an alkali chloride. It was heated at 60° and immersed in benzenesulfonic acid to form a cation exchanger (16). Richards and white (17) have prepared cation exchange membranes from paper and acrylic acid.

Membranes from inorganic precipitates and gels have also been prepared. Weiser prepared copper ferro-and ferricyanide membranes (parchment supported). Malik and Ali (18) have prepared thorium tungstate and molybdate membranes by depositing thorium tungstate and molybdate respectively in pores of a parchment thimble. Malik and Coworkers (19, 20) have also prepared many metal ferrocyanide and ferricyanide membranes like those of cobalt, nickel, chromium, manganese, cadmium and silver.

(iv) Membranes formed by Mechanical treatment:

The simple principle used to prepare these membranes is to bind a polyelectrolyte or a conventional ion exchanger at ordinary or at elevated temperature to a thermoplastic polymer by application of mechanical pressure or to bind two polymers together by mechanical pressure and later to introduce ionogenic groups by following the conventional procedure.

Amberlite IR-120 (powdered) was moulded with a copolymer of vinyl acetate and vinyl chloride and triphenyl phosphate (plasticizer). A roll surface temperature of 130°-150°C was used (21).

A 0.7 mm thick membrane was made by simply pressing at 130°C (200 psi) cross-linked polystyrene resin (quaternary ammonium groups) with polyethylene (22).

Ion exchange membranes have been prepared that are primarily inorganic in nature. The cation exchangers are based on zirconium phosphate as the active material whereas the anion exchangers are based on hydrous thorium oxide. Each type of membrane contains a small quantity of a very high temperature stable organic polymer such as Teflon, Kynar, or polyvinylbutyrol as a binding agent. The active material and the binder are made up into a slurry and cast into membranes form on a glass or Teflon plate using a doctor blade.

Similarly other inorganic membranes have been prepared for example by hot pressing ammonium molybdophosphate with polyethylene powder (23).

Since 1940 much time and effort have been devoted by Marshall and his associates (24, 25, 26) to the investigation of clay membranes. The reason for this lay in the fact that it seemed possible to use them as membrane electrodes. The preparation of clay films by Hauser and Le Beau prompted an examination of their electrochemical properties. Later Mitra (27), Bose (28), Adhikari (29) prepared a number of membranes made from clays.

The membranes used by these authors, were in most cases, made by careful evaporation of supercentrifuged bentonite suspensions followed by controlled heat treatments. Mitra and Bose (loc. cit) had investigated the suitability of a number of other clays, both in their different cationic forms and oxide free states as membrane electrode material.

Wyllie and Patnode (30) used a number of resins and clayey materials for preparation of membranes by the technique of moulding. In some ways they demonstrated the superiority of these membranes over those of Marshall. Such moulded resin membranes had been used by Sinha, Bose (31) and others for the measurment of cationic activities.

Very recently Malik and Singhal (32) had prepared bentonite membranes by the method recommended by Wyllie, Patnode and Sinha (loc. cit) for the preparation of resin membranes. The optimum conditions, viz., the fitness of the clay and bonding powders, ratio of mixing, membrane thickness and the temperature and pressure of moulding were found by trial and error after performing a large number of experiments. The following procedure was finally employed for the preparation of these membranes.

A 200 mesh powder of polystrene was obtained by sieving. It was mixed with a 200 mesh powder of hydrogen bentonite in equal preportion by weight (0.25 gm of each). The mixture was introduced in the electrically heated steel mould of the Apex mount press. When the temperature had risen to 130°C, the heating was stopped and the mixture subjected to a pressure of 3500 lb/sq. in. This pressure was maintained till the mould had cooled down to about 100°C. The pressure was then released, the mould allowed to cool and the moulded disc or membrane removed from the press.

Membranes formed by Photochemical treatment:

Powerful ionizing radiations have been used in this method to bring about the polymerization of monomers incorporated into various materials. In this work polyethylene films have been used by a number of workers. The film was soaked in styrene and treated with γ-rays from Co^{60} (33-39) to form the graft copolymer which was later sulfonated or aminated to form ion selective membrane.

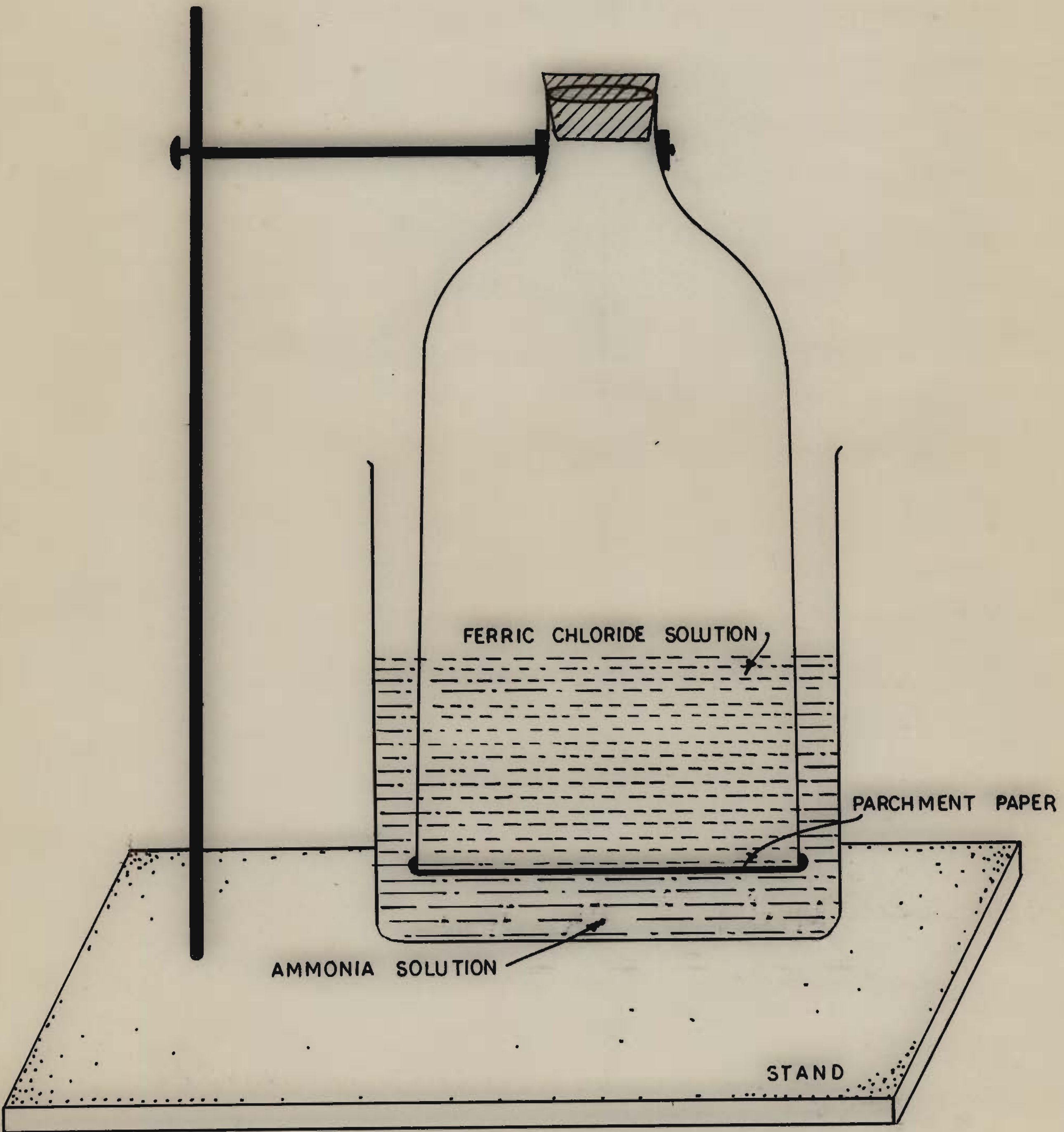

FIG. 3 ASSEMBLY FOR THE PREPARATION OF PARCHMENT SUPPORTED MEMBRANES

Preparation of parchment supported and unsupported ferric oxide, alumina, silica, ferric silicate and aluminium silicate membranes:

(i) Parchment supported ferric oxide membrane

Ferric oxide membrane was prepared by impregnating the parchment paper with iron oxide gel. The paper was first soaked in distilled water and then tied to open glass vessel (cylinder). 25 ml of 0.1M ferric chloride solution was filled in it and then it was suspended in a beaker containing 50 ml of 20 percent ammonia solution for 24 hours. The solutions were then interchanged, ammonia being kept inside and ferric chloride solution outside the vessel(Fig.3). The process was repeated several times until a fine deposit of iron oxide gel(40) was obtained on the parchment paper(Fig.4). The membrane, dark brown in colour, was washed repeatedly with double distilled water for the complete removal of absorbed electrolyte. It was then examined under a microscope for any deformation or crack.

(ii) Ferric oxide unsupported membrane:

Ferric oxide membrane without support was prepared as follows:

Iron oxide gel (40) was prepared by mixing 0.1M ferric chloride (A.R. Grade) solution with 20 percent ammonia solution. It was thoroughly washed with double distilled water for the complete removal of adsorbed electrolyte and the gel dark brown in colour was dried in oven at 110°C for 8 hours. 1.00 gm of fine powder of iron oxide gel was pressed by a compression machine (Fig.5) in the form of a circular disc of diameter 3 cm. and 0.12 mm thickness. The pressure applied was

3000 lb/sq. It was then examined under a microscope for any deformation or crack.

(iii) Parchment supported alumina membrane:

Alumina membrane was prepared by impregnating parchment paper with the gel. The paper was first soaked in distilled water, and then tied carefully on open glass vessel (cylinder) aluminium sulphate solution (10 percent) was filled inside it. It was then suspended in a beaker containing ammonia solution (50 ml, 50 percent) for 24 hours. It was then taken out and washed repeatedly with distilled water to remove the adsorbed electrolytes. The solutions of aluminium sulfate and ammonia were then interchanged, aluminium sulfate outside and ammonia inside.

The process was repeated several times, until a very fine deposit of alumina gel was obtained on the parchment paper (Fig. 4). The membrane thus obtained was white in colour. The membrane was seen under microscope. It had a fine deposition throughout the whole surface and there was no crack or deformation on it.

(iv) Alumina unsupported membrane:

Alumina gel was prepared as follows (41):

Aluminium sulfate (10 percent) was mixed with strong ammonium hydroxide (50 ml) while boiling. The precipitate was washed rapidly with boiling water. The mass was stirred up with 20 ml of a 10 percent acetic acid (sp.gr. 1.049) and then put on the water-bath. A transparent raw gel appeared in five minutes. It was then transferred to an air-oven and dried at about 70°C. Hard transparent grains were obtained.

The gel thus obtained was powdered and then 1 gm pressed in a compression machine by applying a pressure of 3000 lb/sq.in. The membrane thus obtained was 3 cm in diameter and 0.125 mm in thickness. The membrane was white in colour and did not show any deformation or crack under the microscope (Fig.5).

(v) Parchment supported silica membrane:

The membrane was obtained by impregnating silica gel on parchment paper. The parchment paper was first soaked in distilled water and then tied to the open and of a cylindrical glass vessel. 25 ml of sodium silicate solution (sp.gr. 1.16) was filled inside it. The whole assembly was then suspended in a beaker containing 50 ml of 10 percent hydrochloric acid solution for 8 hours. A transparent thin layer of silica was found deposited on parchment paper. It was taken out very carefully and washed repeatedly with hot water in order to remove salt and excess acid.

The solutions of sodium silicate and hydrochloric acid were then interchanged, sodium silicate outside and hydrochloric acid inside the vessel. The process was repeated until a fine uniform deposit of silica gel was obtained (Fig.6) which showed no cracks or deformation under microscope.

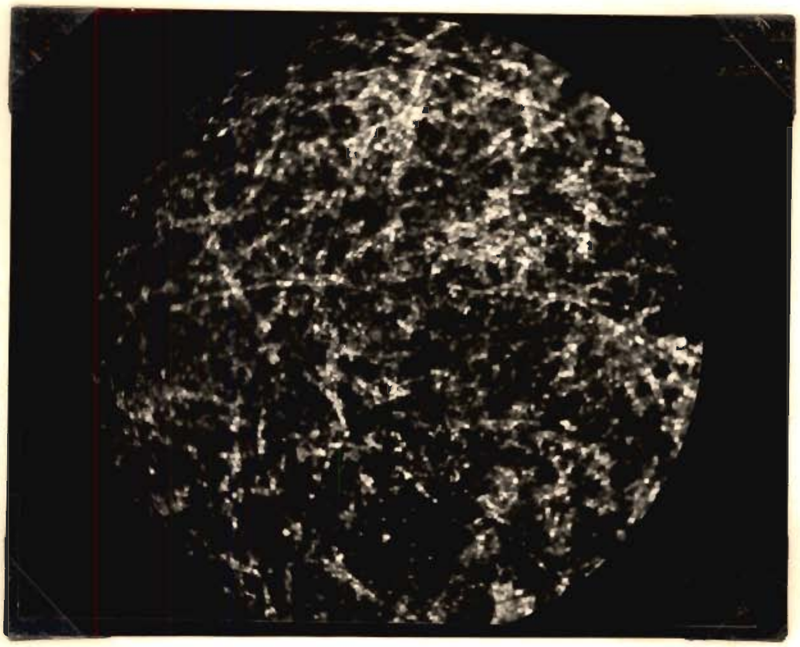

FIG. 4. MICROPHOTOGRAPH OF IRON OXIDE MEMBRANE

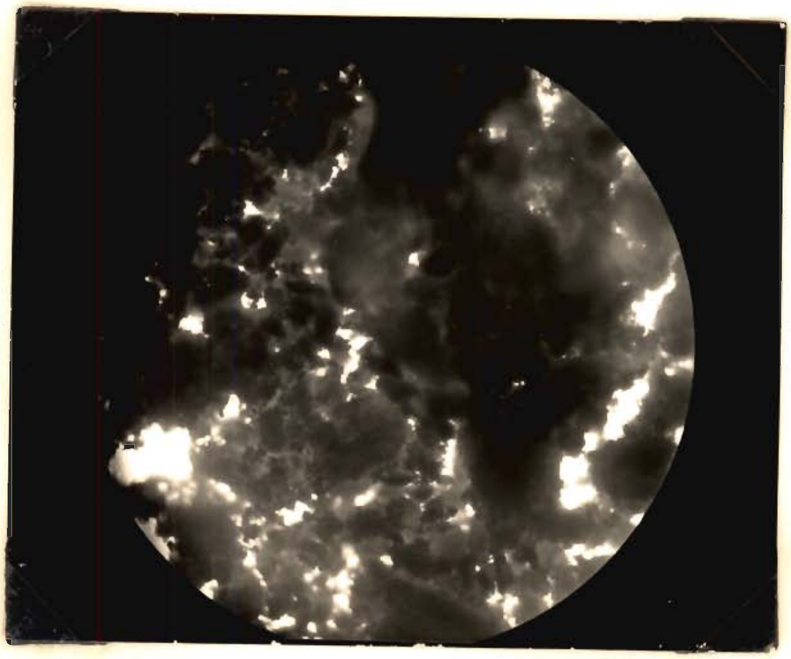

FIG. 5. MICROPHOTOGRAPH OF ALUMINA MEMBRANE

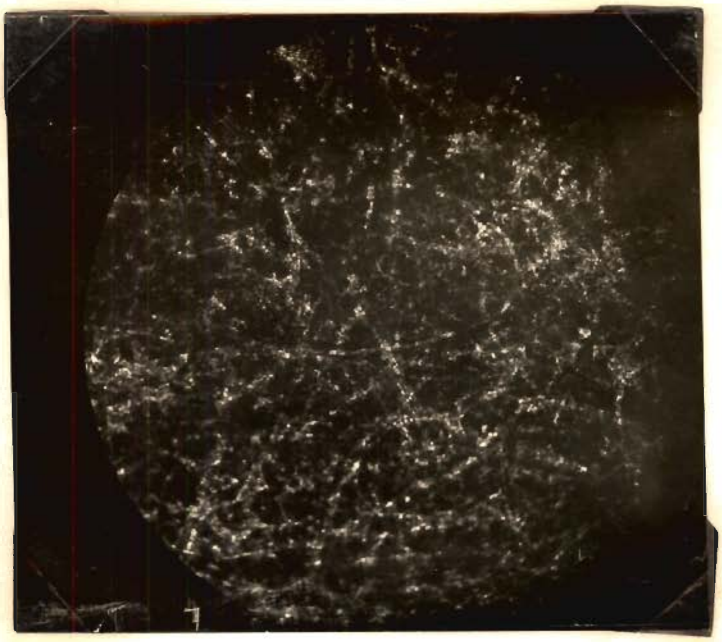

FIG.6. MICROPHOTOGRAPH OF SILICA MEMBRANE

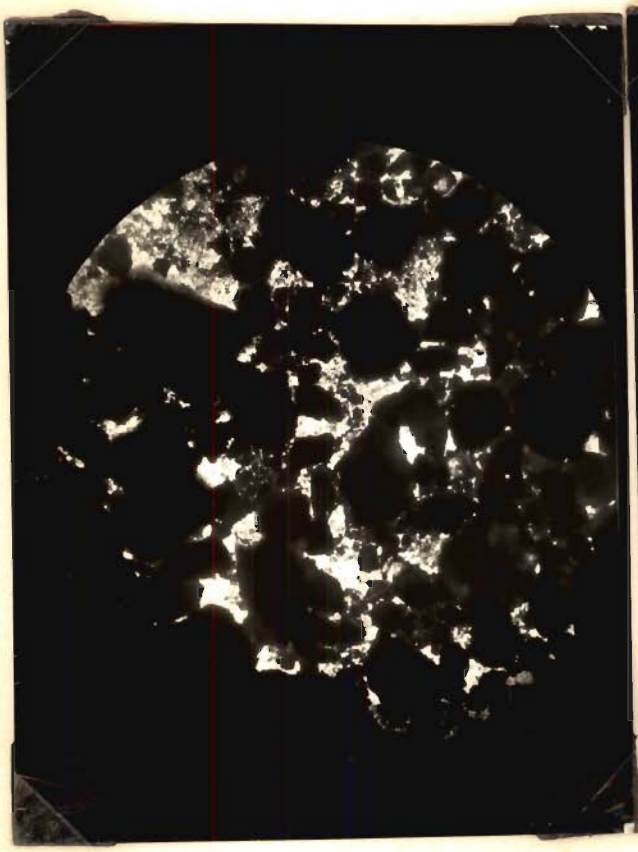

FIG.7 MICROPHOTOGRAPH OF IRON SILICATE MEMBRANE

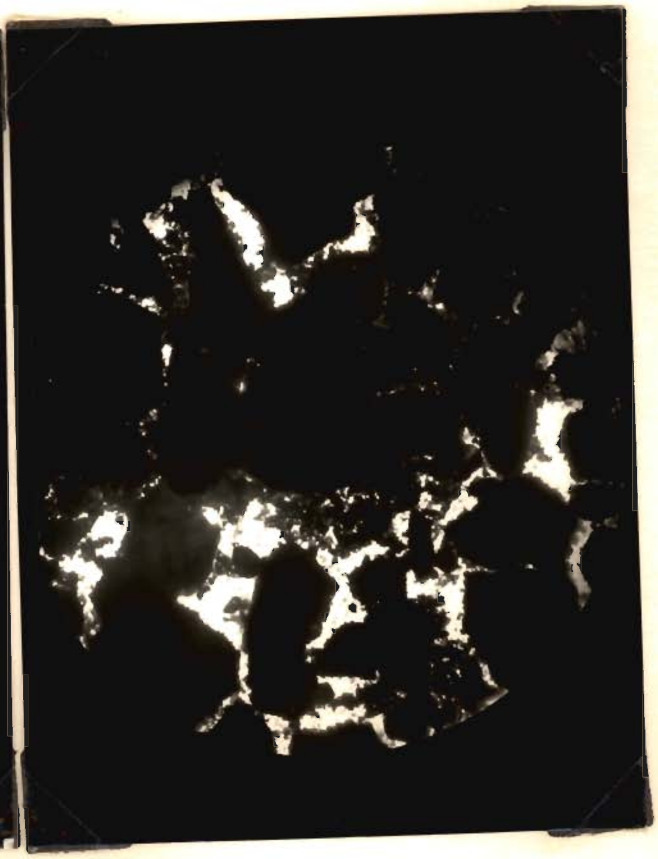

FIG.8. MICROPHOTOGRAPH OF ALUMINIUM SILICATE MEMBRANE

(vi) Silica unsupported membrane:

Patrick's method (42) was employed to prepare the gel. A hot (50°C) 75 ml solution of sodium silicate of sp.gr. about 1.185 was rapidly stirred into an equal volume of a 10 percent solution of hydrochloric acid at the same temperature. After the gel had set (which usually required about an hour) it was broken into pieces and the salt and excess acid were washed out will hot water. Air drying at 75-120°C was employed. Silica gel prepared by this method was hard and glassy. The gel was crushed into fine powder and 1 gm of it was pressed in a mould by a compression machine by applying a pressure of 6000 lb/sq.in. in order to get a thin circular disc. (Fig. 6). The diameter of silica membrane thus obtained was 3.0 cm. and thickness 0.13 mm.

(vii) Parchment supported ferric silicate membrane:

Ferric silicate gel (43) was impregnated on parchment paper in order to get the membrane. Parchment paper soaked in water was tied to an open glass vessel (cylinder) and 25 ml of 0.1M ferric chloride solution was filled in it. The whole assembly was placed in a beaker containing 50 ml of sodium silicate solution (sp.gr.1.16) for 24 hours. It was then taken out and washed well with distilled water in order to remove excess of salt. The solutions were then interchanged, sodium silicate being kept inside and ferric chloride solution outside the vessel. The process was repeated several times in order to get a fine deposit of ferric

FIG. 9. COMPRESSION MACHINE USED FOR PREPARATION OF UNSUPPORTED MEMBRANES

silicate on parchment paper (Fig.7). The membrane, yellow in colour, was washed with distilled water to remove adsorbed electrolyte. It was then examined under a microscope for any deformation or crack.

(viii) Ferric silicate unsupported membrane:

Ferric silicate gel (43) was prepared by mixing 50 ml of 0.1M ferric chloride (A.R. Grade) with 25 ml of sodium silicate solution (sp.gr.1.16). The gel obtained was thoroughly washed and dried at 110°C for 12 hours. 1.00 gm yellow fine powder of iron silicate was pressed in a compression machine in the form of a circular disc of diameter 3 cm. and 0.125 mm thickness. No deformation or cracks were found on membrane while examining under microscope (Fig.7).

(ix) Parchment supported aluminium silicate membrane:

Aluminium silicate gel (44) was prepared by the interaction of basic aluminium sulphate (45) and sodium silicate solution. Basic aluminium sulphate was prepared by titrating 10 percent solution of aluminium sulphate with sodium carbonate to the point at which no permanent precipitate was formed on standing. 25 ml of basic aluminium sulphate solution was taken in an open glass vessel tied with parchment paper soaked in water. It was then suspended in a beaker containing 50 ml of sodium silicate solution (sp.gr.1.16) for 24 hours. Later it was washed with distilled water in order to remove excess salt solutions. The solutions of basic aluminium sulphate and sodium silicate were interchanged, keeping aluminium sulphate outside and sodium silicate inside the vessel. The membrane white in colour was washed gently with double distilled water for the complete removal of salt solutions. It was then examined under microscope for deformation or crack (Fig.8).

(x) Aluminium silicate membrane without support:

100 ml of basic aluminium sulphate solution was mixed with 25 ml of sodium silicate solution (sp.gr.1.16). White gel was obtained which was repeatedly washed with double distilled water in order to remove excess of salts. The gel was dried at 100°C for about 18 hours. 1.00 gm fine white powder was pressed in a compression machine by applying a pressure of 6000 lb/sq.in. in the form of a circular disc of diameter 3 cm. and 0.125 mm thickness (Fig.8).

CHAPTER II

PERMEABILITY MEASURMENTS OF MEMBRANES

Permeability is defined as the property of a porous material which permits the passage or seepage of fluids such as water, salt solutions and/or oil, for example, through its inter connecting voids. The ease with which water or other fluid flows through materials, is of interest to the engineer in varying degrees in the design of structures of any material. The durability of concrete is dependent upon permeability. But, in the solution of great many problems involving earth materials, the permeability may be of primary importance.

Some of the engineering problems in which permeability is of primary importance are as follows:

The rate of settlement of a layer of saturated compressible soil subjected to load is dependent upon the permeability. The sustained rate of flow from wells is dependent upon the permeability of the aquifer. The permeability of soil will determine the spacing of wells and amount of water to be pumped in lowering ground water to facilitate excavation for construction purposes. It also will affect the amount of loss from reservoirs through, under, and around dams. Permeability is a factor in the need for and design of filters to prevent piping or uplift, and to control the hydraulic stability of slopes of earth materials.

The various type of apparatus which are used in soil laboratories for determining coefficients of permeability of soils are called permeameters. They are of two basic designs, the constant head type and the variable head type (1). Numerous subdivisions of the two designs are often mentioned, such as upwardflow and downward-flow types, but these are not of major importance, fundamentally.

The methods used to measure diffusion rates may be broadly classified into two categories:

(i) Steady state method

(ii) Constant flow method

In the first method, the surfaces of a sheet of solid material are maintained in contact with reservoirs of diffusive material at two different fixed concentrations. The net transport is then found by measuring the total rate of movement of material between the reservoirs.

The second method involves subjecting the sample, originally in equilibrium with surrounding reservoir of fixed concentration, to a sudden change in reservoir concentration, and measuring either the concentration distance profiles in the solid or more simply, the change in concentration of the reservoir. Although the apparatus needed for both these types of experiments is usually fairly simple, the analysis of data from the constant flow method is more convenient to do. Besides the constant flow method can provide more information than the steady state one, since the asymptotic value of concentration reached at very long times represents the equilibrium solubility of the diffusing species in the solid material. In contrast, steady state methods customarily provide a measure of the over-all flux rate.

The mechanism by which lipid substances are transported across biological membranes is not very well understood. Various ideas have been presented from time to time, but it has been difficult to make experimental verifications.

There are two general types of path ways through which permeation is presumed to occur in biological membranes, transport through water filled pores and transport through a second phase (lipid in nature) where preferential solubility in the second phase promotes permeation (2, 3). It would seem logical that the second possibility is more likely to hold than the first for water-insoluble substances, nevertheless, evidence has accumulated which would indicate the possibility for some lipid transport through water-filled pores.

In order to consider the permeation of water-insoluble substances through aqueous pores, it is obvious that there must be present a mechanism for solubilization. Fortunately, such mechanisms are known to exist for many of the lipid substances in nature. In the first place, the free fatty acids exist largely as alkali metal salts at physiological pH and in this state are generally water-soluble. Secondly, there is the hydrotropic action of colloidal electrolytes such as the bile salts and alkali metal soaps on the solubilization of many water-insoluble substances. The mechanism by which aqueous solutions of these colloidal electrolytes "dissolve" water-insoluble substances in micelles has long been established, at least in its general aspects (4-6).

There are a few reports in the literature which are concerned with the permeation of micelles and solubilized material through artificial membranes. Dean and Vinograd showed that certain dyes and toluene could be transported through cellophane in the presence of surfactants. More recently a report by Klevens and Carr (7) has shown that micellized substances can diffuse through cellophane membranes, but that the rate can be very slow of the micelles are large. Further it was shown that the solubilization of another substance by micelles slows down considerably their rate of permeation.

The permeation experiments with the collodian membranes and cellophane were carriedout as follows (8).

A measured volume of the solution being tested (usually 10 ml) was placed inside a membrane bag, and a measured volume of water was placed outside. At the beginning of an experiment the liquid levels in the two compartments were essentially the same. All the experiments were carried out at room temperature 22-25°C. From time to time small aliquot samples were removed from both compartments for analysis. The rate at which the system approached equilibrium was then plotted graphically.

Weisers methods employing isotonic solutions for measuring permeability.

Plasmolytic method of preparing isotonic solutions:

Plant cells were employed by De Vries for rough measurment and comparision of osmotic pressure of solution of certain substances. It was observed that the cells were bounded by more or less firm walls lined with membrane permeable to water but impermeable to substances dissolved in the cell sap e.g. certain potassium salts, glucose etc. If such a cell was immersed in a solution of lower osmotic pressure than that of solution inside the cell, no appreciable change was observed in the size of the cell on account of the fact that the rigidity of the cell-walls did not allow the water to flow from outside to inside. But when the cell was immersed in a solution of higher osmotic pressure thanthat of the cell-sap, the cell membrane partially collapsed due to diffusion of water from the interior of the cell to the surrounding solution. This phenomenon was termed as 'Plasmolysis'.

The above principle was used by De Vries (loc.cit) in his method of measuring osmotic pressure. By using cells of the same kind at different concentrations, be determined the concentration at which plasmolysis ceased or was just detectable. Such solutions were called 'Isotonic', that is, solution having the same osmotic pressure. A solution that had an osmotic value higher than that of the cell sap was called 'Hypertonic' solution. A plant cell placed in such a solution was found to show evident plasmolysis. The term 'Hypotonic' was applied to a solution whose osmotic value was lower than that of the cell-sap.

On the above basis Malik and Ali(9) employed the following procedure for the preparation of isotonic solutions needed for the experiments of permeability of membranes. Making use of the plant 'Spirogyra'. They prepared isotonic solutions of KCl, K_2SO_4, Na_2WO_4 and sugar solution etc. and determined the exact strength of above mentioned electrolytes isotonic with the cell-sap.

To perform the diffusion experiments electrolyte solutions were placed inside the ferric tungstate, thorium tungstate membrane thimbles which were suspended in sugar solution in a narrow glass cylinder for 24 hours. The electrolyte inside the thimble was analysed for anions.

<u>Calculations</u>:

0.1M KCl solution was prepared by dissolving 1.865 gms of recrystallised dried sample of KCl in 250 c.c. of double distilled water.

Suppose 0.2M sugar is isotonic with 0.1M KCl then 6.8462 gms of A.R. sucrose was dissolved in 100 c.c.

of distilled water.

To perform diffusion experiments, say, 20 c.c. of 0.1M KCl was placed inside the membrane which was suspended in 50 c.c. of 0.2M sugar solution in a narrow glass cylinder for twenty four hours. Then potassium chloride solution inside the thimble was analysed for chloride ions before and after diffusion against $AgNO_3$.

Let 5 c.c. of KCl before experiment require 9.0 c.c. of $AgNO_3$ and 5 c.c. of KCl after experiment require 2.6 c.c. of $AgNO_3$.

$$\text{Percentage of diffusion} = \frac{(9.0-2.6)}{9.0} \times 100$$

$$= \frac{6.4}{9} \times 100 = 71.1\% \text{ KCl}$$

The method although simple and did not require any elaborate experimental set-up was tedious, time consuming and had a error range too less to give reproducible results. Later on a modified method was developed by Hartung and Willis (1944) for investigating the permeability of copper ferrocyanide membranes to various anions.

Their method too could not take into account all the factors, viz., (i) surface charge on the membrane (ii) adsorption of diffusing ion (iii) valency of anion and (iv) diffusion rate of anion in free solution, on which they considered the diffusion mechanism to depend.

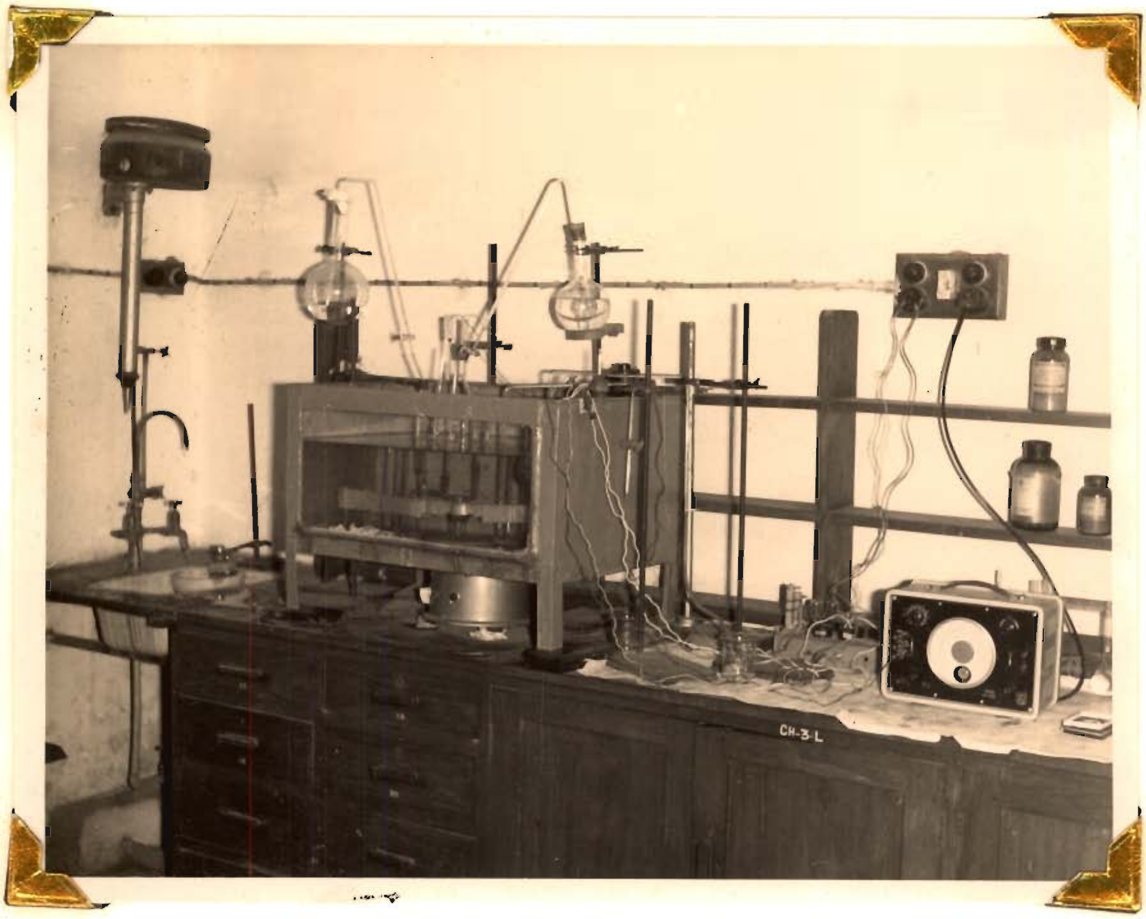

FIG.10. CONSTANT FLOW METHOD OF PERMEABILITY MEASUREMENTS

Permeability measurments by the constant flow method of Willis

Description of the apparatus:

The apparatus is diagramatrically represented in the (Fig. 11). The permeability cell S was in the central section, and consists of twin flat glass vessels with flanges ground to fit together. The internal dimensions of each half cell were approximately 30 mm diameter and giving a volume of about 45 c.c. The lower half of the cell rests on the electromagnetic stirrer plate. The membrane was fitted in between the two half cells and it was sealed.

Freshly distilled water enters from the glass tube through a stop cock A and passes down the tube B and then upto tube C to the constant level head E where the excess is removed by suction. From E the water passes down D to the capillary F. From the capillary the water passes through a wide tube past manometer M into the lower half of the cell. On leaving the cell, the water passes through the stop cock K which is used to regulate the rate of flow of water. The affluent is collected in a measuring cylinder and is analysed by the conductivity measurments.

The solution is supplied from one litre flask through stop cock T, from which it enters the constant level S, and flows continuously through the upper half cell and exits through the stop cock J from which the

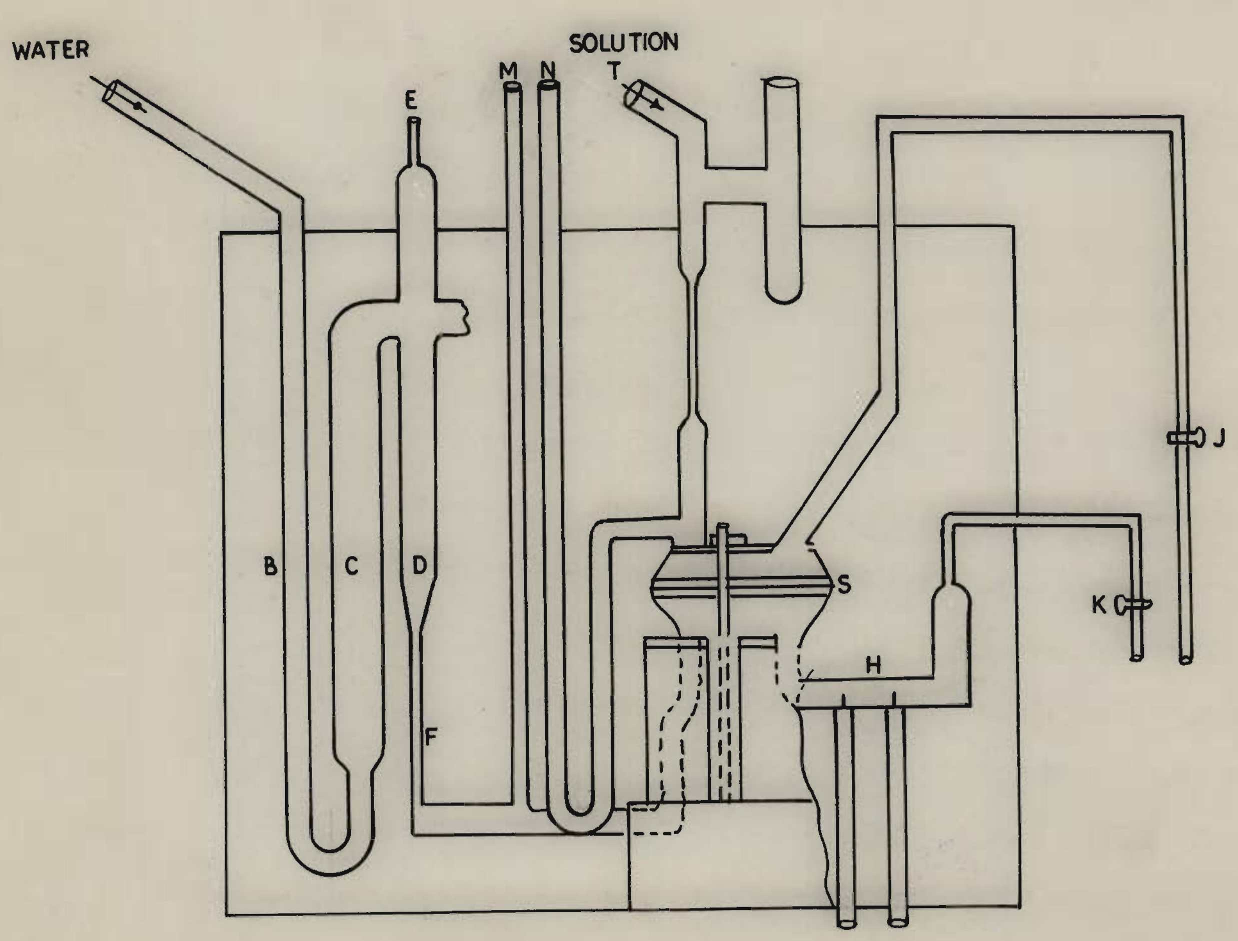

FIG. 11 CONSTANT FLOW METHOD FOR PERMEABILITY MEASUREMENTS

(SCHEMATIC DIAGRAM)

rate of the solution and the level in the manometer N (attached to the upper half cell) was maintained.

The pressures on each side of the membrane were shown by the manometer levels in M and N. A mark was made on the two manometers at equal level and very fine adjustments of pressure were made by changing relative positions of the stop cocks A and K, and T and J in such a way that after a long interval the difference in the levels of the two manometers was very negligible.

The lower half of the cell was stirred by means of a soft iron piece sealed in a glass tube and actuated by the electromagnets G, M and N were covered by small glass caps to prevent entry of dust.

In starting the experiment, the main precaution was to exclude air from the cell. For this purpose cell containing membrane was filled with water and the other components of the assembly were also filled with water. Later all components were fitted in the cell with the help of sockets.

From the upper half the solution was made to flow from stopcock T after opening the stopcock J. The two stopcocks were then adjusted to maintain the marked level in the manometer N. In the same manner stopcock A and T were adjusted to maintain the required level so that the diffusion due to osmosis is checked. The rate of flow of the lower and upper halves were measured by collecting the affluent in measuring cylinders in 20 minutes. The conductivity of this affluent was observed from time to time until it reached a constancy.

From the conductivity data the strength of the solution was found from the calibration curve plotted in conductivity against the known concentration of the electrolyte used.

Checking of the apparatus:

Before starting permeability measurments, the apparatus was thoroughly checked to determine whether it was sufficiently free from inherent sources of error. The following critical examinations were made.

Leakage:

The upper and lower halves of the cell was filled with water and kept for four hours. No leakage was observed. When it was put in a electrolyte solution, the affluent did not show any increase in conductivity which again ensured that there was no leakage in the apparatus.

Rate of flow through lower half of cell:

The rate of flow through the lower half of the cell was maintained constant (150 c.c. per hour) by adjusting the stopcock K.

Rate of stirring in lower half of the cell:

It was observed by Willis in his permeability experiment that stirring increases the permeability, and this effect is attributed to removal of stationary layers from the underside of the membrane, with consequent reduction in the concentration gradient. Keeping this in view, the stirring rate was kept constant by adjusting the control dial of the electromagnetic stirrer, so that the experiment would be made with all the electrolytes under the same condition of stirring.

Rate of flow of solution:

The rate of flow of the solution was adjusted by altering the position of the stopcock J. The rate of flow of the solution was kept 180 c.c. per hour in all the permeability experiments.

Pressure difference across the membrane:

The hydrostatic pressure of the upper and lower halves cell were kept constant by keeping the levels of the liquids in the manometers M and N equal which were adjusted by trial and error of the stopcocks A and K and T and J in turn.

The constant flow method of Willis and Hartung suffers from some drawbacks as mentioned earlier. Therefore it was thought worthwhile to made some improvements in order to get better results.

The improvements were made by decreasing the actual volume of permeability cell enabling equilibrium to be reached more quickly and employing a electromagnetic stirrer for carrying out the experiment under same condition of stirring by adjusting the control dial of electromagnetic stirrer(this avoids the increase in permeability due to variations in stirring as observed by Willis and others).

The permeability of parchment supported and unsupported, ferric oxide alumina, silica, ferric silicate and aluminium silicate membranes to various electrolytes having a common cation (K^+) and anion (Cl^-) was found out by setting up the whole assembly as (Fig.10) mentioned earlier. The permeability values were calculated as described below.

For a particular constant affluent conductivity, the concentration of electrolyte coming down through the membranes was computed from standard concentration-conductance plots of electrolytes (given in Chapter III). Then permeability was calculated in millimoles per hour.

Measurment of membrane potential due to permeability:

It was observed that when a porous medium or gel (the membrane) in which pore walls carry an electric double layer, separated two electrolyte solutions, an electric field (diffusion potential) maintained electroneutrality and brought about the balance of fluxes. The magnitude and sign of the potential depended on the nature of the membrane and the permeating species. If the membrane carried no fixed charge, the potential was the same as the liquid junction potential whereas if the membrane carried some fixed charges, the magnitude of the potential was determined by the concentration of the external solution and its sign by the nature of the fixed charge. However it is found that many membranes considered completely inert, because of the absence of measurable quantity of fixed charge, have a tendency to generate an electric potential.

This was attributed to adsorption of cations or anions to make them anion or cation selective. The work of sollner and others has shown that in the case of nitrocellulose, the electromotive activity was due to the end and stray carboxyl groups of the nitrocellulose (10-15). Membranes like these can be made cation selective or anion selective (16) by making them adsorb large anions or large cations which may be held loosely or firmly. This property is very typical of many uncharged polymer membranes.

Wilbrandt (17) had shown that there is a continuous decrease in the membrane potential of collodion films with increasing permeability. Michaelis (18) was of the opinion that the retardation of anions relative to cation is negatively charged membrane was due to preferential adsorption of anions on the pore walls leading to their immobilisation and consequently acquiring a negative charge.

The membrane potential is commonly taken to be the electromotive force measured between identical reference electrodes (e.g. calomel half-cells), connected by salt bridges with the two solutions on opposite sides of the membrane. This would be a measurment of the true membrane potential only if the liquid junction potentials at the ends of the salt bridges were equal and opposite. It is assumed that this is true when the salt bridge is a saturated potassium chloride solution, although no way to prove this assumption is known. Scatchard (19) made the same assumption in estimating the activities of single ionic species. The results reported by Loeb (20) for membrane potentials in the equilibrium of proteins with electrolytes are all based on this assumption

The method used here in the present studies for the determination of a membrane potentials was that of Michaelis, for concentration potentials, the potential difference of the concentration cell.

$$\mathrm{Hg}\,|\,\mathrm{Hg_2Cl_2}\,|\,\underset{\text{satd.}}{\mathrm{KCl}}\;\Big|_{E_1}\;\underset{C_1}{\text{Electrolyte}}\;\Big|_{\substack{\text{Membrane}\\ E}}\;\underset{C_2}{\text{Electrolyte}}\;\Big|_{E_2}\;\underset{\text{satd.}}{\mathrm{KCl}}\,|\,\mathrm{Hg_2Cl_2}\,|\,\mathrm{Hg}$$

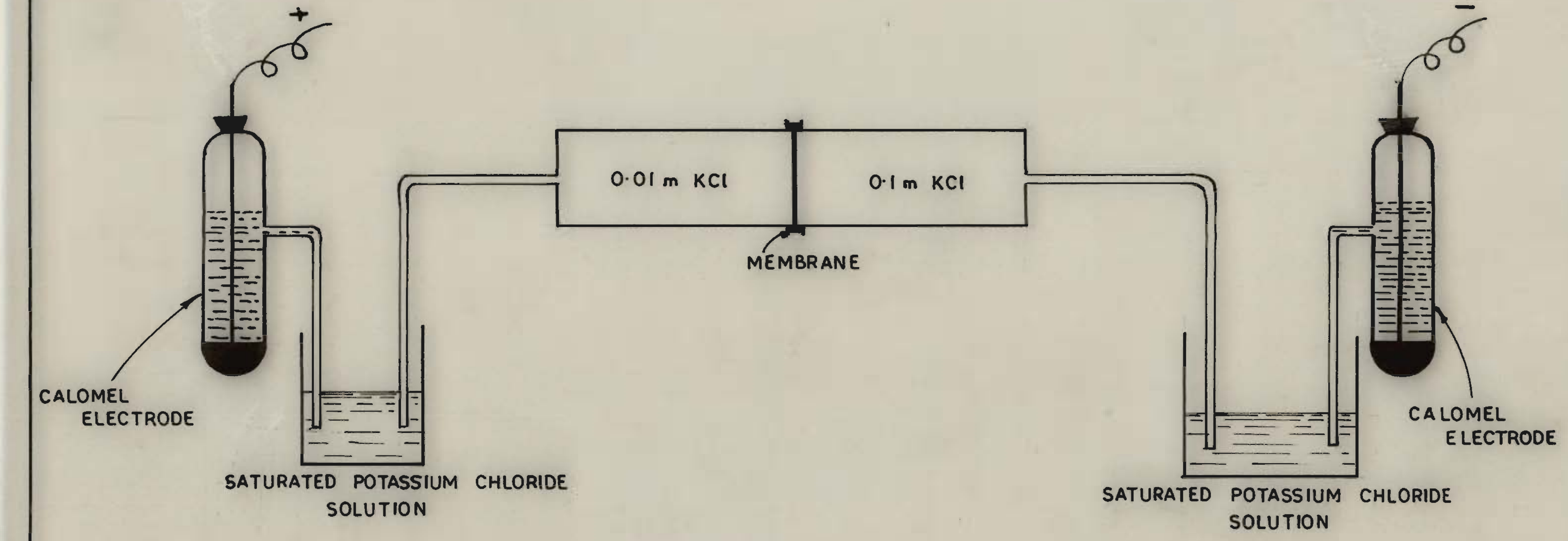

FIG. 12. ASSEMBLY FOR MEMBRANE POTENTIAL MEASURMENTS

Potential measurements due to diffusion of different electrolytes through membranes under study were carried out as follows:

Parchment supported and unsupported ferric oxide, alumina, silica, ferric silicate and aluminium silicate membranes (the preparation of which has already been described in Chapter I) were fitted in between two flanges of membrane potential cell (as shown in Fig. No.12). The same electrolyte was used on both sides of the membrane and the concentration ratio C_1/C_2 was kept 10 throughout, the dilute side (0.01M) always remaining positive. Saturated calomel electrodes were used as reference electrodes. Pye student potentiometer; cat.No.7554 (measurable upto one millivolt) in conjunction with a ballistic galvanometer sensitivity 1.17×10^{-9} amp/mm at one meter and lamp and scale arrangement was used for potential measurements. Measurment of membrane potential shows an initial increase after which it attains a constant value.

CHAPTER III

PERMEABILITY OF PARCHMENT SUPPORTED AND UNSUPPORTED FERRIC OXIDE AND ALUMINA MEMBRANES

Hydrous oxide gels have an important role in colloid chemistry, both theoretical and applied (1). The constitution of the particles in such colloidal systems has been the subject of many enquiries. Hydrous oxide of iron do not hold water in a definite stoichiometric ratio. This idea was extended and developed by a number of people like Duclaux (2), Malfitono (3), Hautzsch and Desch (4) and Linder and Picton (5) showed that the constitution of ferric oxide is 20 $Fe(OH)_3.FeCl_3$ and 45 $Fe(OH)_3FeCl_3$. Pauli represented it by a general formula x $Fe(OH)_3.y.FeOCl.FeO^+$, (Cl^-) for hydrous ferric oxide and herein $x = 32$ to 350 and $y = 4$ to 5.7. Although this formulation may be satisfactory in general way it is difficult to justify the details of the formula since no one has established the existence of $Fe(OH)_3$.

It is now known that alumina gel thrown down from an aluminium salt solution in the hot is hydrous γ-$Al_2O_3.H_2O$. The exact crystal structure of γ-Al_2O_3 is not known.

Thomas and Coworkers (6) have concluded that formation and composition of colloidally dispersed metal oxides, precipitated hydrous oxides etc. may be explained in terms of olation, oxlation and anion penetration.

Inspite of the fact that the colloidal behaviour of aluminium and iron hydrous oxide sols has been so extensively investigated and the composition of these compounds in the gel and other colloidal forms has remained a matter of controversy for a number of years, nothing has been done to study their membrane properties. It was therefore considered worthwhile to carry out investigations in this direction.

EXPERIMENTAL

Iron oxide and alumina membranes were prepared according to the methods described in chapter I. In order to perform the permeability experiments, the membranes were inserted in between the flanges of the permeability cell. The whole assembly for measuring permeability was set as described in chapter II. Temperatures of 20°, 25°, 30° and $35^{\circ} \pm 0.1^{\circ}C$ was maintained in the thermostat housing the permeability cell.

The following solutions of electrolytes were used for determining permeability of membranes.

(i) Electrolytes having a common cation

0.2M KCl, 0.2M KBr, 0.2M KNO_3,
0.2M KCNS and 0.2M K_2SO_4

(ii) Electrolytes having common anion

0.2M NaCl, 0.2M $BaCl_2$, 0.2M $CaCl_2$
0.2M $MgCl_2$, 0.2M $FeCl_3$ and 0.2M $AlCl_3$.

Standard concentration conductance plots of KCl, KBr, KNO_3, K_2SO_4 and KCNS and NaCl, $BaCl_2$, $MgCl_2$, $CaCl_2$, $FeCl_3$ and $AlCl_3$ were obtained from datas given in tables (1 to 11).

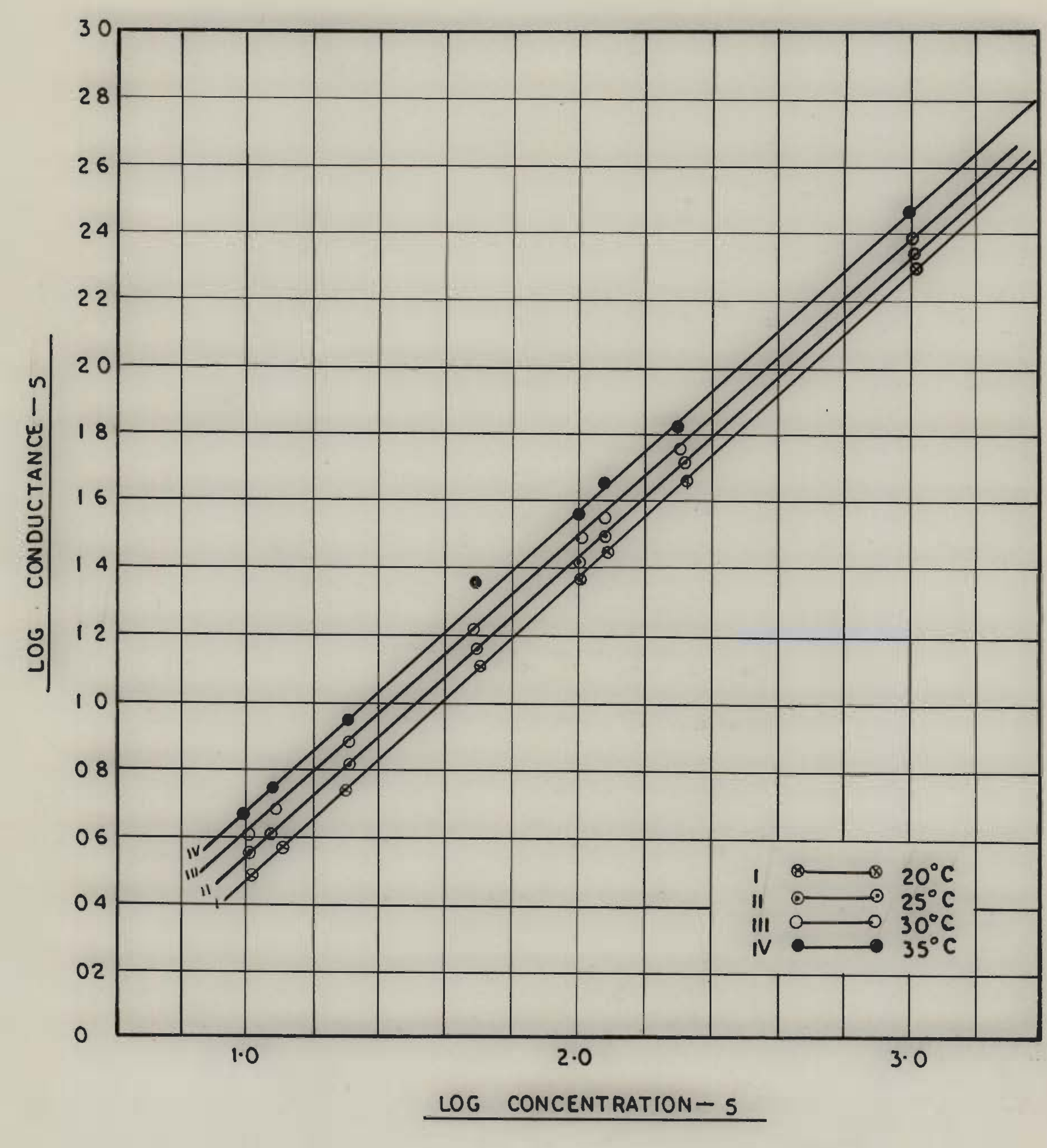

FIG. 13. STANDARD CURVES FOR POTASSIUM CHLORIDE

TABLE No.1

Conductivity of standard potassium chloride solutions at different temperatures.

Concentration (M)	Conductance x 10^5 at 20°C	Conductance x 10^5 at 25°C	Conductance x 10^5 at 30°C	Conductance x 10^5 at 35°C
0.01	248.0	252.0	258.0	264.0
0.002	51.0	53.0	56.0	59.0
0.0010	28.0	30.0	32.0	34.0
0.0005	23.0	25.0	28.0	31.0
0.0002	12.0	14.0	15.0	17.8
0.00012	5.2	6.4	6.8	9.3
0.000012	3.8	4.4	4.6	5.2
0.000015	3.5	4.0	4.2	5.1

Curves were drawn between log (concentration) and log (conductance) at different temperatures (Fig. 13 curves I,II,III,IV).

TABLE No.2

Conductivity of standard potassium bromide solutions at different temperatures:

Concentration (M)	Conductance x 10^5 at 20°C	Conductance x 10^5 at 25°C	Conductance x 10^5 at 30°C	Conductance x 10^5 at 35°C
0.01	220.0	230.0	250.0	270.0
0.002	46.0	50.0	55.0	60.0
0.0012	29.0	32.0	35.0	38.0
0.0010	24.0	27.0	30.0	32.0
0.0005	13.0	15.0	16.0	17.0
0.0002	6.3	6.9	7.6	8.2
0.00012	4.9	5.3	5.9	6.3
0.000010	4.1	4.4	4.9	5.3
0.000012	3.5	3.8	4.2	4.6
0.000015	3.1	3.5	3.8	4.2

Curves were drawn between log (concentration) and log (conductance) at different temperature (Fig. 14 curves I,II,III,IV).

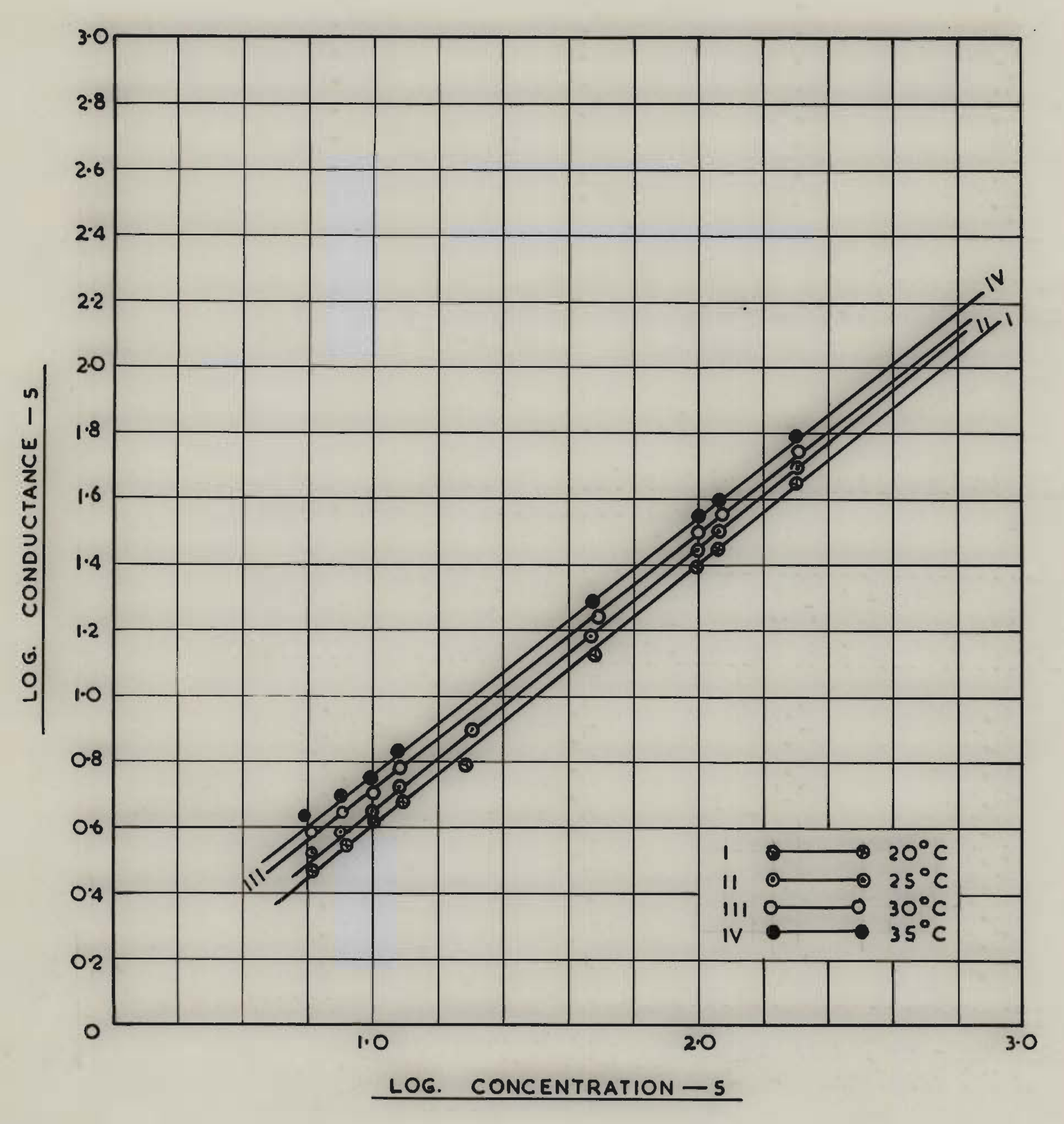

FIG.14. STANDARD CURVES FOR POTASSIUM BROMIDE

TABLE No.3

Conductivity of standard potassium nitrate solutions at different temperatures:

Concentration (M)	Conductance x 10^5 at 20°C	Conductance x 10^5 at 25°C	Conductance x 10^5 at 30°C	Conductance x 10^5 at 35°C
0.01	200.0	230.0	250.0	270.0
0.002	42.0	48.0	51.0	65.0
0.001	28.0	31.0	35.0	39.0
0.0005	23.0	26.0	28.0	31.0
0.0002	12.0	14.0	15.0	17.0
0.00012	6.1	6.5	7.2	8.2
0.000012	3.6	4.2	4.7	5.4
0.000015	3.3	4.0	4.5	5.2

Curves were drawn between log (Concentration) and log (Conductance) at different temperatures (Fig. 15 curves I, II, III, IV).

TABLE No.4

Conductivity of standard potassium thiocyanate solutions at different temperatures:

Concentration (M)	Conductance x 10^5 at 20°C	Conductance x 10^5 at 25°C	Conductance x 10^5 at 30°C	Conductance x 10^5 at 35°C
0.01	192.0	210.0	230.0	245.0
0.002	40.0	45.0	50.0	54.0
0.0012	26.0	28.0	33.0	36.0
0.0010	22.0	25.0	28.0	30.0
0.0005	12.0	14.0	15.0	16.5
0.0002	5.7	6.5	7.2	8.1
0.00012	4.2	4.6	5.2	5.8
0.00001	3.4	3.9	4.2	4.8
0.000012	3.2	3.5	3.8	4.2
0.000015	3.1	3.4	3.7	4.1

Curves were drawn between log (Concentration) and log (Conductance) at different temperatures (Fig. 16 curves I, II, III, IV).

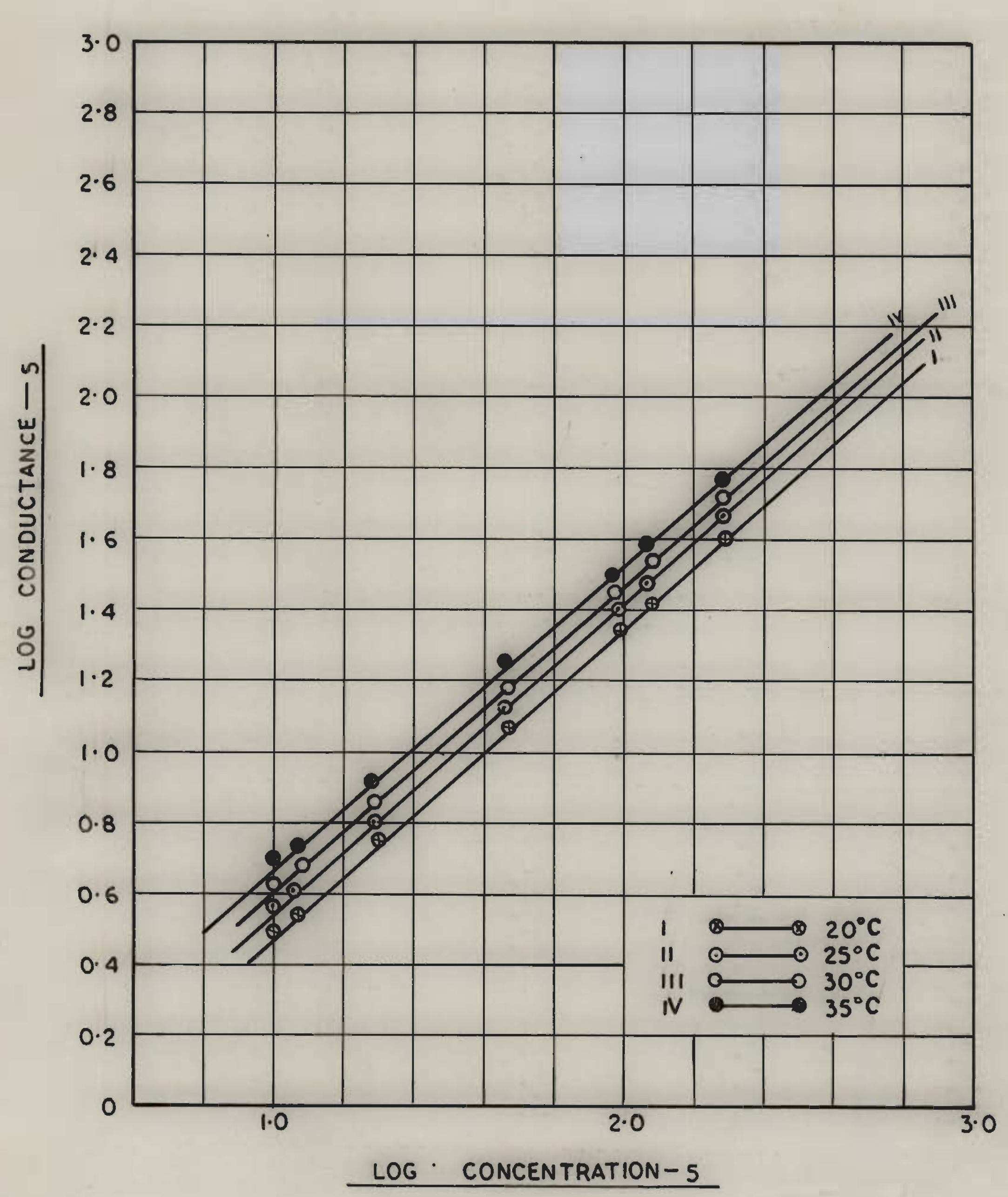

FIG. 15. STANDARD CURVES FOR POTASSIUM NITRATE

TABLE No.5

Conductivity of standard potassium sulphate solutions at different temperatures:

Concentration (M)	Conductance x 10^5 at 20°C	Conductance x 10^5 at 25°C	Conductance x 10^5 at 30°C	Conductanc x 10^5 at 35°C
0.01	215.0	225.5	231.0	245.5
0.002	43.0	50.0	52.0	57.0
0.0010	30.0	32.0	36.0	40.0
0.0005	24.5	30.0	32.0	33.5
0.0002	12.5	16.0	17.5	18.8
0.00012	7.2	8.0	9.1	9.3
0.000012	4.1	4.2	4.6	4.9
0.000015	4.0	4.1	4.3	4.5

Curves were drawn between log (Concentration) and log (Conductance) at different temperatures (Fig. 17 curves I, II, III, IV).

TABLE No.6

Conductivity of standard sodium chloride solutions at different temperatures:

Concentration (M)	Conductance x 10^5 at 20°C	Conductance x 10^5 at 25°C	Conductance x 10^5 at 30°C	Conductanc x 10^5 at 35°C
0.01	240.0	250.0	350.0	380.0
0.002	58.0	66.0	71.0	74.0
0.001	32.0	34.0	38.0	35.0
0.0005	18.0	22.0	29.0	33.0
0.0002	5.0	8.3	10.0	12.0
0.00012	4.5	6.2	6.8	8.1
0.00010	3.8	5.2	5.8	7.5
0.000083	3.4	3.7	5.0	7.0
0.000066	3.0	3.4	4.3	6.2
0.000062	2.5	3.1	3.9	5.8

Curves were drawn between log (Concentration) and log (Conductance) at different temperatures (Fig. 18 curves I, II, III, IV).

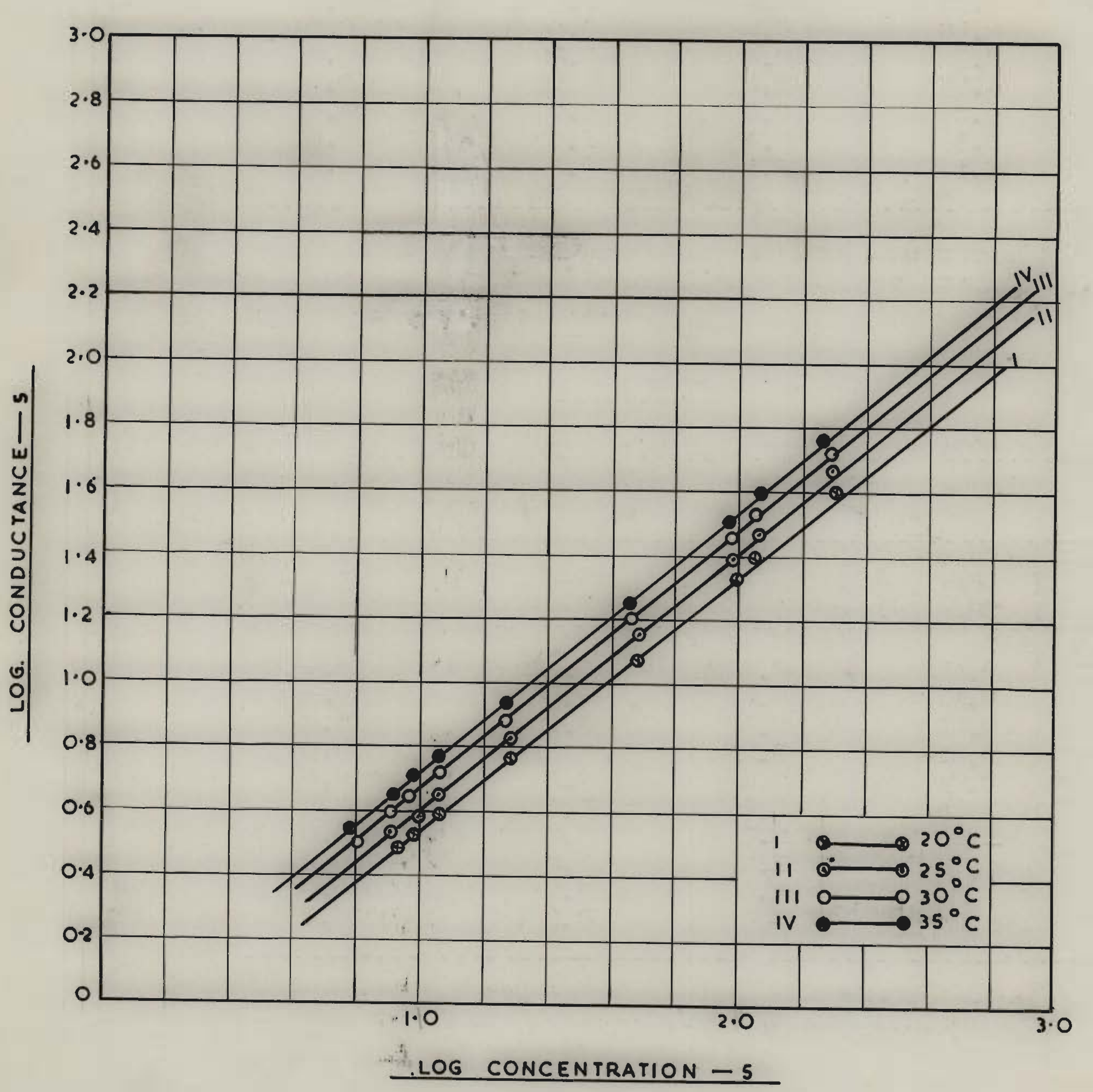

FIG. 16. STANDARD CURVES FOR POTASSIUM THIOCYANATE

TABLE No.7

Conductivity of standard barium chloride solutions at different temperatures:

Concentration (M)	Conductance x 10^5 at 20°C	Conductance x 10^5 at 25°C	Conductance x 10^5 at 30°C	Conductance x 10^5 at 35°C
0.01	238.0	241.0	245.0	251.0
0.002	56.2	59.0	63.0	66.0
0.001	30.0	33.0	37.0	42.0
0.0005	16.0	18.0	20.0	22.0
0.0002	4.7	9.0	10.0	11.0
0.00012	4.2	5.5	6.2	7.1
0.00010	3.4	5.0	5.5	5.8
0.000083	3.2	3.7	4.1	4.7
0.000066	2.5	3.0	3.4	3.7
0.000062	2.3	2.8	3.2	3.4

Curves were drawn between log (Concentration) and log (Conductance) at different temperatures (Fig.19 curves I,II,III,IV).

TABLE No.8

Conductivity of standard calcium chloride solutions at different temperatures:

Concentration (M)	Conductance x 10^5 at 20°C	Conductance x 10^5 at 25°C	Conductance x 10^5 at 30°C	Conductance x 10^5 at 35°C
0.01	243.0	285.0	310.0	340.0
0.002	55.5	66.0	71.0	74.0
0.001	31.2	34.0	38.0	41.0
0.0005	16.6	18.0	19.0	21.0
0.0002	6.6	9.0	10.0	11.1
0.00012	5.8	6.6	8.3	10.0
0.00010	4.0	5.5	6.2	7.1
0.000083	3.3	4.7	5.8	6.6
0.000066	3.0	3.5	4.1	4.5
0.000062	2.8	3.1	3.5	4.0

Curves were drawn between log (Concentration) and log (Conductance) at different temperatures (Fig.21 curves I,II, III, IV).

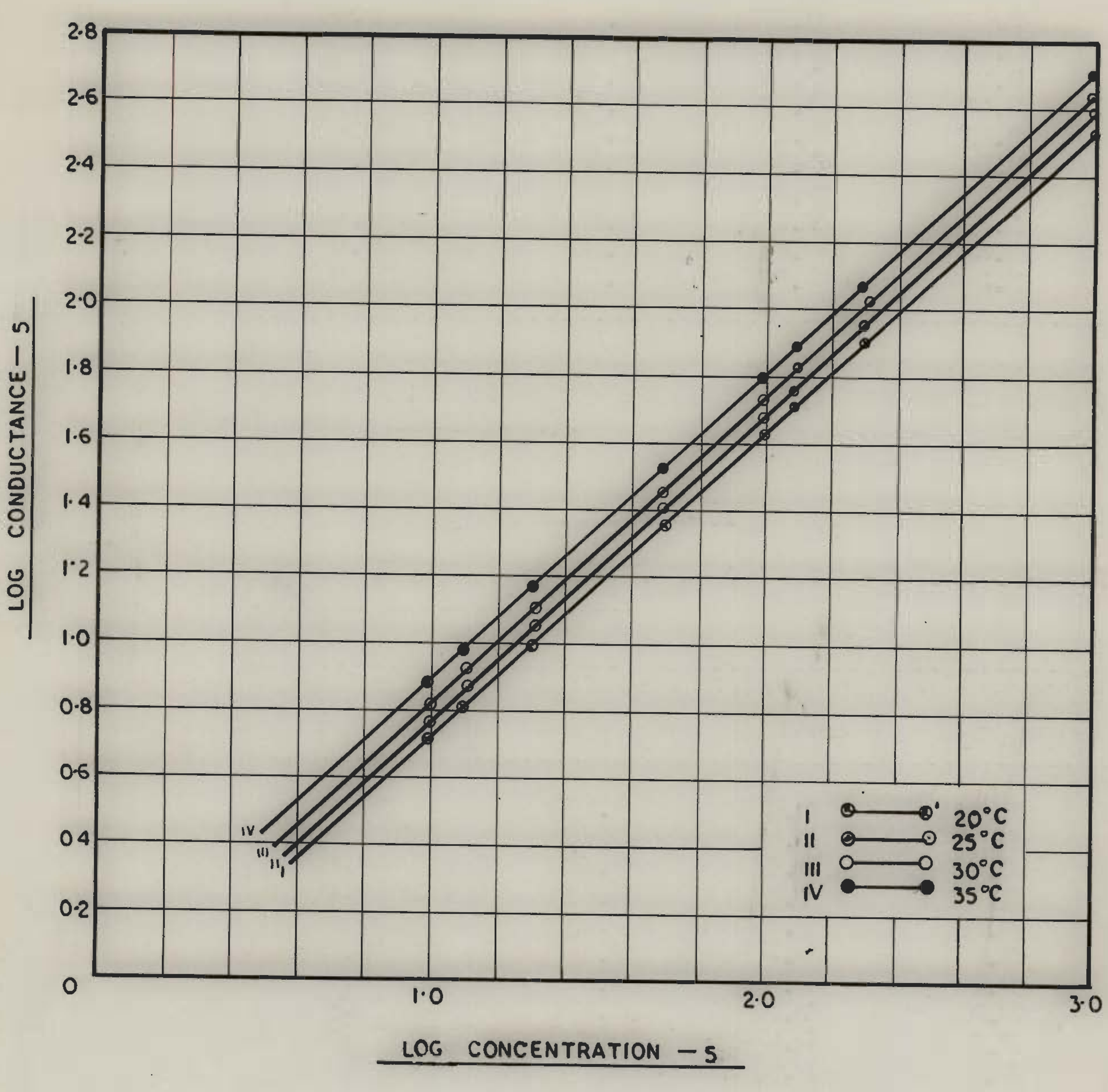

FIG. 17. STANDARD CURVES FOR POTASSIUM SULPHATE

TABLE No.9

Conductivity of standard magnesium chloride solutions at different temperatures:

Concentration (M)	Conductance x 10^5 at 20°C	Conductance x 10^5 at 25°C	Conductance x 10^5 at 30°C	Conductance x 10^5 at 35°C
0.01	312.0	340.0	380.0	450.0
0.002	71.0	83.0	90.0	111.0
0.0012	38.0	43.0	47.0	52.0
0.0010	20.0	22.0	25.0	27.0
0.0005	9.0	11.0	11.1	12.5
0.0002	5.8	6.6	7.6	9.0
0.00012	5.0	5.5	6.2	6.6
0.00001	4.0	5.0	5.5	6.2
0.000012	3.4	4.3	4.7	5.5
0.000015	3.2	3.8	4.3	5.2

Curves were drawn between log (Concentration) and log (Conductance) at different temperatures (Fig.20 curves I,II,III,IV).

TABLE No.10

Conductivity of standard ferric chloride solutions at different temperatures:

Concentration (M)	Conductance x 10^5 at 20°C	Conductance x 10^5 at 25°C	Conductance x 10^5 at 30°C	Conductance x 10^5 at 35°C
0.01	500.0	520.0	580.0	620.0
0.002	160.0	170.0	180.0	210.0
0.001	110.0	125.0	128.0	130.0
0.0005	50.0	55.0	66.0	76.0
0.0002	23.0	26.0	27.0	31.0
0.00012	15.0	16.0	18.0	21.0
0.00010	12.0	13.0	15.0	19.0
0.000083	9.0	11.0	12.5	12.8
0.000063	7.1	8.3	10.0	11.0
0.000062	6.6	7.1	8.3	9.0

Curves were drawn between log (Concentration) and log (Conductance) at different temperatures (Fig.22 curves I,II,III,IV).

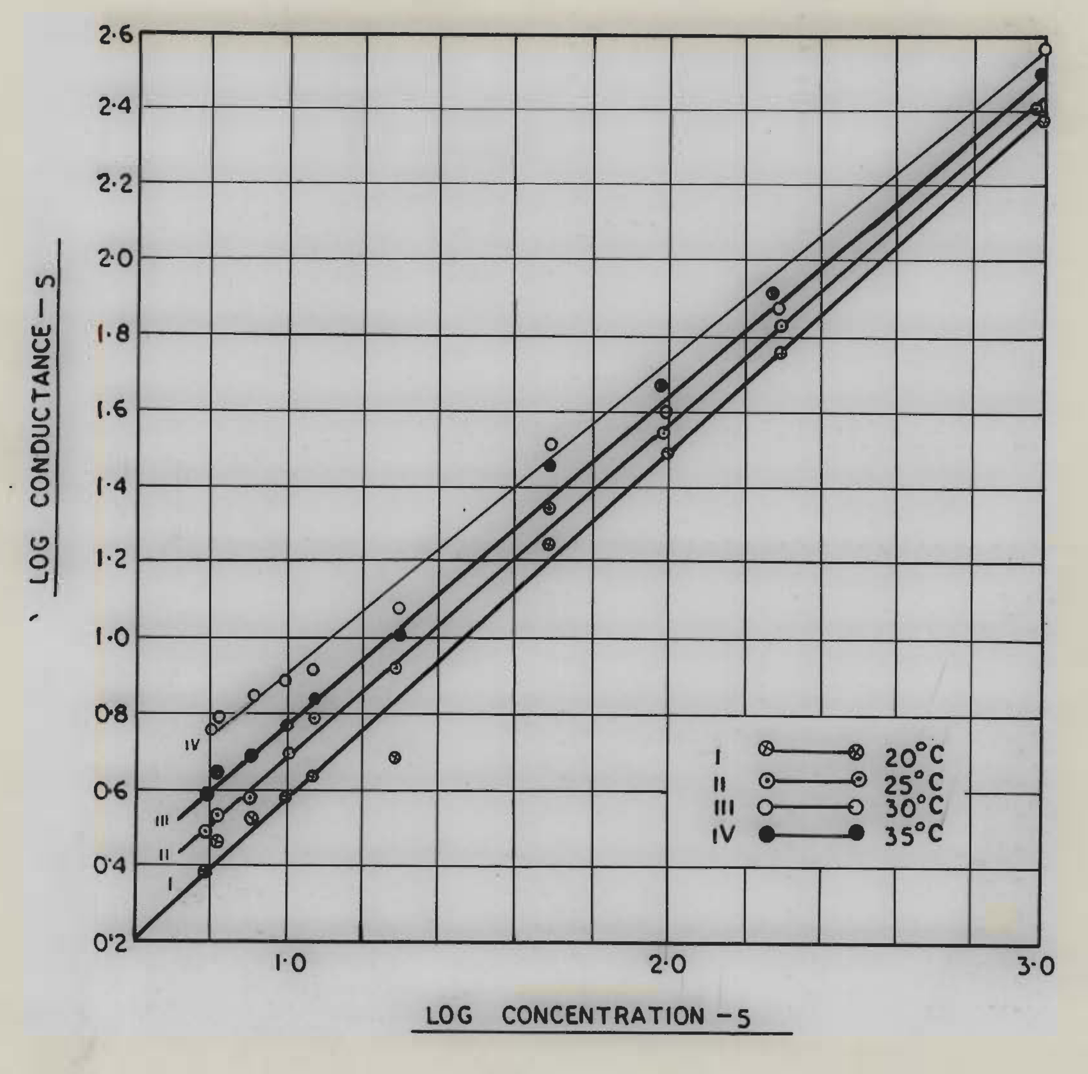

FIG. 18. STANDARD CURVES FOR SODIUM CHLORIDE

TABLE No.11

Conductivity of standard aluminium chloride solutions at different temperatures:

Concentration (M)	Conductance x 10^5 at 20°C	Conductance x 10^5 at 25°C	Conductance x 10^5 at 30°C	Conductance x 10^5 at 35°C
0.01	785.0	853.0	900.0	998.0
0.002	158.0	165.0	260.0	285.0
0.001	100.0	112.0	135.0	245.0
0.0005	47.5	52.0	85.0	100.0
0.0002	20.0	24.5	38.2	56.0
0.00012	13.5	14.8	24.5	45.8
0.00010	10.5	11.0	18.5	24.5
0.000083	7.5	8.0	15.5	20.0
0.000063	6.8	7.5	12.5	18.0
0.000062	5.0	6.0	10.0	16.0

Curves were drawn between log (Concentration) and log (Conductance) at different temperatures (Fig.23 curves I,II,III,IV).

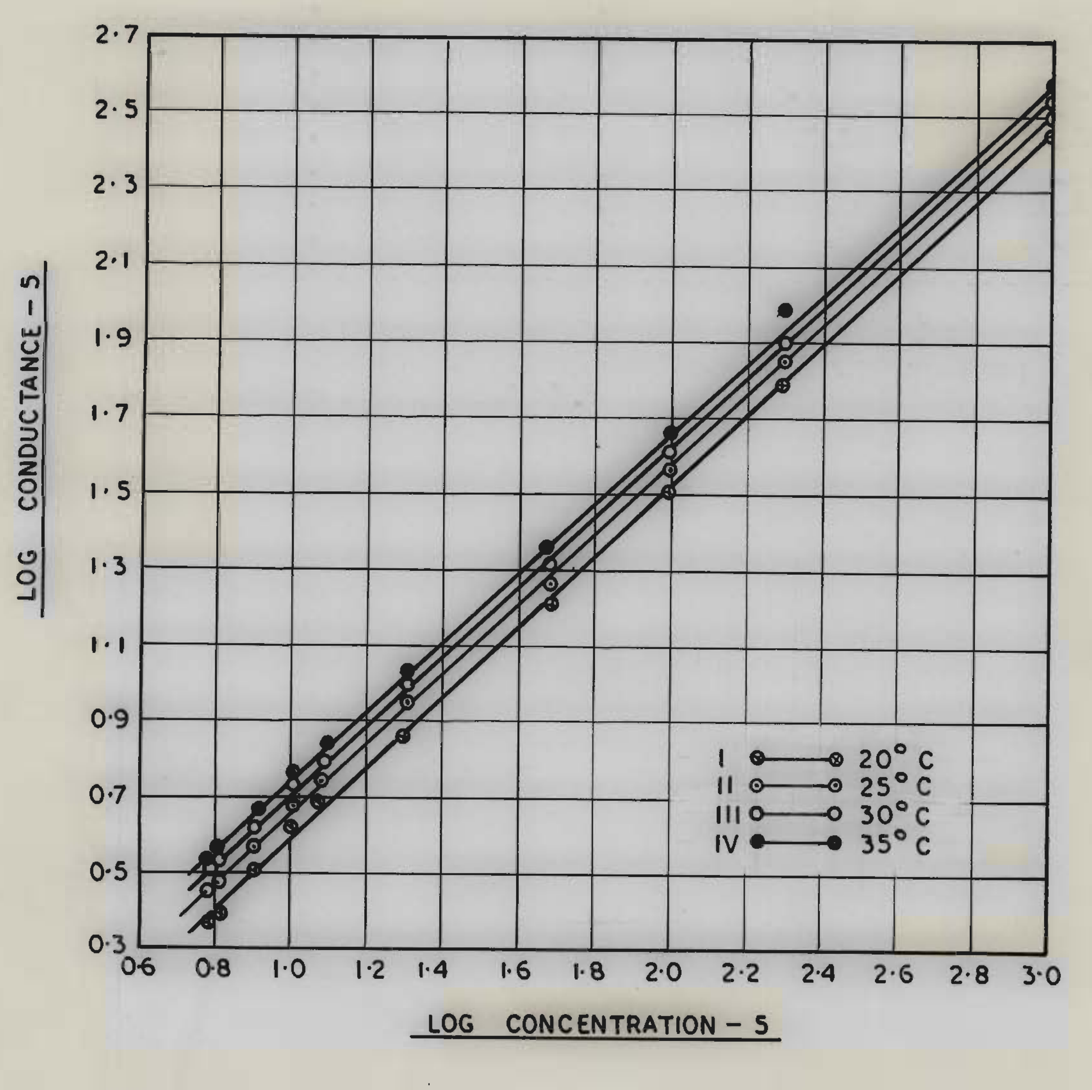

FIG. 19 STANDARD CURVES FOR BARIUM CHLORIDE

The permeability experiments with parchment supported and unsupported iron oxide and alumina membranes were carried out by flowing the electrolytes in the upper half of permeability cell, containing the above mentioned membranes. The thermostat was maintained at the desired temperature. The variations in conductance of affulent with time during the diffusion of electrolyte was observed. The volume of the affulent was kept constant e.g. 150 c.c. per hour. Conductances were measured after every twenty minutes till a constant value was attained. The concentrations were computed from the standard concentration-conductance plots of the electrolytes.

The results on permeability of unsupported iron oxide and alumina membranes in millimoles/hour to various electrolytes having common cation(K^+) and common anion (Cl^-) are given in (Table Nos. 12 to 31).

The results on the permeability of parchment supported iron oxide and alumina membranes are given in condensed (Table Nos.32,34).

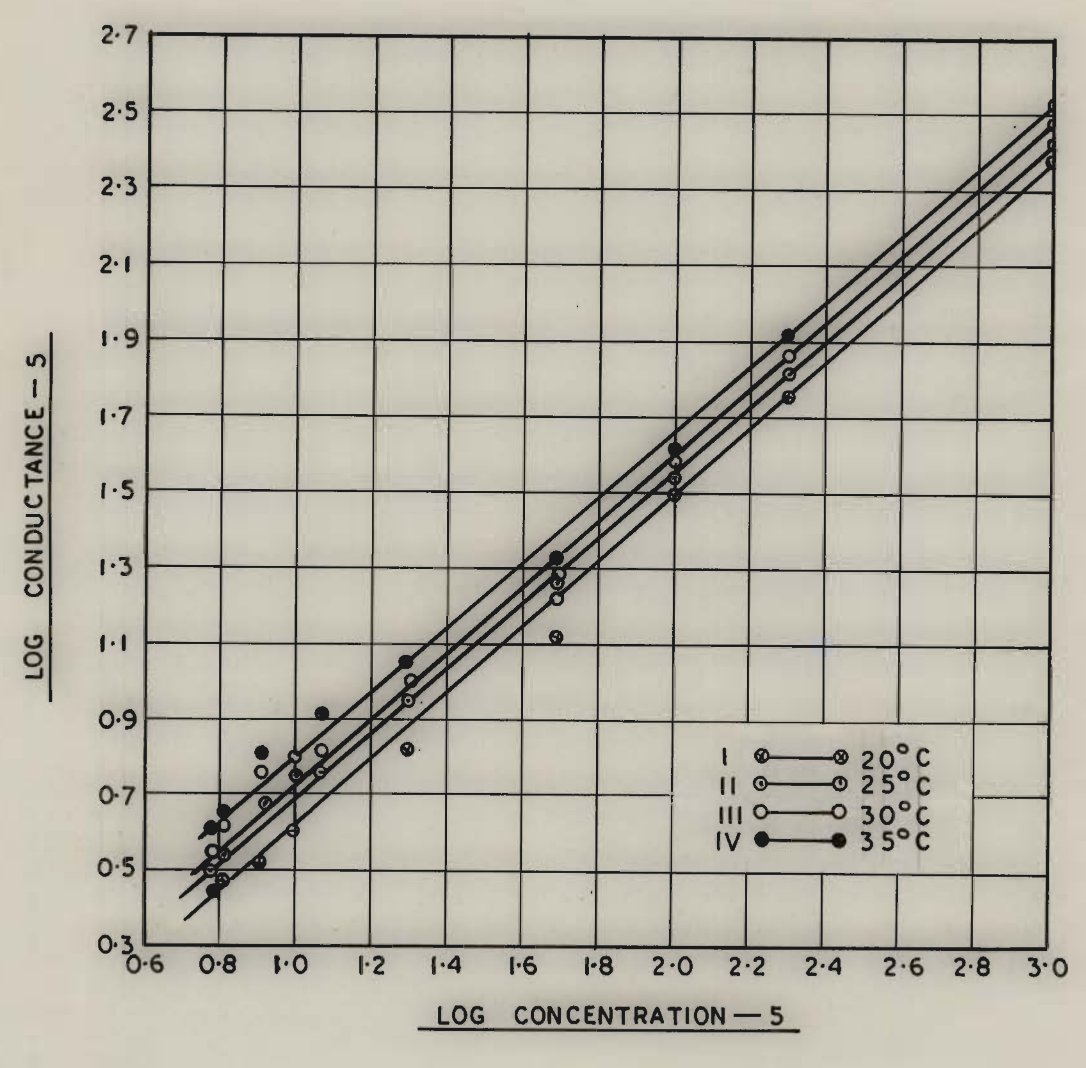

FIG.20 STANDARD CURVES FOR MAGNESIUM CHLORIDE

· Ferric oxide unsupported membranes:

TABLE No.12

Permeability of ferric oxide unsupported membrane to potassium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	9.2×10^{-5}	6.0×10^{-5}	2 hours	0.2188	0.0328
25°	12.5×10^{-5}	9.9×10^{-5}	2 hours	0.3310	0.0496
30°	16.0×10^{-5}	12.0×10^{-5}	2 hours	0.3800	0.0638
35°	26.1×10^{-5}	22.0×10^{-5}	2 hours	0.5490	0.0898

TABLE No.13

Permeability of ferric oxide unsupported membrane to potassium bromide at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken at attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	10.5×10^{-5}	5.3×10^{-5}	2 hours	0.1310	0.0197
25°	13.0×10^{-5}	7.2×10^{-5}	2 hours	0.1995	0.0299
30°	15.5×10^{-5}	12.5×10^{-5}	2 hours	0.3160	0.0332
35°	19.8×10^{-5}	17.5×10^{-5}	2 hours	0.4360	0.0654

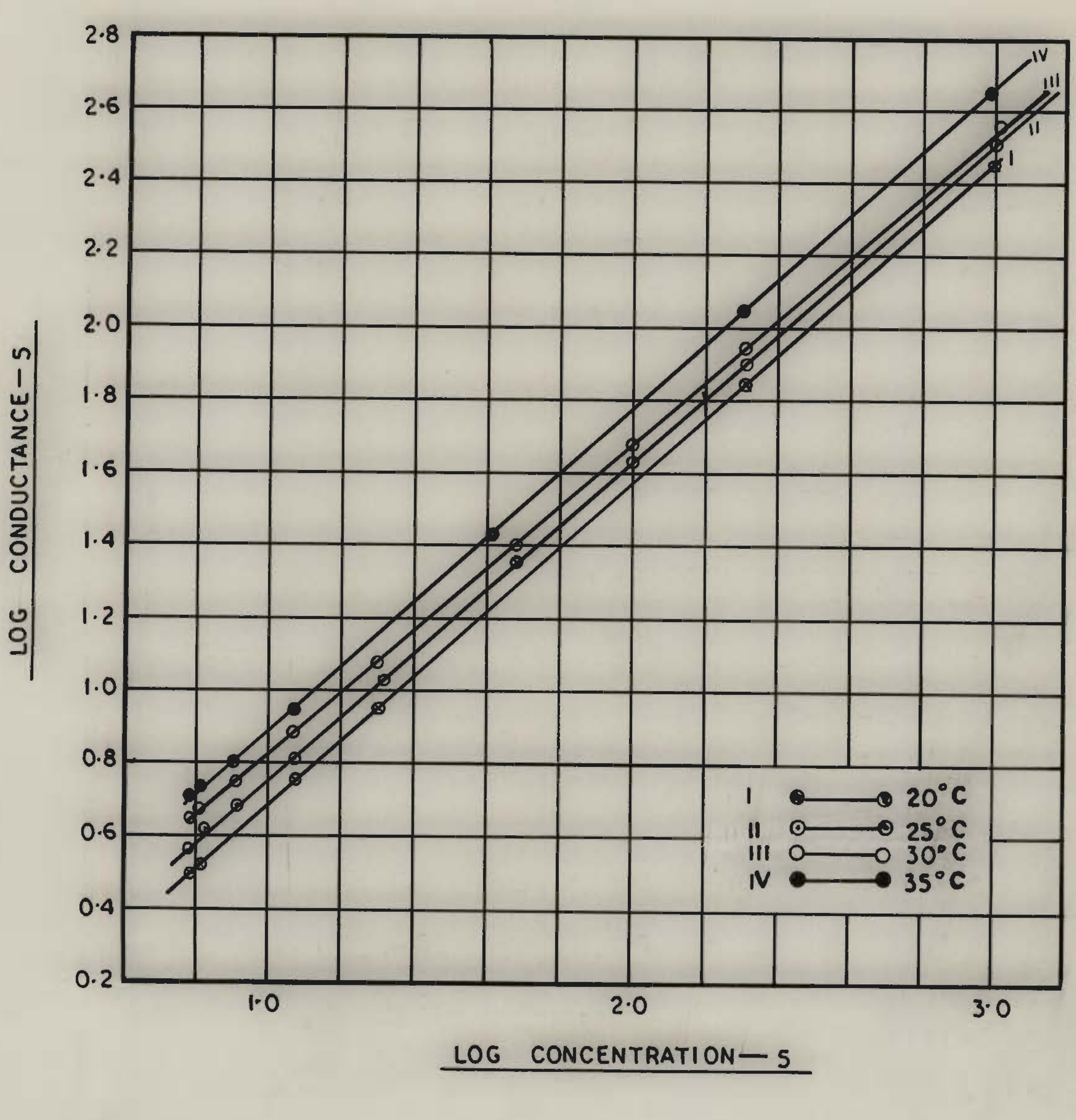

FIG. 21. STANDARD CURVES FOR CALCIUM CHLORIDE

TABLE No.14

Permeability of ferric oxide unsupported membrane to potassium nitrate at different temperatures:

Temperature ^{o}C	Initial conductance of afful ent in mhos	Final conductance of afful ent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of afful ent in millimoles	Permeability in millimoles per hour
20^{o}	$4.8x10^{-5}$	$2.6x10^{-5}$	2 hrs	0.08711	0.0120
25^{o}	$8.3x10^{-5}$	$5.0x10^{-5}$	2 hrs	0.15140	0.0227
30^{o}	$12.5x10^{-5}$	$10.0x10^{-5}$	2 hrs	0.25700	0.0387
35^{o}	$23.5x10^{-5}$	$21.0x10^{-5}$	2 hrs	0.57500	0.0963

TABLE No.15

Permeability of ferric oxide unsupported membrane to potassium thiocyanate at different temperatures:

Temperature ^{o}C	Initial conductance of afful ent in mhos	Final conductance of afful ent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of afful ent in millimoles	Permeability in millimoles per hour
20^{o}	$4.8x10^{-5}$	$2.0x10^{-5}$	2 hrs	0.0501	0.0080
25^{o}	$8.0x10^{-5}$	$4.9x10^{-5}$	2 hrs	0.1200	0.0180
30^{o}	$11.5x10^{-5}$	$10.0x10^{-5}$	2 hrs	0.2510	0.0376
35^{o}	$22.5x10^{-5}$	$19.0x10^{-5}$	2 hrs	0.4365	0.0644

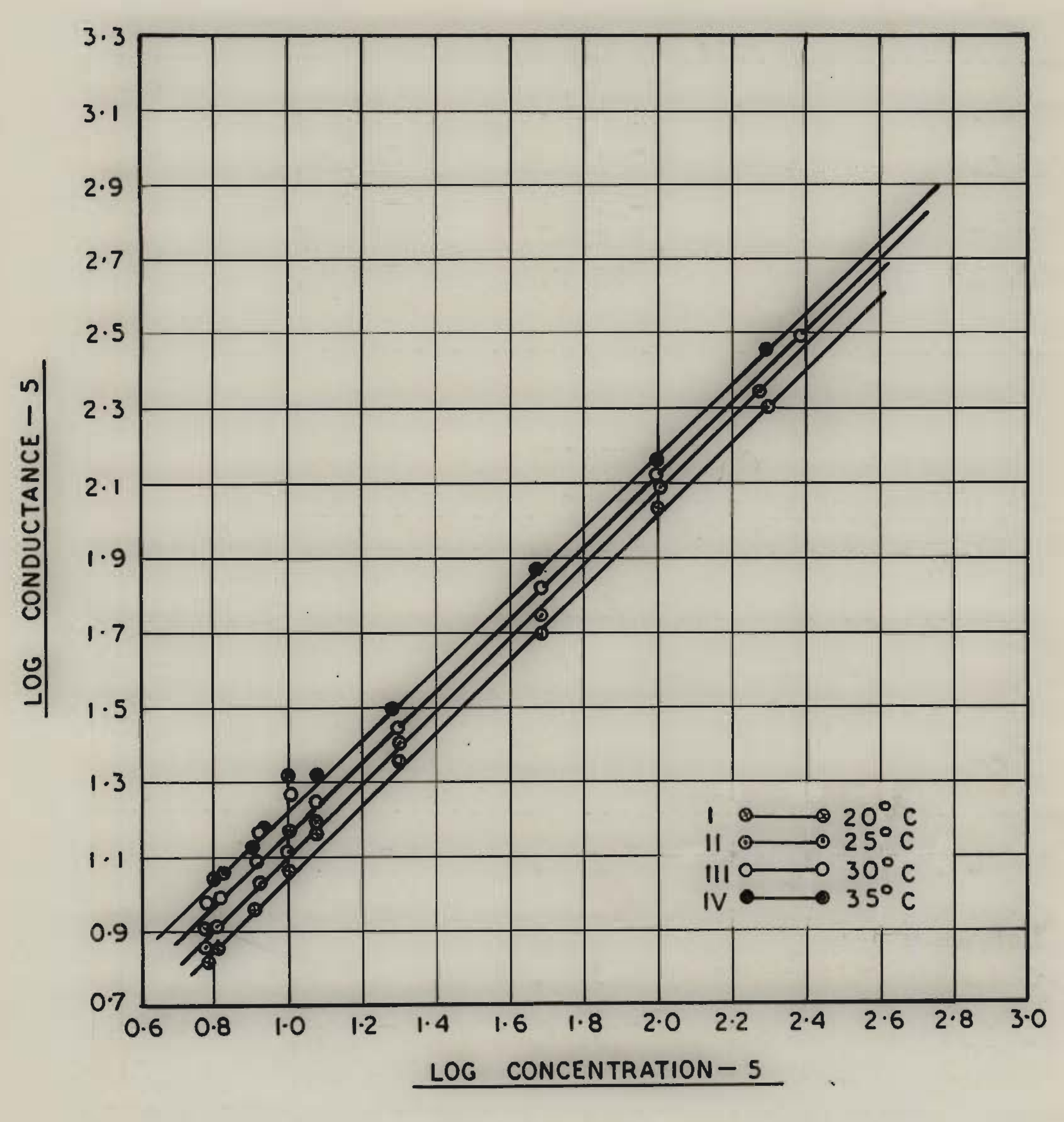

FIG. 22. STANDARD CURVES FOR FERRIC CHLORIDE

TABLE No.16

Permeability of ferric oxide unsupported membrane to potassium sulphate at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	3.8×10^{-5}	3.5×10^{-5}	2 hrs	0.0398	0.0035
25°	7.0×10^{-5}	5.2×10^{-5}	2 hrs	0.0810	0.0124
30°	14.5×10^{-5}	12.0×10^{-5}	2 hrs	0.1580	0.0237
35°	23.5×10^{-5}	22.0×10^{-5}	2 hrs	0.2880	0.0530

TABLE No.17

Permeability of ferric oxide unsupported membrane to sodium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	3.5×10^{-5}	2.9×10^{-5}	2 hrs	0.0501	0.0037
25°	9.2×10^{-5}	8.0×10^{-5}	2 hrs	0.0794	0.0059
30°	17.0×10^{-5}	15.0×10^{-5}	2 hrs	0.2818	0.0191
35°	39.1×10^{-5}	35.0×10^{-5}	2 hrs	0.6607	0.0495

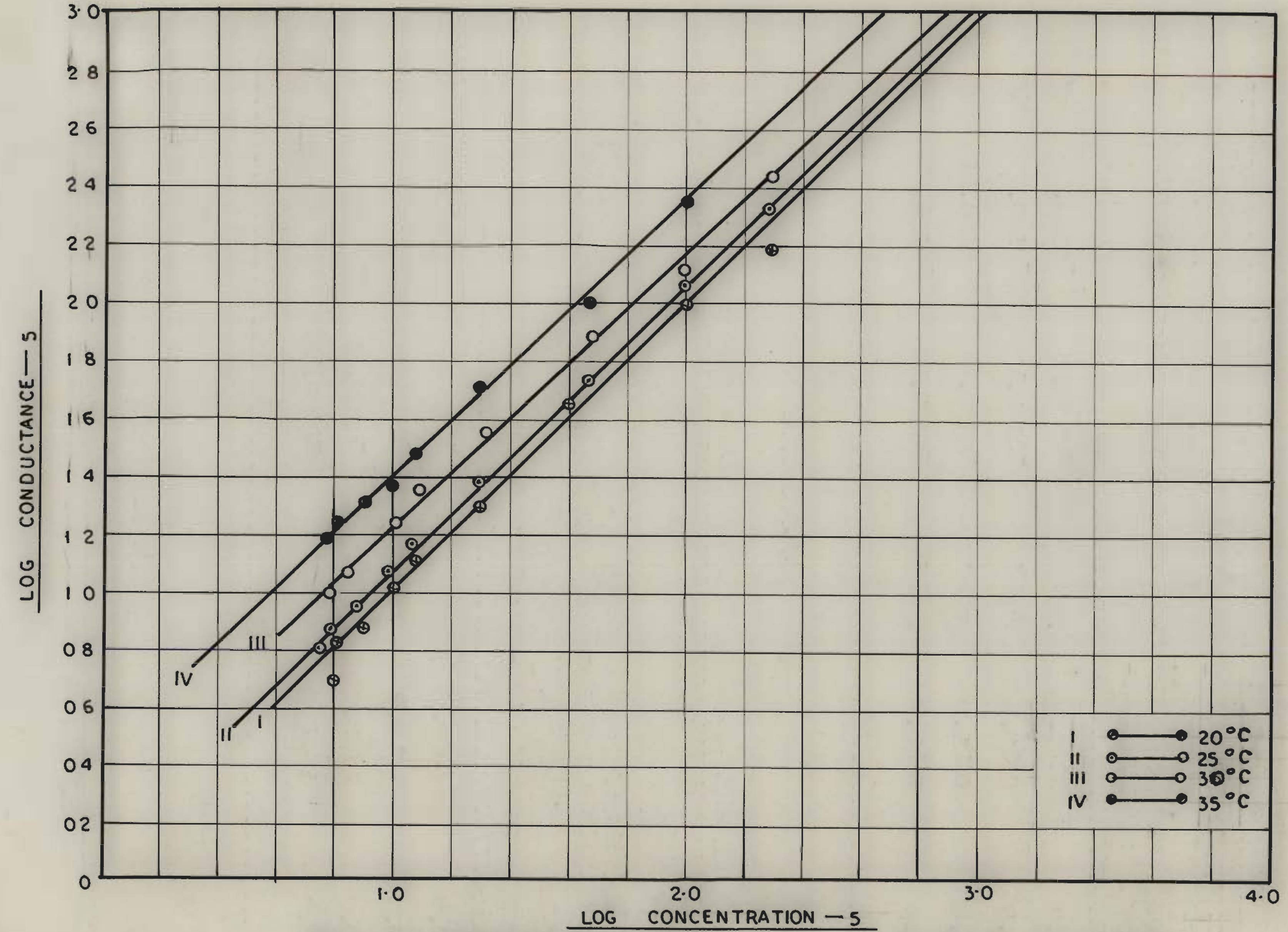

FIG. 23. STANDARD CURVES FOR ALUMINIUM CHLORIDE

TABLE No.18

Permeability of ferric oxide unsupported membrane to barium chloride at different temperatures:

Tempe-rature $^{\circ}C$	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	11.2×10^{-5}	2.0×10^{-5}	2 hrs	0.0398	0.0059
25°	13.0×10^{-5}	12.0×10^{-5}	2 hrs	0.0794	0.0119
30°	17.5×10^{-5}	15.0×10^{-5}	2 hrs	0.2818	0.0422
35°	38.0×10^{-5}	35.0×10^{-5}	2 hrs	0.6607	0.0991

TABLE No.19

Permeability of ferric oxide unsupported membrane to magnesium chloride at different temperatures:

Tempe-rature $^{\circ}C$	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	14.8×10^{-5}	10.5×10^{-5}	2 hrs	0.0524	0.0031
25°	17.6×10^{-5}	15.0×10^{-5}	2 hrs	0.1514	0.0060
30°	23.5×10^{-5}	21.0×10^{-5}	2 hrs	0.2291	0.0137
35°	32.0×10^{-5}	29.0×10^{-5}	2 hrs	0.6026	0.0361

TABLE No.20

Permeability of ferric oxide unsupported membrane to calcium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$6.1x10^{-5}$	$4.1x10^{-5}$	2 hrs	0.0812	0.0043
25°	$7.9x10^{-5}$	$5.9x10^{-5}$	2 hrs	0.1023	0.0055
30°	$8.8x10^{-5}$	$6.5x10^{-5}$	2 hrs	0.5000	0.0077
35°	$10.0x10^{-5}$	$7.5x10^{-5}$	2 hrs	0.8500	0.0130

TABLE No.21

Permeability of ferric oxide unsupported membrane to ferric chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$9.5x10^{-5}$	$8.3x10^{-5}$	2 hrs	0.0711	0.0019
25°	$11.2x10^{-5}$	$9.3x10^{-5}$	2 hrs	0.0724	0.0026
30°	$12.0x10^{-5}$	$9.9x10^{-5}$	2 hrs	0.0660	0.0039
35°	$12.2x10^{-5}$	$10.2x10^{-5}$	2 hrs	0.0800	0.0048

Alumina unsupported membranes:

TABLE No.22

Permeability of alumina unsupported membrane to potassium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeab lity in millimoles per hour
20°	25.5×10^{-5}	18.5×10^{-5}	2 hrs	0.7244	0.1086
25°	30.5×10^{-5}	25.0×10^{-5}	2 hrs	0.8710	0.1306
30°	42.5×10^{-5}	38.0×10^{-5}	2 hrs	1.2590	0.1888
35°	66.0×10^{-5}	62.0×10^{-5}	2 hrs	1.7380	0.2607

TABLE No.23

Permeability of alumina unsupported membrane to potassium bromide at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeabi lity in millimoles per hour
20°	15.0×10^{-5}	12.0×10^{-5}	2 hrs	0.3162	0.0474
25°	23.0×10^{-5}	20.0×10^{-5}	2 hrs	0.6607	0.0991
30°	35.5×10^{-5}	32.0×10^{-5}	2 hrs	1.0470	0.1570
35°	52.0×10^{-5}	48.0×10^{-5}	2 hrs	1.2590	0.2377

TABLE No.24

Permeability of alumina unsupported membrane to potassium nitrate at different temperatures:

Tempe-rature ^{o}C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attain-ing const. value of conductan-ce	Concentration corresponding to const. conductance of afful ent in millimoles	Permeabi-lity in milli-moles per hour
20^{o}	10.5×10^{-5}	8.0×10^{-5}	2 hrs	0.3162	0.0474
25^{o}	18.0×10^{-5}	15.5×10^{-5}	2 hrs	0.5495	0.0824
30^{o}	33.5×10^{-5}	28.5×10^{-5}	2 hrs	1.0470	0.1570
35^{o}	52.0×10^{-5}	49.0×10^{-5}	2 hrs	1.5850	0.2377

TABLE No.25

Permeability of alumina unsupported membrane to potassium thiocyanate at different temperatures:

Tempe-rature ^{o}C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attain-ing const. value of conductan-ce	Concentration corresponding to const. conductance of afful ent in millimoles	Permeabi-lity in milli-moles per hour
20^{o}	6.8×10^{-5}	5.2×10^{-5}	2 hrs	0.1622	0.0243
25^{o}	11.5×10^{-5}	10.0×10^{-5}	2 hrs	0.3162	0.0474
30^{o}	21.2×10^{-5}	18.5×10^{-5}	2 hrs	0.5754	0.0863
35^{o}	39.0×10^{-5}	35.8×10^{-5}	2 hrs	1.0000	0.1500

TABLE No.26

Permeability of alumina unsupported membrane to potassium sulphate at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$16.0x10^{-5}$	$10.5x10^{-5}$	2 hrs	0.0871	0.0130
25°	$15.9x10^{-5}$	$12.0x10^{-5}$	2 hrs	0.1259	0.0188
30°	$18.2x10^{-5}$	$17.0x10^{-5}$	2 hrs	0.2630	0.0374
35°	$37.0x10^{-5}$	$35.0x10^{-5}$	2 hrs	0.5495	0.0824

TABLE No.27

Permeability of alumina unsupported membrane to sodium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$20.0x10^{-5}$	$14.5x10^{-5}$	2 hrs	0.4365	0.0654
25°	$25.0x10^{-5}$	$22.5x10^{-5}$	2 hrs	0.5754	0.0864
30°	$37.0x10^{-5}$	$34.5x10^{-5}$	2 hrs	0.7586	0.1137
35°	$52.0x10^{-5}$	$49.0x10^{-5}$	2 hrs	1.0000	0.1500

TABLE No.28

Permeability of alumina unsupported membrane to barium chloride at different temperatures:

Temperature °C	Initial conductance of afful ent in mhos	Final conductance of afful ent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of afful ent in millimoles	Permeability in millimoles per hour
20°	$20.5x10^{-5}$	$9.0x10^{-5}$	2 hrs	0.5495	0.0722
25°	$30.0x10^{-5}$	$27.5x10^{-5}$	2 hrs	0.8318	0.1247
30°	$45.0x10^{-5}$	$42.5x10^{-5}$	2 hrs	1.0960	0.1644
35°	$78.0x10^{-5}$	$72.0x10^{-5}$	2 hrs	1.8200	0.2930

TABLE No.29

Permeability of alumina unsupported membrane to calcium chloride at different temperatures:

Temperature °C	Initial conductance of afful ent in mhos	Final conductance of afful ent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of afful ent in millimoles	Permeability in millimoles per hour
20°	$21.5x10^{-5}$	$19.0x10^{-5}$	3 hrs	0.4571	0.0717
25°	$28.0x10^{-5}$	$25.0x10^{-5}$	3 hrs	0.5248	0.0787
30°	$42.0x10^{-5}$	$39.0x10^{-5}$	2 hrs	0.7943	0.1190
35°	$55.0x10^{-5}$	$52.0x10^{-5}$	2 hrs	0.8318	0.1247

TABLE No.30

Permeability of alumina unsupported membrane to magnesium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final Conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	23.1×10^{-5}	21.6×10^{-5}	3 hrs	0.3162	0.0474
25°	26.0×10^{-5}	18.5×10^{-5}	3 hrs	0.4365	0.0654
30°	31.0×10^{-5}	29.0×10^{-5}	3 hrs	0.6918	0.1037
35°	52.0×10^{-5}	48.5×10^{-5}	3 hrs	1.0960	0.1643

TABLE No.31

Permeability of alumina unsupported membrane to aluminium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	8.2×10^{-5}	3.1×10^{-5}	3 hrs	0.0288	0.0043
25°	10.2×10^{-5}	5.9×10^{-5}	3 hrs	0.0501	0.0075
30°	17.0×10^{-5}	12.0×10^{-5}	2 hrs	0.0786	0.0113
35°	36.5×10^{-5}	32.0×10^{-5}	2 hrs	0.1259	0.0188

Permeability of pre-treated parchment supported and unsupported iron oxide and parchment supported and unsupported alumina membranes to different electrolytes:

The effect of pre-treated membranes to various electrolytes was studied by soaking the iron oxide and alumina membranes in ferric chloride solution (0.1M) and aluminium chloride solution (0.1M) respectively for 8 hours and the permeability experiments were carrie out at 20°C for comparision with the untreated iron oxide and alumina membranes.

The iron oxide and alumina membranes were also treated with cationic, anionic and non-ionic soap solutions. The membranes were soaked in 10^{-3}M cetyl pyridinium bromide, 10^{-3}M sulphonated phenyl stearic acid and 10^{-3}M lauric acid diethanol amine condensate for 8 hours. The results were compared with those of untreated membranes (Tables No.32 to 34).

The anionic soap viz., sulphonated phenyl stearic acid was prepared by the method recommended by Stirton et.al.(7), cetyl pyridinium bromide, a BDH product, was recrystallised from acetone. The non-ionic soap viz., lauric acid diethanol amine condensate (8) (LDC), was prepared by condensing pure lauric acid (BDH) with diethanol amine.

TABLE No.32

Permeability of parchment supported treated and untreated iron oxide membranes

(Permeability expressed as millimole/hr, electrolyte concentration 0.2M).

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Ferric chloride
KCl	0.0069	0.0068	0.0079	0.0065	0.0041
KBr	0.0045	0.0044	0.0061	0.0028	0.0039
KNO_3	0.0044	0.0043	0.0049	0.0042	0.0037
KCNS	0.0023	0.0023	0.0047	0.0021	0.0012
K_2SO_4	0.0018	0.0017	0.0020	0.0011	0.0011
NaCl	0.0071	0.0062	0.0075	0.0039	0.0030
$MgCl_2$	0.0068	0.0067	0.0072	0.0049	0.0042
$CaCl_2$	0.0043	0.0043	0.0057	0.0041	0.0030
$BaCl_2$	0.0039	0.0039	0.0067	0.0038	0.0029
$FeCl_3$	0.0019	0.0018	0.0041	0.0015	0.0013

TABLE No.33

Permeability of unsupported treated and untreated iron oxide membranes:

(Permeability expressed as millimole/hr, electrolyte concentration 0.2M)

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Ferric chloride
KCl	0.0328	0.0289	0.0644	0.0180	0.0070
KBr	0.0190	0.0189	0.0520	0.0140	0.0112
KNO_3	0.0120	0.0120	0.0239	0.0097	0.0075
KCNS	0.0080	0.0085	0.0339	0.0079	0.0079
K_2SO_4	0.0035	0.0034	0.0083	0.0027	0.0034
NaCl	0.0037	0.0037	0.0068	0.0020	0.0016
$CaCl_2$	0.0043	0.0044	0.0088	0.0032	0.0027
$BaCl_2$	0.0597	0.0580	0.1020	0.0389	0.0289
$MgCl_2$	0.0052	0.0051	0.0098	0.0030	0.0021
$FeCl_3$	0.0019	0.0019	0.0030	0.0016	0.0010

TABLE No.34

Permeability of parchment supported treated and untreated alumina membranes:

(Permeability expressed as millimole/hr, electrolyte concentration 0.2M)

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Aluminium chloride
KCl	0.0597	0.0588	0.0999	0.0421	0.3102
KBr	0.0243	0.0238	0.0682	0.0200	0.0152
KNO_3	0.0237	0.0209	0.0500	0.0197	0.0100
KCNS	0.0130	0.0132	0.0383	0.0100	0.0082
K_2SO_4	0.0065	0.0063	0.0100	0.0040	0.0028
NaCl	0.0309	0.0304	0.0690	0.0210	0.0162
$MgCl_2$	0.0260	0.0270	0.0521	0.0230	0.0141
$BaCl_2$	0.0227	0.0220	0.0440	0.0200	0.0092
$CaCl_2$	0.0150	0.0149	0.0310	0.0082	0.0050
$AlCl_3$	0.0065	0.0064	0.0100	0.0060	0.0038

TABLE No.35

Permeability of unsupported treated and untreated alumina membranes

(Permeability expressed as millimole/hr, electrolyte concentration 0.2M)

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Aluminium chloride
KCl	0.1086	0.0988	0.1370	0.0824	0.0500
KBr	0.0597	0.0590	0.0920	0.0392	0.0213
KNO_3	0.0474	0.0480	0.0800	0.0324	0.0190
KCNS	0.0243	0.0239	0.0521	0.0110	0.0091
K_2SO_4	0.0130	0.0130	0.0320	0.0098	0.0060
NaCl	0.0717	0.0700	0.1000	0.0801	0.0461
$MgCl_2$	0.0474	0.0980	0.0784	0.0683	0.0500
$CaCl_2$	0.0289	0.0299	0.0482	0.0312	0.0234
$BaCl_2$	0.0237	0.0240	0.0460	0.0201	0.0098
$AlCl_3$	0.0150	0.0148	0.0312	0.0100	0.0062

Membrane potential

Membrane potentials due to diffusion of various electrolytes were determined by the method described in chapter II. Potential measurments of ferric oxide and alumina membranes with treated and untreated membranes were made. The results are summerised in tables (36 to 39).

TABLE No.36

Potential of parchment supported treated and untreated iron oxide membranes:

(Potential expressed in millivolts; concentration of electrolyte on two sides of the membrane, 0.1 and 0.01M respectively)

Electrolyte	Untreated membrane	After treatment with Non-ionic soap	Anionic soap	Cationic soap	Ferric chloride
KCl	12.0	13.0	10.5	18.0	19.0
KBr	15.5	15.0	12.0	20.0	21.5
KNO_3	23.0	23.5	18.0	24.0	24.0
KCNS	27.0	27.0	20.0	35.0	37.0
K_2SO_4	38.0	37.0	26.0	42.0	42.5
NaCl	21.0	22.5	16.0	39.0	39.5
$MgCl_2$	35.0	36.0	28.0	42.0	44.5
$CaCl_2$	38.0	38.0	31.5	46.0	48.5
$BaCl_2$	39.0	38.5	34.0	48.5	52.5
$FeCl_3$	53.0	52.5	48.0	55.0	59.0

TABLE No.37

Potential of unsupported treated and untreated iron oxide membranes:

(Potential expressed in millivolts; concentration of electrolyte on two sides of the membrane, 0.1 and 0.01M respectively).

Electrolyte	Untreated membrane	After treatment with Non-ionic soap	Anionic soap	Cationic soap	Ferric chloride
KCl	10.0	10.0	19.0	25.0	28.0
KBr	13.0	13.2	20.0	27.0	29.0
KNO_3	22.5	22.0	23.0	32.0	36.0
KCNS	25.5	25.5	21.0	22.0	32.0
K_2SO_4	30.0	31.5	29.0	44.0	49.0
NaCl	42.0	42.0	40.0	45.0	53.0
$MgCl_2$	49.0	48.9	47.0	53.0	56.0
$CaCl_2$	30.0	30.5	28.5	34.0	38.0
$BaCl_2$	28.0	27.5	26.0	32.0	36.0
$FeCl_3$	54.0	54.0	52.0	56.0	60.0

TABLE No.38

Potential of parchment supported treated and untreated alumina membranes:

(Potential expressed in millivolts; concentration of electrolyte on two sides of the membrane, 0.1 and 0.01M respectively)

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Aluminium chloride
KCl	11.8	11.5	9.0	16.0	21.0
KBr	14.5	14.5	13.0	18.0	22.5
KNO_3	22.5	22.5	21.0	25.5	29.8
KCNS	25.0	24.9	22.5	30.5	35.5
K_2SO_4	35.0	35.0	33.5	39.0	42.5
NaCl	20.0	19.5	18.0	22.5	28.0
$MgCl_2$	34.0	34.0	33.5	38.0	43.5
$CaCl_2$	39.0	38.5	37.0	42.0	46.0
$BaCl_2$	35.0	35.0	34.0	40.0	43.0
$AlCl_3$	42.0	42.1	40.0	48.0	55.0

TABLE No.39

Potential of unsupported treated and untreated alumina membranes:

(Potential expressed in millivolts; concentration of electrolyte on two sides of the membrane, 0.1 and 0.01M respectively).

Electrolyte	Untreated membrane	After treatment with Non-ionic soap	Anionic soap	Cationic soap	Aluminium chloride
KCl	9.0	9.0	8.5	12.5	16.0
KBr	12.0	12.0	11.0	16.0	19.0
KNO_3	18.5	18.0	16.5	22.5	25.5
KCNS	25.0	25.5	24.0	28.0	30.5
K_2SO_4	28.5	28.0	27.6	32.0	35.0
NaCl	15.5	15.0	14.0	18.0	20.0
$MgCl_2$	20.0	20.5	16.0	25.0	30.0
$CaCl_2$	25.5	25.0	21.0	30.0	35.0
$BaCl_2$	24.0	24.5	20.0	30.0	32.5
$AlCl_3$	31.5	31.0	30.0	38.0	48.0

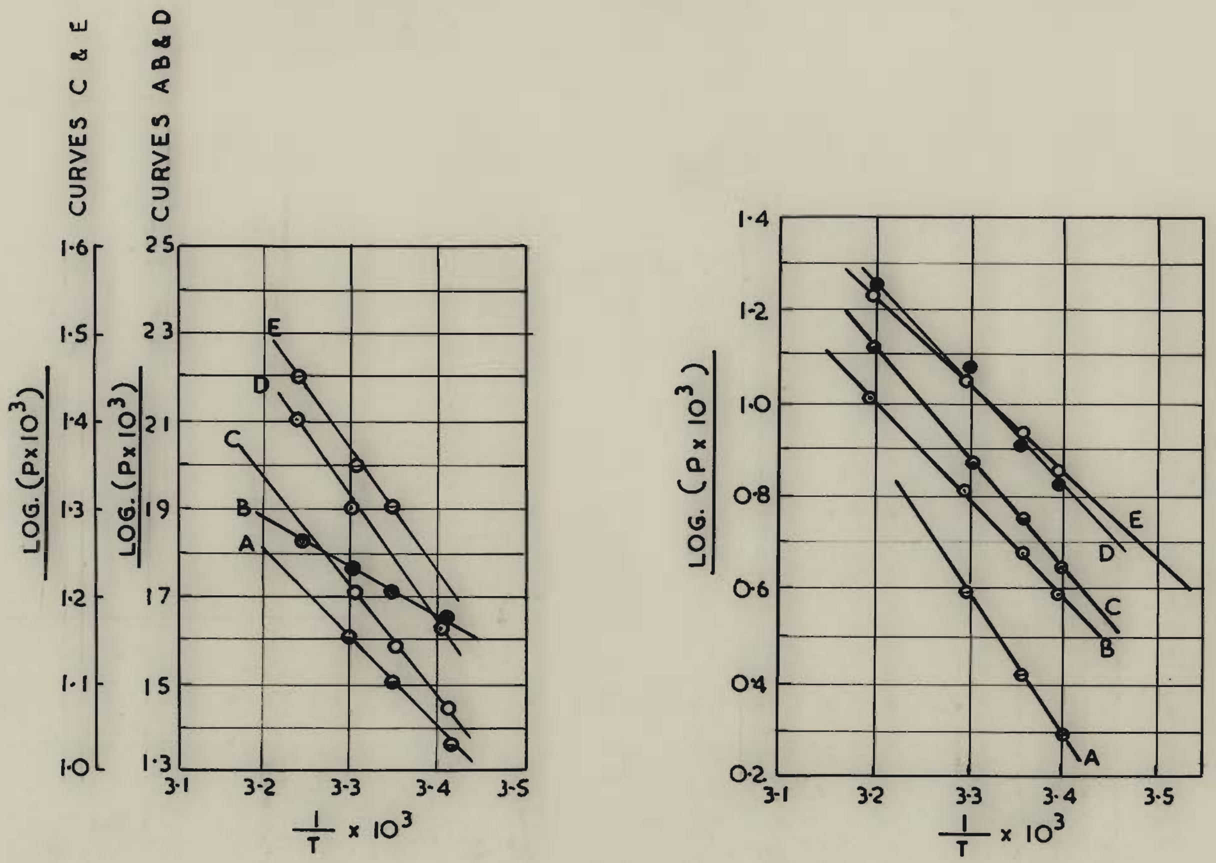

FIG. 24 ACTIVATION ENERGY CURVES FOR PARCHMENT SUPPORTED IRON OXIDE MEMBRANES

Influence of temperature on permeability:

The diffusion rates were found to be highly dependent on temperature showing an increase with rise in temperature. The plots between diffusion values log $(p \times 10^3)$ against $\frac{1}{T} \times 10^3$ for different electrolytes gave straight lines (Fig.24 to 27) relationship from the slopes of which the energy of activation E, of the diffusion process could be calculated.

TABLE No.40

Activation Energy of the diffusion process for different electrolytes in the case of parchment supported iron oxide membranes:

Electrolyte	Activation energy cal./mole	Electrolyte	Activation energy cal./mole
KCl	5673	NaCl	5296
KBr	4712	$BaCl_2$	4767
KNO_3	6112	$MgCl_2$	5112
KCNS	4606	$CaCl_2$	5485
K_2SO_4	6337	$FeCl_3$	7088

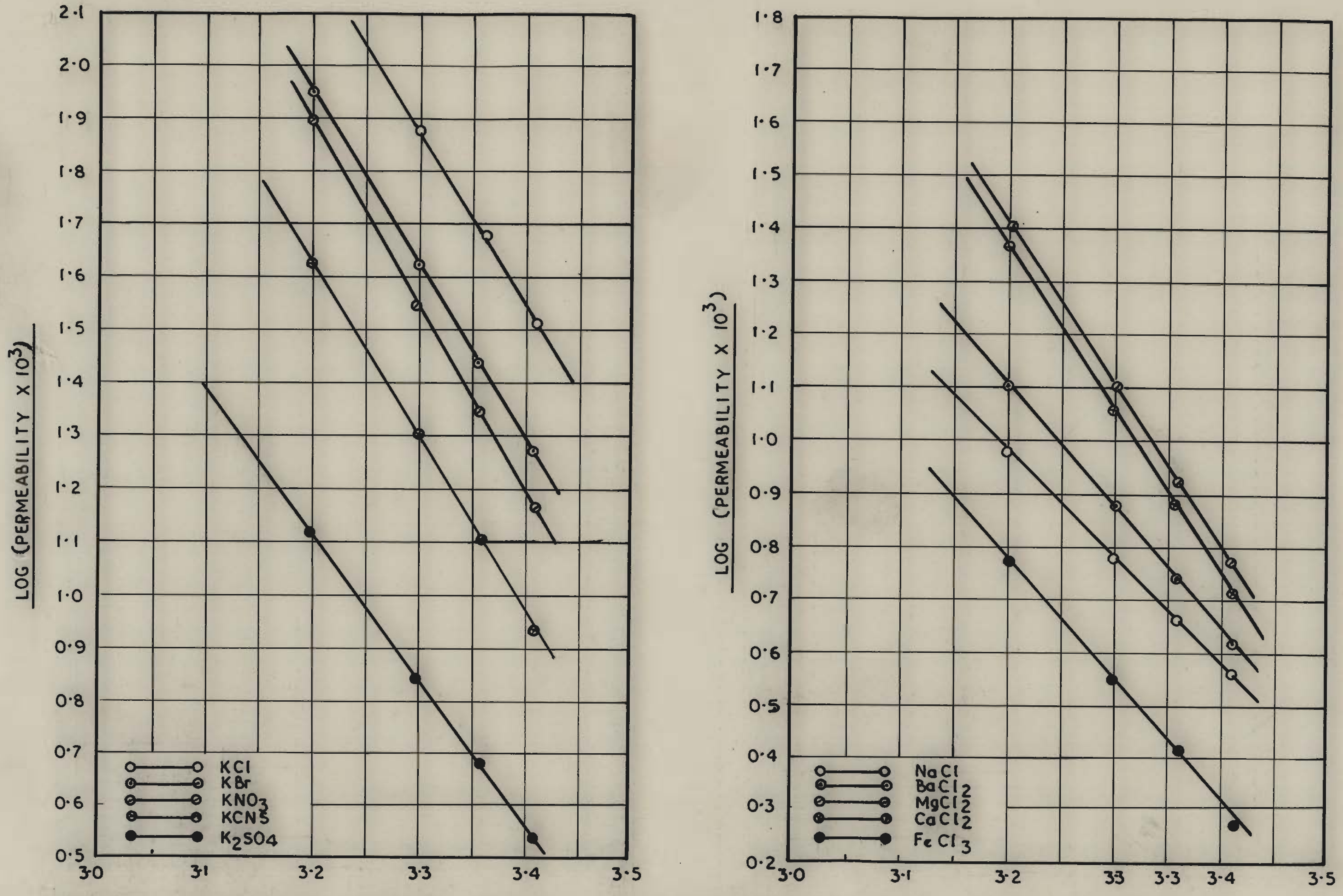

FIG. 25. ACTIVATION ENERGY CURVES FOR UNSUPPORTED FERRIC OXIDE MEMBRANES

TABLE No.41

Activation energy of the diffusion process for different electrolytes in the case of unsupported iron oxide membranes:

Electrolyte	Activation energy cal./mole	Electrolyte	Activation energy cal./mole
KCl	7369	NaCl	4769
KBr	6616	$BaCl_2$	5485
KNO_3	7968	$MgCl_2$	7226
KCNS	7093	$CaCl_2$	7369
K_2SO_4	5895	$FeCl_3$	5298

TABLE No.42

Activation energy of the diffusion process for different electrolytes in the case of parchment supported alumina membranes:

Electrolyte	Activation energy cal./mole	Electrolyte	Activation energy cal./mole
KCl	7830	NaCl	6909
KBr	12436	$BaCl_2$	7000
KNO_3	12486	$MgCl_2$	9672
KCNS	13516	$CaCl_2$	7369
K_2SO_4	13672	$AlCl_3$	9868

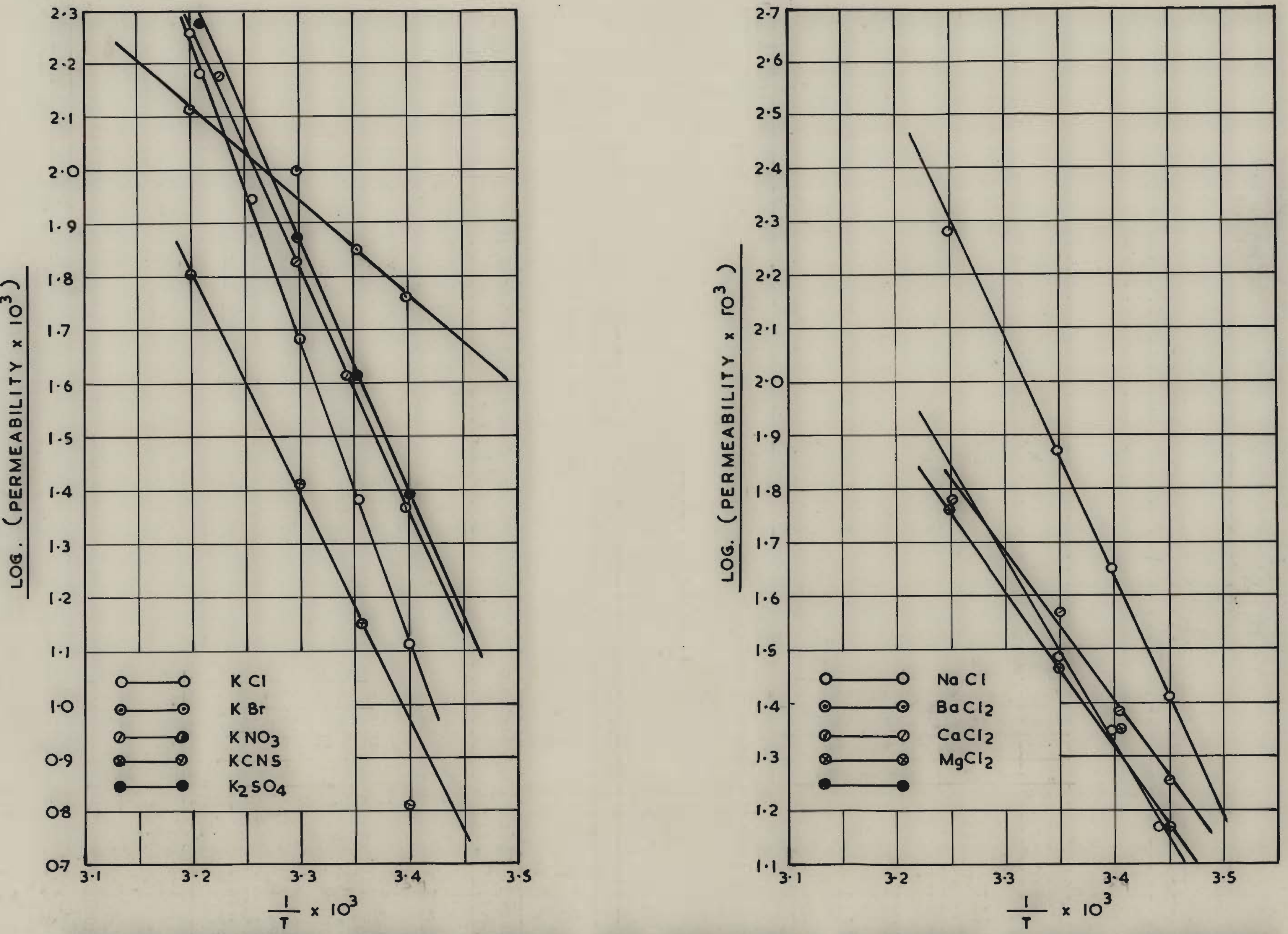

FIG. 26. ACTIVATION ENERGY CURVES FOR PARCHMENT SUPPORTED ALUMINA MEMBRANES

TABLE No.43

Activation energy of the diffusion process for different electrolytes in the case of unsupported alumina membranes:

Electrolyte	Activation energy cal./mole	Electrolyte	Activation energy cal./mole
KCl	8330	NaCl	8212
KBr	9860	$BaCl_2$	8290
KNO_3	9600	$MgCl_2$	9672
KCNS	9672	$CaCl_2$	5152
K_2SO_4	12520	$AlCl_3$	9960

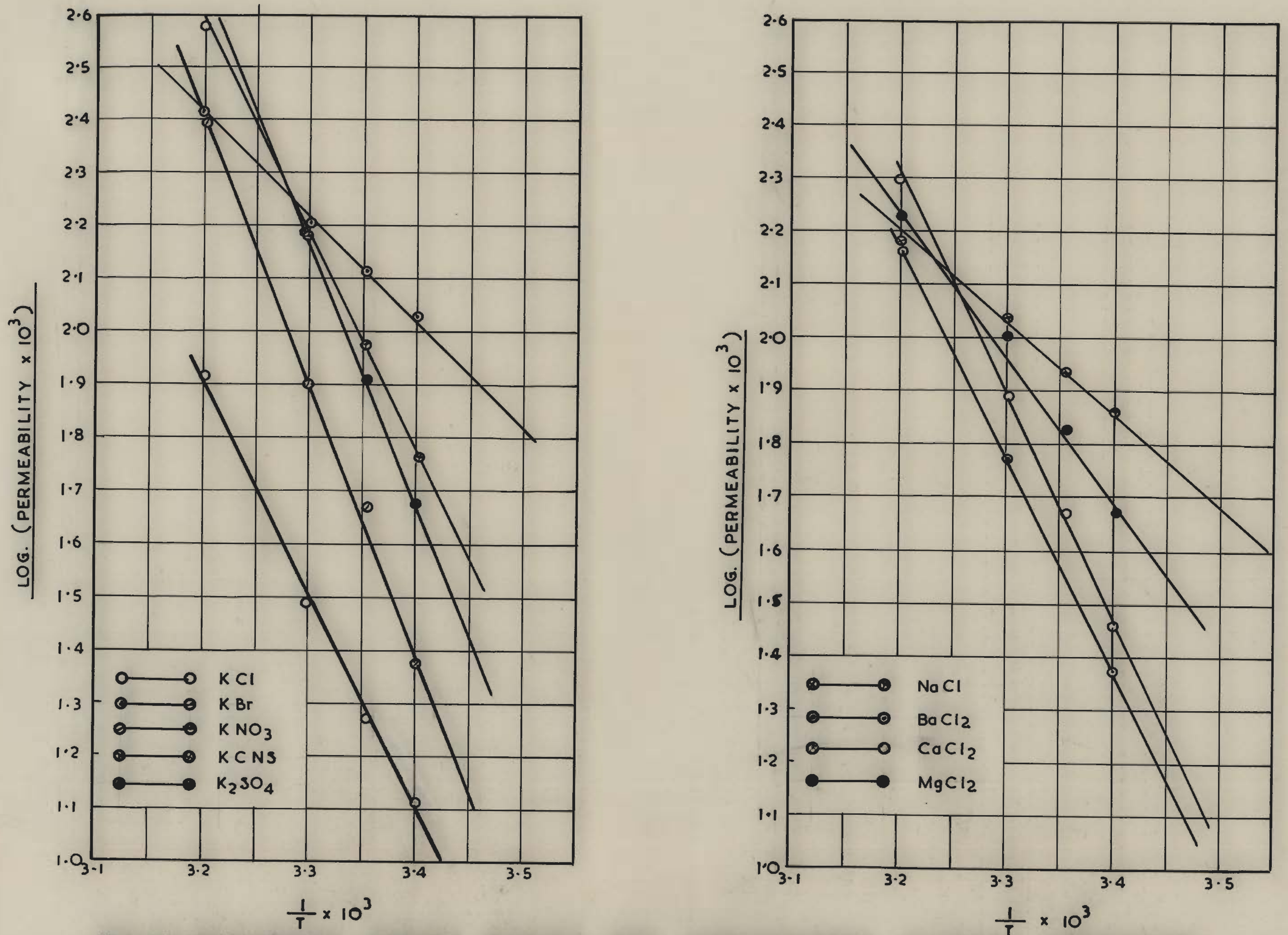

FIG. 27 ACTIVATION ENERGY CURVES FOR UNSUPPORTED ALUMINA MEMBRANES

DISCUSSION

From permeability datas for ferric oxide and alumina (supported and unsupported) it is seen that the order of anions is same in all cases viz., $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$. The cationic sequence for parchment supported iron oxide membrane is $Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Ba^{2+} > Fe^{3+}$ and for unsupported membrane it is $K^+ > Ba^{2+} > Ca^{2+} > Na^+ > Mg^{2+} > Fe^{3+}$. For alumina parchment supported membrane, the order for cations is $K^+ > Na^+ > Mg^{2+} > Ba^{2+} > Ca^{2+} > Al^{3+}$ and $K^+ > Ba^{2+} > Ca^{2+} > Na^+ > Mg^{2+} > Al^{3+}$ for unsupported membrane.

It is evident from permeability data recorded in (Table Nos.32,33 and 34,35) that unsupported ferric oxide and alumina membranes have higher permeability values as compared to parchment supported membranes. Further the magnitude of the permeability values for alumina membranes is higher than the corresponding iron oxide membranes.

It has been observed that there is dissimilarity in the sequence of cations for supported iron oxide and alumina membranes. The cationic sequence in the case of unsupported ferric oxide and alumina membranes is same.

It is also evident from the data recorded in (Table Nos.32 to 35) that the permeability of ions is considerably influenced on treatment of the ferric oxide and alumina membranes with ferric chloride and aluminium chloride solutions respectively. The diffusion of ions is retarded to a great extent. The order of permeability of cations and anions is exactly the same as in untreated ferric oxide and alumina membranes.

It is interesting to note that non-ionic soap (lauric acid diethanol-amine condensate) treated ferric oxide and alumina membranes show no change in the diffusion values. The order of permeability is also uneffected.

Further the cationic soap (cetyl pyridinium bromide) treated ferric oxide and alumina membranes retards the diffusion rate of ions, and the retardation is not to that extent as that of ferric chloride or aluminium chloride treated ferric oxide and alumina membranes. The order of permeability of parchment supported iron oxide and alumina membranes is $Cl^- > NO_3^- > Br^- > CNS^- > SO_4^{2-}$; $K^+ > Na^+ > Ba^{2+} > Ca^{2+} > Mg^{2+} > Fe^{3+}$ and $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$; $K^+ > Mg^{2+} > Ba^{2+} > Na^+ > Ca^{2+} > Al^{3+}$ respectively, while the order of anions and cations for unsupported ferric oxide and alumina membranes is almost the same viz., $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$;
$K^+ > Ba^{2+} > Ca^{2+} > Mg^{2+} > Na^+ > Fe^{3+}$ (for ferric oxide)
$K^+ > Ba^{2+} > Ca^{2+} > Na^+ > Mg^{2+} > Al^{3+}$ (for alumina)

The anionic soap (sulphonated phenyl stearic acid) treated iron oxide and alumina membranes (supported and unsupported) show an increase in the rate of permeation. Here the order of permeability for cations and anions is same as in untreated membranes.

The probable mechanism of diffusion across these membranes will be discussed in Chapter IV alongwith silica ferric silicate and aluminium silicate membranes.

Effect of different electrolytes on membrane potential:

In this study membrane potential shows an increase in initial stage after which it attains a constant value. This reveals that once membrane has attained certain charge (by adsorption of ions from the electrolyte solution) the permeability phenomenon is solely governed by surface forces on the membrane. The observations on pretreated membranes also support this view. It is also possible to interpret results in the light of the views of Meyer and Sievers (loc.cit), who postulated a number of fixed charges due to either adsorption or ionization of membrane material between the fixed ion of the pores and those in the bulk of the solution.

The potential values in the case of supported membranes (Table Nos.36 and 38) are higher as compared to potential values of unsupported membranes (Table Nos. 37 and 39). This supports the view that higher the permeability lower will be the potential attained. The order of potential values of different anions and cations for parchment supported and unsupported iron oxide and alumina membrane are just the reverse of permeability values viz., $SO_4^{2-} > CNS^- > NO_3^- > Br^- > Cl^-$ (for all membranes) $Fe^{3+} > Ba^{2+} > Ca^{2+} > Mg^{2+} > K^+ > Na^+$; $Fe^{3+} > Mg^{2+} > Na^+ > Ca^{2+} > Ba^{2+} > K^+$ (for parchment supported and unsupported iron oxide membranes) and $Al^{3+} > Ca^{2+} > Ba^{2+} > Mg^{2+} > Na^+ > K^+$; $Al^{3+} > Mg^{2+} > Na^+ > Ca^{2+} > Ba^{2+} > K^+$ (for parchment supported and unsupported alumina membranes).

The cationic soap treated membranes as expected gives higher potential values (Table Nos.32 to 35) than untreated membranes. The order of potential values for different ions in the case of parchment supported iron oxide and alumina membranes is:
$SO_4^{2-} > CNS^- > NO_3 > Br^- > Cl^-$ (for all membranes)
$Fe^{3+} > Ba^{2+} > Ca^{2+} > Mg^{2+} > Na^+ > K^+$(for parchment supported iron oxide); $Fe^{3+} > Mg^{2+} > Na^+ > Ca^{2+} > Ba^{2+} > K^+$ (for unsupported iron oxide membrane) and $Al^{3+} > Ca^{2+} > Ba^{2+} > Mg^{2+} > Na^+ > K^+$ (for parchment supported alumina membrane); $Al^{3+} > Mg^{2+} > Na^+ > Ca^{2+} > Ba^{2+} > K^+$ (for unsupported alumina membranes).

From above it is clear that the order of potential values is reverse of permeability order. Further potential values in the case of supported membranes are higher since their permeability is low as compared to unsupported membranes. Similar behaviour was observed with non-ionic soap solution, ferric chloride and aluminium chloride treated ferric oxide and alumina membranes respectively. Potential values in the non-ionic soap treated membranes are same in magnitude as that of untreated membranes while ferric chloride treated ferric oxide membrane and aluminium chloride treated alumina membrane gives higher potential values. The order of potential values for anions and cations is same as in untreated membranes.

Anionic soap (sulphonated phenyl stearic acid) treated ferric oxide and alumina membranes gave low potential values due to decrease in positive charge of the membrane. The order is same as in the case of untreated membranes.

The values of energy of activation (Table Nos. 40 to 43) for the diffusion process of different electrolytes is higher than free diffusion of electrolytes like KCl (0.2M) reported in literature is 4400 cal./mole. These results confirm the values by Tolliday, Woods, and Hartung (9) of 5100 cal./mole for KCl and 5900 cal./mole for K_2SO_4 (0.2M).

CHAPTER IV

PERMEABILITY OF PARCHMENT SUPPORTED AND UNSUPPORTED SILICA, FERRIC SILICATE AND ALUMINIUM SILICATE MEMBRANES

Extended studies on silica gel were first made by van Bemmelen (1). According to him, the gel has a solid frame work consisting of fine capillaries which extend in all directions and which are filled with a liquid. When the dehydrating process has continued to a certain stage, the liquid in the capillaries begins to drawn out and gas or vapour replaces the liquid. It is this condition that causes opaqueness. Transparency again results when the liquid has been completely withdrawn from the capillaries and they collapse, thereby removing the gas or vapor phase. When water is again restored to the gel the cycle is reversed.

Zsigmondy (2) repeated the experiments of van Bemmelen and by using improved apparatus he was able to show the phases of dehydration more exactly and in greater detail. Anderson (3) continued the study of the dehydration of silica gels and presented data for the approximate size of the capillary tubes. He considered the range to be from 2.75 to 5.49 m with silica-water gels before drying. Anderson also made a study of the imbibition of certain fluids by dehydrated silica gel and found that when the capallaries are full of alcohal their apparent size ranges from 2.42 to 5.15 m . With imbibed benzene, the range is from 2.70 to 5.98 m and this indicates that the size of the capillaries is approximately independent of the fluid imbibed. Anderson's results support the theory that a permanent solid structure is present in a silica gel.

Patrick and Grimm (4) after making an extended series of determinations with silica gel, concluded that a distinction should be made between capillary adsorption, and adsorption from a plane surface. The liquid that is held by surface adsorption is very small in comparision to that which is held or condensed in the capillaries of a very porous substance.

The Silicates:

The complexity of the natural and artificial silicate presented a problem which proved quite insoluble by chemical methods alone. The application of x-ray crystallographic methods, however, has served to reveal certain broad principles upon which the structures of the silicates are based.

Amongst the obstacles to the study of the silicate has been, in the past, the difficulty of assigning to the compounds correct and significant molecular formulae. This difficulty arises from several causes. In the first place, since the analytical data for such complex materials may be compatible with several different molecular formulae, the uncertainity which is inherent at to the homogeneity and reproducibility of material of natural origin limits the possibility of decisive formulation on analytical grounds alone. Secondly, as is well known, the question is complicated by the isomorphous replacement of one element by another in the simple sense of Mitscherlich's law. Thus, magnesium, calcium, ferrous iron and other bivalent metals may replace one another mutually to a greater or lesser extent, as also may Al^{3+} and Fe^{3+} or OH^- and F^-.

The consideration of the silicate garden, for which materials are widely available at novelty counters, is a good introduction to the subject of the chemical reactions of soluble silicates. If a very soluble hydrated crystal of a heavy metal salt, for example, ferric chloride or cobaltic nitrate is put into a silicate solution it is quickly covered by a gelatinous envelope more or less permeable to water and of a colour dependent upon the metal salt. Under osmotic pressure the water tends to move from the silicate solution into the envelope where it dissolves more of the metallic salt. The envelope thus bursts under this pressure, exposing more salt solution to the silicate. A new area of permeable membrane is then formed, while the original envelope has in the meantime become harder, the pressure by osmosis therefore bursts the membrane most recently formed. The process continues, causing the typical fungoid or plant-like growths. For example, when cobaltous nitrate $Co(NO_3)_2.6H_2O$ is dropped into a 20 per-cent solution of $Na_2O{:}3.3\ SiO_2$, a reaction immediately occurs at the interface with the deposition of a blue gelatinous envelope around the crystal. As the diffusion process continues, the envelope tends to grow upward because the salt solution within the envelope usually contains a bubble of gas, presumably air displaced from the crystal surface. Ferric chloride $FeCl_3.6H_2O$, is one of the best salts for demonstrating this with silicate solutions in the range $Na_2O:2SiO_2$ to $Na_2O:3.3SiO_2$.

The character of the growth depends not only on the salt chosen but on the ration of alkali to silica in the silicate solution and still more on the amount of water in the system. These variables all affect the composition and the permeability of the precipitated layer, the rate of transition from sol to gel, and the strenth of the envelope.

When heavy metal salts and soluble silicates are brought together in solutions sufficiently dilute to prevent the entire solidification of the mass, precipitates are formed but, as Jordis (5) found, these precipitates may not contain all the silica and both heavy metal and silica can be found in the clear supernatant liquid. In one case it was found that when a solution of ferric chloride was poured into a solution of metasilicate, a precipitate formed, but if the solutions were mixed in the reverse manner there was no precipitate. Ferric salts are especially prone to react with the more siliceous silicates to form colloidal suspensions.

The precipitation of iron and aluminium salts with silicate solutions and the reaction of the precipitates with acids and bases have been extensively studied by Puri (6), whose primary interest is in the analogies between them and the natural soil. Titration curves were obtained by plotting equivalents of ferric chloride and aluminium chloride in the role of acids and sodium hydroxide and sodium metasilicate as alkalies against pH. Washed silica gel and precipitates of iron and aluminium with soluble silicates, when titrated with alkalies gave similar families of curves which indicated their acid character. Soil colloids and iron and aluminium silicates are regarded as acidoids which, to the extent that their surfaces are in contact with reactive solutions, behave like soluble acids. Puri(7) has worked out the analogies with soil colloids in a long series of experiments from which it is clear that starting with silicate solutions and soluble iron and aluminium salts, soils with properties closely similar to natural soils can be artificially produced.

It has been pointed out by Murata (8) and Schlecht (9) that, in aluminium silicates in which the ratio of Si:Al exceeds 2:1, there is a continuous network of silica which remains intact after aluminium ions are removed by acid. If the structure contains a greater proportion of aluminium cations, there is no continous silica network; when the aluminium ions are removed from such a structure by acid, the silica fragments pass into solution as soluble silicic acid.

From the purely physico-chemical point of view the colloidal behaviour of silica, aluminium silicate and ferric silicate has been extensively investigated. But interestingly enough the problem concerning the composition of these compounds in the gel and other colloidal forms has not been satisfactorily worked out. The same holds good, probably to a larger degree, with regard to their membrane properties. The latter aspect forms the main theme of the investigation described in this chapter.

EXPERIMENTAL

The permeability of silica, ferric silicate, and aluminium silicate membranes to various electrolytes e.g. 0.2M KCl, 0.2M KBr, 0.2M KNO_3, 0.2M KCNS, 0.2M K_2SO_4 and 0.2M NaCl, 0.2M $BaCl_2$, 0.2M $CaCl_2$, 0.2M $MgCl_2$ (0.2M $FeCl_3$ in the case of ferric silicate membranes, 0.2M $AlCl_3$ in the case of aluminium silicate membranes) were carried out by flowing the electrolytes in the upper half of the cell.

The thermostat was maintained at the desired temperature. The variations in conductance of affulent with time during the diffusion of electrolyte was observed. The volume of the affulent was kept constant e.g. 150 c.c. per hour. Conductances were measured after every twenty minutes till a constant value was attained. The concentrations were computed from the standard concentration-conductance plots of the electrolytes.

The results on permeability with unsupported silica, ferric silicate and aluminium silicate membranes are given in following tables and the results with parchment supported membranes are given in (Table No. 30 to 35).

Silica unsupported membrane

TABLE No.1

Permeability of silica unsupported membrane to potassium chloride at different temperatures:

Temperature ^{o}C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20^{o}	$9.8x10^{-4}$	$7.2x10^{-4}$	2 hrs	3.3110	0.3278
25^{o}	$12.5x10^{-4}$	$10.2x10^{-4}$	2 hrs	4.1840	0.4184
30^{o}	$18.0x10^{-4}$	$15.2x10^{-4}$	2 hrs	6.3100	0.5679
35^{o}	$24.0x10^{-4}$	$21.8x10^{-4}$	2 hrs	8.3000	0.9234

TABLE No.2

Permeability of silica unsupported membrane to potassium bromide at different temperatures:

Temperature ^{o}C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20^{o}	$8.2x10^{-4}$	$6.8x10^{-4}$	2 hrs	3.0200	0.2899
25^{o}	$10.8x10^{-4}$	$8.7x10^{-4}$	2 hrs	3.9810	0.4180
30^{o}	$12.5x10^{-4}$	$9.6x10^{-4}$	2 hrs	4.1690	0.5252
35^{o}	$15.2x10^{-4}$	$12.2x10^{-4}$	2 hrs	4.7860	0.6891

TABLE No.3

Permeability of silica unsupported membrane to potassium nitrate at different temperatures:

Temperature $^{\circ}C$	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	8.9×10^{-5}	4.7×10^{-5}	2 hrs	0.2607	0.0260
25°	9.0×10^{-5}	7.1×10^{-5}	2 hrs	0.2188	0.0295
30°	12.0×10^{-5}	10.0×10^{-5}	2 hrs	0.3020	0.0407
35°	18.2×10^{-5}	14.2×10^{-5}	2 hrs	0.3631	0.0522

TABLE No.4

Permeability of silica unsupported membrane to potassium thiocyanate at different temperatures:

Temperature $^{\circ}C$	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	6.5×10^{-5}	4.0×10^{-5}	3 hrs	0.1148	0.0172
25°	6.5×10^{-5}	5.4×10^{-5}	3 hrs	0.1514	0.0227
30°	8.2×10^{-5}	6.9×10^{-5}	3 hrs	0.1738	0.0260
35°	12.5×10^{-5}	10.2×10^{-5}	3 hrs	0.2399	0.0360

TABLE No.5

Permeability of silica unsupported membrane to potassium sulphate at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$5.6\text{x}10^{-5}$	$4.8\text{x}10^{-5}$	2 hrs	0.0871	0.0128
25°	$11.0\text{x}10^{-5}$	$8.0\text{x}10^{-5}$	2 hrs	0.1380	0.0207
30°	$19.2\text{x}10^{-5}$	$16.8\text{x}10^{-5}$	2 hrs	0.2630	0.0394
35°	$29.1\text{x}10^{-5}$	$26.2\text{x}10^{-5}$	2 hrs	0.4365	0.0654

TABLE No.6

Permeability of silica unsupported membrane to sodium chloride at different temperatures: .

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$5.5\text{x}10^{-5}$	$4.7\text{x}10^{-5}$	2 hrs	0.1259	0.0154
25°	$12.0\text{x}10^{-5}$	$7.6\text{x}10^{-5}$	2 hrs	0.1660	0.0210
30°	$19.0\text{x}10^{-5}$	$12.5\text{x}10^{-5}$	2 hrs	0.2188	0.0295
35°	$22.0\text{x}10^{-5}$	$19.3\text{x}10^{-5}$	2 hrs	0.3162	0.0426

TABLE No.7

Permeability of silica unsupported membrane to barium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	6.2×10^{-5}	4.0×10^{-5}	3 hrs	0.1202	0.0093
25°	9.3×10^{-5}	7.5×10^{-5}	3 hrs	0.1738	0.0130
30°	12.5×10^{-5}	9.2×10^{-5}	3 hrs	0.1820	0.0163
35°	18.9×10^{-5}	15.3×10^{-5}	3 hrs	0.2291	0.0200

TABLE No.8

Permeability of silica unsupported membrane to magnesium chloride at different temperatures:

Temperature oC	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	8.1×10^{-5}	5.0×10^{-5}	3 hrs	0.1202	0.0180
25°	9.1×10^{-5}	8.2×10^{-5}	3 hrs	0.1820	0.0273
30°	15.0×10^{-5}	12.0×10^{-5}	3 hrs	0.2512	0.0376
35°	24.5×10^{-5}	21.0×10^{-5}	3 hrs	0.3981	0.0597

TABLE No.9

Permeability of silica unsupported membrane to calcium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$6.8x10^{-5}$	$4.9x10^{-5}$	3 hrs	0.0724	0.0086
25°	$10.2x10^{-5}$	$5.9x10^{-5}$	3 hrs	0.1074	0.0125
30°	$12.5x10^{-5}$	$8.3x10^{-5}$	3 hrs	0.1259	0.0151
35°	$15.1x10^{-5}$	$12.3x10^{-5}$	3 hrs	0.1660	0.0199

Ferric silicate unsupported membrane

TABLE No.10

Permeability of ferric silicate unsupported membrane to potassium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$59.0x10^{-5}$	$55.0x10^{-5}$	2 hrs	2.5120	0.3768
25°	$92.0x10^{-5}$	$89.0x10^{-5}$	2 hrs	3.6310	0.5446
30°	$129.0x10^{-5}$	$125.0x10^{-5}$	2 hrs	4.1690	0.6255
35°	$198,0x10^{-5}$	$190.0x10^{-5}$	2 hrs	6.1660	0.9249

TABLE No.11

Permeability of ferric silicate unsupported membrane to potassium bromide at different temperatures:

Temperature ^{o}C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20^{o}	45.0×10^{-5}	40.0×10^{-5}	3 hrs	1.8200	0.2730
25^{o}	110.0×10^{-5}	95.5×10^{-5}	3 hrs	3.4670	0.5200
30^{o}	151.0×10^{-5}	140.0×10^{-5}	3 hrs	7.2440	1.0866
35^{o}	218.0×10^{-5}	215.0×10^{-5}	3 hrs	10.9600	1.6440

TABLE No.12

Permeability of ferric silicate unsupported membrane to potassium nitrate at different temperatures:

Temperature ^{o}C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20^{o}	33.0×10^{-5}	30.0×10^{-5}	3 hrs	1.4450	0.2067
25^{o}	49.0×10^{-5}	45.8×10^{-5}	3 hrs	1.9950	0.2992
30^{o}	68.0×10^{-5}	65.0×10^{-5}	3 hrs	2.5120	0.3768
35^{o}	98.0×10^{-5}	92.0×10^{-5}	3 hrs	3.3110	0.4964

TABLE No.13

Permeability of ferric silicate unsupported membrane to potassium thiocyanate at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	15.0×10^{-5}	12.0×10^{-5}	3 hrs	0.4786	0.0713
25°	24.0×10^{-5}	20.0×10^{-5}	3 hrs	0.7943	0.1191
30°	41.0×10^{-5}	39.0×10^{-5}	3 hrs	1.3800	0.1828
35°	56.8×10^{-5}	54.5×10^{-5}	3 hrs	1.7380	0.2607

TABLE No.14

Permeability of ferric silicate unsupported membrane to potassium sulphate at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	9.9×10^{-5}	6.9×10^{-5}	2 hrs	0.1318	0.0197
25°	15.8×10^{-5}	12.5×10^{-5}	2 hrs	0.1995	0.0299
30°	28.0×10^{-5}	24.0×10^{-5}	2 hrs	0.3802	0.0590
35°	46.0×10^{-5}	42.0×10^{-5}	2 hrs	0.6310	0.0946

TABLE No.15

Permeability of ferric silicate unsupported membrane to sodium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	10.0×10^{-5}	7.6×10^{-5}	3 hrs	0.2188	0.0328
25°	15.2×10^{-5}	13.1×10^{-5}	3 hrs	0.2754	0.0413
30°	25.0×10^{-5}	21.2×10^{-5}	3 hrs	0.4365	0.0654
35°	48.0×10^{-5}	42.0×10^{-5}	3 hrs	0.8318	0.1247

TABLE No.16

Permeability of ferric silicate unsupported membrane to barium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	11.1×10^{-5}	7.1×10^{-5}	3 hrs	0.1905	0.0285
25°	15.0×10^{-5}	12.5×10^{-5}	3 hrs	0.3311	0.0496
30°	23.0×10^{-5}	20.0×10^{-5}	3 hrs	0.5012	0.0751
35°	32.0×10^{-5}	29.0×10^{-5}	3 hrs	0.6918	0.1037

TABLE No.17

Permeability of ferric silicate unsupported membrane to magnesium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$8.0\text{x}10^{-5}$	$5.0\text{x}10^{-5}$	3 hrs	0.1202	0.0180
25°	$12.0\text{x}10^{-5}$	$9.9\text{x}10^{-5}$	3 hrs	0.2188	0.0328
30°	$17.0\text{x}10^{-5}$	$13.8\text{x}10^{-5}$	3 hrs	0.2754	0.0413
35°	$25.0\text{x}10^{-5}$	$20.9\text{x}10^{-5}$	3 hrs	0.4169	0.0625

TABLE No.18

Permeability of ferric silicate unsupported membrane to calcium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$12.0\text{x}10^{-5}$	$9.0\text{x}10^{-5}$	2 hrs	0.1995	0.0299
25°	$16.0\text{x}10^{-5}$	$13.0\text{x}10^{-5}$	2 hrs	0.2512	0.0376
30°	$21.0\text{x}10^{-5}$	$18.0\text{x}10^{-5}$	2 hrs	0.3162	0.0474
35°	$38.0\text{x}10^{-5}$	$32.0\text{x}10^{-5}$	2 hrs	0.5012	0.0751

TABLE No.19

Permeability of ferric silicate unsupported membrane to ferric chloride at different temperatures:

Temperature °C	Initial conductance of afflulent in mhos	Final conductance of afflulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of afflulent in millimoles	Permeability in millimoles per hour
20°	10.5×10^{-5}	7.0×10^{-5}	3 hrs	0.0660	0.0099
25°	15.2×10^{-5}	11.5×10^{-5}	3 hrs	0.0912	0.0136
30°	21.2×10^{-5}	18.9×10^{-5}	3 hrs	0.1259	0.0188
35°	31.5×10^{-5}	27.5×10^{-5}	3 hrs	0.1660	0.0249

Aluminium silicate unsupported membranes:

TABLE No.20

Permeability of aluminium silicate unsupported membrane to potassium chloride at different temperatures:

Temperature °C	Initial conductance of afflulent in mhos	Final conductance of afflulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of afflulent in millimoles	Permeability in millimoles per hour
20°	51.0×10^{-6}	48.0×10^{-5}	3 hrs	2.2910	0.3740
25°	61.0×10^{-5}	59.5×10^{-5}	3 hrs	2.7540	0.4131
30°	93.0×10^{-5}	89.0×10^{-5}	3 hrs	3.1620	0.4743
35°	149.8×10^{-5}	145.0×10^{-5}	3 hrs	4.1690	0.6253

TABLE No.21

Permeability of alminium silicate unsupported membrane to potassium bromide at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	51.2×10^{-5}	45.0×10^{-5}	3 hrs	1.9950	0.2999
25°	62.0×10^{-5}	59.0×10^{-5}	3 hrs	2.4550	0.3682
30°	80.2×10^{-5}	78.0×10^{-5}	3 hrs	3.8900	0.5751
35°	128.0×10^{-5}	120.0×10^{-5}	3 hrs	5.0120	0.7518

TABLE No.22

Permeability of aluminium silicate unsupported membrane to potassium nitrate at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	45.0×10^{-5}	38.0×10^{-5}	3 hrs	1.8200	0.2730
25°	63.0×10^{-5}	57.8×10^{-5}	3 hrs	2.5120	0.3768
30°	85.0×10^{-5}	79.0×10^{-5}	3 hrs	2.8840	0.4326
35°	116.0×10^{-5}	112.8×10^{-5}	3 hrs	3.9810	0.5971

TABLE No.23

Permeability of aluminium silicate unsupported membrane to potassium thiocyanate at different temperatures:

Temperature °C	Initial conductance of afful ent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$22.5x10^{-5}$	$19.0x10^{-5}$	4 hrs	0.8710	0.1306
25°	$33.0x10^{-5}$	$29.5x10^{-5}$	4 hrs	1.0720	0.1608
30°	$46.0x10^{-5}$	$42.5x10^{-5}$	4 hrs	1.5850	0.2377
35°	$72.0x10^{-5}$	$68.0x10^{-5}$	4 hrs	2.5120	0.3768

TABLE No.24

Permeability of aluminium silicate unsupported membrane to potassium sulphate at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$42.0x10^{-5}$	$38.4x10^{-5}$	2 hrs	0.7943	0.1185
25°	$61.0x10^{-5}$	$54.5x10^{-5}$	2 hrs	1.0960	0.1644
30°	$72.0x10^{-5}$	$69.9x10^{-5}$	2 hrs	1.3180	0.1977
35°	$89.0x10^{-5}$	$82.5x10^{-5}$	2 hrs	1.5850	0.2377

TABLE No.25

Permeability of aluminium silicate unsupported membrane to sodium chloride at different temperatures:

Temperature $^{\circ}C$	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$19.5x10^{-5}$	$15.0x10^{-5}$	3 hrs	0.4571	0.0685
25°	$27.0x10^{-5}$	$23.0x10^{-5}$	3 hrs	0.5754	0.0863
30°	$39.5x10^{-5}$	$35.0x10^{-5}$	3 hrs	0.7943	0.1191
35°	$55.2x10^{-5}$	$53.5x10^{-5}$	3 hrs	1.0960	0.1639

TABLE No.26

Permeability of aluminium silicate unsupported membrane to barium chloride solution at different temperatures:

Temperature $^{\circ}C$	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attainling const value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	$11.3x10^{-5}$	$8.0x10^{-5}$	3 hrs	0.2188	0.0328
25°	$17.2x10^{-5}$	$14.9x10^{-5}$	3 hrs	0.3631	0.0544
30°	$25.0x10^{-5}$	$21.0x10^{-5}$	3 hrs	0.5012	0.0751
35°	$45.0x10^{-5}$	$40.0x10^{-5}$	3 hrs	0.8318	0.1247

TABLE No.27

Permeability of aluminium silicate unsupported membrane to calcium chloride solution at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of afful ent in millimoles	Permeability in millimoles per hour
20°	15.0×10^{-5}	11.0×10^{-5}	3 hrs	0.2512	0.0366
25°	20.5×10^{-5}	16.8×10^{-5}	3 hrs	0.3311	0.0496
30°	31.0×10^{-5}	21.9×10^{-5}	3 hrs	0.4365	0.0654
35°	41.0×10^{-5}	34.9×10^{-5}	3 hrs	0.5495	0.0824

TABLE No.28

Permeability of aluminium silicate unsupported membrane to magnesium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	22.5×10^{-5}	14.0×10^{-5}	3 hrs	0.3981	0.0597
25°	26.8×10^{-5}	18.5×10^{-5}	3 hrs	0.4677	0.0701
30°	31.2×10^{-5}	25.5×10^{-5}	3 hrs	0.6026	0.0903
35°	46.0×10^{-5}	39.0×10^{-5}	3 hrs	0.8710	0.1306

TABLE No.29

Permeability of aluminium silicate unsupported membrane to aluminium chloride at different temperatures:

Tempe-rature $^{\circ}C$	Initial conductance of afflulent in mhos	Final conductance of afflulent in mhos	Time taken in attain-ing const. value of conductan-ce	Concentration corresponding to const. conductance of afflulent in millimoles	Permeabi-lity in milli-moles per hour
20°	$11.2x10^{-5}$	$8.5x10^{-5}$	2 hrs	0.0831	0.0124
25°	$16.8x10^{-5}$	$14.2x10^{-5}$	2 hrs	0.1096	0.0164
30°	$28.8x10^{-5}$	$25.8x10^{-5}$	2 hrs	0.1585	0.0237
35°	$52.0x10^{-5}$	$48.5x10^{-5}$	2 hrs	0.1995	0.0299

Permeability of pre-treated silica ferric silicate and aluminium silicate membranes to different electrolytes:

The effect of pre-treated membranes to various electrolytes was studied by soaking the ferric silicate membranes in ferric chloride solution (0.1M) and aluminium silicate membranes in aluminium chloride solution (0.1M) respectively, for 8 hours and the permeability experiments were carried out at 20°C for comparision with the un-treated membranes.

The silica, ferric silicate and aluminium silicate membranes were also treated with cationic, anionic and non-ionic soap solution. The membranes were soaked in 10^{-3}M cetyl pyridinium bromide, 10^{-3}M sulphonated phenyl stearic acid and 10^{-3}M lauric acid diethanol amine condensate for 8 hours. The results were compared with those of untreated membranes (Table No.30-35).

TABLE No.30

Permeability of parchment supported silica membranes:

(Permeability expressed as millimoles/hour; electrolyte concentration 0.2M).

Electrolyte	Untreated membrane	After treatment with Non-ionic soap	Anionic soap	Cationic soap
KCl	0.2100	0.1900	0.2789	0.1400
KBr	0.1523	0.1323	0.2223	0.1100
KNO_3	0.0180	0.0160	0.0258	0.0138
KCNS	0.0158	0.0140	0.0220	0.0100
K_2SO_4	0.0100	0.0091	0.0160	0.0060
NaCl	0.0138	0.0112	0.0185	0.0100
$BaCl_2$	0.0071	0.0053	0.0105	0.0048
$MgCl_2$	0.0150	0.0120	0.0210	0.0099
$CaCl_2$	0.0061	0.0052	0.0088	0.0042

TABLE No.31

Permeability of unsupported silica membranes:

(Permeability expressed as millimoles/hour; electrolyte concentration 0.2M)

Electrolyte	Untreated membrane	After treatment with		
		Non-ionic soap	Anionic soap	Cationic soap
KCl	0.3278	0.3000	0.3800	0.2892
KBr	0.2899	0.2561	0.3366	0.2366
KNO_3	0.0260	0.0190	0.0289	0.0182
KCNS	0.0172	0.0151	0.0262	0.0158
K_2SO_4	0.0120	0.0100	0.0200	0.0092
NaCl	0.0154	0.0076	0.0210	0.0112
$BaCl_2$	0.0093	0.0082	0.0120	0.0042
$MgCl_2$	0.0180	0.0092	0.0256	0.0105
$CaCl_2$	0.0086	0.0071	0.0119	0.0031

TABLE No.32

Permeability of parchment supported Ferric silicate membranes:

(Permeability expressed as millimoles/hour; electrolyte concentration 0.2M)

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Ferric chlorid
KCl	0.3389	0.3264	0.4999	0.3012	0.2801
KBr	0.2600	0.2580	0.3800	0.2154	0.1891
KNO_3	0.1208	0.1169	0.2538	0.1000	0.0920
KCNS	0.0513	0.0481	0.0914	0.0318	0.0268
K_2SO_4	0.0118	0.0110	0.0772	0.0102	0.0090
NaCl	0.0245	0.0211	0.0450	0.0144	0.0096
$BaCl_2$	0.0200	0.0169	0.0400	0.0102	0.0069
$MgCl_2$	0.0230	0.0175	0.0276	0.0128	0.0090
$CaCl_2$	0.0168	0.0152	0.0236	0.0084	0.0056
$FeCl_3$	0.0125	0.0110	0.0250	0.0063	0.0040

TABLE No.33

Permeability of unsupported ferric silicate membrane:

(Permeability expressed as millimoles/hour; electrolyte concentration 0.2M)

Electrolyte	Untreated membrane	After treatment with		
		Non-ionic soap	Anionic soap	Cationic soap
KCl	0.3768	0.3568	0.4985	0.3165
KBr	0.2730	0.2589	0.3730	0.2386
KNO_3	0.2067	0.1896	0.3268	0.1598
KCNS	0.0713	0.0600	0.0816	0.0498
K_2SO_4	0.0197	0.0158	0.0297	0.0123
NaCl	0.0328	0.0300	0.0756	0.0158
$BaCl_2$	0.0285	0.0248	0.0570	0.0140
$MgCl_2$	0.0299	0.0254	0.0598	0.0150
$CaCl_2$	0.0180	0.0168	0.0360	0.0090
$FeCl_3$	0.0099	0.0082	0.0198	0.0046

TABLE No.34

Permeability of parchment supported aluminium silicate membrane:

(Permeability expressed as millimoles/hour; electrolyte concentration 0.2M)

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Aluminium chloride
KCl	0.3400	0.3200	0.3890	0.3300	0.3100
KBr	0.2633	0.2530	0.3248	0.2528	0.2230
KNO_3	0.2300	0.2100	0.3000	0.2089	0.1580
KCNS	0.1158	0.1043	0.2568	0.1020	0.0081
K_2SO_4	0.1000	0.0089	0.1823	0.0089	0.0058
NaCl	0.0499	0.0388	0.0998	0.0244	0.0240
$BaCl_2$	0.0288	0.0269	0.0576	0.0144	0.0132
$MgCl_2$	0.0295	0.0273	0.0590	0.0152	0.0139
$CaCl_2$	0.0255	0.0238	0.0510	0.0123	0.0122
$AlCl_3$	0.0100	0.0089	0.0200	0.0050	0.0038

TABLE No.35

Permeability of unsupported aluminium silicate membranes:

(Permeability expressed as millimoles/hour; electrolyte concentration 0.2M)

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Aluminium chloride
KCl	0.3740	0.3610	0.3890	0.3540	0.3500
KBr	0.2999	0.2665	0.3000	0.2689	0.2580
KNO_3	0.2730	0.2430	0.2828	0.2520	0.2460
KCNS	0.1306	0.1280	0.1408	0.1280	0.1260
K_2SO_4	0.1185	0.1034	0.1299	0.1095	0.0098
NaCl	0.0685	0.0565	0.1370	0.0365	0.0265
$BaCl_2$	0.0366	0.0328	0.0632	0.0189	0.0168
$MgCl_2$	0.0597	0.0412	0.1094	0.0248	0.0220
$CaCl_2$	0.0328	0.0265	0.0656	0.0168	0.0148
$AlCl_3$	0.0124	0.0110	0.0248	0.0620	0.0600

Membrane potentials of parchment supported and unsupported silica, ferric silicate and aluminium silicate membranes:

Potential measurments with different electrolytes were carried out with treated and untreated silica, ferric silicate and aluminium silicate membranes (parchment supported and unsupported) by the method described in Chapter II. The results are tabulated below:

TABLE No.36

Potential of parchment supported silica membranes

(Potential expressed in millivolts; concentration of electrolyte on two sides of the membrane, 0.1 and 0.01M respectively)

Electrolyte	Untreated membrane	After treatment with Non-ionic soap	Anionic soap	Cationic soap
KCl	45.0	46.0	47.5	41.0
KBr	47.5	48.0	49.0	45.0
KNO_3	52.0	54.5	57.0	50.0
KCNS	54.0	56.0	58.0	52.5
K_2SO_4	58.0	59.0	61.5	56.0
NaCl	56.8	57.0	58.0	54.0
$BaCl_2$	62.5	63.5	64.0	60.0
$MgCl_2$	55.0	57.0	58.0	52.5
$CaCl_2$	69.0	70.0	71.5	65.0

TABLE No.37

Potential of unsupported silica membranes

(Potential expressed in millivolts; concentration of electrolyte on two sides of the membrane; 0.1 and 0.1M respectively)

Electrolyte	Untreated membrane	After treatment with		
		Non-ionic soap	Anionic soap	Cationic soap
KCl	41.5	42.0	43.5	39.5
KBr	42.0	42.5	44.8	40.0
KNO_3	43.0	44.0	46.0	41.0
KCNS	43.5	45.0	47.0	42.0
K_2SO_4	45.0	46.5	48.5	43.0
NaCl	44.5	45.5	49.0	42.0
$BaCl_2$	47.0	48.0	49.5	46.0
$MgCl_2$	43.8	44.5	46.0	41.5
$CaCl_2$	48.5	50.5	52.5	45.5

TABLE No.38

Potential of parchment supported ferric silicate membranes:

(Potential expressed in millivolts; concentration of electrolyte on two sides of the membrane; 0.1M and 0.01M respectively)

Electrolyte	Untreated membrane	After treatment with Non-ionic soap	Anionic soap	Cationic soap	Ferric chloride
KCl	35.0	36.5	33.0	38.0	40.0
KBr	36.0	37.0	35.0	39.0	41.0
KNO_3	36.5	37.5	35.5	39.5	42.0
KCNS	37.5	38.5	36.0	40.0	41.5
K_2SO_4	39.0	40.5	38.0	41.5	42.0
NaCl	37.0	38.0	36.0	39.0	40.5
$BaCl_2$	39.0	40.5	38.0	40.5	42.0
$MgCl_2$	42.0	43.5	41.0	43.0	44.0
$CaCl_2$	40.0	42.0	39.0	41.0	43.0

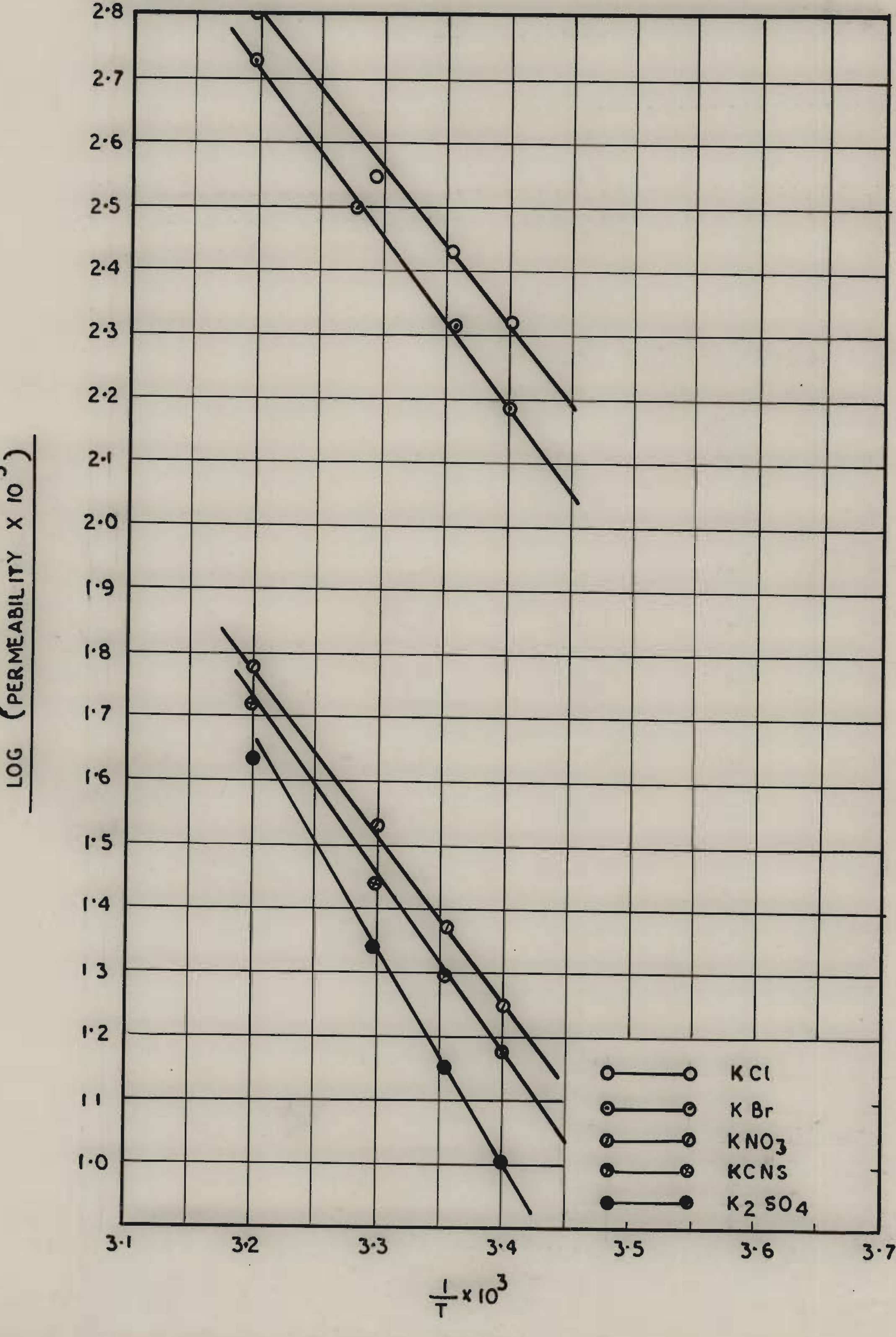

FIG. 28 a. ACTIVATION ENERGY CURVES FOR PARCHMENT SUPPORTED SILICA MEMBRANES

TABLE No.39

Potential of unsupported ferric silicate membranes

(Potential expressed in millivolts; concentration of electrolyte on two sides of the membrane; 0.1 and 0.01M respectively)

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Ferric chloride
KCl	31.0	32.0	29.5	33.5	40.0
KBr	32.0	33.0	30.5	34.0	41.5
KNO_3	33.5	34.0	31.0	35.0	42.5
KCNS	34.0	35.5	33.0	36.5	44.0
K_2SO_4	36.0	37.0	35.0	38.0	46.0
NaCl	35.0	36.0	34.0	37.0	45.0
$BaCl_2$	36.5	37.5	35.5	38.5	46.5
$MgCl_2$	38.0	39.0	37.0	40.5	42.0
$CaCl_2$	37.0	38.0	36.0	39.0	43.5

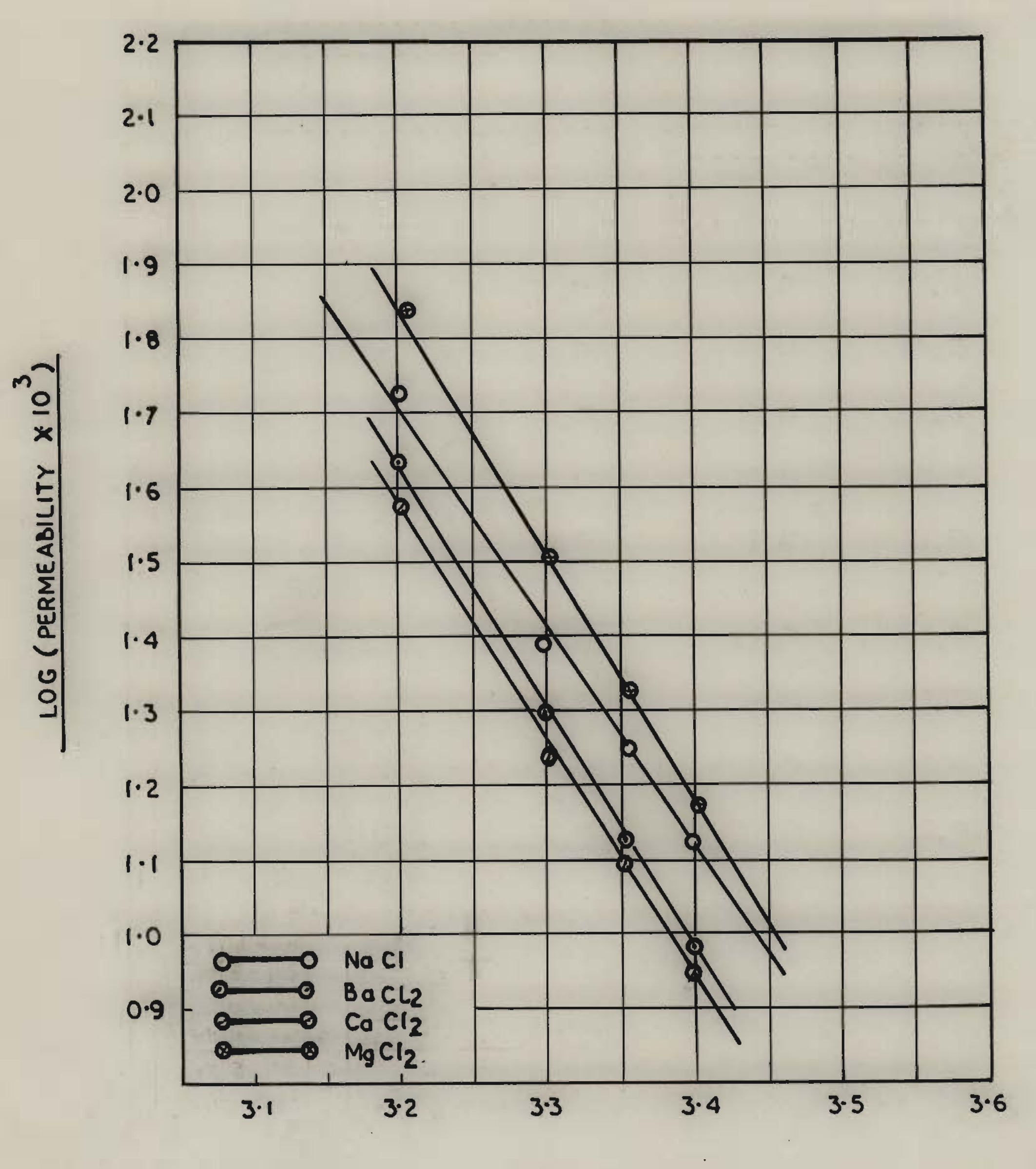

FIG. 28 b. ACTIVATION ENERGY CURVES FOR PARCHMENT SUPPORTED SILICA MEMBRANES

TABLE No.40

Potential of parchment supported aluminium silicate membranes

(Potential expressed in millivolts; concentration of electrolyte on two sides of the membrane; 0.1 and 0.01M respectively)

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Aluminium chloride
KCl	36.5	37.0	34.5	38.0	39.5
KBr	37.0	38.0	36.0	39.0	40.5
KNO_3	38.5	39.0	36.5	40.5	41.0
KCNS	39.0	40.5	38.0	41.0	42.0
K_2SO_4	41.0	41.5	40.0	42.0	42.5
NaCl	45.5	46.5	44.0	47.0	48.0
$BaCl_2$	46.5	47.5	45.5	48.5	49.8
$MgCl_2$	46.0	47.0	46.0	48.0	49.5
$CaCl_2$	47.0	48.0	48.0	49.0	50.5
$AlCl_3$	49.5	50.0	49.0	52.0	54.0

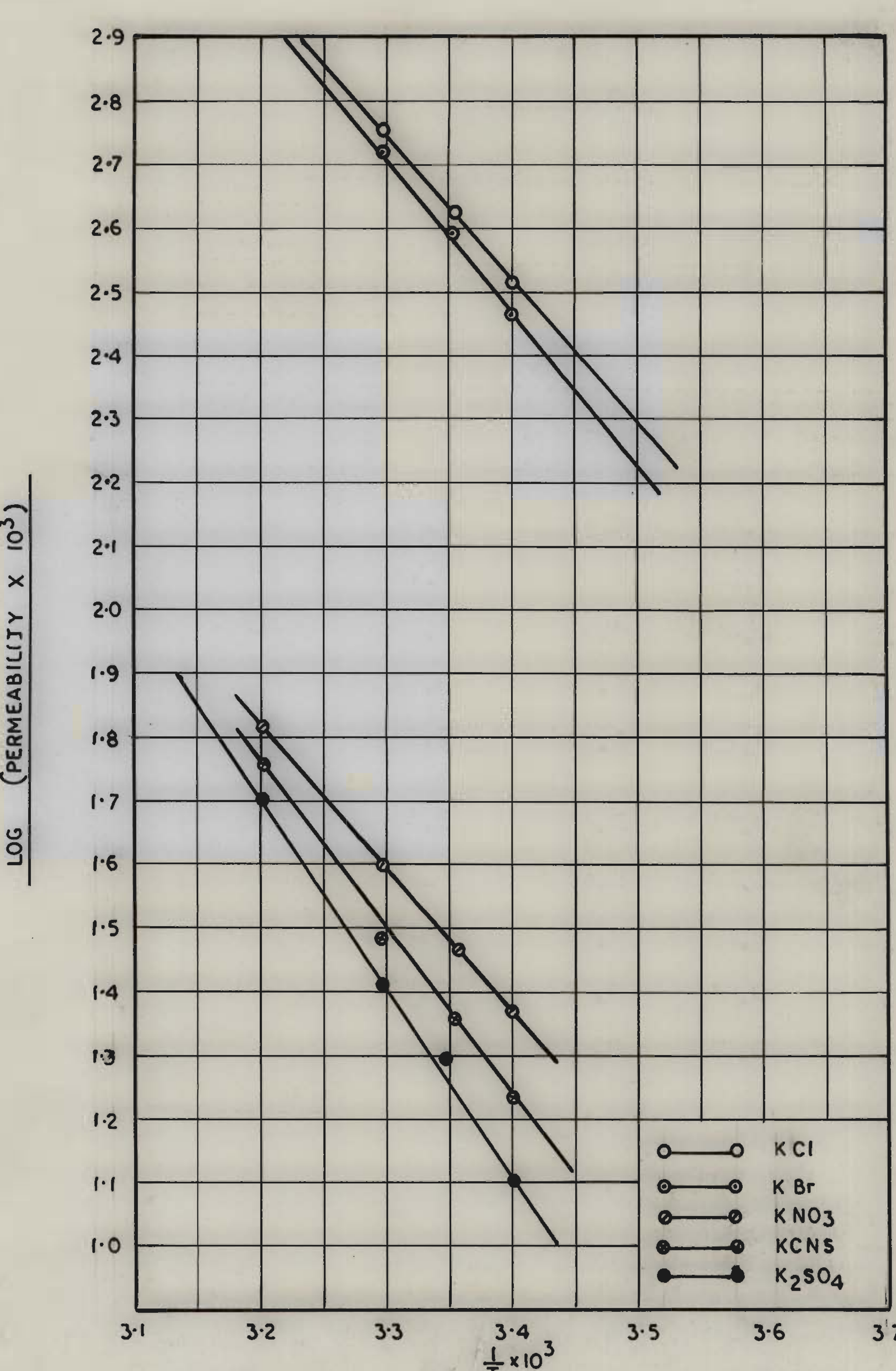

FIG. 29 a. ACTIVATION ENERGY CURVES FOR UNSUPPORTED SILICA MEMBRANES

TABLE NO.41

Potential of unsupported aluminium silicate membranes:

(Potential expressed in millivolts; concentration of electrolyte on two sides of the membrane; 0.1 and 0.01M respectively)

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Aluminium chloride
KCl	23.5	24.0	20.0	25.5	27.5
KBr	25.0	26.5	21.0	27.0	29.0
KNO_3	26.0	27.0	23.0	28.0	29.5
KCNS	28.0	29.5	24.5	30.0	32.0
K_2SO_4	30.5	31.0	26.0	32.0	35.0
NaCl	36.5	37.0	32.5	38.0	42.5
$BaCl_2$	37.0	38.0	35.5	39.0	43.0
$MgCl_2$	36.8	37.0	35.8	38.0	42.8
$CaCl_2$	38.0	39.0	37.0	40.5	41.5
$AlCl_3$	40.5	41.5	39.0	43.0	45.0

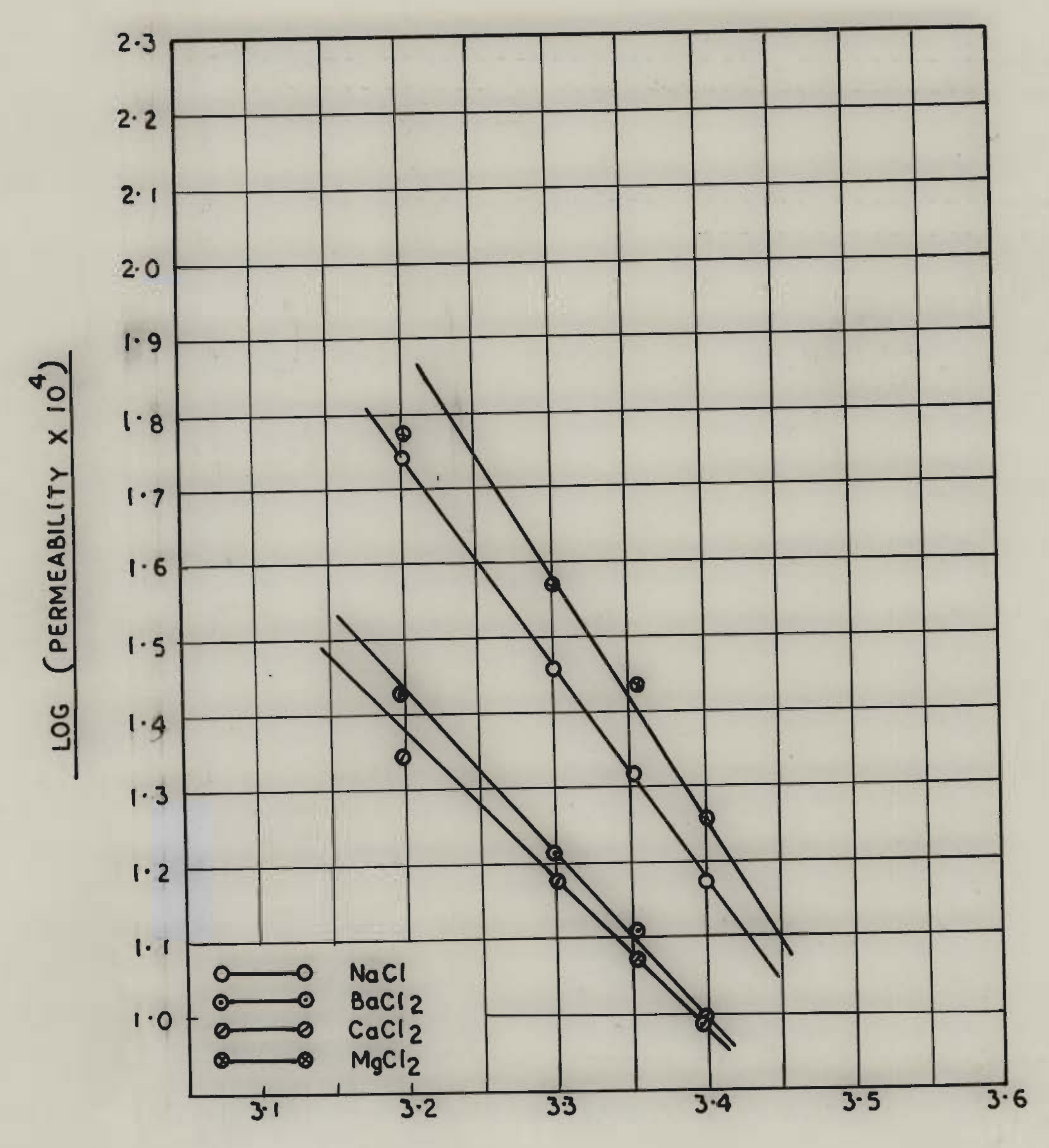

FIG.:29 b. ACTIVATION ENERGY CURVES FOR UNSUPPORTED SILICA MEMBRANES

Activation energy of the diffusion process for different electrolytes in the case of parchment supported and unsupported silica, ferric silicate and aluminium silicate membranes:

The activation energy values of the diffusion process were calculated from the slopes of plots between log $(p\times10^3)$ verses $\frac{1}{T}\times10^3$ where p is permeability and T is absolute temperature (Fig 28 to 33).

TABLE No.42

Activation energy of the diffusion process for different electrolytes in the case of silica membranes:

Electrolyte	Activation energy cal/mole in case of parchment supported silica membranes	Activation energy cal/mole in case of unsupported silica membranes
KCl	5689	5301
KBr	6113	5689
KNO_3	5896	5487
KCNS	6340	6330
K_2SO_4	7979	6831
NaCl	6831	6580
$BaCl_2$	7979	4941
$MgCl_2$	7372	4769
$CaCl_2$	7519	7450

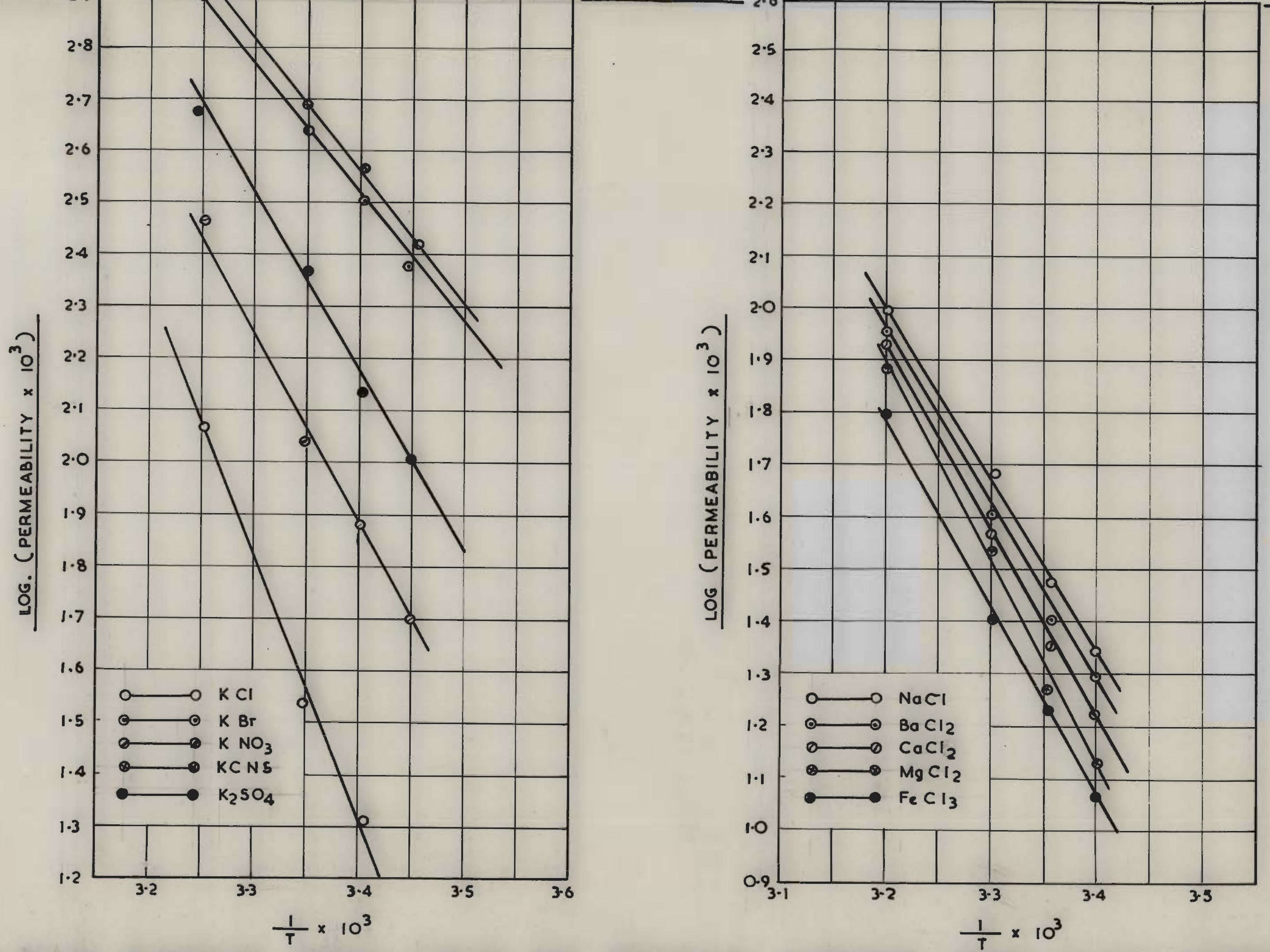

FIG. 30. ACTIVATION ENERGY CURVES FOR PARCHMENT SUPPORTED FERRIC SILICATE MEMBRANES

TABLE No.43

Activation energy of the diffusion process for different electrolytes in the case of ferric silicate membranes:

Electrolyte	Activation energy c cal/mole in case of parchment supported ferric silicate membranes	Activation energy cal/mole in case of unsupported ferric silicate membranes
KCl	5896	5825
KBr	6003	6000
KNO_3	8310	6340
KCNS	8310	8298
K_2SO_4	12820	8310
NaCl	7667	6340
$BaCl_2$	7979	7990
$CaCl_2$	9445	4769
$MgCl_2$	8664	6340
$FeCl_3$	7821	6831

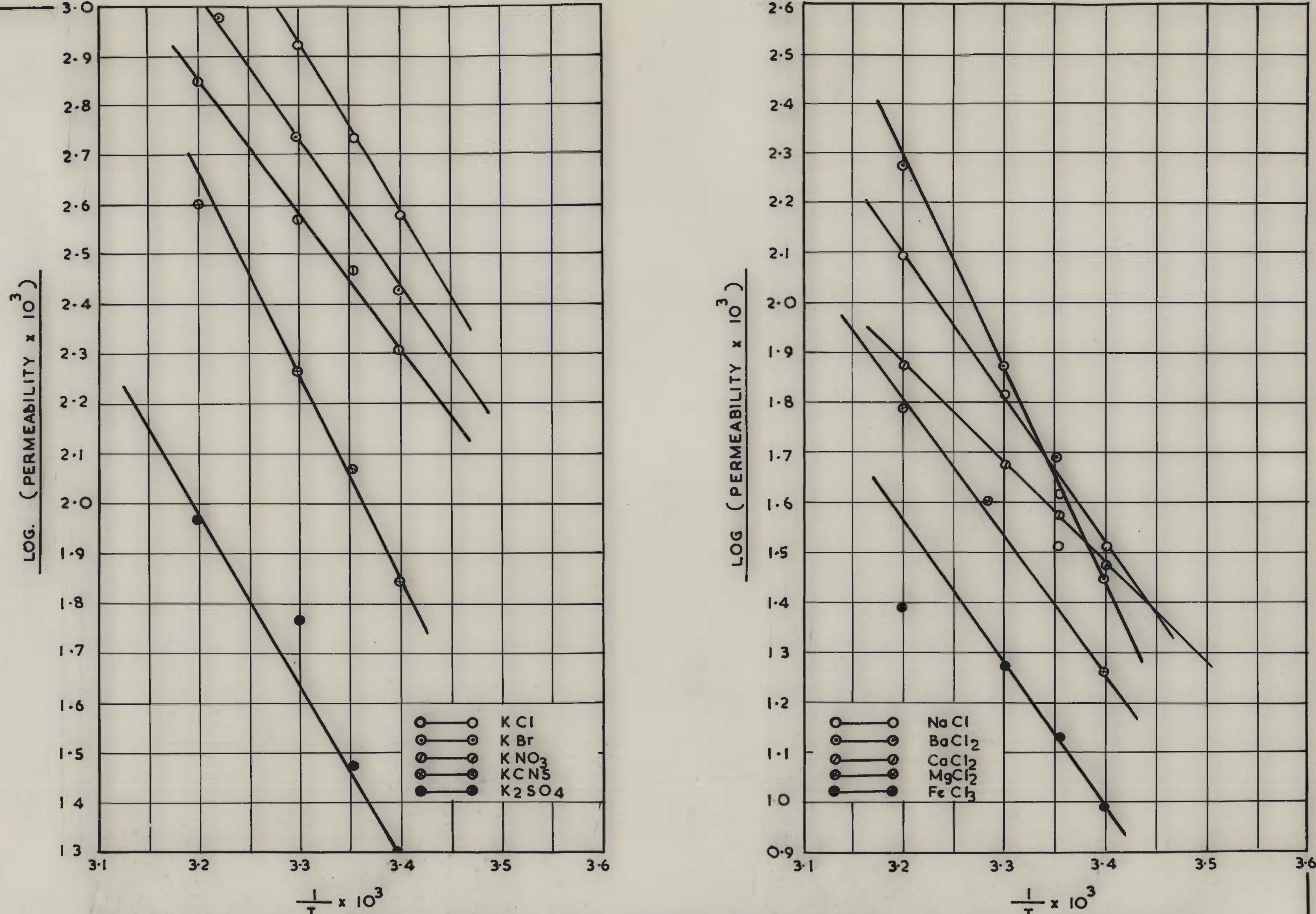

FIG.31 ACTIVATION ENERGY CURVES FOR UNSUPPORTED FERRIC SILICATE MEMBRANES

TABLE No.44

Activation energy of the diffusion process for different electrolytes in the case of aluminium silicate membranes:

Electrolyte	Activation energy cal/mole in case of parchment supported aluminium silicate membranes	Activation energy cal/mole in case of unsupported aluminium silicate membranes
KCl	7372	7094
KBr	7667	7519
KNO_3	8310	4769
KCNS	7886	5116
K_2SO_4	9879	5487
NaCl	8310	5689
$BaCl_2$	9658	5301
$CaCl_2$	7886	5689
$MgCl_2$	7979	4769
$AlCl_3$	12695	7094

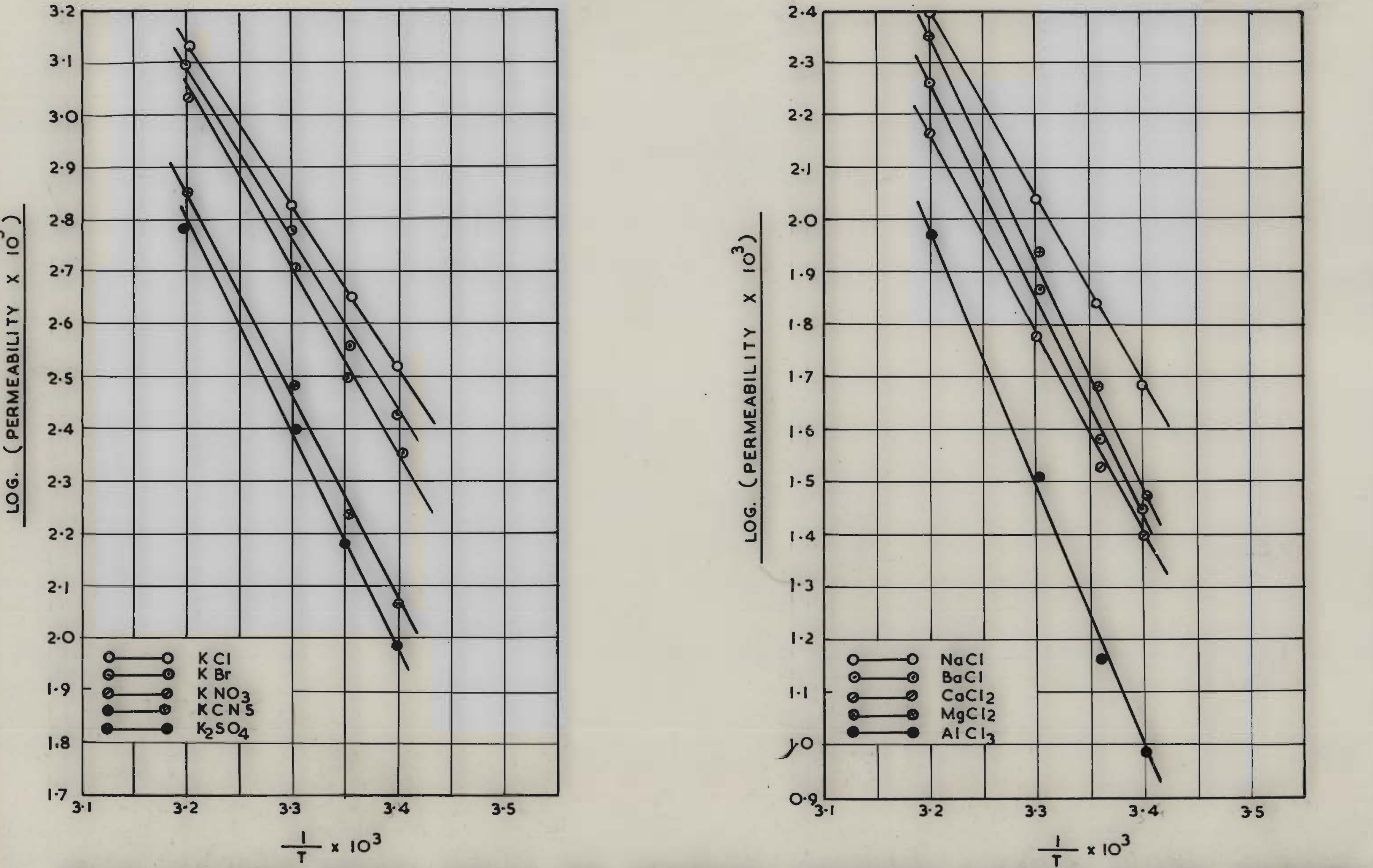

FIG. 32 ACTIVATION ENERGY CURVES FOR PARCHMENT SUPPORTED ALUMINIUM SILICATE MEMBRANES

DISCUSSION.

The membranes under investigation, viz., silica, ferric silicate and aluminium silicate are neither semipermeable nor are of selective permeability. These can, however, be classed under membranes of various degree of selective permeability as would be clear from a discussion on their permeability which follows.

The mechanism of diffusion across these membranes, unlike semipermeable membrane, would depend both on the membrane structure and on the electrical forces arising from the interplay of membranes and solutions of electrolytes. From the structural view point these membranes should be of porous character made up of solid material which would act as sieves on a molecular scale. Their permeability behaviour would, however, be different from those of coal (10) and activated carbon (11). On the other hand they would behave like electrically charged zeolities (12) and other synthetic membranes (13), which can retard ion diffusion to different degrees or may prevent their flow altogether.

The membranes under discussion are positively charged having hydrogen or aluminium or iron firmly attached to the fixed part of the double layer. The other characteristic of the double layer associated with such colloidal systems namely the existence of chloride counter ions distributed in the liquid part of the fixed layer will be met with here also.

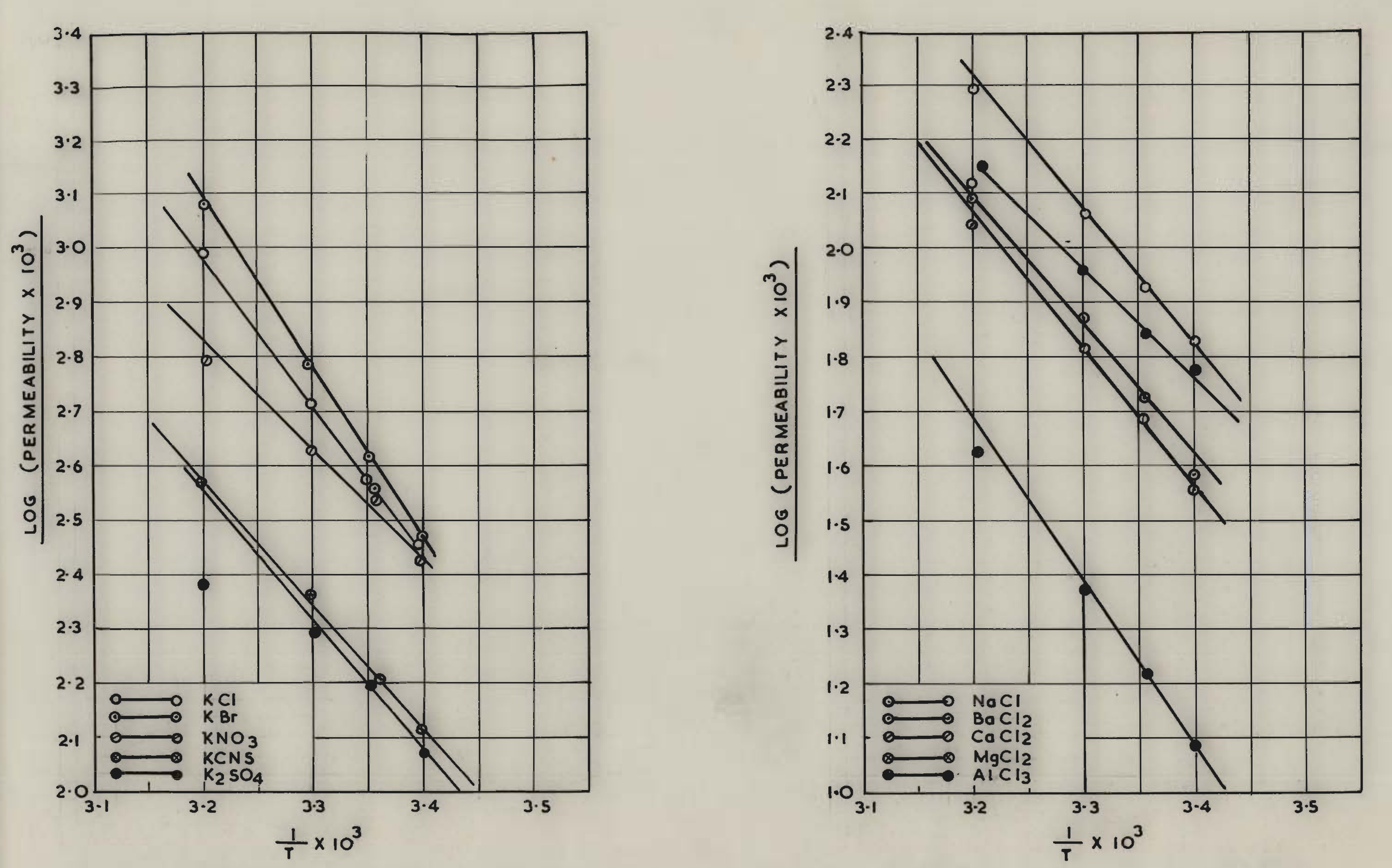

FIG. 33. ACTIVATION ENERGY CURVES FOR UNSUPPORTED ALUMINIUM SILICATE MEMBRANES

Although the double layer would exist on the capillary pores the extent to which the electrical forces would influence the diffusion of ions through them would depend on the diameter of the pores, the picture becoming more complicated with membranes of heteroporosity (14) when the membranes potential would be the resultant of the interaction of the different individual pore potential. Even if we consider our membranes to be homoporous (which appears highly improbable) those prepared with parchment support would show heteroporosity and a difference would exist between the permeability behaviour of unsupported and parchment supported membranes.

The electrochemical characteristics of membranes of high porosity is not limited to concentration potential (membrane potential) but also on the rate of electroosmosis across them (15). The latter would be governed by the electrokinetic (zeta) potential of the membrane, the higher the concentration potential and the higher the rate of electroosmosis, the greater the "electrochemical activity" of a membrane of given porosity.

The performance of the membrane would also be influenced on impregnation by foreign material. They can influence the pore capillary in different manners. (i) decrease the thickness of the electrical double layer thereby bringing about a decrease in charge

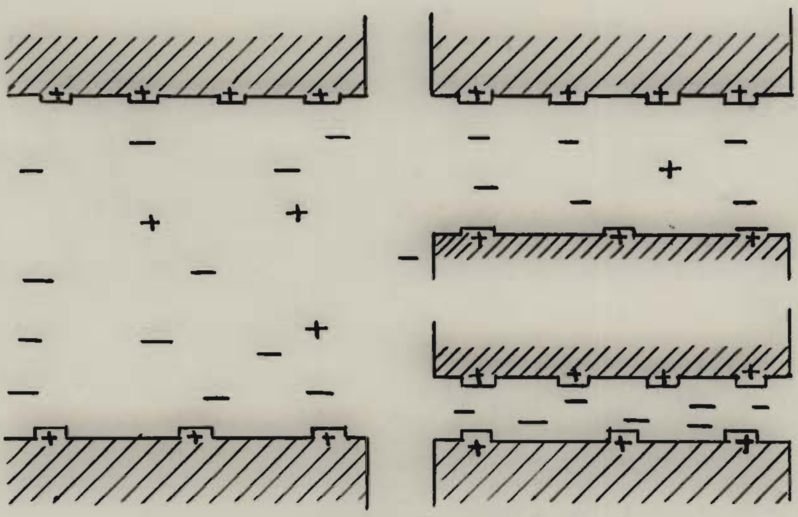

FIG. 34 a.

DISTRIBUTION OF IONS IN PORES OF DIFFERENT DIAMETERS AT THE SAME CONCENTRATION OF OUTSIDE ELECTROLYTE SOLUTION

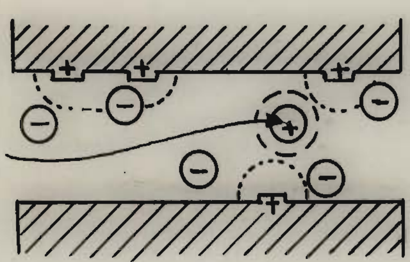

FIG. 34.b.

INFLUENCE OF LOCATION OF FIXED CHARGES AT THE WALLS OF A WIDER PORE.

(ii) more effective impregnation may result in charge neutralisation and subsequent reversal of charge on the fixed part of the double layer (iii) adsorption of the molecule (uncharged proteins, non-ionic soaps) or macromolecular ions (from polyelectrolytes, proteins, ionic surfactants) etc. resulting in enhanced activation of the membrane due to adsorption (iv) retardation in the diffusion process by charges of the same sign that are fixed at the walls of the pore.

After considering the structural factors- including both the geometry of the pores and the electrical potentials existing on the wall of the pore (membrane potential) and at large distances from the wall (ζ-potential)- the next thing to be considered is the electrical forces arising from the interplay of membranes and solution of electrolytes passing through them.

Normally in the case of positively charged membrane the diffusion of anions should be for more than the cations. This would mean that there would be large number of negative ions and lesser number of positive ions at one particular instant. The nember of positive ions would,however, become less with the decreasing diameter of the pore and with extremely narrow capillaries only diffusion of anions should take place (Fig.34a). This partial anion selectivity would also depend upon the concentration of the solution, it becoming more prominent with dilute solutions than concentrated ones (due to larger number of cations getting opportunity to diffusion than in dilute solutions).

The blockage of the passage of ions in the case of a positively charged membrane should take place on treatment with cations. Here too the extent of blockage would depend upon the pore size. With wider pores the proximity of the cations to the wall would not result in complete blockage unless the impregnated cation got located in some special way right half of (Fig.34b).

The passage of ions through the pores of the membrane would also depend on the charge and the hydration of ions. Polyvalent ions will experience greater electrostatic forces than the univalent ions. Ions undergoing hydration would effect the permeability in two ways (i) by virtue of their size (ii) on the extent to which the electrical forces of the membrane can pierce through the hydrated shell. The position of ions in the Hofmeister series should, therefore, influence the diffusion process.

From (Table No.30) it is also evident that the permeability values for anions (having a common cation K^+) are higher than for cations (having a common anion Cl^-). The only exception being $MgCl_2$ whose permeability value is larger than sodium chloride.

The lower permeability values for the different cations, K^+; Na^+; Ba^{++}; Ca^{++} is understandable in the case of a positively charged membrane which would markedly restrict their movement. The diffusion to cations does not follow the order of the size of the cation Na^+ (1.0A°) > Ca^{2+} (1.05A°) > K^+ (1.33A°) > Ba^{2+} (1.38A°). On the other hand the order for the hydrated ions is followed K^+ (1.19A°) > Na^+ (1.76A°) > Ba^{2+} (2.78A°) > Ca^{2+} (3.00A°).

It may therefore, be concluded that the positively charged silica membrane becomes permeable to cations because of their hydrated form. The movement across the membrane would have been either negligible or very much restricted if they had remained unhydrated.

The large permeability value for Mg^{2+} may be due to its very small ionic size 0.75A° as against 1.38A° for Ba^{2+} or 1.05A° for Ca^{2+}. It appears that the pores in the silica membrane are wide enough to allow the diffusion of very small ions without the electrical forces being operative.

With anions the charge on the membrane should mainly effect the diffusion process. This is true for the univalent anions. The permeability values are higher than for cations due to the electrostatic driving force. However, hydration also plays an important role since the order of permeability: $Cl^- > Br^- > NO_3^- > CNS^- >$. SO_4^{2-} is the same as their position in the lyotropic series. It implies that anions which would hydrate easily would diffuse quickly than others.

The behaviour of the sulphate ions is altogether different. Here the permeability value is very low inspite of the fact that a large electrical driving force should operate due to two negative charges on the ion. It appears that a very large hydration shell envelopes the ion (which is evident from its position in the lyotropic series) resulting in the reduction of the electrostatic driving force which would subsequently retard diffusion.

It has been observed that the permeability values (both for anions and cations) are higher in the case of unsupported membranes as compared to parchment supported ones. This is quite obvious because the ions, in this case, have to diffuse through two layers, one after the other. Even if the membrane material covers the pores of the parchment paper, the permeability values should decrease since heteroporosity characteristic of the membrane would increase due to interaction between different individual pore potentials.

<u>Ferric silicate and aluminium silicate membranes</u>:

The order of permeability of the cations (with common anion Cl^-) and anions (with common cation K^+) is the same as in the case of silica membranes viz.,

Anions: $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$ (for ferric and aluminium silicate membranes)

Cations: $K^+ > Na^+ > Mg^{2+} > Ba^{2+} > Ca^{2+} > Fe^{3+}$ (for ferric silicat membranes)

$K^+ > Na^+ > Mg^{2+} > Ba^{2+} > Ca^{2+} > Al^{3+}$ (for aluminium silicate membranes)

Here too we find that the permeability values are higher for anions than cations and although similar explanation based on the size of hydrated ions, position in lyotropic series, electrostatic driving force magnitude of membrane potential etc. can be given for membrane permeability, the strikingly large difference in the permeability value of the silica membrane on the one hand and the iron and aluminium silicate membrane on the other is not easy to explain.

A comparision of the(Tables No. 30-35)would reveal that the permeability values for cations (Na^+, Ba^{2+}, Ca^{2+}) are very much higher for aluminium and ferric silicate membrane than for silica membrane. This difference is not so much evident in the case of Cl^- and Br^- ions but is quite appreciable for NO_3^- , CNS^- (Tables No.32-35).

The enhanced permeability of aluminium silicate and ferric silicate membranes may be due to larger pore size. But if this would have been the only factor then the permeability values of Cl^- and Br^- ions for iron and aluminium silicates should have also been higher than those for the silica membrane. But this is not so, on the other hand the values for these two anions differ very little from one another for these three membranes.

To account for the difference in the permeability behaviour of the aluminium and ferric silicates for the cations we have to find an explanation in terms of structure. These compounds may be given the empirical formulae: $\overset{I}{M_2}O.Al_2O_3.n\ SiO_2.m\ H_2O$ or

$$\overset{I}{M_2}O.Fe_2O_3.n\ SiO_2.m\ H_2O$$

(where M may be an alkali metal ion). The ratio of $\overset{I}{M_2}O:Al_2O_3$ or $\overset{I}{M_2}O:Fe_2O_3$ is unity, which means that the structures are all based on AlO_4 or SiO_4 tetrahedran linked to each of four other tetrahedra by sharing the four apical oxygen atom. According to the empirical rule of Lowenstein (16) AlO_4 tetrahedra can be joined in this way to SiO_4 tetrahedra only, never to another AlO_4. This means that n in the oxide formula cannot be less then two in the completed aluminosilicate framework. The framework thus carries a net negative charge (the magnitude of the charge depending on the number of Al or Fe atoms in it). The enhanced permeability for cations can thus be explained on the basis of some residual negative charges present on the walls of the membrane pores.

It is not easy to explain the high values for the nitrate and thiocyanate ions. May be that the hydration of these ions is increased when these come in contact with ferro-and aluminosilicate structures.

Influence of impregnation of membranes with soaps:

Silica, ferric silicate and aluminium silicate membranes (supported and unsupported) impregnated by non-ionic soap (lauric acid diethanolamine condensate) decreases permeability values to very small extent (Table Nos.30-35). It appears that soap influences pore capillary through adsorption (formation of a monolayer on the wall) thereby decreasing the pore size. This would result in the decrease of permeability of both anions and cations. The order of permeability is, however, not effected and remains the same as in the case of untreated membranes.

The cationic soap (cetyl pyridinium bromide) treated membranes retard the diffusion of anions and cations to a much greater extent than the non-ionic soap treated membranes. The permeability data (Table Nos.30-35) would show that this effect is more marked with cations than with anions.

Impregnation with cationic soaps would effect its performance in two ways: (i) adsorption of large cations (cetyl pyridinium ion) on the pores of the walls, resulting in an increase charge on the membrane (ii) blockage of the passage of the ions by charges of the same sign as on the membranes, the extent of blockage depending on the pore size, narrow pores being blocked more easily than the wider ones. The second factor influences the diffusion of both anions and cations resulting in decrease in permeability. The second factor would facilitate the diffusion of anions due to electrostatic driving force with the result that appreciable diffusion takes place inspite of the blockage of passage.

In contrast to cationic soaps, impregnation of membranes by anionic soaps (sulphonated phenyl stearic acid) results in an increase in permeability values both for cations and anions. But the cations move faster than the anions (Table Nos.30-35). Here the adsorption of soap ions (which carry a opposite to the charge on the walls of the pores) does not result in the blockage of the path. On the other hand it would result in charge neutratisation (and perhaps charge reversal if impregnation is carried out effectively). This would cause enhanced cation permeability which was originally restricted due to high positive charge on the membrane.

The above discussion, based on adsorption, put forward to explain the permeability behaviour of impregnated soap membranes should however, be used with caution due to large number of factors involved therein. Firstly, we have to see the nature of adsorption visa vis the c.m.c. of the soap; secondly, the adsorbability of the various soaps, the ionic soaps adsorbing more readily than the non-ionic ones. Again factors like the interaction of soap with the membrane material (formation of soap-silica complex) or the existence of a monolayer just adjacent to the charged double layer has to be taken into account.

Ferric chloride treated ferric silicate and aluminium chloride treated aluminium silicate membranes:

The behaviour of ferric chloride treated ferric silicate membranes and aluminium chloride treated aluminium silicate membranes should be expected to be the same as cationic soap treated membranes. This is what has been observed. The diffusion of both cations and anion is reduced (Table Nos.30-35). Blockage of passage by ions of the same sign and an increase in the positive charge on the walls of the membranes form the basis of explaining their permeability behaviour in this case also. As before here too, the decrease in the permeability of cations is more marked than anions.

Effect of different electrolytes on membrane potential:

Higher potential values are realised in the case of parchment supported silica, ferric silicate and aluminium silicate membranes as compared to unsupported membranes. A comparision of the permeability and potentia datas of supported and unsupported membranes (Table Nos. 30-35 and 36-41) would reveal that the potential values are indirectly proportional to permeability values, higher the permeability value lower the membrane potential and vice versa. The order of membrane potential for parchment supported and unsupported silica membranes for different anions and cations is as follows:

Anions: $SO_4^{2-} > CNS^- > NO_3^- > Br^- > Cl^-$

Cations: $Ca^{2+} > Ba^{2+} > Mg^{2+} > Na^+ > K^+$

The order realised is just the reverse of permeability values both for supported and unsupported membranes. Further the potential values of electrolytes having common cation are less than electrolytes having common anion.

The potential values for ferric silicate and aluminium silicate membranes (supported and unsupported) due to diffusion of different electrolytes are recorded in (Table Nos. 38-41). The order of potential values in the case of ferric silicate (supported and unsupported membranes to various ions is: $SO_4^{2-} > CNS^- > NO_3^- > Br^- > Cl^-$; $Fe^{3+} > Mg^{2+} > Ca^{2+} > Ba^{2+} > Na^+ > K^+$ and in the case of aluminium silicate (supported and unsupported) the order of anions and cations is: $SO_4^{2-} > CNS^- > NO_3^- > Br^- > Cl^-$; $Al^{3+} > Ca^{2+} > Mg^{2+} > Ba^{2+} > Na^+ > K^+$.

In all these cases it is observed that sequence of anions and cations for potential values is almost just the reverse of sequence of anions and cations for permeability values as mentioned earlier. However, the potential values are lower in the case of anions than cations.

Potential of soap impregnated silica, ferric silicate and aluminium silicate membranes:

Non-ionic soap (lauric acid diethanol amine condensate) treated supported and unsupported silica, ferric silicate and aluminium silicate membranes increase the potential values of diffusion process of different electrolytes although the order of potential values for different anions and cations is same for respective membranes as mentioned earlier (Table Nos.36-41). It appears that the treatment of membranes with non-ionic soaps increases the thickness of double layer so that higher potential values are observed.

The cationic soap (cetyl pyridinium bromide) treated supported and unsupported silica, ferric silicate and aluminium silicate membranes show high potential values (the order of potential values however remains unaffected). This is quite likely since treatment with cationic soaps would result in a increase in charge on the membrane.

The anionic soap (sulphonated phenyl stearic acid) treated membranes show a decrease in potential values than untreated membranes (the order of potential values for different anions and cations remain the same). The decrease in potential values may be explained on the fact that addition of surfactant of opposite charge would decrease the thickness of the electrical double layer and subsequent decrease in charge. Low potential values are, therefore, realised with anionic soap treated membrane.

Fe^{3+}ions treated ferric silicate and Al^{3+}ions treated aluminium silicate membranes give very high potential values as compared to untreated membranes. The same explanation as put forward for cationic soap treated membranes can be put forward here also.

It is worth noting that the results on membrane potential support most of the arguments put forward to to explain the permeability behaviour of different treate membranes.

Activation energy of the diffusion process for different electrolytes:

The values of energy of activation for the diffusion of different electrolytes in the case of parchment supported and unsupported silica, ferric silicate and aluminium silicate membranes are higher than the free diffusion of KCl (0.2M) reported in literature as 4400 cal./mole. The values are in accordance with that obtained by Tolliday, Hartung and Woods (loc.cit). The results may be explained in terms of the highly charged nature of the membranes.

Permeability of alumina and ferric oxide membranes:

Most of the explanations put forward for the permeability of silica, ferric and aluminium silicate membranes hold good in the case of ferric oxide and alumina membranes also since these are positively charged Here too the permeability values for anions (having a common cation K^+) are higher than those for cations. The positive charge on the membrane would have restricted the movement of cations to a very great extent but for their hydration is responsible for diffusion.

The diffusion of anions is controlled by their position in the Hofmeister series, the order being: $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$. Moreover, since the membrane walls are positively charged the movement of anions is facilitated, sulphate ion is again an exception here.

The unsupported iron oxide and alumina membranes have higher permeability values as compared to parchment supported ones. Not only the introduction of a support hinders the diffusion but the enhanced heteroporosity of the membrane also restricts the movement of the ions.

Unlike silica, ferric silicate and aluminium silicate impregnation with non-ionic soaps does not bring about any change in the permeability values. The possibility of adsorption at capillary pores or on the walls of the pores is, therefore ruled out here. This may be attributed to narrow width of the membrane pores (the assumption is valid because the permeability values with alumina and silica membranes are much smaller than silica, aluminium silicate and ferric silicate membranes).

Inpregnation with cationic soaps decrease the permeability while treatment with anionic soap increase it. The anions, however, move faster across cation soap impregnated membrane. The decrease in permeability may be attributed to blockage of the passage by ions of the same sign (cetyl pyridinium ion) on the membrane. However, since the soap cations also get adsorbed on the walls of the pores, the charge increases and the blockage does not restrict the movement to such an extent as it would normally do.

Anionic soap treated membranes increase the permeability both for cations and anions. However, the cations move faster than the anions. Charge neutralisation leading to charge reversal on the walls of the pore is responsible for this behaviour. Since ions having charge opposite to that on the membrane are involved, the blockage of the pores cannot be envisaged. Therefore, unlike cationic soap treated membranes, the permeability is not decreased.

The effect of impregnation with ferric chloride (in case of ferric oxide membrane) and aluminium chloride (in case of alumina membrane) is just the same as observed in cationic soap treated membranes.

The results on membrane potential of iron oxide and alumina membranes support most of the arguments put forward to explain the permeability behaviour of different treated membranes.

CHAPTER V

FERRIC OXIDE, ALUMINA, SILICA, FERRIC SILICATE AND ALUMINIUM SILICATE MEMBRANE ELECTRODES

Although the Debye-Hückel theory gives expressions for the activities of single ions in solution, no method is known with which single ion activities can be measured. One cannot measure the potential of a single reversible electrotes which would depend on the activity of the ion to which the electrode is reversible. A cell consisting of two electrodes must be used. If the two electrodes are reversible to the anion and to the cation in the system respectively, only the product of the cation and anion activity can be derived from the measured emf. Combining a reversible electrode with a non-specific calomel electrode with salt bridge as the reference electrode does not supply any answer either, since the potential at the liquid junction with the reference electrode cannot be evaluated without making assumptions about the single-ion activities. Also, osmotic measurments give activity products only.

Agreement between theory and experiment mentioned above has therefore been obtained for ion-activity products only and not for single ion-activities.

A splitting of experimentally determined ion-activity products into single-ion activities would be entirely arbitrary. Nevertheless, in the description and the interpretation of many experiments, the use of single-ion activities is very convenient. Although such single-ion activities would not be thermodynamically determined, they do have a physical meaning, and they can be computed in principle from electrostatic theory. Certain arbitrary agreements have therefore been adopted regarding the evaluation of single ion-activities, and the adopted values have been chosen to agree as closely as possible with the result of the Debye-Hückel theory and its refinements.

Activity from the Donnan Equilibrium:

Experimental determination of the activity of single ion species seems to be more promising. Several proceedures have been developed. An indirect method was employed by Schuffelen and Loosjes (1) for activity measurments in suspensions. For determination of say, potassium, the following relation was utilized:

$$pH_{susp.} - pH_{soln.} = pK_{susp.} - pK_{soln.}$$

From the measured pH in suspension and solution and the pK calculated or determined in the solution, pK of the suspension was calculated.

This method is a direct application of the Donnan equilibrium, which appears by comparision of (2) with (3). The crucial point of Schuffelen's procedure (loc.cit) is the accuracy and interpretation of the suspension pH. As is well known, the pH of clay and soil suspension effect of Wiegner and Pallmann. They established by potentiometric and inversometric measurments a linear relationship within certain limits, between the hydrogen ion concentration and the content of colloids in the suspension. The significance of the calculated $(K^+)_{susp.}$ is naturally subject to the same uncertainity as the pH value. The inconsistent opinions of several investigators as to the significance of potentiometric measurments of ion activities in clay and soil suspensions and the influence of liquid junction potentials make the situation somewhat confusing. To what extent the $(K^+)_{susp.}$ is relevant to natural soils is an unsolved and still more delicate problem.

The membrane electrode method:

Of considerable scientific and practical interest is the use of permselective membranes as "membrane electrodes" which was demonstrated twenty years ago(4).

The potential usefulness of membrane electrodes was first recognized by Haber (5) after Nernst and Riesenfeld (6) had shown that any interphase (membrane) which in a concentration cell selectively allows the reversible transfer of only a single ion species from the one solution to the other gives rise to a potential and acts electromotively in a manner strictly analogous to a conventional reversible electrode for this ion.

For many years the only membrane electrode of practical usefulness was the glass electrode until Marshall and collaborators (7) succeeded in the preparation of clay membranes which, though sluggish in their electromotive response, are useful in the determination of the activities of univalent and in some instances also of bivalent cations.

Permselective membranes, by virtue of their ability to act electromotively in the presence of a single species of critical ions like specific reversible electrodes, may be used for the electrometric determination of ion activities in such solutions. By their use it becomes possible to determine (with the restriction indicated) the activities of many ions for which specific reversible electrodes do not exist (8) as with many anions, F^-, NO_3^-, CH_3COO^-, ClO_3^-, ClO_4^-, IO_3^-, etc. or where specific reversible electrodes of the conventional type involve considerable experimental difficulties, as with the alkali and alkaline earth cations Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{++}, Ca^{++}, etc. and with NH_4^+. For cation determinations the strong-acid-type sulfonated polystyrene collodian membranes (9) will be preferable in the future to the oxidized collodian membranes originally used.

Membrane potentials are usually measured indirectl using cells of the type:

$$-\mathrm{RE}(1)\ \Big|\ M^{z+}(\{M^{z+}\}_1)\ \Big|\ \begin{array}{l}\text{Cation-selective}\\ \text{membrane}\end{array}\Big|\ M^{z+}(\{M^{z+}\}_2)\ \Big|\ \mathrm{RE}(2)+$$

where RE represents a reference half cell M for any cation and $\{M^{z+}\}_1 > \{M^{z+}\}_2$. If R.E (1) and RE (2) have identical electrode potentials the potential difference across the cell is equal to the membrane potential E. If the membrane is completely impermeable to anions then.

$$E = \frac{RT}{nF} \ln \frac{\{M^{z+}\}_1}{\{M^{z+}\}_2} .$$

Thus if the activity of the cation on one side of the membrane is known, that on the other can be calculated.

For example in the case of clay membrane electrodes developed by Marshall which acts as a reversible electrodes for a variety of cation depending on their composition, the ionic activity was calculated from the emf of the following cell:

$Hg, Hg_2Cl_2, Na(K/or\ Ca)Cl \mid Membrane \mid Na(K\ or\ Ca)Clay, Hg_2\ Cl_2\ Hg$

according to the Nernst relation:

$$E = \frac{RT}{nF} \ln \frac{a_{(solution)}}{a_{(clay)}}$$

These electrodes are made by attaching to the end of a glass tube a thin but strong clay membrane obtained by heating a thin flake of clay. The tube is filled with a salt solution of known cation activity, and the clay membrane is equilibrated with this solution to bring it in the corresponding cation form. The electrode is placed in the liquid in which the cation activity must be determined, together with a reference electrode. At the membrane of the electrode, the solutions of known and unknown cation activity are separated by the clay membrane and a membrane potential is created which is a function of the ratio of the cation activities on either side of the membrane. The choice of the cation species in the solution in the electrode determines the cation for which the electrode acts as a reversible electrode. Owing to possible imperfections of the membrane, the electrode requires calibration with solutions of known cation activity.

Marshall's method for activity measurment is limited to systems containing one or two cation species. But in natural clays and soils, which always contain several exchangeable ion species, the possibility of determining all the cations present is of great value. Peech and Scott have attempted to do this by measuring the membrane potential (E) between a montmorillonite suspension and its equilibrium solution.

Marshall's and Peech's procedures are subject to the same sources of error as Schuffelen's method. They work with very dilute suspensions, and the measured activity is a function of the intermicellar solution and the exchanger phase rather than of the latter alone. The bearing of the results upon natural soils is therefore questionable. This is particularly true of systems containing ions of different valence where the ion distribution is markedly affected by dilution of the system.

Although membrane electrodes have been successfully used to measure activities of cations of Groups I A and II A they have a number of inherent disadvantages. In some systems, the potential is very sensitive to the rate of stirring (10). Moreover, since the potential usually depends on the activities of all species that can interact with the membrane, the interpretation is very complicated if more than one kind of cation is present wheather on the same side or on different sides of the cell (11). Reliable measurments have so far been restricted largely to solutions which contain a single cation in such cases, the use of a constant ionic medium to centrol activity coefficients is precluded.

Membrane electrodes have been used to study the interaction of alkali metal and alkaline earth ions with polyelectrolytes such as proteins (12) and soaps (13) and to determine the equilibrium constants of alkali metal phosphate complexes. If membranes specific to a certain cation can be developed to a high degree of accuracy, membrane electrodes may become extremely useful for studying equilibria among complexes of cations of subgroups I A and II A.

Ion-exchange membrane electrodes (13) have been used in studies on the activity of cations and anions in milk and the interaction of the salts common in milk with casein sols.

Mitra and Chatterjee (14) have developed clay membrane electrodes for the determination of copper ion activities from colloidal systems. They (15) have also prepared clay membrane electrodes for the determination of Zn, Mn and Co ion activities similar to those used previously.

The existing literature does not provide enough data on anion activity determination from membrane electrode systems. It was, therefore, considered worthwhile to carryout investigations in this direction. Ferric oxide, alumina, ferric silicate and aluminium silicate membrane electrodes were used for this purpose. Two aspects of the problem have been studied: (i) determination of the activity of Cl^- ions in solutions of KCl of different concentrations (ii) to determine the activity of the counter ions in positively charged hydrous oxide sols and ferric silicate and aluminium silicate sols of different dilutions and during slow coagulation.

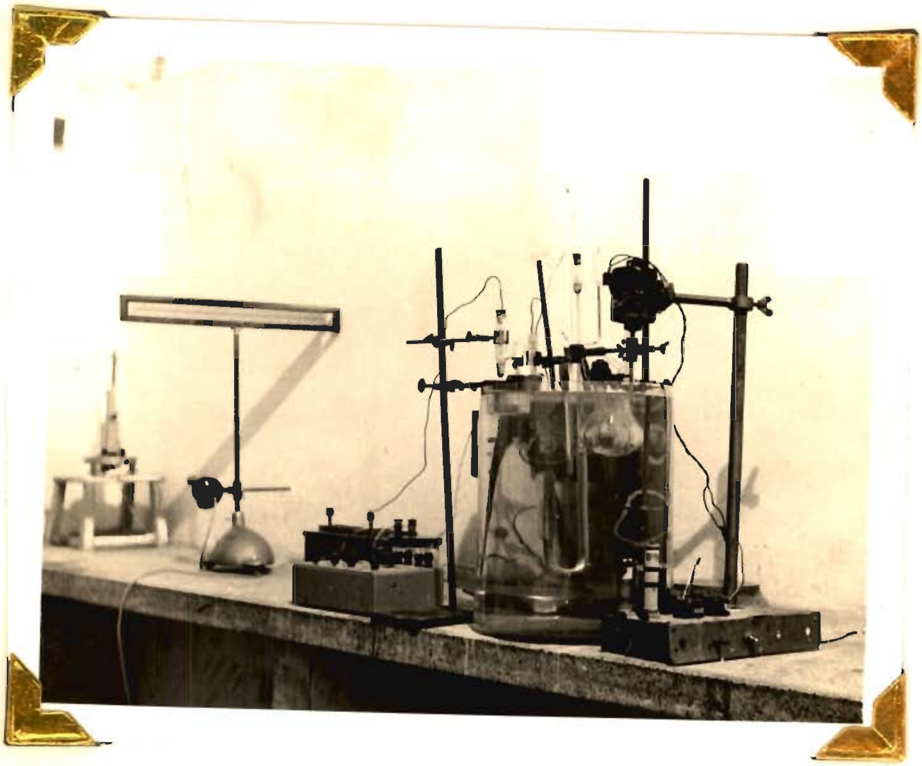

FIG.35. ASSEMBLY OF MEMBRANE ELECTRODES SYSTEM

EXPERIMENTAL

Preparation of ferric oxide, alumina, silica, ferric silicate and aluminium silicate membrane electrodes:

Ferric oxide, alumina, silica, ferric silicate and aluminium silicate membranes were prepared as described in Chapter I. The electrodes of the respective membranes were made as follows (16).

Each membrane was cemented to the end of five separate glass tubes by Araldite adehesive. The tubes were filled with salt solution of known anion activity and were fitted in rubber corks bearing two holes. The other hole was provided for the introduction of reference electrode in the solution kept in 50 ml beaker.

The tube was filled with solution of known anion activity. It was placed in a 50 ml beaker containing the liquid whose anion activity was to be determined. Two reference electrodes were used, one was put in the tube containing salt solution of known anion activity and the other was dipped through the second hole of rubber cork in the liquid of unknown activity. The assembly is shown in(Fig.No.35).

Checking of membrane electrode:

Owing to the possible imperfection of the membrane, the membrane electrode required checking with solutions of known anion activity above the membrane and solutions of unknown anion activity below it.

The unknown solution was analysed and activity corresponding to concentration was found out from standard table (17). The theoretical value of anion activity was compared with experimentally determined anion activity value. The agreement of two values within experimental error gave clear indication of proper working of membrane electrode. The concentration of the potassium chloride solution was checked by Mohr's method.

TABLE No.1

Ferric oxide membrane electrode
Known Cl^- ion activity = 0.086M

Concentration of unknown anion activity solution (KCl) (M)	Potential in volts	Experimental Cl^- ion activity	Theoretical Cl^- ion activity	Percent error
0.01	0.058	0.0092	0.0093	1.0
0.005	0.082	0.0046	0.0047	1.0
0.002	0.094	0.0019	0.0019	1.0
0.001	0.189	0.00095	0.00097	1.0

TABLE No.2

Alumina membrane electrode
Known Cl^- ion activity = 0.086 M

Concentration of unknown anion activity solution (KCl) (M)	Potential in volts	Experimental Cl^- ion activity	Theoretical Cl^- ion activity	Percent error
0.01	0.057	0.0092	0.0093	1.0
0.005	0.075	0.0045	0.0047	1.6
0.002	0.093	0.0019	0.0019	1.0
0.001	0.185	0.00096	0.00097	1.0

TABLE No.3

Ferric silicate membrane electrode
Known Cl^- ion activity = 0.086 M

Concentration of unknown anion activity solution (KCl) (M)	Potential in volts	Experimental Cl^- ion activity	Theoretical Cl^- ion activity	Percent error
0.01	0.056	0.00925	0.0093	0.8
0.005	0.075	0.00465	0.0047	0.8
0.002	0.094	0.0019	0.0019	1.0
0.001	0.124	0.00096	0.00097	1.0

TABLE No.4

Aluminium silicate membrane electrode
Known Cl^- ion activity = 0.086M

Concentration of unknown anion activity solution (KCl) (M)	Potential in volts	Experimental Cl^- ion activity	Theoretical Cl^- ion activity	Percent error
0.01	0.056	0.00925	0.0093	0.8
0.005	0.076	0.0046	0.0047	1.0
0.002	0.092	0.0018	0.0019	1.0
0.001	0.123	0.00096	0.00097	1.0

Determination of Cl^- ion activity during the dilution and coagulation of ferric oxide, alumina, ferric silicate and aluminium silicate sols by their membrane electrodes:

(1) Ferric oxide membrane electrode:

The ferric oxide membrane electrode was prepared as described earlier. Ferric oxide sol was prepared by the method recommended by Krecke (18). 250 ml of double distilled water was heated to boiling in 500 ml pyrex beaker and to this was added 2-3 drops of 30 percent ferric chloride solution, gradually with constant stirring. The colloidal solution, brick red in colour was obtained. Its pH was adjusted to 2.5 by dialysis and measured by Cambridge pH meter.

For the estimation of the sol (19) 20 ml of the sol was taken in a clean beaker and it was evaporated to dryness on a water bath. The dried mass was dissolved in minimum amount of concentrated nitric acid and then diluted with water. Ammonium hydroxide was added gradually till complete precipitation of ferric hydroxide occurs. The precipitate was filtered, washed, ignited and weighed as Fe_2O_3.

In order to see the effect of dilution of sol, the standard KCl in which the Cl^- ion activity was 0.00925 was filled in the membrane electrode tube and 10 ml of ferric oxide sol of various concentrations was kept below membrane in 50 ml beaker. The whole assembly of ferric oxide membrane electrode was kept in a thermostat regulated at constant temperature, 25° ± 0.1°C.

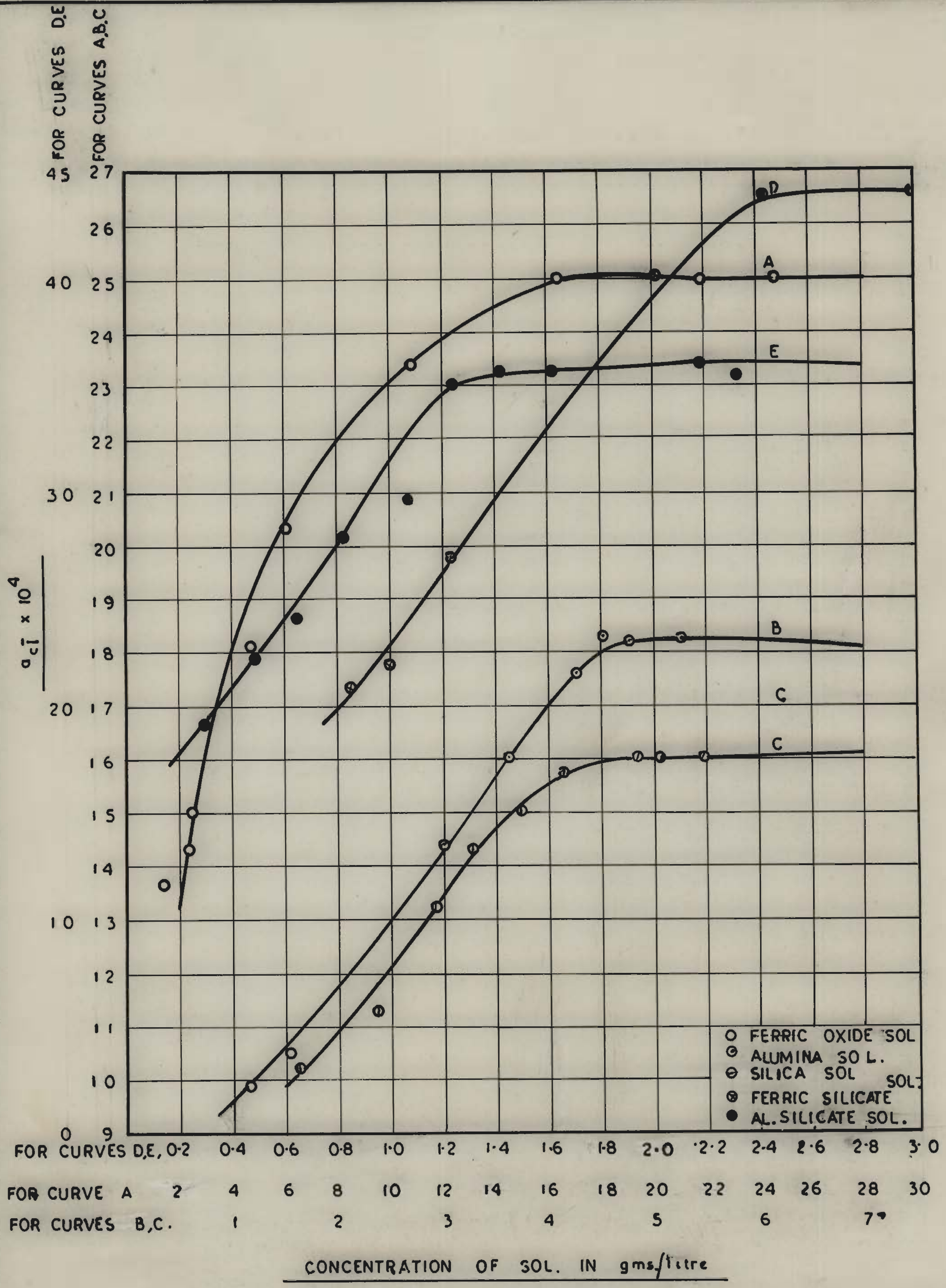

FIG 36. EFFECT OF DILUTION OF SOLS

Pye Student potentiometer, cat.No.7354 (measurable upto one millivolt) in conjunction with a ballastic galvanometer sensitivity 1.17×10^{-9} amp/mm at one meter and lamp and scale arrangement was used for potential measurments. The potential values are recorded in Table No.5. The Cl^- ion activities in different concentrations of sol were calculated in the usual way with the help of Nernst-equation:

$$E = \frac{RT}{nF} \ln \frac{a(\text{known})}{a(\text{unknown})}$$

TABLE No.5

Cl^- ion activity at different dilutions of ferric-oxide sol:

Concentration of the ferric oxide sol in gms/litre	Potential in volts	$a_{cl^-} \times 10^4$
24.08	0.034	24.8
20.10	0.033	24.8
16.50	0.034	24.8
10.80	0.035	23.7
7.20	0.037	22.1
6.30	0.039	20.2
4.82	0.043	18.1
2.77	0.047	15.0
2.52	0.048	14.3
1.52	0.049	13.6

Fig.36

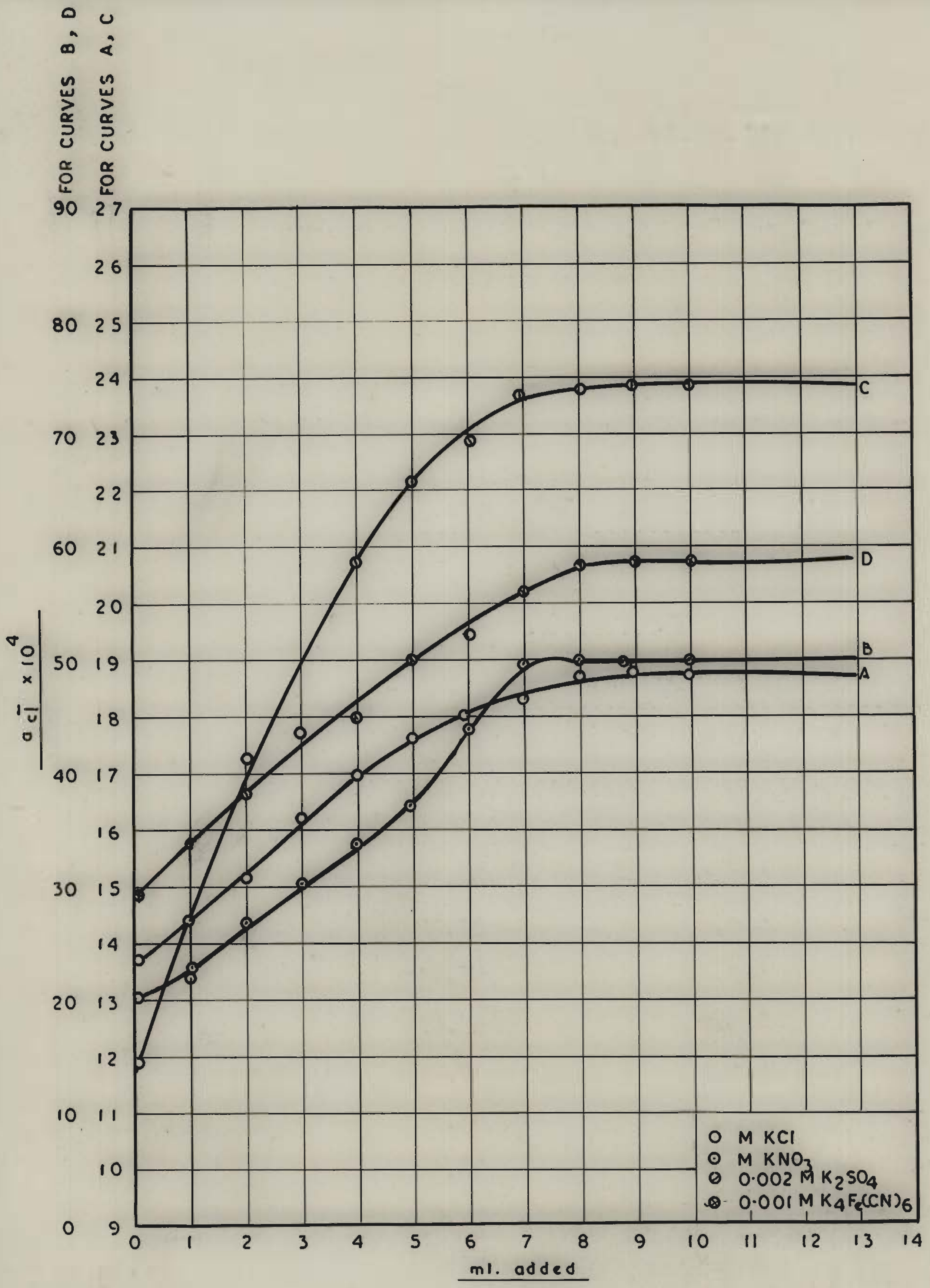

FIG. 37. EFFECT OF ADDITION OF ELECTROLYTES TO FERRIC OXIDE SOL.

For studying the coagulation of ferric oxide sol, the standard KCl in which the Cl^- ion activity was 0.00925 filled in the tube containing membrane at the end and 10 ml of ferric oxide sol was taken in 50 ml beaker.

Electrolytes KCl, KNO_3, K_2SO_4, $K_4Fe(CN)_6$ were then added in small lots to the ferric oxide sol and the total volume everytime was kept 20 ml. After each addition of electrolyte, potential values were recorded and Cl^-ion activity determined by using Nernst equation. The whole assembly was kept in thermostat maintained at 25° ± 0.1°C. The results are tabulated below:

TABLE No.6

Variation in Cl^-ion activities with gradual addition of (M) potassium chloride to ferric oxide sol:

Volume of KCl added to 10 ml of ferric oxide sol, total volume 20 ml	Potential in volts	$a_{cl^-} x10^4$
0.0	0.035	23.77
1.0	0.032	26.67
2.0	0.028	31.33
3.0	0.025	35.16
4.0	0.022	39.45
5.0	0.020	43.25
6.0	0.019	44.26
7.0	0.018	46.34
8.0	0.017	48.53
9.0	0.017	48.53
10.0	0.017	48.53

Fig. 37

TABLE No.7

Variation in Cl^- ion activities with gradual addition of (M) potassium nitrate to ferric oxide sol:

Volume of KNO_3 added to 10 ml of ferric oxide sol, total volume 20 ml	Potential in volts	$a_{cl^-} \times 10^4$
0.0	0.039	20.18
1.0	0.036	22.70
2.0	0.032	26.67
3.0	0.029	29.92
4.0	0.026	33.57
5.0	0.024	36.81
6.0	0.019	44.26
7.0	0.016	49.66
8.0	0.016	49.66
9.0	0.016	49.66
10.0	0.016	49.66

Fig.37

TABLE No.8

Variation in Cl^- ion activities with gradual addition of (0.002M) potassium sulphate to ferric oxide sol:

Volume of K_2SO_4 added to 10 ml of ferric oxide sol, total volume 20 ml	Potential in volts	$a_{cl^-} \times 10^4$
0.0	0.052	11.96
1.0	0.050	13.37
2.0	0.044	16.60
3.0	0.042	18.03
4.0	0.040	20.70
5.0	0.037	22.18
6.0	0.036	22.70
7.0	0.035	23.77
8.0	0.035	23.77
9.0	0.035	23.77
10.0	0.035	23.77

Fig.37

TABLE No.9

Variation in Cl^- ion activities with gradual addition of (0.001M) potassium ferrocyanide to ferric oxide sol:

Volume of $K_4Fe(CN)_6$ added to 10 ml of ferric oxide sol, total volume 20 ml	Potential in volts	$a_{cl^-} \times 10^4$
0.0	0.030	29.42
1.0	0.027	33.57
2.0	0.021	41.30
3.0	0.020	43.25
4.0	0.019	44.26
5.0	0.016	49.66
6.0	0.015	52.00
7.0	0.013	55.72
8.0	0.012	58.34
9.0	0.012	58.34
10.0	0.012	58.34

Fig. 37

Alumina membrane electrode:

Alumina membrane electrode was prepared as mentioned earlier. Alumina sol was prepared as described below:

The method described by H.B. Weiser (20) was followed. 10 gms of aluminium chloride (E. Merck) was dissolved in 500 c.c. of conductivity water and the resulting solution was heated to boiling. Aluminium hydroxide was precipitated with slight excess of ammonia and mixture was boiled for five minutes. The precipitate was taken in centrifuge tube and suspended in conductivity water. The suspension was centrifuged for 15 minutes. The supernatant liquid was poured off and conductivity water was again added and precipitate was washed. The process of washing was repeated many times. The precipitate was then transferred to a 500 c.c. pyrex beaker and suspended with conductivity water. The suspension was then heated to boiling. The precipitate of $Al(OH)_3$ was peptized to alumina sol by adding gradually 0.2N HCl (in 1 c.c. portion) boiling the solution for ten minutes between each addition. The pH of alumina sol was lowered to 2.00 by the addition of requisite amount of 0.1N HCl. The concentration of colloidal solution was determined gravimetrically as Al_2O_3.

The effect of dilution of alumina sol on Cl^- activity was studied by taking a standard KCl solution (in which the Cl^- ion activity is 0.00925) in membrane electrode tube and 10 ml of alumina sol of different concentrations was kept below the membrane in 50 ml beaker. The whole assembly was kept in a thermostat regulated at 25 ± 0.1°C. The potential values were recorded by using students potentiometer (the details of which are given earlier) and Cl^- ion activities at different concentrations of alumina sol were calculated by using Nernst equation.

TABLE No.10

Cl^- ion activity at different concentrations of alumina sol:

Concentration of the alumina sol in gms/litre	Potential in volts	$a_{cl^-} \times 10^4$
5.32	0.042	18.03
4.815	0.042	18.03
4.50	0.0418	18.03
4.30	0.043	17.62
3.67	0.0458	16.07
3.00	0.047	14.32
2.68	0.052	11.96
2.41	0.054	11.38
1.52	0.055	10.62
1.20	0.057	10.0

Fig. 36

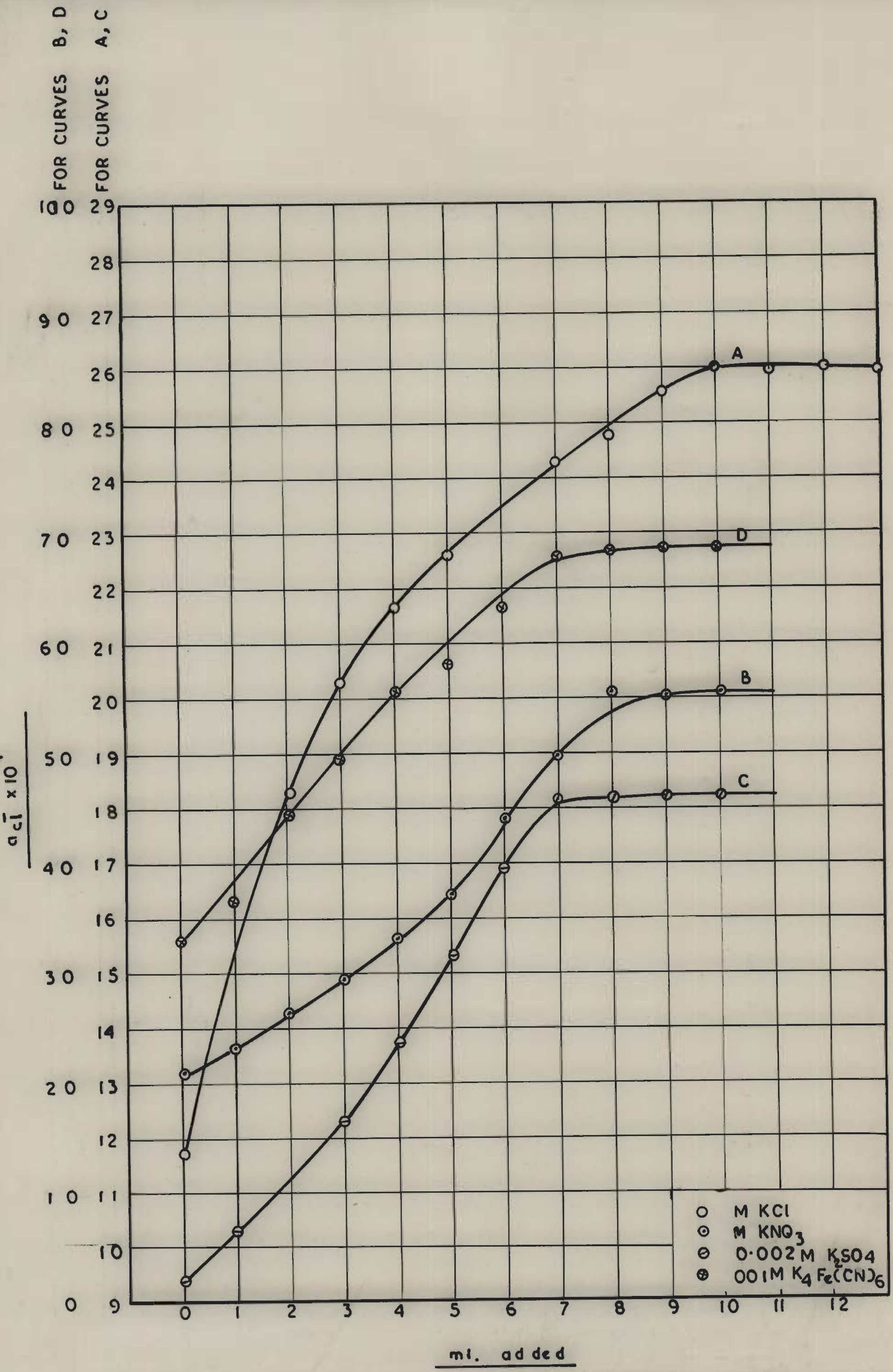

FIG. 38. EFFECT OF ADDITION OF ELECTROLYTES TO ALUMINA SOL.

For making the coagulation study of alumina sol by the addition of different electrolytes KCl solution of Cl^- ion activity was 0.00925 was taken in the membrane tube and the sol containing varying acounts of coagulating electrolytes, viz., KCl, KNO_3, K_2SO_4, $K_4Fe(CN)_6$ were added in small quantities to the sol and potential values recorded after the addition of electrolytes. All the measurments were carried out by keeping the whole assembly in a thermostat regulated at 25 ± 0.1°C. The data are recorded in tables given below:

TABLE No.11

Variation in Cl^- ion activities with gradual addition of (M) potassium chloride to alumina sol:

Volume of KCl added to 10 ml of alumina sol, total volume 20 ml	Potential in volts	$a_{cl^-} x10^4$
0.0	0.049	11.7
1.0	0.039	18.0
2.0	0.038	18.45
3.0	0.035	20.7
4.0	0.034	21.6
5.0	0.033	22.6
6.0	0.032	23.17
7.0	0.031	24.3
8.0	0.029	26.0
9.0	0.027	28.5
10.0	0.026	29.1
11.0	0.026	29.1
12.0	0.026	29.1

Fig.38

TABLE No.12

Variation in Cl^-ion activities with gradual addition of (M) potassium nitrate solution to alumina sol:

Volume of KNO_3 added to 10 ml of alumina sol, total volume 20 ml	Potential in volts	$a_{cl^-} x10^4$
0.0	0.038	20.89
1.0	0.036	22.70
2.0	0.032	26.67
3.0	0.029	29.92
4.0	0.026	33.57
5.0	0.024	36.51
6.0	0.019	44.26
7.0	0.016	49.66
8.0	0.013	55.72
9.0	0.013	55.72
10.0	0.013	55.72

Fig.38

TABLE No.13

Variation in Cl^-ion activities with gradual addition of (0.002M) potassium sulphate solution to alumina sol:

Volume of K_2SO_4 added to 10 ml of alumina sol, total volume 20 ml	Potential in volts	$a_{cl^-} x10^4$
0.0	0.098	9.44
1.0	0.096	10.33
2.0	0.095	10.72
3.0	0.091	12.30
4.0	0.088	13.8
5.0	0.085	15.49
6.0	0.083	16.98
7.0	0.081	18.20
8.0	0.081	18.20
9.0	0.081	18.20
10.0	0.081	18.20

Fig.38

TABLE No.14

Variation in Cl^- ion activities with gradual addition of (0.001M) potassium ferrocyanide to alumina sol:

Volume of $K_4Fe(CN)_6$ added to 10 ml of alumina sol, total volume 20 ml	Potential in volts	$a_{cl^-} \times 10^4$
0.0	0.026	33.57
1.0	0.024	36.81
2.0	0.019	44.26
3.0	0.016	49.66
4.0	0.013	55.72
5.0	0.012	58.34
6.0	0.010	63.97
7.0	0.008	68.55
8.0	0.008	68.55
9.0	0.008	68.55
10.0	0.008	68.55

Fig.38

Silica membrane electrode:

The silica membrane electrode was prepared by the method described earlier.

Silica sol (21) was prepared by diluting 40 c.c. of concentrated hydrochloric acid with 125 c.c. of double distilled water. 75 c.c. of sodium silicate solution (sp.gr.1.16) was added to the dilute acid with constant stirring. The mixture was dialysed till the pH of the sol reaches to 1.5. The silica content was determined gravemetrically by evaporating 5 c.c. sol in a weighed crucible to dryness and then igniting until the weight was constant.

TABLE No.15

Cl^- ion activity at different concentrations of silica sol:

Concentration of the silica sol in gms/litre	Potential in volts	$a_{cl^-} \times 10^4$
22.20	0.045	16.07
20.40	0.045	16.07
18.00	0.045	16.07
16.85	0.046	15.70
15.200	0.047	15.0
13.18	0.048	14.3
11.845	0.050	13.37
9.56	0.054	11.38
6.52	0.056	10.47

Fig. 36

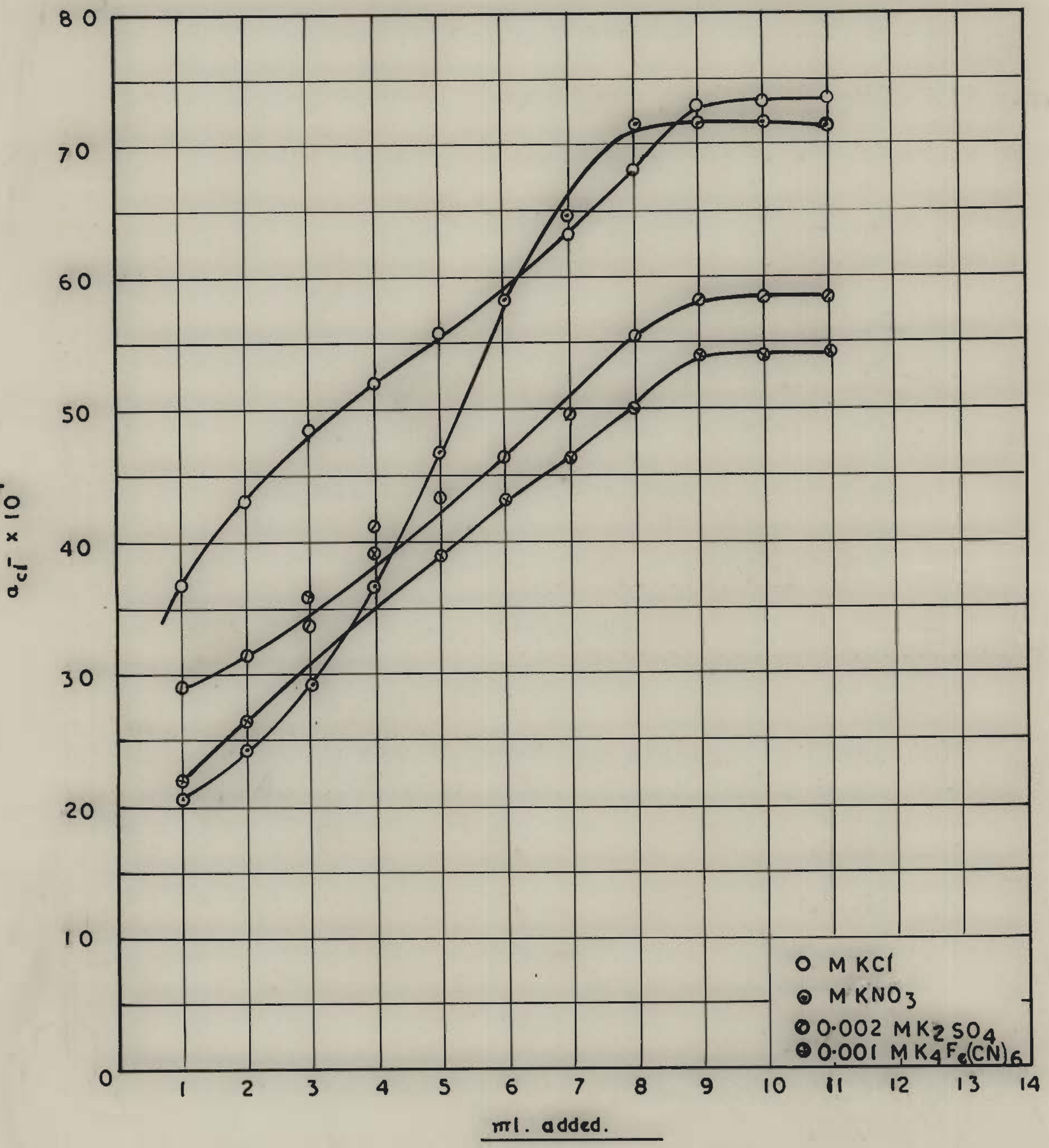

FIG. 39. EFFECT OF ADDITION OF ELECTROLYTES TO SILICA SOL.

The coagulation of silica sol by addition of different electrolytes was made by taking KCl solution of ion activity 0.00925 in the membrane electrode. Electrolytes KCl, KNO_3, K_2SO_4 and $K_4Fe(CN)_6$ were then added in small quantities to the silica sol and potential values recorded. All the experiments were carried out in a thermostat maintained at 25 ± 0.1°C.

TABLE No.16

Variation in Cl^- ion activity with gradual addition of (M) potassium chloride solution to silica sol:

Volume of KCl added to 10 ml of silica sol, total volume 20 ml	Potential in volts	$a_{cl^-} \times 10^4$
0.0	0.024	36.81
1.0	0.020	43.25
2.0	0.017	48.53
3.0	0.015	52.00
4.0	0.013	55.72
5.0	0.012	58.34
6.0	0.010	63.97
7.0	0.008	68.55
8.0	0.006	73.45
9.0	0.006	73.45
10.0	0.006	73.45

Fig.39

TABLE No.17

Variation in Cl^- ion activity with gradual addition of (M) potassium nitrate to silica sol:

Volume of KNO_3 added to 10 ml of silica sol, total volume 20 ml	Potential in volts	$a_{cl^-} \times 10^4$
0.0	0.038	20.89
1.0	0.031	24.31
2.0	0.029	29.92
3.0	0.024	36.81
4.0	0.018	46.34
5.0	0.012	58.34.
6.0	0.009	68.55
7.0	0.008	68.55
8.0	0.007	71.78
9.0	0.007	71.78
10.0	0.007	71.78

Fig.39

TABLE No.18

Variation in Cl^- ion activity with gradual addition of (0.002M) potassium sulphate to silica sol:

Volume of K_2SO_4 added to 10 ml of silica sol, total volume 20 ml	Potential in volts	$a_{cl^-} x 10^4$
0.0	0.029	29.92
1.0	0.028	31.33
2.0	0.026	33.57
3.0	0.021	41.30
4.0	0.020	43.25
5.0	0.018	46.34
6.0	0.016	49.66
7.0	0.013	55.72
8.0	0.012	58.34
9.0	0.012	58.34
10.0	0.012	58.34

Fig.39

TABLE No.19

Variation in Cl^- ion activity with gradual addition of (0.001M) potassium ferrocyanide to silica sol:

Volume of $K_4Fe(CN)_6$ added to 10 ml of silica sol, total volume 20 ml	Potential in volts	$a_{cl^-} \times 10^4$
0.0	0.040	20.70
1.0	0.032	26.67
2.0	0.025	35.16
3,0	0.023	38.55
4.0	0.022	39.45
5.0	0.020	43.25
6.0	0.018	46.34
7.0	0.016	49.66
8.0	0.014	54.45
9.0	0.014	54.45
10.0	0.014	54.45

Fig.39

Ferric silicate membrane electrode:

Ferric silicate membrane electrode was prepared by the method described earlier.

Ferric chloride solution (100 c.c.) having 4.3 g. atoms of chlorine per litre, diluted to 400 c.c. with distilled water, was taken to prepare the colloid(22) Sodium silicate solution (193.9 c.c.) having 12.4 moles of SiO_2 per litre was taken and diluted to 1550 c.c. with distilled water. This diluted sodium silicate solution was gradually added to ferric chloride solution with constant stirring. The precipitate of iron silicate formed was peptized by hydrochloric acid and a yellowish red sol of iron silicate resulted. After adding 1200 c.c. of sodium silicate solution the precipitate formed refused to be peptised and a slight precipitation was visible. Hence, the sol was prepared by using lesser amount of sodium silicate solution than the equivalent quantity. The sol thus prepared contained an excess of ferric chloride and it was kept for dialysis. The pH of the sol was 2.40.

In order to see the effect of dilution of sol, the standard KCl of Cl^- ion activity 0.00925 was kept in the membrane tube and 10 ml of iron silicate sol of different concentrations was kept below the membrane in 50 ml beaker. The whole assembly of iron silicate membrane electrode was kept in a thermostat regulated at constant temperature 25 ± 0.1°C. Potential values were recorded and Cl^- ion activities calculated. The results are tabulated below:

TABLE No.20

Cl^- ion activity at different concentrations of iron silicate sol:

Concentration of the sol gms/litre	Potential in volts	$a_{cl^-} \times 10^4$
3.2540	0.016	44.66
3.0080	0.016	44.66
2.5460	0.019	44.26
2.3348	0.025	35.16
2.0000	0.027	33.57
1.8588	0.030	29.42
1.2680	0.035	23.77
1.0080	0.037	22.18
0.8456	0.0385	20.95
0.4100	0.039	20.23

Fig.36

The coagulation of ferric silicate sol by addition of different electrolytes was made by taking KCl solution in which Cl^- ion activity was 0.00925 in the membrane tube and ferric silicate sol was taken below the membrane. Electrolytes KCl, KNO_3, K_2SO_4 and $K_4Fe(CN)_6$ were then added in small quantities to the ferric silicate sol and potential values were recorded

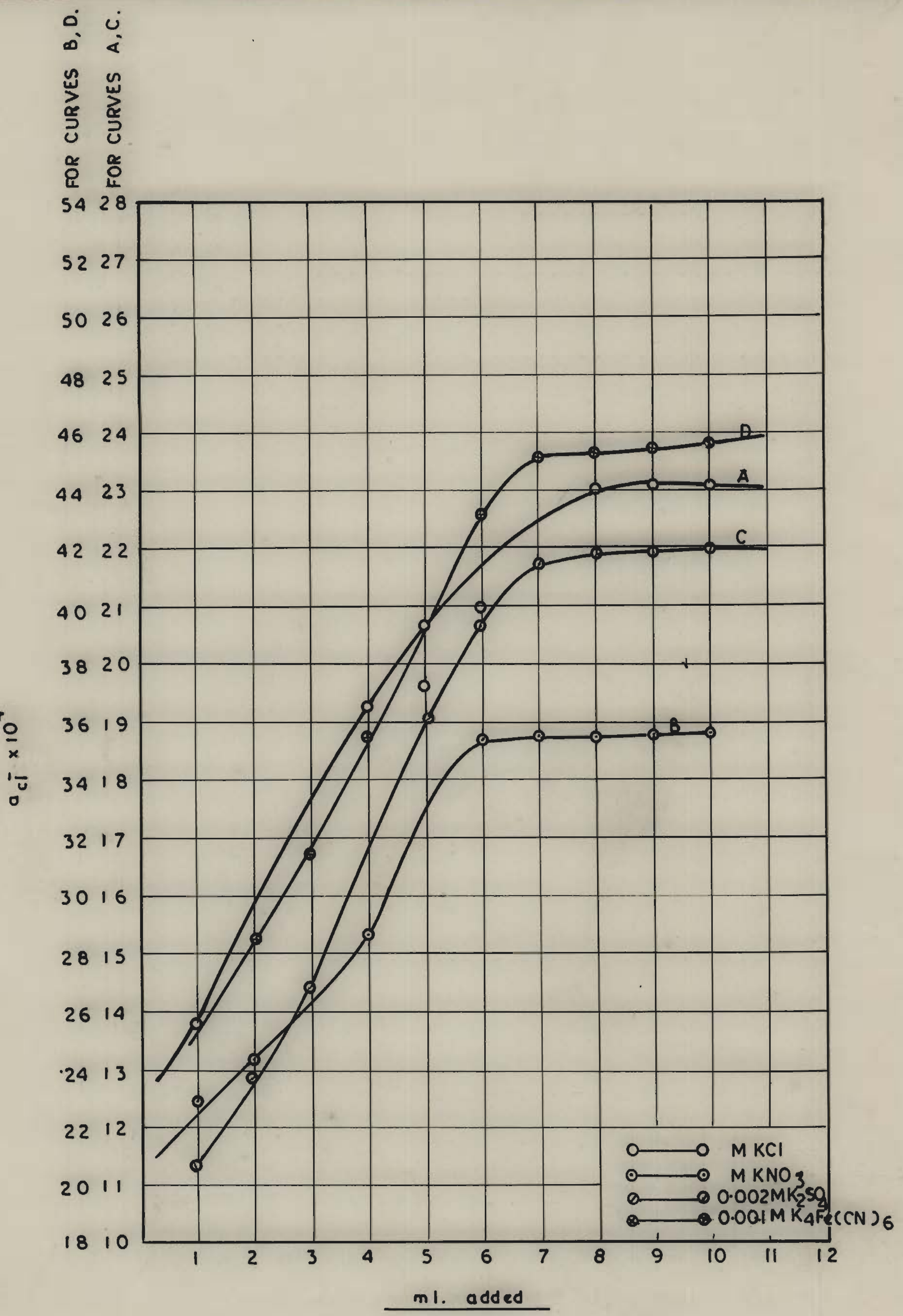

FIG. 40. EFFECT OF ADDITION OF ELECTROLYTES TO FERRIC SILICATE SOL.

All the experiments were carried out in thermostat maintained at 25 ± 0.1°C.

TABLE No.21

Variation in Cl^- ion activity with gradual addition of (M) potassium chloride solution to iron silicate sol:

Volume of KCl added to 10 ml of ferric silicate sol, total volume 20 ml	Potential in volts	$a_{cl^-} \times 10^4$
0.0	0.054	11.38
1.0	0.051	12.76
2.0	0.050	13.37
3.0	0.047	14.32
4.0	0.042	18.03
5.0	0.040	19.77
6.0	0.039	19.95
7.0	0.038	20.89
8.0	0.037	22.18
9.0	0.037	22.18
10.0	0.037	22.18

Fig. 40

TABLE No.22

Variation in Cl^- ion activity with gradual addition of (M) KNO_3 to iron silicate sol:

Volume of KNO_3 added to 10 ml of ferric silicate sol, total volume 20 ml	Potential in volts	$a_{cl^-} \times 10^4$
0.0	0.042	18.03
1.0	0.040	20.70
2.0	0.037	22.18
3.0	0.036	22.70
4.0	0.035	23.77
5.0	0.032	26.67
6.0	0.029	33.57
7.0	0.029	33.57
8.0	0.029	33.57
9.0	0.029	33.57
10.0	0.029	33.57

Fig.40

TABLE No.23

Variation in Cl^- ion activity with gradual addition of (0.002M) potassium sulphate to iron silicate sol:

Volume of K_2SO_4 added to 10 ml of ferric silicate sol, total volume 20 ml	Potential in volts	$a_{cl^-} x 10^4$
0.0	0.057	10.00
1.0	0.056	10.47
2.0	0.052	11.96
3.0	0.050	13.37
4.0	0.047	14.32
5.0	0.042	18.03
6.0	0.040	19.77
7.0	0.038	20.89
8.0	0.038	20.89
9.0	0.038	20.89
10.0	0.038	20.89

Fig. 40

TABLE No.24

Variation in Cl^- ion activity with gradual addition of (0.001M) potassium ferrocyanide sol:

Volume of $K_4Fe(CN)_6$ added to 10 ml of ferric silicate sol, total volume 20 ml	Potential in volts	$a_{cl^-} x10^4$
0.0	0.035	23.77
1.0	0.033	26.06
2.0	0.032	26.67
3.0	0.030	29.42
4.0	0.027	33.57
5.0	0.025	35.16
6.0	0.021	41.30
7.0	0.020	43.25
8.0	0.020	43.25
9.0	0.020	43.25
10.0	0.020	43.25

Fig.40

Aluminium silicate membrane electrode:

The aluminium silicate membrane electrode was prepared by the method described earlier.

Aluminium silicate sol (23) was prepared by the interaction of basic aluminium sulphate (24) and sodium silicate solution. Basic aluminium sulphate was prepared by titrating 10 percent solution of sluminium sulphate with sodium carbonate to the point at which no permanant precipitate was formed on standing. Very thin sodium silicate solution (sp.gr.1.10) was gradually added to basic aluminium sulphate solution with constant stirring. The precipitate of aluminium silicate was peptized by hydrochloric acid and a white sol of aluminium silicate resulted.

The effect of dilution of aluminium silicate sol was studied by taking standard KCl (Cl^- ion activity 0.00925) in the membrane tube and 10 ml of aluminium silicate sol of different concentrations was kept below membrane in 50 ml beaker. The whole assembly was kept in a thermostat maintained at 25 ± 0.1°C. Results are tabulated below:

TABLE No.25

Cl^- ion activity at different concentrations of aluminium silicate sol:

Concentration of sol gm/litre	Potential in volts	$a_{cl^-} \times 10^4$
2.1980	0.025	35.16
1.6280	0.025	35.16
1.4250	0.025	35.16
1.2220	0.028	33.57
1.0890	0.030	29.42
0.8890	0.032	26.67
0.6520	0.034	24.80
0.4580	0.035	23.77
0.2110	0.039	19.95
0.1523	0.046	18.45

Fig.36

For coagulation study of aluminium silicate sol by different electrolytes, the standard KCl solution of known Cl^- ion activity (0.00925) was filled in the membrane tube. KCl, KNO_3, K_2SO_4 and $K_4Fe(CN)_6$ were then added in small quantities to the aluminium silicate sol and potential values recorded after each addition of electrolyte. All the experiments were carried out in a thermostat regulated at 25 ± 0.1°C. The data are recorded in following tables:

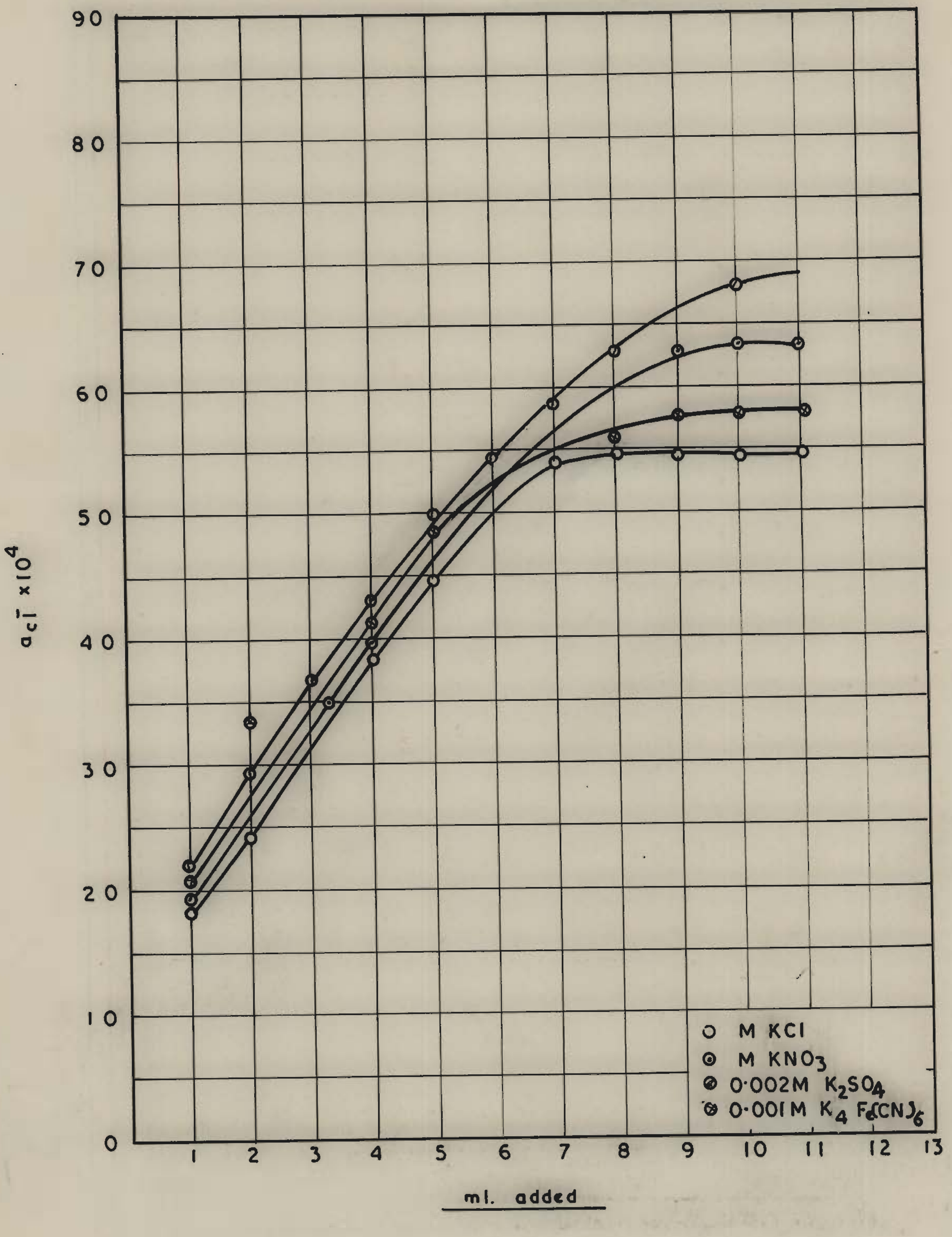

FIG. 41 EFFECT OF ADDITION OF ELECTROLYTES TO ALUMINIUM SILICATE SOL.

TABLE No.26

Variation in Cl^- ion activities with gradual addition of (M) potassium chloride to aluminium silicate sol;

Volume of KCl added to 10 ml of aluminium silicate sol, total volume 20 ml	Potential in volts	$a_{Cl^-} \times 10^4$
0.0	0.042	18.03
1.0	0.035	23.77
2.0	0.025	35.16
3.0	0.023	38.55
4.0	0.019	44.26
5.0	0.017	48.53
6.0	0.014	54.45
7.0	0.014	54.45
8.0	0.014	54.45
9.0	0.014	54.45
10.0	0.014	54.45

Fig. 41

TABLE No.27

Variation in Cl⁻ion activities with gradual addition of (M) potassium nitrate to aluminium silicate sol:

Volume of KNO_3 added to 10 ml of aluminium silicate sol, total volume 20 ml	Potential in volts	$a_{cl^-} x 10^4$
0.0	0.039	19.95
1.0	0.029	33.57
2.0	0.024	36.81
3.0	0.022	39.45
4.0	0.019	44:26
5.0	0.017	48.53
6.0	0.016	49.66
7.0	0.013	55.72
8.0	0.010	63.97
9.0	0.010	63.97
10.0	0.010	63.97

Fig.41.

TABLE No.28

Variation in Cl^- ion activity with gradual addition of (0.002M) potassium sulphate to aluminium silicate sol:

Volume of K_2SO_4 added to 10 ml of aluminium silicate sol, total volume 20 ml	Potential in volts	$a_{cl^-} x 10^4$
0.0	0.037	22.18
1.0	0.030	29.42
2.0	0.025	35.16
3.0	0.020	43.25
4.0	0.020	49.66
5.0	0.016	54.45
6.0	0.014	58.34
7.0	0.012	63.97
8.0	0.010	68.55
9.0	0.009	68.55
10.0	0.009	68.55

Fig.41.

TABLE No.29

Variation in Cl^- ion activity with gradual addition of (0.001M) potassium ferrocyanide to aluminium silicate sol:

Volume of $K_4Fe(CN)_6$ added to 10 ml of aluminium silicate sol, total volume 20 ml	Potential in volts	$a_{Cl^-} \times 10^4$
0.0	0.040	19.77
1.0	0.031	32.10
2.0	0.029	33.57
3.0	0.025	35.16
4.0	0.025	41.30
5.0	0.021	44.26
6.0	0.019	49.66
7.0	0.016	55.72
8.0	0.013	58.34
9.0	0.012	58.34
10.0	0.012	58.34

Fig. 41.

DISCUSSION.

Zeolite mineral and clay membranes and those employing synthetic material have been successfully employed to determine the ion activity of alkali and alkaline earth ions. For example, Marshall's clay electrodes (25) can be used to determine the ion activity of various cations by setting up a cell of the type:

$$\mathrm{Hg}\,|\,\mathrm{Hg_2Cl_2}\,|\,\mathrm{Na(K/or\ Ca)Cl}\,|\,\underset{\text{membrane}}{\mathrm{Clay}}\,|\,\mathrm{Na(K\ or\ Ca)Clay}\,|\,\mathrm{Hg_2Cl_2}\,|\,\mathrm{Hg}$$

and applying the Nernst relationship. These electrode systems, though very useful, possess high Ohmic resistance (1-10 mega ohm), require several hours or days to attain equilibrim and are stable for limited period only.

Just in line with the above argument, membrane systems can be theoretically visualised which can be employed to determine activity of anions in a solution. For this positively charged membranes can be prepared. Membranes of this type can be: ferric oxide, alumina, silica, ferric silicate and aluminium silicate with chloride ions in the liquid part of the double layer and can, therefore, be employed for determining the chloride ion activity in solutions.

The above mentioned membranes suffer from one drawback that they are not permselective (this is evident from permeability studies described in Chapter III and IV)

But they are quite stable and unlike the clay membranes attain equilibrium within 15 to 20 minutes. It has, however, been observed that they can be used for the determination of Cl^- ion activity inspite of their non-permselective nature since the permeability of the chloride ions is far greater than other anions and especially the cations.

From (Table Nos.1 to 4) it is clear that Cl^- ion activity in potassium chloride solution can be determined with the ferric oxide, alumina, silica, ferric and aluminium silicate membrane electrodes over a narrow concentration range viz., 0.01M to 0.001M. The performance becomes faulty with solutions of concentration 0.001M and 0.01M. The results were comparable with those obtained by Mohr's method, the error ranging between 1.0 to 1.5 per cent.

Amongst the five membranes, the ferric oxide and aluminium silicate membrane electrodes give better accuracy (within 1.0 per cent) than others. If higher permeability of chloride ions would have been the criterion for better performance, then ferric silicate should have worked equally well. This, however, could not be confirmed on the basis of these estimations.

Positively charged colloidal solutions like those of alumina and ferric oxide have got Cl^- as the counter ions. Their activity changes with dilution and during the coagulation process-a fact which was observed by Weiser (26) on the basis of potentiometric studies using calomel electrodes. The results obtained by him were checked by employing membrane electrodes reversible with respect to anions.

Variation in Cl^- ion activity during the dilution of ferric oxide, alumina, ferric silicate and aluminium silicate sols:

Result on the Cl^- ion activity of ferric oxide, alumina, ferric silicate, amd aluminium silicate sols of varying concentrations reveal that the counter ion activity increases with increase in the concentration of the sol. The plots between sol concentration and Cl^- ion activity give a parabolic curve (Fig.No.36). From this it may be concluded that more exchangeable counter ions are available from dilute sols than the concentrated ones.

Variation in Cl^- ion activity during the coagulation of ferric oxide, alumina, ferric silicate andaluminium silicate sols by the gradual addition of electrolytes:

The increase in the activity of Cl^- ions in the ferric oxide, alumina, ferric silicate and aluminium silicate sols by gradual addition of M KCl, M KNO_3, 0.002M K_2SO_4 and 0.001M $K_4Fe(CN)_6$ supports the phenomenon of ion exchange which are the chloride ions in the outer shells of the double layers of these sols.

The plots between concentration of electrolyte added and Cl^- ion activity again give parabolic curves. This means that after the addition of a certain concentration of the coagulating electrolyte the exchange phenomenon stops and the colloidal particles become uncharged or possess only a small residual charge. The coagulation will then be independent of the concentration and the valency of the precipitating ions. The nature of the curves (Fig.No.37 to 41) is almost the same as realised by Weiser (loc.cit) using calomel electrodes. These results give definite evidence of the exchange of counter ions and subsequent adsorption of coagulating ions during the coagulation of a hydrophobic sol.

RESUME

RESUME

Artificial membranes are well known for their importance as models for physiological studies. These have also found use in fundamental studies like those on osmosis, Donnan membrane equilibria, concentration potential, reversible electrode system for measuring ion activities etc. Besides large amount of work primarily concerned with the preparation of membranes has been done to make them useful in industry and technology, incorporating chemical operation like demineralisation by electrolysis, salt filtration, purification by ion exchange etc.

The artificial membranes are broadly classified as (a) homogenous membranes, and (b) heterogenous membranes.

Under the head of homogenous membranes comes polymethacrylic acid (PMA), phenolsulfonic acid (PSA), and polystyrene sulfonic acid which have been proved very useful. Cellulose acetate and oil films also constitute the same class of artificial membranes. These membranes have been very useful for demineralization of saline water and as models for biological membranes.

Heterogenous membranes are subdivided into

(i) non-reinforced membranes which are prepared by employing suitable casting techniques for solutions of membrane forming substances.

(ii) Woven-fabric backed membranes, the preparatior of these membranes.involves in four steps (a) solublization of monomers in suitable solvents (b) impregnation of cloth with the solution of monomer or partially polymerized gel (c) curing the complete polymerization with or without pressure and (d) introduction of inogenic groups by conventional procedures like sulfonation or chloromethylation followed by amination.

(iii) Membranes formed by chemical treatment: These membranes are formed by impregnating parchment film with membrane forming material. Weiser (1930) prepared parchment supported copper ferro and ferricyanide membranes. Malik and Coworkers (1961 to 1963) have prepared a large number of metal ferrocyanide and other gel forming membranes by impregnating their gels or precipitates in parchment paper.

(iv) Membranes formed by mechanical treatment- The simple principle used to prepare these membranes is to bind a polyelectrolyte or a conventional ion exchanger at ordinary or elevated temperatures to a thermoplastic polymer by application of mechanical pressure or to bind two polymer together by mechanical pressure and later to introduce ionogenic groups by following the conventional procedure. Amberlite IR-120 (powdered) was moulded with a polymer of vinyl acetate and vinyl chloride and triphenyl phosphate (plasticizer). Inorganic membranes have been prepared for example by hot pressing ammonium . molybdophosphate with polyethylene powder. Marshall and his associates (1939,1942,1948) prepared many clay films by same procedure as mentioned above. Very recently Malik and Singhal (1962) had prepared bentonite membranes by the method recommended by Wyllie, Patnode and Sinha (1950).

(v) Membranes formed by photochemical treatment- Powerful ionizing radiations have been used in this method to bring about the polymerization of monomers incorporating into various materials. In this work polyethylene film was soaked in styrene and treated with -rays from Co^{60} to form the graft copolymer which was later sulfonated or aminated to form ion selective membranes.

Inorganic gel forming systems which may provide useful membrane material for fundamental studies, have not been fully exploited. Investigations described in the thesis deals with this aspect. Membranes employed for the investigation are metal hydrous oxide, ferric silicate and aluminium silicate membranes and were obtained with and without parchment support.

Preparation of membranes:

Parchment supported ferric oxide, alumina, silica, ferric silicate and aluminium silicate membranes were prepared by impregnating the parchment paper with respective gels. The procedure adopted is as follows: The paper was first soaked in distilled water, and then tied carefully on open glass vessel (bell jar type).

25 ml., 0.1M $FeCl_3$ solution or aluminium sulphate (10 per cent) solution was filled inside it for the preparation of ferric oxide or alumina membranes and it was then suspended in a beaker containing ammonia solution (50 ml; 10 or 50 per cent) for 24 hours. It was then taken out and washed repeatedly with distilled water to remove the adsorbed electrolyte. The solutions of ferric chloride or aluminium sulphate were then interchanged, ferric chloride or aluminium chloride outside and ammonia inside. The process was repeated several times, until a very fine deposit of ferric oxide or alumina gel was obtained on the parchment paper. The membranes were examined under microscope for any deformation or crack. The same procedure was followed for the preparation of ferric silicate and aluminium silicate membranes.

For the preparation of unsupported ferric oxide, alumina, silica, ferric silicate and aluminium silicate following procedure was adopted.

Iron oxide, alumina, silica, ferric silicate and aluminium silicate gels were prepared. 1.00 gm of the respective gels were pressed by a compression machine in the form of a circular disc of very small thickness say 0.12 mm. The pressure applied was 3000 lb/sq. inch. The membranes were then seen under microscope in order to see crack or deformation.

Permeability measurments:

Permeability is defined as the property of a porous material which permits the passage or seepage of fluids such as water, salt solutions and/or oil for example, through its inter connecting voids. Permeability of fluids is of primary importance in many engineering problems such as in the settlement of a layer of saturated compressible soil subjected to load is dependent upon the permeability. Permeability is a factor in the need for and design of filters to prevent piping or uplift and to control the hydraulic stability of slopes of earth materials.

The various type of apparatus which are used in soil laboratories for determining coefficients of permeability of soils are called permeameters. They are of two basic designs, the constant head type and the variable head type. Numerous subdivisions of the two designs are often mentioned, such as upwardflow and downwardflow types, but these are not of major importance, fundamentally.

Methods used to measure rate of diffusion are broadly classified in two categories (i) steady state method and (ii) constant flow type.

In the first method, the surfaces of a sheet of solid material are maintained in contact with reservoirs of diffusive material at two different fixed concentrations. The second method involves subjecting the sample, originally in equilibrium with surrounding reservoir of fixed concentration, to a sudden change in reservoir concentration, and measuring either the concentration distance profiles in the solid or more simply, the change in concentration of the reservoir. Although the apparatus needed for both these types of experiments is usually fairly simple, the analysis of data from the constant flow method is more convenient to do.

The permeation experiments with the collodion membranes and cellophane were carried out as follows:

A measured volume of the solution being tested (usually 10 ml) was placed inside a membrane bag, and a measured volume of water was placed outside. At the beginning of an experiment the liquid levels in the two compartments were essentially the same. All the experiments were carried out at room temperature 22-25°C. From time to time small aliquot samples were removed from both compartments for analysis. The rate at which the system approached equilibrium was then plotted graphically.

Weiser's method (loc.cit) employing isotonic solutions for measuring permeability was employed by Malik and Ali (loc.cit). Making use of the plant "Spirogyra", they prepared isotonic solutions of KCl, K_2SO_4, Na_2WO_4 and sugar solution etc. and determined the exact strength of above mentioned electrolytes isotonic with the cell-sap. To perform the diffusion experiments electrolyte solutions were placed inside the ferric tungstate, thorium tungstate membrane thimbles which were suspended in sugar solution in a narrow glass cylinder for 24 hours. The electrolyte inside the thimble was analysed for anions.

The above method although simple and did not require any elaborate experimental set-up was tedious, time consuming and had an error range too large to give reproducible results. Later on a modified method was developed by Harting and Willis (1942) for investigating the permeability of copper ferrocyanide membranes to various anions.

Their method too could not take into account all the factors, viz., (i) surface charge on the membrane (ii) adsorption of diffusing ions (iii) valency of anion and (iv) diffusion rate of anion in free solution, on which they considered the diffusion mechanism to depend.

The apparatus used for diffusion of ions in our studies was similar in construction to that described by Hartung and Willis (loc.cit) and had some improvements over it. It had the following special features: (i) larger membranes could be utilised (ii) actual volume of permeability cell could be decreased to enable equilibrium to be reached more quickly (iii) the lower half of the cell could be stirred and (IV) the essential parts of apparatus, the rates of flow and the hydrostatic pressure on either side of the membrane could be rigidly controlled. The permeability cell consisted of twin flat glass (pyrex) vessels with flanges ground together. The internal dimensions of each half cell were approximately 50 mm. in diameter and 4 mm. in depth. The rate of flow was normally 150 ml per hour. The solution of the electrolyte was allowed to flow contineously through the top of the cell in essentially the same manner as for the lower half cell. The normal rate of flow was maintained 200 ml per hour. The hydrostatic pressure on each side of the membrane was always kept equal by adjusting the rate of flow of solution and conductivity water across the membrane. The affulent coming out was analysed conductometrically. Knowing the rate of flow and concentration of the affulent coming out of the lower half cell (from concentration-conductance curves) the permeability values at a particular temperature were calculated.

Before starting permeability measurments, the apparatus was throughly checked to determine wheather it was sufficiently free from inherent sources of error. The following critical examinations were made (i) Leakage: the upper and lower halves of the cell was filled with water and kept for four hours in order to check leakage. When it was put in a electrolyte solution, the affulent did not show any increase in conductivity which ensured that there was no leakage in the apparatus. (ii) Rate of flow through lower and upper half of cell: the rate of flow through the lower half of the cell was maintained constant (150 ml per hour) and through upper half (200 ml per hour) by adjusting stopcocks. (iii) Rate of stirring in lower half of the cell: it was observed by Willis in his permeability experiments that stirring increases the permeability, and this effect is attributed to removal of stationary layers from the underside of the membrane, with consequent reduction in the concentration gradient. Keeping this in view, the stirring rate was kept constant by adjusting the control dial of the electromagnetic stirrer, so that the experiment would be made with all the electrolytes under the same condition of stirring (iv) Pressure difference across the membrane: the hydrostatic pressure of the upper and lower halves cell were kept constant by keeping the levels of the liquids in the manometers equal which were adjusted with the help of stopcocks.

Ferric oxide and alumina membranes:

Ferric oxide and alumina membranes (supported and unsupported) were prepared by the method described earlier and permeability of membranes to various electrolytes having common cation and common anion was studied. From data on permeability of ferric oxide and alumina (supported and unsupported) membranes it was seen that the order of permeability was $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$ for anions. The cationic sequence for parchment supported iron oxide membrane was $Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Ba^{2+}$ Fe^{3+} and for unsupported membrane it was $K^+ > Ba^{2+} > Ca^{2+} >$

$Na^+ > Mg^{2+} > Fe^{3+}$. For alumina parchment supported membrane, the order for cations was $K^+ > Na^+ > Mg^{2+} > Ba^{2+}$ $Ca^{2+} > Al^{3+}$ and $K^+ > Ba^{2+} > Ca^{2+} > Na^+ > Mg^{2+} > Al^{3+}$ for unsupported membrane.

Permeability values for unsupported membranes are higher as compared to parchment supported membranes. Furthermore the magnitude of the permeability values for alumina membranes was higher than the corresponding iron oxide membranes. It was interesting to note that non-ionic soap (lauric acid diethanol-amine condensate) treated ferric oxide and alumina membranes did not show any change in the diffusion values. The order of permeability values for different ions also remained uneffected.

The cationic soap treated (cetyl pyridinium bromide) treated ferric oxide and alumina membranes retarded the diffusion rate, but retardation was much more marked with ferric chloride treated ferric oxide and aluminium chloride treated alumina membranes. The order is same as mentioned earlier. On the other hand unlike cationic soap treated membranes, anionic soap (sulphonated phenyl stearic acid) treated iron oxide and alumina membranes (supported and unsupported) showed an increase in the rate of permeation. Here also the order for different ions remained uneffected.

The probable mechanism of diffusion across these membranes is dealt along with silica, ferric silicate membranes (given later).

Effect of different electrolytes on membrane potential:

These studies revealed that the concentration potential (membrane potential) shows an increase in initial stage after which it attains a constant value. It means that once membrane has attained certain charge (by adsorption of ions from the electrolyte solution) the permeability phenomenon is solely governed by surface forces on the membrane.

The potential values in the case of parchment supported membranes were higher as compared to potential values of unsupported membranes. This supports the view that higher the permeability lower will be the potential attained. The order of potential values of different anions and cations for parchment supported and unsupported iron oxide and alumina membranes were just the reverse of permeability values, viz., $SO_4^{2-} > CNS^- > NO_3^- > Br^- > Cl^-$ (for all membranes), $Fe^{3+} > Ba^{2+} > Ca^{2+} > Mg^{2+} > K^+ > Na^+$; $Fe^{3+} > Mg^{2+} > Na^+ > Ca^{2+} > Ba^{2}$ K^+ (for parchment supported and unsupported iron oxide membranes) and $Al^{3+} > Ca^{2+} > Ba^{2+} > Mg^{2+} > Na^+ > K^+$; $Al^{3+} > Mg^{2+} > Na^+ > Ca^{2+} > Ba^{2+} > K^+$ (for parchment supported and unsupported alumina membranes).

The cationic soap treated membranes, as expected, gave higher potential values than untreated membranes. The order of potential values for different ions in the case of parchment supported iron oxide and alumina membranes was $SO_4^{2-} > CNS^- > NO_3^- > Br^- > Cl^-$ (for all membranes), $Fe^{3+} > Ba^{2+} > Ca^{2+} > Mg^{2+} > Na^+ > K^+$; $Fe^{3+} > Mg^{2+} > Na^+ > Ca^{2+} > Ba^{2+} > K^+$ (for parchment supported and unsupported iron oxide membranes) and $Al^{3+} > Ca^{2+} > Ba^{2+} > Mg^{2+} > Na^+ > K^+$; $Al^{3+} > Mg^{2+} > Na^+ > Ca^{2+} > Ba^{2+} > K^+$ (for parchment supported and unsupported alumina membranes).

Potential values in the non-ionic soap treated membranes were of the same magnitude as that of untreated membranes while ferric chloride treated ferric oxide membrane and aluminium chloride treated alumina membrane give higher potential values than cationic soap treated membranes. The order of potential values for different anions and cations was the same as mentioned earlier.

Anionic soap treated ferric oxide and alumina membranes gave low potential values but the order both for cations and anions remained uneffected.

The values of energy of activation of diffusion process for different electrolytes is higher than values of free diffusion of electrolytes like KCl (0.2M) reported in literature 4400 cal./mole.

The mechanism of diffusion of silica, ferric silicate and aluminium silicate membranes:

Silica, ferric silicate and aluminium silicate membranes are neither semipermeable nor show selective permeability but can be classed under membranes of various degrees of selective permeability. The mechanism of diffusion will be based on the membrane structure and on the electrical forces arising from the interplay of membranes and solutions of electrolytes. These membranes should be of porous character which would act as sieves on a molecular scale. They behave like electrically charged zeolities but differ from coal and activated carbon.

These membranes are positively charged having hydrogen or aluminium or iron ions firmly attached to the fixed part of the double layer. The other characteristic of the double layer associated with such colloidal systems namely the existence of chloride counter ions distributed in the liquid part of the fixed layer will be met with here also.

The permeability values for anions (having common cation K^+) were higher than for cations (having a common anion Cl^-). The only exception being $MgCl_2$, whose permeability value was larger than sodium chloride.

The lower permeability values for different cation K^+, Na^+, Ba^{2+}, Ca^{2+} is understandable in the case of a positively charged membrane which would markedly restrict their movement. The diffusion to cations did not follow the order of the size of the cations $Na^+ (1.0A^o) > Ca^{2+}(1.05A^o) > K^+(1.33A^o) > Ba^{2+}(1.38A^o)$. On the other hand the order for the hydrated ions was followed $K^+(1.19A^o) > Na^+(1.76A^o) > Ba^{2+}(2.78A^o) > Ca^{2+}(3.00A^o)$.

Hence it was concluded that the positively charged silica membrane becomes permeable to cations because of their hydrated form. The movement across the membrane would have been either negligible or very small if the cation had remained unhydrated.

The large permeability value for Mg^{2+} may be due to its very small ionic size 0.75A° as against 1.38A° for Ba^{2+} or 1.05A° for Ca^{2+}. This shows that silica membranes have pores wide enough to allow the diffusion of very small ions without the electrical forces being operative.

The permeability values are higher for anions than cations due to electrostatic driving force. However hydration also plays an important role since the order of permeability $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$ is the same as their position in the lyotropic series. It implies that anions which would hydrate easily would diffuse quickly than others. The permeability value of SO_4^{2-} ion is very low inspite of the fact that a large electrical driving force should operate due to two negative charges on the ion.

The permeability values for different ions are higher in the case of unsupported membranes as compared to parchment supported since in the later case the ions have to diffuse through two layers one after the other and geometry of the membranes becoming more complicated due to membrane heteroporosity.

The order of permeability values for cations (with common anion Cl^-) and anions (with common cation K^+) in ferric silicate and aluminium silicate is the same as in silica membranes. Here too we find.that the permeability values are higher for anions than cations and similar explanation based on the size of the hydrated ions, position in lyotropic series, electrostatic driving force, magnitude of membrane potential can be given for membrane permeability. The strikingly large difference in the permeability value of the silica membrane on the one hand and the iron and aluminium silicate on the other is not easy to explain except in terms of the difference in the structure of the membrane materials.

The permeability values for cations (Na^+, Ba^{2+}, Ca^{2+}) are very much higher for aluminium and ferric silicate membrane than for silica membrane. This difference is not so much evident in the case of Cl^- and Br^- ions but is quite appreciable in the case of NO_3^-, CNS^-.

The enhanced permeability of ferric silicate and aluminium silicate membranes to cations may be explained as follows:

These compounds may be given the empirical formulae $\overset{I}{M}_2O.Al_2O_3.nSiO_2.mH_2O$ or $\overset{I}{M}_2O.Fe_2O_3.nSiO_2.mH_2O$ (where M may be an alkali metal ion). The ratio of $\overset{I}{M}_2O:Al_2O_3$ or $\overset{I}{M}_2O:Fe_2O_3$ is unity, which means that the structures are all based on AlO_4 or SiO_4 tetrahedron linked to each of four other tetrahedra by sharing the four apical oxygen atom. According to empirical rule of Lowenstein (loc.cit)

AlO_4 tetrahedra can be joined in this way to SiO_4 tetrahedra only, never to another AlO_4. This means that n in the oxide formula cannot be less than two in the completed alumina silicate framework. The framework thus carries a net negative charge (the magnitude of the charge depending on the number of Al or Fe atoms in it). The enhanced permeability for cations can thus be explained on the basis of some residual negative charges present on the walls of the membrane pores. High permeability values for the nitrate and thiocyanate ions could not, however, be accounted for.

Soap impregnated silica, ferric silicate and aluminium silicate membranes:

The impregnation of membranes (supported and unsupported) with non-ionic soap (lauric acid diethanolamine condensate) decreased the permeability values to very small extent. This might be explained by assuming that soap influences pore capillary through.adsorption (formation of a monolayer on the wall), thereby decreasing the pore size and hence a decrease in permeability values was realised. The order of permeability value for anions and cations was the same as in untreated membranes.

The cationic soap (cetyl pyridinium bromide) treated membranes retarted the diffusion of anions and cations to a greater extent than the non-ionic soap treated membranes. The effect was more marked with cations than anions. Impregnation of cationic soap would effect its performance in two ways (i) adsorption of large cations (cetyl pyridinium bromide) on the pores of the walls, resulting in an increase in charge on the membrane (ii) blockage of the passage of the ions by charges of the same sign as on the membranes, the extent of blockage depending on the pore size, narrow pores being blocked more easily than the wider ones. The second factor influences the diffusion of both anions and cations resulting in a decrease in permeability.

The anionic soap treated membranes gave higher permeability values as compared to untreated membranes both for cations and anions. But the cations moved faster than anions. This may be explained in terms of charge neutralisation and to some extent in terms of charge reversal if impregnation is carried out more effectively.

Ferric chloride treated ferric silicate and aluminium chloride treated aluminium silicate membranes:

The behaviour of ferric chloride treated ferric silicate and aluminium chloride treated aluminium silicate is same as cationic soap treated membranes. Blockage of passage of the same sign and an increase in the positive charge on the walls of the membrane can again form the basis of explaining the experimental results.

Effect of different electrolytes on membrane potential:

Higher potentials are realised in the case of parchment supported silica, ferric silicate and aluminium silicate membranes as compared to unsupported membranes. Permeability and potential data of supported and unsupported membranes would reveal that the potential values are inversely indirectly proportional to permeability, higher the permeability value, lower the membrane potential and vice versa. The order of membrane potential for parchment supported and unsupported silica membranes is as follows: $SO_4^{2-} > CNS^- > NO_3^- > Br^- > Cl^-$; $Ca^{2+} > Ba^{2+} > Mg^{2+} > Na^+ > K^+$. The order realised is just the reverse of permeability values both for supported and unsupported membranes. Furthermore potential values for anions are less than cations.

The potential values for ferric silicate and aluminium silicate (supported and unsupported) show that the order of cations and anions is the just reverse of the sequence of anions and cations for permeability.

Potential of soap impregnated silica, ferric silicate and aluminium silicate membranes:

Non-ionic soap (lauric acid diethanolamine condensate) treated supported and unsupported membranes increases the potential values although the order remains uneffected. It appears that the treatment of membranes with non-ionic soaps increases the thickness of double layer so that higher potential values are observed.

The cationic soap (cetyl pyridinium bromide) treated supported and unsupported silica, ferric silicate and aluminium silicate membranes show high potential values (the order of potential values for ions remains uneffected). This is quite likely since treatment with cationic soap would result in a increase in charge on the membrane.

The anionic soap (sulphonated phenyl stearic acid) treated membranes show a decrease in potential values than untreated membranes (the order remains same). The decrease is due to the fact that addition of surfactant of opposite charge would decrease the thickness of the electrical double layer and subsequent decrease in charge.

Fe^{3+} ions treated ferric silicate and Al^{3+} ions treated aluminium silicate membranes give very high potential values as compared to untreated membranes. The same explanation as put forward for cationic soap treated membranes can be put forward here also.

Mechanism of permeability of ferric oxide and alumina membranes:

Most of the explanations put forward for the permeability of silica, ferric and aluminium silicate hold good in the case of ferric oxide and alumina membranes since these are also positively charged. The permeability values for anions are higher as that of cations. The positive charge on the membrane would have restricted the movement of cations to a very great extent but for their hydration the cations move through membranes.

The diffusion of anions is controlled by their position in the Hofmeister series, the order being $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$. Positively charged membrane walls facilitate the movementof anions, the sulphate ion being exception.

The unsupported iron oxide and alumina membranes are more permeable than supported because the later hinders the diffusion due to heteroporosity of the membranes.

Unlike silica, ferric silicate and aluminium silicate impregnation with non-ionic soaps does not bring about any change in permeability value therefore the idea of adsorption at capillary pores or on the walls of the pores is ruled out here. This may be attributed to narrow width of the membrane pores (the assumption is valid because permeability values of ferric oxide and alumina membranes are low than silica, ferric silicate and aluminium silicate membranes).

The decrease in permeability values due to impregnation of cationic soap may be attributed to blockage of passage of ions of the same sign (cetyl pyridinium ion) on the membrane. The increase in permeability due to impregnation of anionic soap may be explained in terms of charge neutralisation leading to the charge reversal on the walls of the pores.

The effect of impregnation with ferric chloride (in the case of ferric oxide membrane) and aluminium chloride (in the case of alumina membranes) is just the same as observed in cationic soap treated membranes.

It is worth mentioning that the results on membrane potential support most of the arguments put forward to explain the permeability behaviour of different treated membranes.

Activation energy of the diffusion process:

Activation energy values in the case of parchment supported and unsupported ferric oxide, alumina, silica, ferric silicate and aluminium silicate membranes are higher than the free diffusion of electrolytes like that of KCl (0.2M) reported in literature 4400 cal./mole, The results may be explained in terms of the highly charged nature of the membranes.

Ferric oxide, alumina, ferric silicate and aluminium silicate membrane electrodes:

Ferric oxide, alumina, silica, ferric silicate and aluminium silicate membranes were prepared as described earlier. Membranes were cemented to the end of glass tubes by Araldite adhesive. The tubes were filled with salt solutions of known anion activity and were fitted in rubber corks bearing two holes. The other hole was provided for the introduction of reference electrode in the solution of unknown anion activity kept in 50 ml beaker. Owing to the possible imperfection of the membrane, the membrane electrodes were checked with solution of known anion activity (KCl) above the membrane and unknown anion activity solution (KCl) below the membrane. Later unknown solution (KCl) was analysed by Mohr's method and activity of anion corresponding to concentration was compared with experimentally determined anion activity.

It was found that the working of electrodes is proper over a narrow range of concentration viz., 0.01M to 0.001M and performance becomes faulty with solutions of concentration $< 0.001M$ and $> 0.01M$. The ferric oxide and aluminium silicate membrane electrode give better accuracy (within 1.0 per cent) than others.

These membranes have many advantages over Marshall's (loc.cit) clay membranes inspite of the fact that they are not permselective. Unlike clay membranes they do not decompose and attain equilibrium quickly: 15 to 20 minutes. Since the permeability of chloride ions for greater than other anions (and especially the cations) they have been found useful for determination of Cl^- ion activity in fairly dilute solutions.

Positively charged colloidal solutions like those of alumina and ferric oxide have got Cl^- as the counter ions. Their activity changes with dilution and during the coagulation process - a fact which was observed by Weiser (loc.cit) on the basis of potentiometric studies using calomel electrodes. This was checked by employing membrane electrodes reversible with respect to anion.

Results on the Cl^- ion activity of ferric oxide, alumina, silica, ferric silicate and aluminium silicate sols of varying concentrations reveal that the counter ions activity increases with increase in the concentration of the sol. The plots between sol concentration and Cl^- ion activity gives a parabolic curve which show that more exchangeable counter ions are available from dilute sols than the concentrated ones.

The gradual addition of M KCl, M KNO_3, 0.002M K_2SO_4, 0.001M $K_4Fe(CN)_6$ to ferric oxide, alumina, silica, ferric silicate and aluminium silicate sols supports the phenomenon of ion exchange which are the chloride ions in the outer-shells of the double layers of these sols.

The plots between concentration of electrolyte added and Cl^- ion activity give parabolic curves. This means that after the addition of certain concentration of the coagulating electrolyte the exchange phenomenon stops and the colloidal particles becomes uncharged or possess only a small residual charge. The coagulation will then be independent of the concentration and the valency of the precipitating ions. The results give definite evidence of the exchange of counter ions and subsequent adsorption of coagulating ions during the coagulation of hydrophobic sol.

APPENDIX

A large number of heavy metal ferro-and ferricyanides of different colours and shade (with possible utility as pigments) have been prepared, their colloidal properties studied and their composition ascertained. Bhattacharya and Malik did extensive work not only on the composition of zinc, manganese, cobalt, nickel ferrocyanides, but also studied their adsorptive and hydrolytic properties and colloidal behaviour (1,2). Other aspects of metal ferrocyanogen complexes studied by Malik included changes in conductivity, pH and zeta potential of copper ferrocyanide sol (3,4,5), permeability of cobalt, nickel and silver ferricyanide membranes (6), sol-gel transformation of zinc ferrocyanide (7) and Prussian and Turnbulls blues (8). The colloidal studie's enumerated above gave many interesting informations hitherto unknown for these compounds. These are (i) zinc, manganese, cobalt, nickel and iron ferrocyanide precipitate pass over into stable colloids by using excess of potassium ferrocyanide (ii) viscosity variations with dialysis of these sols give almost identical curves thereby pointing towards the similarity in their composition, (iii) parchment supported membranes of cobalt, nickel and silver ferricyanides can be obtained by depositing the respective gels, the rate of diffusion of various electrolytes through them being in the reverse order of their adsorption, (iv) conductivity changes during coagulation can be correlated with the exchangeable H^+ counter ions and provide evidence for the phenomenon of adsorption, surface reaction and chemical interaction between the precipitating and stabilising ions (ferrocyanide ions) etc.

Very recently Malik and Coworkers did many interesting studies on the colloidal behaviour and membrane properties of Cr, Co, Zn, Ni, Mn ferrocyanides (9,10,11).

The literature reveals the fact that investigations on metal ferrocyanogen complexes have covered a wide field of study, renging from the older concepts based on chemical analysis and physico-chemical properties of the precipitates to the more recent ones, evolved on the basis of such studies as the application of modern electro-chemical techniques (polarography, amperometry, coulometry, exchange reaction etc.), importance of the metal ferrocyanide reactions in analytical work and on the catalytic decomposition of the alkali ferrocyanides have been achieved by these studies, but there still exists large scope for further studies. For example, one of the metal ferrocyanide which has not so far been systematically studied is aluminium ferrocyanide.

Very few references (12,13) are available in the literature on the colloidal behaviour of aluminium ferrocyanide. The work so far done does not take into account the various complexities inherent in the nature and composition of this compound. Moreover interesting information on the surface properties of these precipitates can be obtained by preparing their sol and gels and by investigating the permeabilit of its membrane for different electrolytes. The following studies on aluminium ferrocyanide was, therefore, undertaken: (i) preparation of aluminium ferrocyanide sol and study of its slow coagulation and variations in viscosity with dialysis (ii) permeability of aluminium ferrocyanide parchment supported membranes to anions and cations including effect of soap treated membranes on permeability and membrane potential studies.

Colloidal Aluminium Ferrocyanide

Reagents:

Potassium ferrocyanide (A.R.) was dissolved in double distilled water and strength determined by titrating against potassium permangnate (14) solution. Aluminium chloride (E. Merck) was taken and it was dissolved in double distilled water. Its strength (15) was determined gravimetrically after weighing as Al_2O_3.

Preparation of aluminium ferrocyanide sol:

Double decomposition method was adopted for the preparation of sol. The amounts of aluminium chloride and potassium ferrocyanide required to give 5 gms of aluminium ferrocyanide were calculated from the following stoichiometric relationship.

$$4\ AlCl_3 + 3\ K_4Fe(CN)_6 = Al_4\left[Fe(CN)_6\right]_3 + 12\ KCl$$

Calculated amounts of the reactants were mixed in the ratio 1 equivalent of $AlCl_3$: 6/5 equivalent of $K_4Fe(CN)_6$. The sol could only be obtained when $K_4Fe(CN)_6$ solution was gradually added to diluted $AlCl_3$ solution with constant stirring. The sol obtained was light greenish white in colour. It was dialyzed in a parchment bag keeping distilled water in the outer vessel. The sol on examination in Burton's type electrophoresis apparatus was found to be negatively charged.

Time of slow coagulation:

Experiments were performed with three different concentrations of the sol, viz., A, A/2 and A/4 using different electrolytes. 5 c.c. of the aluminium ferrocyanide sol was taken in clean dried pyrex test tubes and varying amounts of electrolytes (M KCl, 0.02M $BaCl_2$, 0.01M $AlCl_3$, 0.002M $Th(NO_3)_4$) were added. The total volume was made upto 10 ml by the addition of doubly distilled water. The concentrations of various electrolytes used for the coagulation experiments were so adjusted that the minimum time required for coagulation was near about 30 minutes in each case. Sols of the three different concentrations A, A/2, A/4 were taken and the time at which the sol particles left the surface of the sol was taken as the time of coagulation. Coagulation experiments were carried out at controlled pH (4.65).

TABLE No.1

Precipitation concentration in mM/litre for different electrolytes for aluminium ferrocyanide sol:

Concentration of sol	Electrolytes			
	KCl	$BaCl_2$	$AlCl_3$	$Th(NO_3)_4$
A(5 gms/litre)	300	5	1.8	0.7
A/2(2.5gms/litre)	285	3	0.8	0.4
A/4(1.25gms/litre)	252	2	0.7	0.2

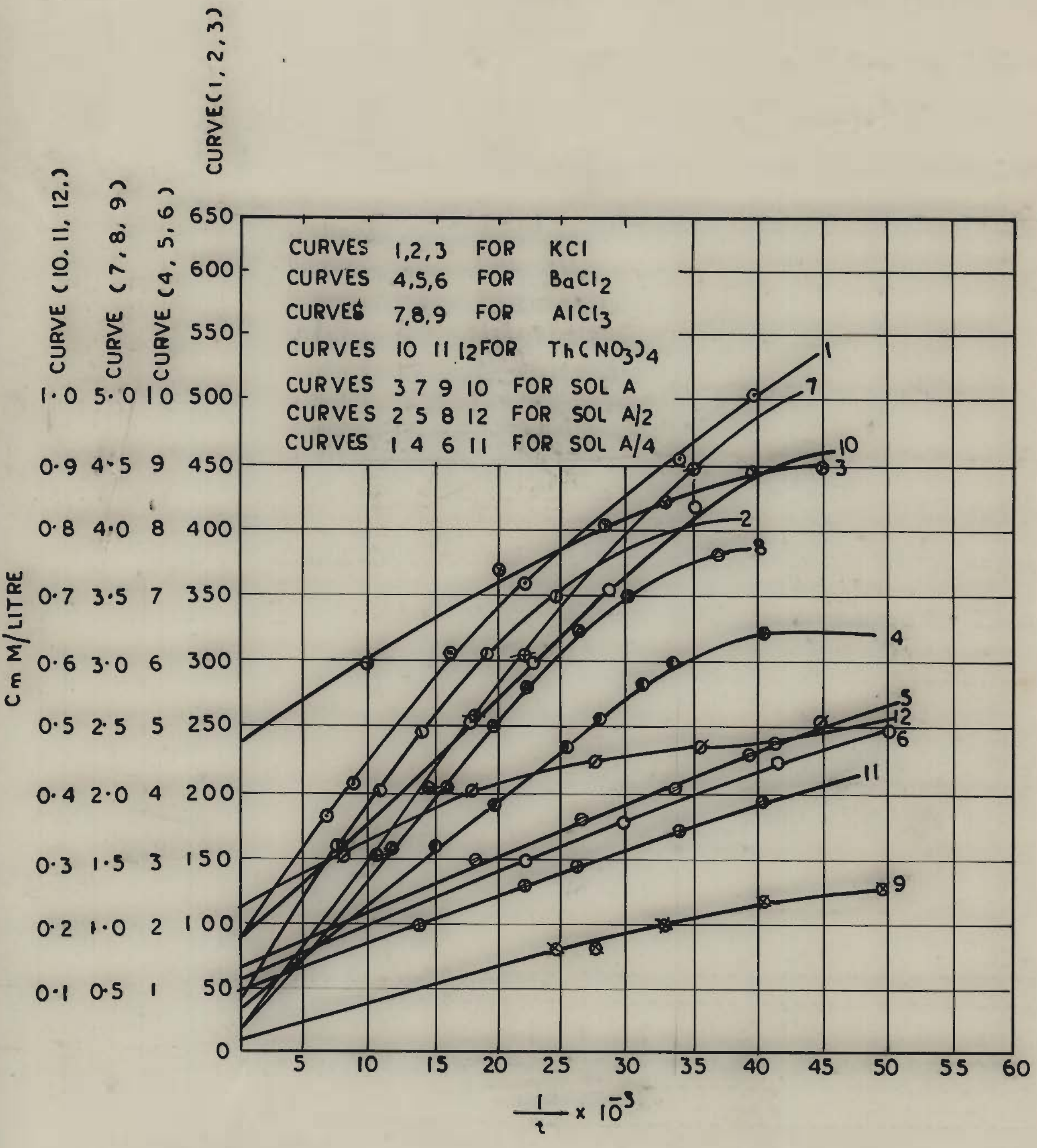

FIG. 42. CURVES CONCENTRATION(t) Vs $\frac{1}{t}$

Determination of constants of Bhattacharya's equation:

The relation established by Bhattacharya and Bhattacharya (16) between the concentration 'c' of the coagulating electrolyte and the time of coagulation 't' of copper ferrocyanide, ferric oxide and As_2S_3 sols is as under:

$$c = a + \frac{m.\frac{1}{t}}{n + \frac{1}{t}} \qquad (i)$$

where a, m and n are constants.

The equation assumes the following linear form on simplification $\frac{1}{c-a} = \frac{n}{m}.t + \frac{1}{m}$ (ii)

Accordingly a verification of the equation can be obtained from the coagulation data if the plots between $\frac{1}{c-a}$ and t give a straight line. 'a' in equation (ii) is obtained from the intercepts on the c-axis from the plots of c and $\frac{1}{t}$ (Fig. 42)

In the case of slow coagulation data of aluminium ferrocyanide sol the plots between $\frac{1}{c-a}$ and t gave straight line (Fig. 43) thereby providing the validity of Bhattacharya's equation.

The values of the constants in the Bhattacharya's equation for aluminium ferrocyanide are tabulated below.

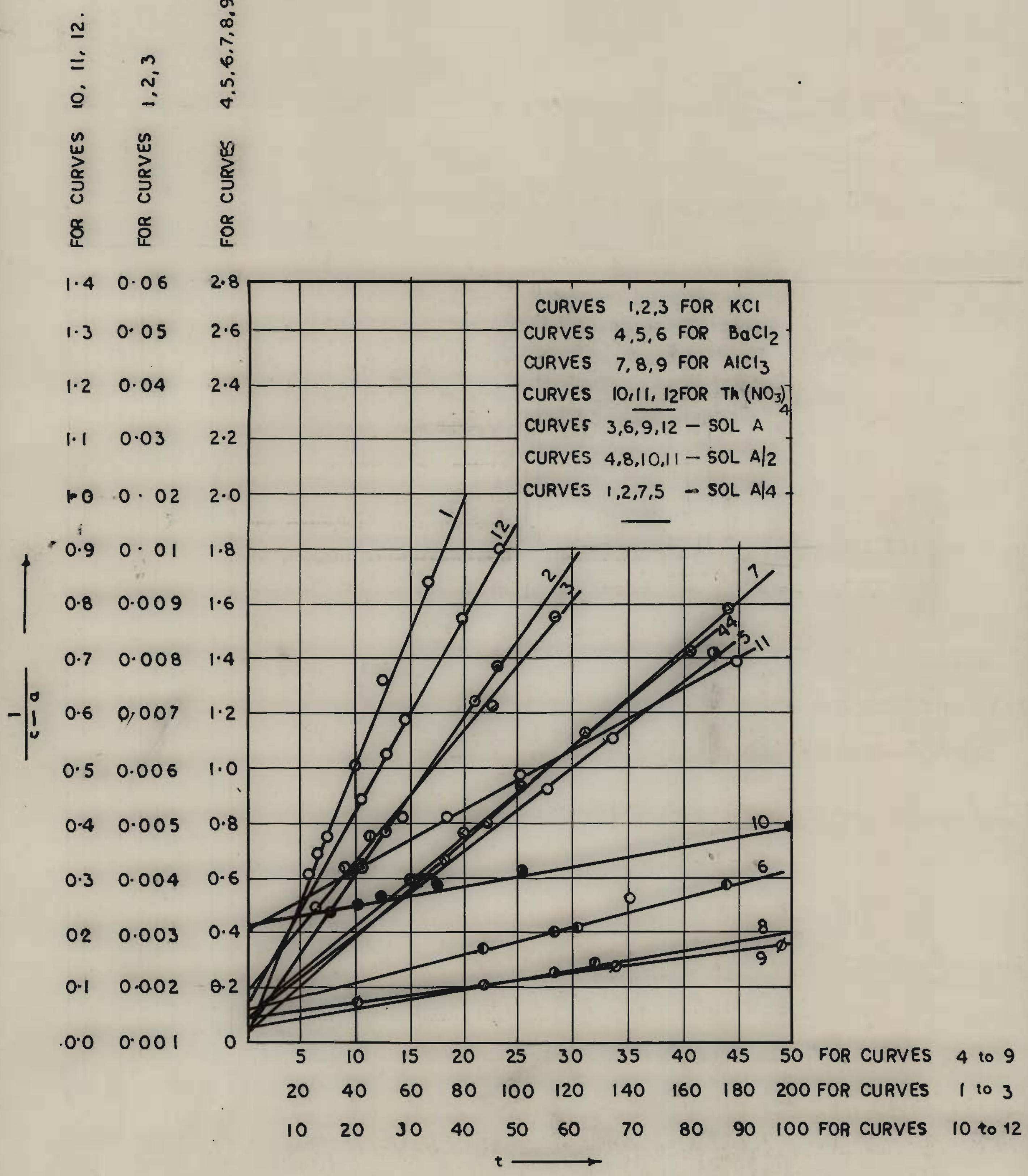

FIG. 43 CURVES $\frac{1}{c-a}$ Vs TIME OF COAGULATION (t)

TABLE No.2

Constants of Bhattacharya's equation for Aluminium ferrocyanide sol:

Concentration of sol	Electrolyte	a (mM/litre)	m (mM/litre	n (min.$^{-1}$)
A	M KCl	15	75.5	75.0
A/2	M KCl	12	89.9	82.0
A/4	M KCl	10	106.2	100.0
A	0.2M $BaCl_2$	1.7	9.0	2.34
A/2	0.2M $BaCl_2$	1.3	12.5	10.37
A/4	0.2M $BaCl_2$	1.1	16.6	12.94
A	0.01M $AlCl_3$	0.20	12.5	1.75
A/2	0.01M $AlCl_3$	0.15	16.6	2.82
A/4	0.01M $AlCl_3$	0.10	25.0	21.5
A	0.002M $Th(NO_3)_4$	0.48	4.7	0.79
A/2	0.002M $Th(NO_3)_4$	0.23	5.0	2.85
A/4	0.002M $Th(NO_3)_4$	0.10	16.6	29.8

Viscosity experiments:

Scarpa's (17) method modified by Farrow (18) and improved by Prasad, Mehta and Desai (19) was employed. The formula used is given below:

$$\eta = \frac{P^4}{8LV} \times \frac{t_1 t_2}{t_1 + t_2} = K \times \frac{t_1 t_2}{t_1 + t_2}$$

where t_1 and t_2 are the times required for filling and emptying the bulb of viscometer under a constant pressure P, V the volume of the bulb R and L are the radius and length of the capillary respectively. The value of the viscometer constant, K was determined under the same condition of temperature and pressure by measuring t_1 and t_2 for a liquid of known viscosity.

500 c.c. of the sol was prepared and 100 c.c. of the sol was kept in three different dialyzing bags for dialysis. The dialysis was done by changing distilled water at fixed intervals. One bag contained sol A, the second sol A/2 and the third contained sol A/4. Measurments were made at temperatures 30°, 35°, 40°, 45° ± 0.1°C (Fig.44). The results are summarized below.

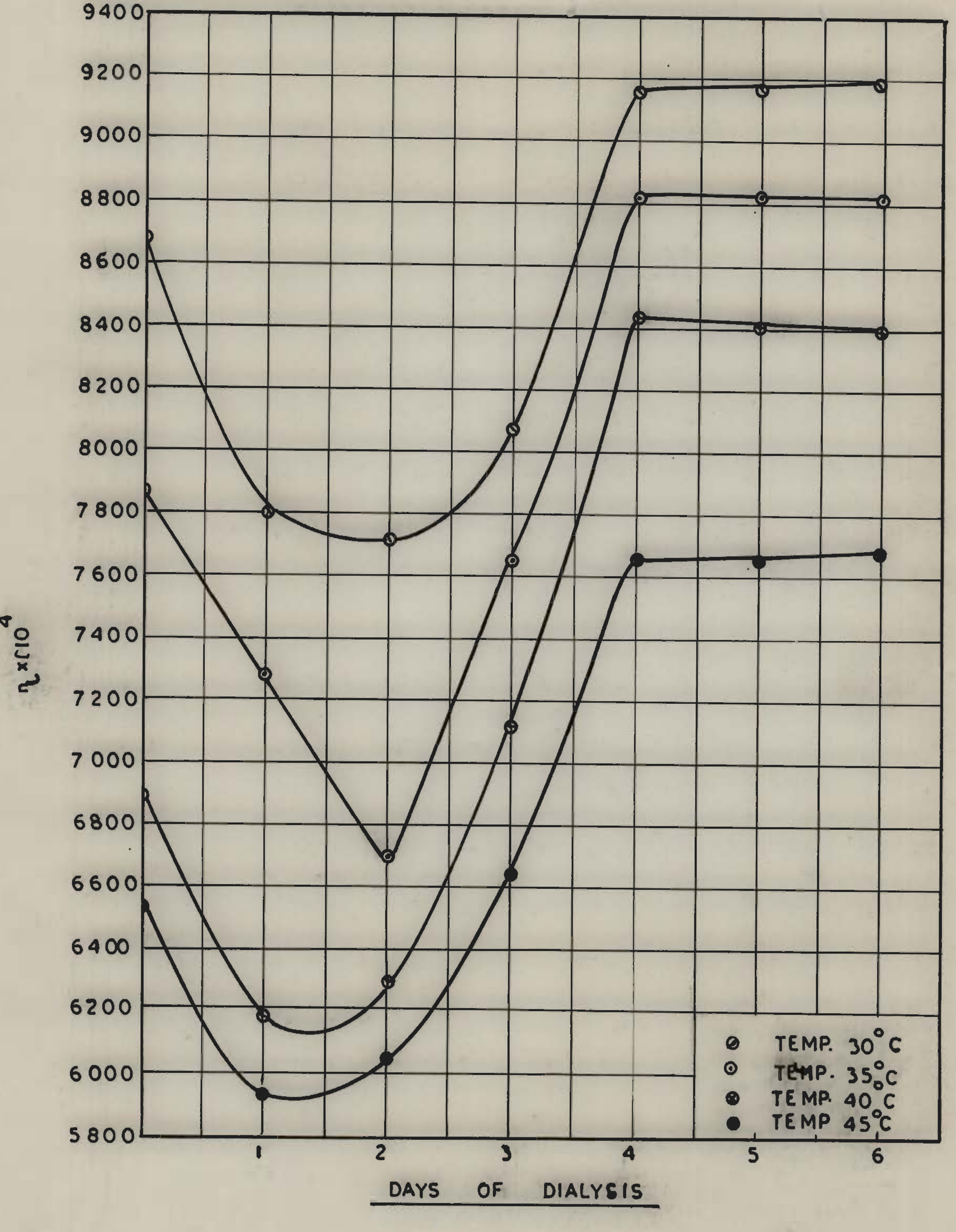

FIG.44 VARIATION IN VISCOSITY WITH DAYS OF DIALYSIS

TABLE No.3

Changes in viscosity of aluminium ferrocyanide sol with days of dialysis at different temperatures:

Temperature °C	Viscosity of undialysed sol in centipoise	Viscosity of sol (in centipoise after dialysis of				
		First day	Second day	Third day	Forth day	Fifth day
30°	0.8696	0.7817	0.7735	0.8087	0.9189	0.9183
35°	0.7891	0.7305	0.6517	0.7679	0.8837	0.8820
40°	0.6917	0.6197	0.6301	0.7136	0.8453	0.8400
45°	0.6554	0.5935	0.6073	0.6650	0.7660	0.7650

FIG.45. MICROPHOTOGRAPH OF ALUMINIUM FERROCYANIDE MEMBRANE

Preparation of Aluminium Ferrocyanide membrane:

Aluminium ferrocyanide membrane was prepared by impregnating the parchment paper with the reactants of the gel. The paper was first soaked in distilled water, and then tied to a bell jar. 0.2M solution of potassium ferrocyanide was filled in it and was then suspended in a beaker containing 0.2M aluminium chloride solution for 48 hours. It was then taken out and washed well with double distilled water. Later the solutions were interchanged, aluminium chloride was kept inside and potassium ferrocyanide outside the vessel. The process was repeated several times, until a fine deposit of aluminium ferrocyanide was obtained on the parchment paper. The membrane thus obtained was greenish white in colour. The membrane was also checked under microscope for any deformation or crack(Fig.45).

The permeability of aluminium ferrocyanide membrane was carried out by using the constant flow technique of Willi's, the details of which had already been given in Chapter II. The wet membrane as such was fitted between two flanges of permeability cell and measurments were carried out by using different electrolytes in the upper half of cell. The thermostat was maintained at the desired temperature. The variations in conductance of affulent with time during the diffusion of electrolyte was observed. The volume of the affulent was kept constant e.g. 150 c.c. per hour.

Conductances were measured after every twenty minutes till a constant value was attained. The concentrations were computed from the standard concentration-conductance plots of the electrolytes, given in Chapter III.

The electrolytes used in the upper half of the cell for permeability measurments are as under!

(i) Electrolytes having common cation

0.2M KCl, 0.2M KBr, 0.2M KNO_3, 0.2M K_2SO_4

(ii) Electrolytes having common anion

0.2M NaCl, 0.2M $BaCl_2$, 0.2M $CaCl_2$, 0.2M $MgCl_2$.

The results on permeability of parchment supported aluminium ferrocyanide membranes in millimoles per hour to various electrolytes having common cation and common anion are summarised below:

TABLE No.4

Permeability of aluminium ferrocyanide parchment supported to potassium chloride at different temperatures

Temperature °C	Initial conductance of affulent in mhos	Final Conductance of affulent in mhos	Time taken in attaining constant value of conductance	Concentration corresponding to constant conductance in millimoles	Permeability in millimoles per hour
20°	50.0×10^{-5}	47.8×10^{-5}	3 hours	2.291	0.3436
25°	69.0×10^{-5}	59.0×10^{-5}	3 hours	2.754	0.4131
30°	82.0×10^{-5}	89.0×10^{-5}	3 hours	3.162	0.4743
35°	145.0×10^{-5}	144.8×10^{-5}	3 hours	4.169	0.6253

TABLE No.5

Permeability of parchment supported aluminium ferrocyanide membrane to potassium bromide at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hou
20°	10.1×10^{-5}	5.2×10^{-5}	3 hours	0.1310	0.0197
25°	13.2×10^{-5}	7.2×10^{-5}	3 hours	0.1994	0.0298
30°	15.4×10^{-5}	12.4×10^{-5}	3 hours	0.3160	0.0331
35°	19.4×10^{-5}	17.2×10^{-5}	3 hours	0.4361	0.0654

TABLE No.6

Permeability of parchment supported aluminium ferrocyanide membrane to potassium nitrate at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final Conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	4.5×10^{-5}	2.5×10^{-5}	2 hours	0.0871	0.0120
25°	8.2×10^{-5}	5.0×10^{-5}	2 hours	0.1514	0.0227
30°	12.4×10^{-5}	10.1×10^{-5}	2 hours	0.2570	0.0387
35°	23.2×10^{-5}	21.0×10^{-5}	2 hours	0.5750	0.0963

TABLE No.7

Permeability of parchment supported aluminium ferrocyanide membrane to potassium thiocyanate at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration (corresponding to const. conductance of affulent in millimoles	Permeability in mill moles per hour
20°	4.8×10^{-5}	2.0×10^{-5}	2 hours	0.0501	0.0080
25°	8.1×10^{-5}	4.8×10^{-5}	2 hours	0.1200	0.0180
30°	11.2×10^{-5}	10.0×10^{-5}	2 hours	0.2510	0.0376
35°	23.0×10^{-5}	18.9×10^{-5}	2 hours	0.4365	0.0644

TABLE No.8

Permeability of parchment supported aluminium ferrocyanide membrane to potassium sulphate at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in mill imoles per hour
20°	4.2×10^{-5}	3.4×10^{-5}	2 hours	0.0398	0.0035
25°	7.0×10^{-5}	5.2×10^{-5}	2 hours	0.0810	0.0124
30°	14.8×10^{-5}	12.1×10^{-5}	2 hours	0.1580	0.0237
35°	23.8×10^{-5}	22.1×10^{-5}	2 hours	0.2880	0.0530

TABLE No.9

Permeability of parchment supported aluminium ferrocyanide membrane to sodium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	19.9×10^{-5}	15.0×10^{-5}	3 hours	0.4571	0.0685
25°	28.0×10^{-5}	23.0×10^{-5}	3 hours	0.5754	0.0863
30°	38.5×10^{-5}	34.9×10^{-5}	3 hours	0.7943	0.1191
35°	52.0×10^{-5}	53.6×10^{-5}	3 hours	1.0960	0.1639

TABLE No.10

Permeability of parchment supported aluminium ferrocyanide membrane to barium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in millimoles per hour
20°	11.2×10^{-5}	8.0×10^{-5}	3 hours	0.2188	0.0328
25°	17.1×10^{-5}	14.9×10^{-5}	3 hours	0.3631	0.0544
30°	24.9×10^{-5}	21.0×10^{-5}	3 hours	0.5012	0.0751
35°	44.5×10^{-5}	40.0×10^{-5}	3 hours	0.8318	0.1247

TABLE No.11

Permeability of parchment supported aluminium ferrocyanide membrane to calcium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. value of conductance	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in milli-moles per hour
20°	12.0×10^{-5}	9.0×10^{-5}	3 hours	0.1995	0.0299
25°	16.0×10^{-5}	13.0×10^{-5}	3 hours	0.2512	0.0378
30°	21.0×10^{-5}	18.0×10^{-5}	3 hours	0.3162	0.0474
35°	38.0×10^{-5}	32.0×10^{-5}	3 hours	0.5012	0.0751

TABLE No.12

Permeability of parchment supported aluminium ferrocyanide membrane to magnesium chloride at different temperatures:

Temperature °C	Initial conductance of affulent in mhos	Final conductance of affulent in mhos	Time taken in attaining const. conductance value of	Concentration corresponding to const. conductance of affulent in millimoles	Permeability in milli-moles per hour
20°	8.9×10^{-5}	6.1×10^{-5}	3 hours	0.1600	0.0240
25°	9.9×10^{-5}	8.2×10^{-5}	3 hours	0.1820	0.0273
30°	15.0×10^{-5}	12.0×10^{-5}	3 hours	0.2512	0.0376
35°	24.9×10^{-5}	21.0×10^{-5}	3 hours	0.3981	0.0597

TABLE No.13

Permeability of parchment supported treated and untreated aluminium ferrocyanide membranes:

(Permeability expressed in millimoles/hour, electrolyte concentration 0.2M).

Electrolyte	Untreated membrane	After treatment with		
		Non-ionic soap	Anionic soap	Cationic soap
KCl	0.3436	0.3430	0.2560	0.3820
KBr	0.0197	0.0200	0.0120	0.0225
KNO_3	0.0120	0.0120	0.0090	0.0182
KCNS	0.0080	0.0079	0.0060	0.0100
K_2SO_4	0.0035	0.0034	0.0018	0.0082
NaCl	0.0685	0.0679	0.0598	0.0720
$BaCl_2$	0.0328	0.0328	0.0309	0.0392
$CaCl_2$	0.0299	0.0298	0.0266	0.0330
$MgCl_2$	0.0240	0.0239	0.0210	0.0290

TABLE No.14

Potential of parchment supported treated and untreated aluminium ferrocyanide membranes:

(Potential expressed in millivolts; concentration of electrolyte on two sides of the membrane, 0.1 and 0.01M respectively).

Electrolyte	Untreated membrane	After treatment with		
		Non-ionic soap	Anionic soap	Cationic soap
KCl	25.0	25.0	27.5	23.5
KBr	27.0	27.5	29.0	26.0
KNO_3	28.5	28.0	31.5	27,5
KCNS	32.0	32.0	34.0	31.0
K_2SO_4	38.5	38.0	39.5	36.0
NaCl	20.5	20.5	24.8	21.5
$BaCl_2$	23.0	23.0	25.5	24.0
$CaCl_2$	25.8	28.0	27.5	26.0
$MgCl_2$	32.0	32.0	34.5	33.5

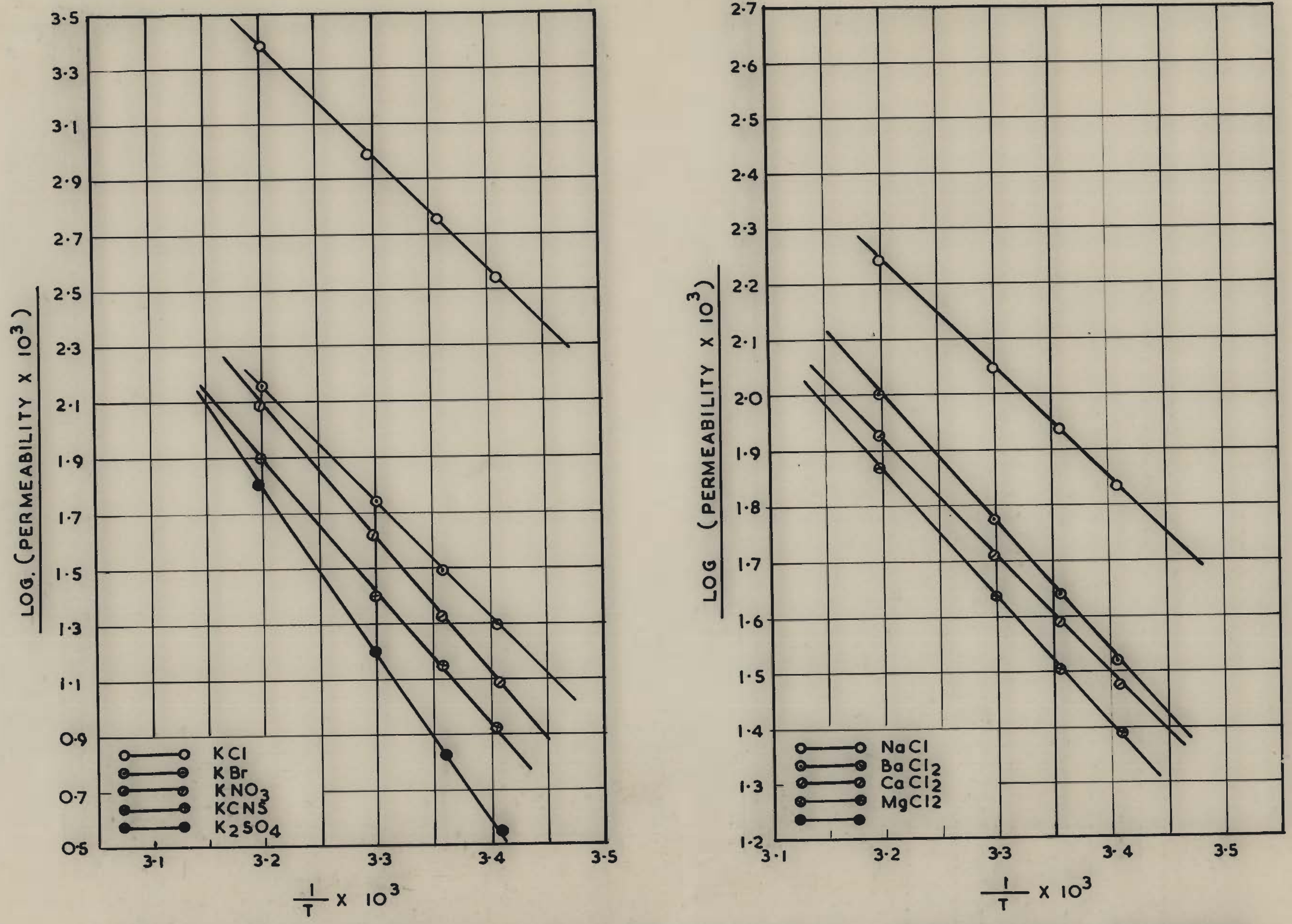

FIG. 46. ACTIVATION ENERGY CURVES FOR ALUMINIUM FERROCYANIDE MEMBRANES

Influence of temperature on the permeability of aluminium ferrocyanide membrane:

The diffusion rates were found to be highly dependent on temperature showing an increase with rise in temperature. The plots between log $(p \times 10^3)$ against $\frac{1}{T} \times 10^3$ (Fig.46) gave in all cases straightline relationship from the slopes of which the energy of activation E, of the diffusion process was calculated (Table No.15).

TABLE No.15

Activation energy of the diffusion process of different electrolytes through parchment supported aluminium ferrocyanide membranes:

Electrolyte	Activation energy cal./mole	Electrolyte	Activation energy cal./mole
KCl	4534	NaCl	4450
KBr	4969	$BaCl_2$	4820
KNO_3	4859	$MgCl_2$	4600
KCNS	5662	$CaCl_2$	5505
K_2SO_4	7120		

DISCUSSION

The precipitation concentration in mM/litre (Table No.1) for the various electrolytes required for coagulating the sol gave the order of the coagulating power as:

$Th^{4+} > Al^{3+} > Ba^{2+} > K^{+}$

It appears from our results (Table No.2) that Bhattacharyas equation, viz., $c = a + \frac{m.\frac{1}{t}}{n + \frac{1}{t}}$ is applicable in the case of aluminium ferrocyanide sol at all the three dilutions. The value of 'a' which we term critical stability concentration shows a normal variation with the valency of the precipitating ions in that it decreases, as the valency of the precipitating ion increases. The obvious physical interpretation of 'a(as seen in the (Fig.No.42) is the value of 'c' at $\frac{1}{t} = 0$ and hence 'a' is the maximum amount of electrolyte which can be added to the sol without effecting any coagulation. In other words we may call it the critical stability concentration of the electrolyte for the particular sol.

In visualising the physical significance of the constant m as seen in (Fig.No.43) is as follows. In the equation if $\frac{1}{t}$ is taken indefinitely large, the limiting value of 'c' becomes a+m. Hence m is that concentration of the electrolyte which should be added above the critical concentration 'a' in order to coagulate the sol immediately or in other words a+m is the limiting value of the electrolyte concentration where the region of slow coagulation merges into that of rapid coagulation.

Again if we put $t = \frac{1}{n}$ the equation becomes $c = a + \frac{m.n}{n+n}$ or $c-a = \frac{m}{2}$ which means that $\frac{m}{2}$ is the amount of electrolyte in excess of the critical stability concentration 'a' required to coagulate the sol in time $t= \frac{1}{n}$. Hence we can say that 'n' is the reciprocal of the time in which the sol will coagulate when the excess of electrolyte above the critical stability concentration is only half of the excess required to coagulate the sol immediately.

The empirical equation of Bhattacharya (et.al) may be based on the theoretical considerations developed by Verwey and Overbeek (20) for the interaction of two charged units as shown by Ghosh et.al (21) and Coworkers. Therefore n has the dimensions of frequency whilst m has that of concentration. Hence the value of the constant n is directly related to the attractive force between two aggregating colloidal particles. Further for a rapid or instantaneous coagulation m becomes equal to $(c-a) \sim c$ as a or coagulating concentration is small compared to c. In other words m refers to the concentration of the coagulating electrolyte when the stability factor is defined by the repulsive force hence an increase in the valency of the ion (from the monovalent to polyvalent) will result in the decrease of repulsive force and m will decrease.

The viscosity time of dialysis curves exhibit appreciable changes in viscosity (Fig.No.44). From the curves it is inferred that the viscosity first decreases during the first two days and then continuously increases after the second day, showing tendency of attaining constancy with prolonged dialysis. The variations of such nature may be attributed to factors like gradual removal of stabilizing ions and the hydrolysis of the complex on dialysis. Normally the removal of the stabilizing ions would result in a decrease in charge and consequent increase in viscosity. Since a decrease in viscosity is observed in the initial stages, it seems that second factor is operative here and the hydrolysed soluble ions go to increase the charge on the colloid. A highly charged system would show little tendency for the aggregation of the particle and hence the viscosity would decrease. After sufficient dialysis the hydrolysis is stopped and the dialysis process is then controlled by the removal of stabilizing ions. This would result in an increase in viscosity. Finally the magnitude of hydration, corresponding to the minimum charge required to keep the sol stable is reached and a constancy in viscosity is attained.

The variations in viscosity with time of dialysis in the case of aluminium ferrocyanide sol are quite different from those of other sols like cobalt, nickel, manganese ferrocyanides studied by Malik and Co-workers (22). This is quite evident from the fact that aluminium ferrocyanide is more complex in nature than the more familiar metal ferrocyanides.

Mechanism of diffusion across aluminium ferrocyanide membrane:

The permeability of aluminium ferrocyanide membrane to different electrolytes having a common cation and anion respectively shows that the order of rate of diffusion for anions is:

$Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$ and for cations $K^+ > Na^+ > Ba^{2+} > Ca^{2+} > Mg^{2+}$

It is also clear from permeability data recorded in (Table No.13) that the rate of penetration of cations is more than anions. This shows clearly that membrane is negatively charged and hence allows cations more easily to pass through it while anions are not easily passed due to repulsive force.

Further it is evident from above that the sequence for anions is according to their size, the ions of smaller size (Cl^- and Br^-) pass through more easily than the bigger ones (CNS^-, SO_4^{2-}).

The cationic sequence shows that the diffusion of hydrated ionic radii which are much smaller for K^+ (1.19A°) and Na^+ (1.76A°) is high than those of Ba^{2+} (2.78A°), Ca^{2+} (3.00A°) and Mg^{2+} (3.32A°). The diffusion of unhydrated ions cannot be visualised since Na^+ (1.00A°) and K^+ (1.33A°) are much large than Mg^{2+} (0.75A°) or even Ca^{2+} (1.05A°).

It is interesting to note that non-ionic soap (lauric acid diethonol-amine condensate) treated aluminium ferrocyanide membranes show no change in the diffusion values (Table No.13). This shows that the absence of any kind of charge or exchange adsorption does not allow the non-ionic soap to come in the vicinity of the membrane.

The anionic soap treated (sulphonated phenyl stearic acid) membrane retards the movement of anions and cations to a appreciable extent (Table No.13). The retardation of anions is more than cations. It appears that the development of large negative force, the anions are much retarded and cation to a least extent. The sequence of anions and cations is same as above.

It is also observed from the (Table No.13) that cationic soap (cetyl pyridinium bromide) renders membrane more permeable to anions and cations. Althoug the increase in rate of diffusion of anions is more than cations. The charge neutralisation by cationic soap renders membrane more permeable. Here also the sequence of anions and cations remains same.

Effect of different electrolytes on membrane potential

The potential values due to diffusion of electrolytes through aluminium ferrocyanide membrane are recorded in (Table No.14). It is evident from datas for anions and cations that potential values are higher for anions and less for cations. This is good in agreement with the fact that higher the potential lower will be the permeability. The order of potential values for anions and cations is: -

Anions: $SO_4^{2-} > CNS^- > NO_3^- > Br^- > Cl^-$

Cations: $Mg^{2+} > Ca^{2+} > Ba^{2+} > Na^+ > K^+$.

No change in potential values is observed in the case of non-ionic soap (lauric acid diethanol amine condensate) treated aluminium ferrocyanide membrane. The order of potential values is same as above.

The cationic soap treated membrane as expected gives lower potential values (Table No.14). It is obvious that the charge neutralisation is responsible for decreasing the thickness of double layer and hence a decrease in potential values is realised. The decrease in potential values is more in the case of anions than cations. The order of potential values for different anions and cations is safe.

Anionic soap (sulphonated phenyl stearic acid) treated membranes gives higher potential values as compared to untreated membranes (Table No.14). The increase in potential values is due to large negative force developed on membrane. Although the potential values are low for cations.

It is obvious that the values of activation energy (Table No.15) p231. for the diffusion of electrolytes in the case of aluminium ferrocyanide membrane is more than activation energy from free diffusion of electrolytes. For example the activation energy of free diffusion of KCl (0.2M) cited in literature is 4400 cal./mole which is less than calculated in the present study. The results can be explained on highly charged nature of the membrane.

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CHAPTER I

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Permeability of Electrolytes Through Parchment Supported Iron Oxide Membranes*

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Permeability measurements with various electrolytes, viz. KCl, K_2SO_4, KNO_3, $KCNS$, KBr, $NaCl$, $BaCl_2$, $MgCl_2$ and $FeCl_3$ on parchment supported iron oxide membranes have been carried out using the constant flow method. The results show that the order of permeability of anions and cations is $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$ and $Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Ba^{2+} > Fe^{3+}$ respectively. The above order of permeability which differs from the order of free diffusion indicates that the free diffusion of ions is greatly restricted due to the imposition of the membrane. It is also observed that the permeability of electrolytes is greatly influenced if the membrane is pretreated with ferric chloride, or cationic and anionic soap solutions. Membranes pretreated with ferric chloride and anionic soap solutions are less permeable than those treated with cationic soap solutions. Measurement of membrane potential shows an initial increase after which it attains a constant value and the order of membrane potential values for the above anions and cations is reverse of the order of permeability, thus indicating that greater the membrane potential lower the permeability and vice versa. Activation energies of the diffusion process for the various electrolytes have also been calculated.

MEMBRANE phenomenon is very complex and a number of controlling factors have been listed from time to time to explain it. According to Teorell[1] the problem can be approached from the following angles: (i) ionic transport; (ii) membrane potential; (iii) electrical conductivity; (iv) ionic distribution equilibria; and (v) the spatial distribution of ions and potentials across the membrane. Various other theories have also been put forward by other workers[2-4]. During the course of our studies on the permeability of electrolytes through various inorganic membranes we deduced a simple relationship between permeability and membrane potential giving a relatively simple picture of transport phenomenon across artificially prepared parchment supported membranes.

The present communication deals with the permeability measurements of the various electrolytes on parchment supported iron oxide membranes carried out using the constant flow method of Hartung and Willis[5]. The work reported here, besides incorporating the usual data on permeability and membrane potential, also describes the results of the investigations on membranes pretreated with ferric ions, and cationic and anionic soap solutions.

Materials and Methods

Preparation of membrane — Parchment supported ferric oxide membrane was prepared as follows. Distilled water soaked parchment paper disc was suspended in a cylinder containing a solution of ferric chloride (25 ml., 0·1*M*). The whole assembly was placed in a beaker containing ammonia solution (50 ml., 20 per cent) for 24 hr. The solutions were then interchanged, ammonia being kept inside and ferric chloride solution outside the vessel. The process was repeated several times until a fine deposit of iron oxide gel was obtained on the parchment paper. The membrane, dark brown in colour, was washed repeatedly with double distilled water for the complete removal of absorbed electrolyte. It was then examined under a microscope for any deformation or crack. The wet membrane as such was fitted between the two flanges of permeability cell.

Apparatus and experimental procedure — The diffusion experiments were carried out using constant flow method[5]. This method gave accurate results for the diffusion rates. The apparatus used in this study was similar in construction to that described by Hartung and Willis[5]. It had the following special features: (i) larger membranes could be employed; (ii) actual volume of permeability cell could be decreased to enable equilibrium to be reached more quickly; (iii) the lower half of the cell could be stirred; and (iv) the essential parts of apparatus, the rates of flow and the hydrostatic pressure on either side of the membrane could be rigidly controlled. The permeability cell consisted of twin flat glass (pyrex) vessels with flanges ground together. The internal dimensions of each half cell were approximately 50 mm. in diameter and 4 mm. in depth. The rate of flow was normally 100 ml. per hour. The solution of the electrolyte was allowed to flow continuously through the top of the cell in essentially the same manner as for the lower half. The normal rate of flow was maintained at 200 ml. per hour. The hydrostatic pressure on each side of the membrane was always kept equal by adjusting the rate of flow of solution and conductivity water across the membrane. The effluent coming out was analysed conductometrically. Knowing the rate of flow and concentration of the effluent coming out of the lower half cell (from concentration-conductance curves) the permeability values at a particular temperature were calculated.

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Permeability of various electrolytes through pretreated membranes — In order to find the effect of pretreated membrane on the permeability of different electrolytes the permeability measurements were carried out at 20°C. with membranes soaked in 0·1*M* ferric chloride solution, $10^{-3}M$ sulphonated phenyl stearic acid, $10^{-3}M$ cetyl pyridinium bromide and $10^{-3}M$ lauric acid diethanolamine condensate for 24 hr. The results were compared with those obtained on untreated membranes.

The anionic soap, viz. sulphonated phenyl stearic acid was prepared by the method of Stirton *et al.*[6] Cetyl pyridinium bromide, a BDH product, was recrystallized from acetone. The non-ionic soap, viz. lauric acid diethanolamine condensate[7] (LDC), was prepared by condensing pure lauric acid (BDH) with diethanolamine.

Membrane potential measurements — In order to get better insight into the mechanism of permeability phenomenon it was thought worthwhile to carry out experiments on membrane potential. The method used for determining membrane potential, *E*, was the same as described by Michaelis[8] for concentration potential difference of the concentration cell.

$$\text{Hg}\ \ \text{Hg}_2\text{Cl}_2\ \ \underset{\text{Sat.}}{\text{KCl}}\ \ \underset{C_1}{\text{Electrolyte}}\ \overset{\text{Membrane}}{\Big|}\ \underset{C_2}{\text{Electrolyte}}\ \ \underset{\text{Sat.}}{\text{KCl}}\ \ \text{Hg}_2\text{Cl}_2\ \ \text{Hg}$$

The value of *E* was measured with the help of a students' potentiometer. The same electrolyte was used on both sides of the membrane and the concentration ratio C_1/C_2 was kept equal to 10 throughout, the dilute side (0·01*M*) always remaining positive.

Determination of the membrane potential was made with freshly prepared, treated and untreated membranes. The variation in potential with time was determined. The experiments were repeated with fresh solutions of electrolyte and the maximum potential attained was recorded.

Results and Discussion

Effect of different electrolytes on permeability of the treated and untreated membranes — The two main factors, which should be taken into consideration while determining the permeability of ions through membranes are: (i) charge on the membrane pores, due to either adsorption or ionization of the membrane material which act as barrier to the diffusing ions; and (ii) sieve action whereby the screening of ions according to their size takes place, larger ions diffusing out more slowly than the smaller ones and vice versa.

Considering the permeability of different anions and cations for the membrane under study, it is seen that the order of permeability of the anions and cations is: $Cl^- > Br^- > NO_3^- > CNS^- > SO_4^{2-}$ and $Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Ba^{2+} > Fe^{3+}$ respectively. The above sequence indicates that the free diffusion of ions is greatly restricted due to imposition of the membrane since no where the order of free diffusion, viz. $SO^{2-} > Br > Cl > NO_3^- > CNS^-$ is realized.

The difference in the permeability values may also be related to the sieving effect of the membrane so that the ions of smaller size pass through easily and the movements of bigger ones is appreciably hindered.

It is evident from the data recorded in Table 1 that the permeability of electrolytes is considerably influenced when the membrane is pretreated with ferric chloride or soap solutions. The treatment of membrane with ferric chloride rendered the membrane less permeable without influencing the order of permeability. Such a behaviour can be explained on the basis of the strong adsorption of Fe^{3+} ions, almost to complete saturation by these ions, by the membrane surface thereby retarding the movements of anions and cations due base exchange (cation) and other surface reactions (anion). For example large electrostatic forces should exist between the bivalent anions and the ferric ions with the result that the diffusion of the univalent anion is much less retarded in comparison to the bivalent, say sulphate ion.

It is interesting to note that cationic soap (cetyl pyridinium bromide) treated membrane also retards the diffusion rate of anions and cations although the diffusion values are somewhat higher in magnitude than in the case of ferric chloride treated membrane. The order of permeability for different anions and cations in this case is $Cl^- > NO_3^- > Br^- > CNS^- > SO_4^{2-}$ and $K^+ > Na^+ > Mg^{2+} > Ca^{2+} > Ba^{2+} > Fe^{3+}$ respectively. This again shows that the membrane takes up a large positive charge on it by the adsorption of

TABLE 1 — PERMEABILITY OF DIFFERENT ELECTROLYTES ON IRON OXIDE MEMBRANES

(Permeability expressed as millimole/hr; electrolyte conc. 0·2*M*)

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Ferric chloride
KCl	0·0069	0·0068	0·0079	0·0065	0·0041
KBr	0·0045	0·0044	0·0061	0·0028	0·0039
KNO_3	0·0044	0·0036	0·0049	0·0042	0·0037
KCNS	0·0023	0·0023	0·0047	0·0021	0·0012
K_2SO_4	0·0018	0·0016	0·0020	0·0011	0·0014
NaCl	0·0071	0·0062	0·0075	0·0039	0·0030
$MgCl_2$	0·0068	0·0063	0·0072	0·0049	0·0042
$CaCl_2$	0·0043	0·0045	0·0057	0·0041	0·0030
$BaCl_2$	0·0039	0·0030	0·0067	0·0038	0·0029
$FeCl_3$	0·0019	0·0018	0·0041	0·0015	0·0013

TABLE 2 — POTENTIAL OF IRON OXIDE MEMBRANES

(Potential expressed in mV; Conc. of electrolyte on two sides of the membrane, 0·1 and 0·01*M* respectively)

Electrolyte	Untreated membrane	After treatment with			
		Non-ionic soap	Anionic soap	Cationic soap	Ferric chloride
KCl	12·0	13·0	10·5	18·0	19·0
KBr	15·5	15·0	12·0	20·0	21·5
KNO_3	23·0	23·5	18·0	24·0	24·0
KCNS	27·0	27·0	20·0	35·0	37·0
K_2SO_4	38·0	37·0	26·0	42·0	42·5
NaCl	21·0	22·5	16·0	39·0	39·5
$MgCl_2$	35·0	36·0	28·0	42·0	44·5
$CaCl_2$	38·0	38·0	31·5	46·0	48·5
$BaCl_2$	39·0	38·5	34·0	48·5	52·5
$FeCl_3$	53·0	52·5	48·0	55·0	59·0

positively charged cetyl pyridinium ion. But the higher diffusion value compared to ferric chloride treated membrane in this case is rather anomalous. It appears that the soap hinders the permeability of the solvent to a great extent with the result that the solutions permeates in a concentrated form through the membrane giving apparently higher permeability values.

A definite increase in permeability, compared to that of untreated membrane, is observed with anionic soap (sulphonated phenyl stearic acid) treated membranes although the order again remains the same. In this case the possibility of exchange adsorption is very small and purely physical forces appear to influence the permeability phenomenon. The dominant role of electrostatic forces controlling the diffusion phenomenon although should be given due emphasis, it cannot be the only factor. These forces help in creating a close contact between the positively charged membrane surface and the anion of the surfactant but the presence of the latter should modify the surface properties of the membrane in a manner as to retard the passage of the solvent. Under such conditions enhanced permeability should be expected.

With non-ionic soaps there is no change in permeability values. Although this soap should also modify the surface properties of the membrane, the absence of electrostatic forces or exchange adsorption does not allow the non-ionic soaps to come in the vicinity of the membrane.

Effect of different electrolytes on membrane potential — In this study membrane potential shows an initial increase after which it becomes constant. This fact shows that once the membrane has attained a certain charge (after adsorbing ions from the electrolyte solution) the permeability phenomenon is solely governed by surface forces on the membrane. Our results on pretreated membranes reported above support this view. The results can also be interpreted in the light of the views of Meyer and Sievers[9] who postulated a number of fixed charges due to either adsorption or ionization of membrane material between the fixed ion of the pores and those in the bulk of the solution.

The experimental observations (Table 2) on membrane potential for anions and cations show an order reverse to that of permeability, viz. $Cl^- < Br^- < NO_3^- < CNS^- < SO_4^{2-}$ and $K^+ < Na^+ < Mg^{2+} < Ca^{2+} < Ba^{2+} < Fe^{3+}$ respectively.

The cationic soap treated membrane, as expected, gives higher potential than untreated membrane due to adsorption of cetyl pyridinium ions. Similar behaviour is observed with ferric chloride treated membranes.

The treatment of the membrane with anionic soaps decreases the potential values whereas the potential values almost remain unchanged with non-ionic soap treated membranes. Although the mechanism involved in all the three cases is not clear, the values of the membrane potential obtained with treated membranes support the view that greater the potential, lesser the permeability and vice versa.

Influence of temperature on permeability — The diffusion rates are found to be highly dependent on temperature showing an increase with rise in temperature. The plots between diffusion values, log $(p \times 10^3)$ against $\frac{1}{T} \times 10^3$ (Figs. 1 and 2) give in all the cases straightline relationships from the slopes of which the energy of activation, E, of the diffusion process, could be calculated (Table 3).

The value of energy of activation for the free diffusion of KCl ($0{\cdot}2M$) reported in literature is

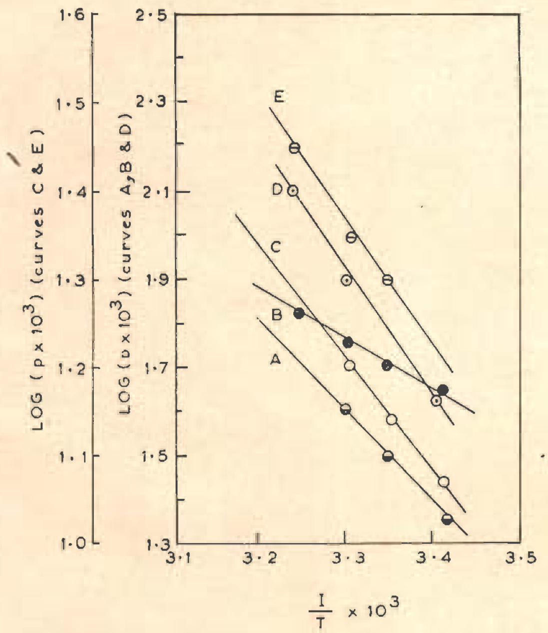

Fig. 1 — Plots of log $(p \times 10^3)$ versus $1/T \times 10^3$ for various electrolytes (anionic) [(A) KCNS; (B) KBr; (C) KCl; (D) KNO_3; and (E) K_2SO_4]

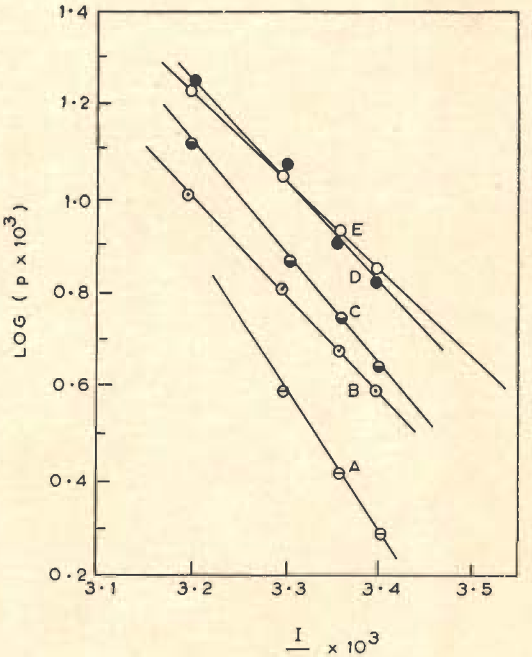

Fig. 2 — Plots of log $(p \times 10^3)$ versus $1/T \times 10^3$ for various electrolytes (cationic) [(A) $FeCl_3$; (B) $BaCl_2$; (C) $CaCl_2$; (D) $MgCl_2$; and (E) NaCl]

TABLE 3 — ACTIVATION ENERGY OF THE DIFFUSION PROCESS FOR DIFFERENT ELECTROLYTES

Electrolyte	Activation energy cal./mole	Electrolyte	Activation energy cal./mole
KCl	5673	NaCl	5296
K_2SO_4	6337	$BaCl_2$	4767
KNO_3	6112	$CaCl_2$	5485
KCNS	4606	$MgCl_2$	5112
KBr	4712	$FeCl_3$	7088

3600 cal./mole and is lower than that calculated in the present study. The results can again be explained in terms of the highly charged nature of the ferric oxide membrane.

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