NON-EQUILIBRIUM THERMODYNAMICS OF COUPLED FLOW PROCESSES THROUGH POROUS MEDIA

A THESIS SUBMITTED
IN PARTIAL FULFILMENT OF THE REQUIREMENT
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
M. GEORGE ABRAHAM

CHEMISTRY GROUP
BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE
PILANI (RAJASTHAN)
1977

CERTIFICATE

This is to certify that the thesis entitled 'Non-equilibrium Thermodynamics of Coupled Flow Processes Through Porous Media' submitted by Shri M. George Abraham, I.D. No. 74S83501, for award of Ph.D. degree of the Birla Institute of Technology and Science, Pilani, embodies original work done by him under my supervision.

R.C. Srivastava

(R.C. Srivastava) 25.7.77
Professor of Chemistry
Birla Institute of Technology and Science
Pilani.

Pilani

Date 25-7-'77

ACKNOWLEDGEMENTS

I am thankful to Professor R.C. Srivastava, M.Sc., Ph.D., F.R.I.C.(London), Professor of Chemistry, Birla Institute of Technology and Science, Pilani, for his help and guidance during the entire course of this work.

I am also thankful to Dr. Abhay K. Jain for the valuable discussion I had with him, during the course of this work.

Thanks are due to the Director, Birla Institute of Technology and Science, and the Group Leader of Chemistry Discipline for providing the necessary facilities.

Financial assistance from the Council of Scientific and Industrial Research, New Delhi, in the form of a Junior Research Fellowship first and later a Senior Research Fellowship is greatly acknowledged.

The help received from Messers G.D. Sharma and K.M. Sharma, Glass Blowing Section, in the fabrication of apparatus and H.C. Pant, Reprography Section, in the preparation of thesis figures is acknowledged

My thanks are due to Mr. Ram Kumar for typing the thesis with diligent care.

The help of my friends in various ways deserve special mention.

George Abraham

Pilani

(M.George Abraham)

Date 25-7-'77

CONTENTS

****

PREFACE

Non-equilibrium thermodynamics is one of the most powerful tools for the study of coupled flow processes through porous media. The non-equilibrium thermodynamic treatment is mostly phenomenological in nature and treats the barrier, which may be a porous plug or a membrane, natural or synthetic, very much like a black box and one may only deduce its mechanism and function from observations of input and output data. The conclusions thus drawn would obviously be of a rather general nature but the price of this generality is that not much can be learnt about the mechanism of the phenomenon. It is for this reason that several mechanistic models have been proposed of which Speigler's frictional model is the one that has attracted attention in recent years.

The studies reported in chapter II on the electro-osmosis of liquid mixtures have been designed to throw light on the validity of Speigler's frictional model in addition to verifying the Onsager's formalism. The transport data have been further utilised to verify the non-equilibrium thermodynamic theory of electro-kinetic energy conversion developed by Osterle and co-workers, and Kedem and Caplan.

Kedem and Katchalsky developed a theory for the permeability of composite membranes on the basis of non-equilibrium thermodynamics. This theory was intended for biological membranes which are composite structures consisting of several layers of substances differing in composition and permeability characteristics. Since the study of flow through such composite porous media (e.g. porous soils or rocks having layered structure) is quite important in geo-sciences, it is of interest to explore the extent to which the theory of Kedem and Katchalsky can be made applicable to them. This precisely is the aim of studies reported in chapters III and IV.

Of course in chapter I a brief summary of the postulates and methodology of thermodynamics of irreversible processes on which the studies recorded in subsequent chapters are based has been given.

(M.George Abraham)

CHAPTER I

NON-EQUILIBRIUM THERMODYNAMICS OF FLOW THROUGH POROUS MEDIA

NON-EQUILIBRIUM THERMODYNAMICS OF FLOW THROUGH POROUS MEDIA

I.1 INTRODUCTION

The study of the physics of flow through porous media has become basic for many scientific and engineering applications, quite apart from the interest it holds for its purely scientific aspects. Such diversified fields as soil mechanics, ground water hydrology, petroleum engineering, water purification, industrial filteration, ceramic engineering powder metallurgy, and study of gas masks all rely heavily upon it as fundamental to their individual problems. All these branches of science and engineering have contributed a vast amount of literature on the subject (Carman, 1956; Engelund, 1953; Houpeurt, 1957; Lacey and Loeb, 1972; Muskat, 1937; 1949; Scheidegger, 1960, 1963; Speigler, 1966; Todd, 1959; Tuwiner, 1962).

The thermodynamics of irreversible processes (TIP) describes a relatively recent branch of macroscopic physics which has achieved great significance for its applications, particularly in the physics of flow through porous media. The extensive application of TIP principles in the field of membrane phenomena is seen in the literature (Eisenmann, 1972; Helfferich, 1962; Hwang and Kammermeyer, 1975; Katchalsky and Curran, 1965; Lakshminarayanaih, 1969; Mears, 1976; Scatchard, 1964; Schlogl, 1956; Sollner, 1964; Speigler, 1962; Staverman, 1952).

I.2 THERMODYNAMICS OF IRREVERSIBLE PROCESSES

A co-ordinated theory of thermodynamics of Irreversible processes (TIP) based on the fundamental work of Onsager has been developed over the past 25 years (Casimir, 1945; De Groot, 1966; Meixner, 1959; Prigogine, 1947). The 'thermodynamics of irreversible processes', should be described more exactly as 'the thermodynamic phenomenological theory of irreversible processes' for it consists of a thermodynamic and a phenomenological part. The thermodynamic part of the theory proceeds via the same method as classical thermodynamics; even the terms 'entropy flow' and 'entropy production', so characteristic of the new theory, develop from a consistent elaboration and definition of the concepts of classical thermodynamics. The phenomenological part of the theory introduces new postulates from the point of view of macroscopic physics, that is, the 'phenomenological equations' and the 'Onsagers reciprocal relations' which are justified by exprience like the first and second laws of thermodynamics.

A. An outline of the principles of the TIP Theory

A convenient starting point for discussing the essential features of TIP is the second law of thermodynamics. The law contains essentially three statements

a) Entropy S is a variable of state for a system in equilibrium.

b) In order to calculate the entropy difference ΔS between two states I and II of a system one must devise a path from one state to the other completely via equilibrium states. Then

$$\Delta S = \int_{I}^{II} d_e S$$

is independent of the patch and

$$d_e S = \frac{dQ}{T} \qquad (I.1)$$

where $d_e S$ is the externally supplied entropy, dQ is the heat absorbed by the system and T the absolute temperature.

c) If the system follows a path via non-equilibrium states, the process is called 'irreversible' and then

$$dS > d_e S \quad \text{or} \quad dS = d_e S + d_i S \qquad (I.2)$$

where $d_i S$ in the entropy produced inside the system by irreversible processes.

The first basic assumption made in TIP is that in a system not in equilibrium, but not too far from equilibrium, the entropy is still a well defined variable of state and can be calculated in principle by integrating the local entropy over the volume of the system, with the local entropy s calculated from the local temperature T, pressure p, energy u, volume v and the chemical potential μ_i of the components by Gibb's relation

$$Tds = du + pdv - \sum_i \mu_i dn_i \qquad (I.3)$$

where n_i is the number of moles of component i.

The fundamental function which measures the irreversibility of a processes is the rate of entropy production σ for the non-isothermal process or the dissipation function $\phi = T\sigma$ for isothermal processes. The TIP theory further postulates that σ, the rate of entropy production, can be expressed as a sum of products of fluxes (J_i) and conjugate forces (X_i), each of which represent an irreversible process in the system;

$$\sigma = \sum_i J_i X_i \qquad (I.4)$$

The forces and their conjugate fluxes can be of diverse nature. For instance, a temperature gradient as a force X_i induces a conjugate heat flux, an electrical potential gradient as a force causes the flow of electric current as a flux, a chemical potential gradient as a force results in a diffusional flow of material as a flux, a pressure gradient gives rise to a flow of material as a flux, the affinity brings about the flow due to chemical reaction, etc.

The equation (I.4) for entropy production σ is used for choosing conjugate fluxes and forces. Considerable freedom, however, is allowed in choosing the forces and the fluxes. It is important that their products should have the dimensions of energy/time the same as the dissipation function (this latter rule can be used to test the self consistency of the system).

The fourth postulate of TIP which confines its use to relatively slow processes, states that a linear relationship exists between the fluxes and all the forces which operate in the system. This postulate is based on the emprical observation that many of the phenomenological laws of physics are linear relationships.

In general, the relationship between fluxes and forces can be expressed as

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \qquad (I.5)$$

The above equations are known as the phenomenological equations where L_{ij} terms are proportionality factors, known as phenomenological coefficients. If several irreversible processes take place simultaneously then each flux will depend on all the forces present and vice versa. The phenomenological coefficients can be described as straight coefficients, correlating fluxes and conjugate forces or cross coefficients, relating a particular flux with the non-conjugate forces.

Numerous transformations of the phenomenological equations into more convenient forms are possible as a consequence of their linearity. Thus one may write the forces as a linear function of flows;

$$X_i = \sum_{j=1}^{n} R_{ij} J_j \quad (i = 1,2....n) \qquad (I.6)$$

and R_{ij} are the resistance coefficients. In general R_{ij} and L_{ij} are related by the equation

$$R_{ij} = \frac{|L|_{ij}}{|L|} \qquad (I.7)$$

in which $|L|$ in the determinant of the matrix of the coefficients L_{ij} and $|L|_{ij}$ in the minor of the determinant corresponding to the terms L_{ij}.

In equation (I.5) it is implied that a linear coupling between all forces and all fluxes participating in irreversible processes in the system is possible. But this needs a critical scrutiny because it is an important question whether coupling can exist between fluxes and forces of different tensorial orders. Consider an isothermal system with a scalar flux J_s and a conjugate scalar force X_s, and a vectorial flow J_v and the corresponding vectorial force X_v. The dissipation function ϕ in this case is

$$\phi = J_s X_s + J_v X_v \qquad (I.8)$$

The phenomenological relations for the fluxes as functions of force can be written as

$$J_s = L_{ss} X_s + L_{sv} X_v \qquad (I.9)$$

$$J_v = L_{vs} X_s + L_{vv} X_v \qquad (I.10)$$

In equations (I.9) and (I.10) the coefficient L_{ss}, relating the scalar force X_s to the scalar flow J_s, is itself a scalar. The coefficient L_{sv} must be a vector in order to give a scalar flow through the inner product with the vectorial force X_v; L_{vs} must also be a vector in order to produce a vectorial resultant J_v, when multiplied by scalar X_s. Finally, L_{vv} is a tensor of second order which transforms the vector X_v into the vector J_v.

The general coupling described in these equations may occur in an anisotropic system in which there is no spatial symmetry. However, in systems endowed with certain symmetry properties and especially in isotropic systems for which the properties at equilibrium are the same in all directions not all modes of coupling are possible. It can be shown that flows and forces of different tensorial order are not coupled. This leads in the isotropic case, to a reduction of the equations to the simplified form

$$J_s = L_{ss} X_s$$

$$J_v = L_{vv} X_v$$

and the coefficient L_{vv} becomes a scalar.

The reason for this behaviour is that in an isotropic system a reversal of sign of all the coordinate axes must leave all the phenomenological coefficients invariant. Since L_{ss} is scalar, it fulfils this requirement automatically, but the vector L_{sv} and L_{vs} would change sign upon inversion of the coordinate system; L_{sv} and L_{vs} can remain invariant only if both are equal to zero or if no coupling exists between scalar flows and vectorial forces and between vectorial flows and scalar forces. The requirement that L_{vv} be invariant under any rotation of the co-ordinate system leads to the conclusion that for isotropic systems, L_{vv} must be a scalar. This requirement that there be no coupling between scalar and vectorial quantities may be called the Curie-Prigogine principle (De Groot, 1966; Prigogine, 1968) since it is based on the considerations of Curie regarding cause and effect relations in static systems of different symmetry, and was extended by Prigogine to irreversible systems in flow. An important conclusion from this principle is that simultaneous diffusion and chemical reaction cannot be coupled phenomenologically in an isotropic system.

A further postulate of TIP states that the cross phenomenological coefficients those that relate the reciprocal fluxes and forces are equal, i.e.

$$\left.\begin{array}{ll} & L_{ij} = L_{ji} \\ \text{or} & R_{ij} = R_{ji} \end{array}\right| \qquad \text{(I.11)}$$

These are known as Onsager's Reciprocal Relations.

Thus the postulates underlying the TIP theory can be summariezed as follows:

i) In a closed system which undergoes irreversible processes the entropy always increases. The entropy is divisible into two terms, the entropy flow and entropy production.

ii) A local thermodynamic equilibrium can exist at any point and time in the system.

iii) The magnitude of the entropy production is measured by σ, the rate of entropy production for non isothermal systems or ϕ the dissipation function for isothermal systems. These can be expressed as a sum of the products of the fluxes representing the irreversible processes, and the conjugate forces causing the fluxes.

iv) A linear relationship between each flow and all forces in the system.

v) The matrix of the phenomenological coefficients are symmetrical, i.e., the reciprocal coefficients are equal $(L_{ij} = L_{ji})$.

Oster, Pearlson, and Katchalsky (1971) have suggested an alternative approach to irreversible processes. This is phenomenological in nature and is based on the theory of electrical networks. This in fact is revival of the pioneering ideas of Meixner (1963) who for the first time suggested an analogy between irreversible transport processes and electrical networks. The formalism developed by Oster, Perelson and Katchalsky has been named as Network Thermodynamics (Oster, et.al. 1971, 1973a,b; Rattee and Breuer, 1974).

B. Network Thermodynamics

Most irreversible processes can be expressed as a product of two variables, an effort variable 'e' and a flow variable 'f'. In electrical networks these variables are of course voltage difference and current, in mechanics force and velocity, in chemical reaction affinity and rate of the reaction and so on. The product of the two variables is an energy production rate (e times f) which is made of two components: a utilizable energy(reversible energy or storage) and a dissipated energy (entropy production). The time integral of either of the two quantities is generally easier to measure by experiment than the variables themselves. In a diffusional process the time integral of the material flow is Δq (t)and the amount of material transported during time t

$$\Delta q(t) = \int_0^t e(t) f(t) dt \qquad (I.12)$$

which is an easily measurable quantity.

Any such system can be represented by a network of finite number modes and branches. The kinetic process which takes place in the system can then be characterized as a sum of products e_i and f_i representing the effort and flow variable respectively for the ith branch of the network.

As an example, the transport of material from a Reservior I into Reservior II through a membrane can be represented by the scheme shown in Fig. [1.1]. The process through the membrane can be subdivided into three elements

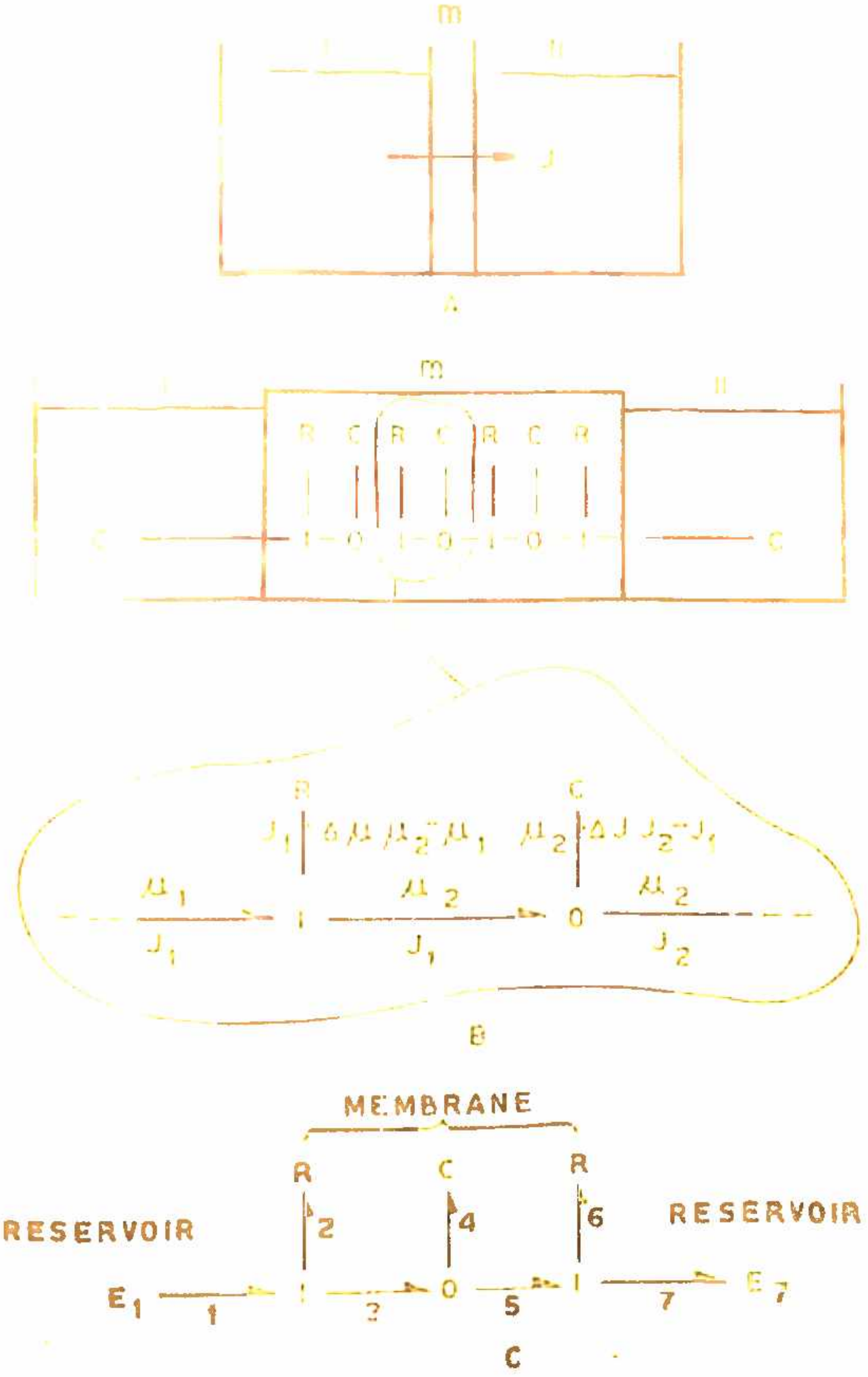


FIG. 1.1 SCHEMATIC REPRESENTATION OF TRANSPORT OF MATERIAL THROUGH A MEMBRANE (OSTER et al, 1971)

in series

i) the flux across the reservior I - membrane interfare,

ii) the flow inside the membrane, and

iii) the flow across the second interface into reservior II.

Each elementary process can be represented by two network elements in series: a dissipative process, i.e., a resistance

(denoted $\overset{R}{-1-}$)

and a storage process, or capacitance

(denoted by $\overset{C}{-0-}$)

The presence of a resistance and capacitance in series signify the fact that across the membrane, drops in both the chemical potential and the flow of material J occur. The values of the network elements, that of the resistance R_m and the capacitance C_m can be expressed in terms of measurable experimental quantities. Thus,

$$R_m = \frac{RT\,\Delta x}{D_m(N_i/V)} \tag{I.13}$$

and

$$C_m = \frac{(N_i/V)\,\Delta x}{RT} \tag{I.14}$$

where R_m is the membrane resistance, C_m is the membrane capacitance Δx is the thickness of the membrane, N_i is the number of moles of permeant in the membrane and D_m is the diffusion coefficient of the permeant in the membrane.

The time course of the transport process across the membrane can thus be described by an equation very similar to the one used to represent alternating electric currents, except that the electric potentials E are replaced by the chemical potentials

$$\frac{d\mu_m}{dt} = \frac{2}{R_m C_m}(\langle\mu\rangle - \mu_m) = \frac{(\langle\mu\rangle - \mu_m}{\tau_m} \qquad (I.15)$$

where $\langle\mu\rangle$ the mean chemical potential in the system is defined as

$$\langle\mu\rangle = \frac{\mu^{I} + \mu^{II}}{2} \qquad (I.16)$$

and τ_m, the relaxation time of the process by

$$\tau_m = \frac{R_m C_m}{2}$$

C. The Steady State

Among the irreversible processes a special role is played by those in which the state variables of the system are independent of time. These may be called non-equilibrium stationary states. If no restraints are imposed on the system it acheives, after a sufficiently long time, a state of equilibrium. On the other hand, if a number of constant restraints are imposed, such as a constant gradient of temperature, a constant gradient of chemical or electrical potential, a steady state is attained. In the steady state all flow corresponding to the forces on which no restraint is imposed vanish, while the flows corresponding to the fixed forces assume a constant value independent of time. In a steady state all functions of the state become independent of time and hence the change of entropy of the system with time vanishes, i.e.

$$dS/dt = d_eS/dt + d_iS/dt = 0$$

or

$$d_eS/dt = - d_iS/dt \qquad \text{(I.17)}$$

but since for any state of the system $d_iS/dt > 0$, $d_eS/dt < 0$. This conclusion means that the entropy production in a stationary system must be compensated by the liberation of entropy to the surroundings. In other words, non-equilibrium steady states cannot occur in isolated systems which do not permit exchange of entropy with the surroundings.

In an interesting analysis of the approach to the steady state, Prigogine (1947, 1968) has shown that during an irreversible process taking place in a system the entropy production assumes the minimal value compatible with the restrictions imposed on the system. Moreover, if as a result of some fluctuation, the system deviates from the steady state the internal changes tend to bring it back to its initial state. Thus there exists a situation analogue to that observed in stable equilibria which are governed by Le Chatelier principle of moderation (Klein, 1960; Schlogl, 1956). The stationary processes are therefore in a stable state. The actual deduction of Prigogine's theorem of minimum entropy production can be seen in the excellent monographs by De Groot (1966), Katchalsky and Curran (1965), Prigogine (1968). A critical discussion on the domain of validity of Prigogine's theorem of minimum entropy production has been presented by Denbigh (1951a, 1952a).

So long as the number of forces and fluxes is small one can visualise the steady state, i.e., which of the fluxes would balance each other. But when the number of fluxes and forces become large such a visualisation becomes difficult and it is in such situations that Prigogine's theorem becomes really useful. It may be kept in mind that since Prigogine's theorem is deduced considering linear laws and Onsager's relations, its domain of validity cannot exceed the domain of validity of linear laws and Onsager's relation.

Summarizing, the procedure followed in the application of the theory is simple. The Gibbs equation with the help of law of conservation of mass and energy is transformed in the form of equation (I.4), for the system under consideration. From the equation for entropy production thus deduced, conjugate fluxes and forces are spotted out and the rate equations in the form of linear and homogeneous equation (I.5) is written. Then the condition of steady state is applied and the expressions for various steady state phenomena are obtained, the magnitude of which are evaluated from suitable experiments. The Onsager's relations give the connection between various cross effects. It may be kept in mind that this formalism is applicable only so long as the system is in the neighbourhood of equilibrium, i.e., upto first order perturbations (De Groot, 1966; De Groot and Mazur, 1962; Fitts, 1962; Prigogine, 1968).

In the following sections the applications of the TIP theory; briefly discussed in the earlier sections, to processes in heterogeneous (discontinuous) systems are discussed.

I.3 APPLICATIONS OF TIP THEORY TO PROCESSES IN HETEROGENOUS (DISCONTINUOUS) SYSTEMS!

As 'processes in heterogeneous (discontinuous) systems' we deal with irreverisble processes which relate to the exchange of mass, electricity, and heat between two homogeneous subsystems ('phases'). Let the two phases be isotropic. Let electrification and magnetisation as well as interfacial phenomena be excluded. Moreover, let the total system be closed, i.e., let no exchange of matter take place with the surroundings, so that mass exchange takes place only between the two (open) phases. Furthermore, chemical reactions shall be excluded from consideration because everything important about reactions occurs either in the frame work of homogeneous systems or in the frame work of continuous systems.

The two homogeneous subsystems are separated from each other either by a material phase boundary or by a 'valve'. The valve can be a narrow opening, a capillary, a system of capillaries, a membrane, etc. The subsystems, separated by such a valve, can correspond to two different states of the same type of phases, such as two media which exhibit different pressure and temperature but are the same with reference to their state of aggregation and chemical nature. Here the discontinuous system represents a limiting case of a continuous system and certain simplications in the thermodynamic description result (Haase, 1969).

In order that the methods of TIP can be applied to the present case, it must be assumed that the exchange of matter,electricity and heat between the two systems parts occurs slowly in comparison to the equilisation of temperature, pressure, concentrations and electrical potential inside each phase (Haase, 1969). Then each of the two subsystems remains homogeneous, even during the course of the irreversible processes, i.e., each phase remains in internal thermal and mechanical equilibrium and has uniform composition and uniform potential. Temperature, pressure, concentrations and potential change discontinuously on crossing the phase boundary and are otherwise functions of time only. This eliminates solid phases from consideration since, in practice, the above conditions can be realized only for fluid systems. Mazur and Overbeek (1951) applied TIP theory and deduced expressions for various electro-osmotic effects. The non-equilibrium thermodynamic treatment of electro-osmotic effect, which is summarized below, is quite general and does not make use of double layer model (De Groot, 1966; Haase, 1969; Katchalsky and Curran, 1965; Lakshminarayaniah, 1969).

Keeping in view the nature of the work embodied in this thesis, which is presented in the subsequent chapters, we shall discuss the electro-osmotic phenomena (simultaneous transport of matter and electricity) and the thermo-osmotic phenomena (simultaneous transport of heat and mass) on the basis of TIP.

A. Electrokinetic Phenomena

Electrokinetic phenomena was observed as early as the 19th century (Abrahamson, 1934; Adams, 1941; Overbeek, 1952). To study the electro-kinetic phenomena experimentally two compartments 1 and 2 separated by a porous barrier are used. Let each compartment contain n_i $(i = 1,2....n)$ components, carrying Z_iF charge per unit mass. Temparature and concentrations are kept uniform throughout the complete system. Applying Gibbs equilibrium and laws of conservation of mass and energy to all its part, the dissipation function for a discontinuous system may be derived.

Conservation of mass and charge are given by

$$dn_i^1 + dn_i^2 = 0 \ (i = 1,2,....n) \tag{I.18}$$

and

$$\sum_{i=1}^{n} Z_iF\ dn_i^1 + \sum_{i=1}^{n} Z_iF\ dn_i^2 = 0 \tag{I.19}$$

respectively. Electrical current flowing from compartment 1 to 2 is given by

$$I = -\sum_{i=1}^{n} Z_iF\ dn_i^1/dt = \sum_{i=1}^{n} Z_iF\ dn_i^2/dt \tag{I.20}$$

The conservation of energy for the system gives

$$dU = dU^1 + dU^2 = dQ - P^1 dV^1 - P^2 dV^2 + (\phi^1 - \phi^2) I \, dt \qquad (I.21)$$

where dQ is the heat absorbed from the surroundings. From the Gibbs equation the change of total entropy can be obtained,

$$TdS = TdS^1 + TdS^2 = dU^1 + dU^2 + P^1 dV^1 + P^2 dV^2$$
$$- \sum_i \mu_i^1 \, dn_i^1 - \sum_i \mu_i^2 \, dn_i^2 \qquad (I.22)$$

substitution of equations (I.20) and (I.21) into (I.22) gives

$$TdS = dQ - \sum_i \mu_i^1 \, dn_i^1 - \sum_i \mu_i^2 \, dn_i^2 - \phi^1 \sum_i Z_i F \, dn_i^1 - \phi^2 \sum_i Z_i F \, dn_i^2$$
$$\ldots\ldots \quad (I.23)$$

which because of equation (I.18) gives

$$TdS = dQ - \sum_{i=1}^{n} (\mu^1 + Z_i F \, \phi^1 - \mu_i^2 - Z_i F \, \phi^2) \, dn_i^1 \qquad (I.24)$$

From equation (I.2) and (I.1) it is obvious that the second term on the right hand side of equation (I.24) is equal to $T \, d_i S$. Therefore,

$$d_i S = - \sum_{i=1}^{n} \Delta (\mu_i + Z_i F \, \phi) \, dn_i^1 / T \qquad (I.25)$$

Since $\Delta\mu_i = \bar{V}_i \Delta P$ for our system, the dissipation function is given by

$$\phi = T \frac{d_i S}{dt} = - \sum_i^n \bar{V}_i \Delta P \, dn_i^1/dt - \sum_i^n z_i F \Delta\phi \, dn_i^1/dt \qquad (I.26)$$

where $\bar{V}_i$ in the specific volume of the component i.

Equation (I.26) enables us to spot out the fluxes and forces in the system by remembering that the dissipation function is the sum of the product of the fluxes J_i and forces X_i (Equation (I.4)). Thus it follows that the volume flow J and the current flow I are given by

$$J = - \sum_i^n \bar{V}_i \, dn_i^1/dt \qquad (I.27)$$

and

$$I = - \sum_i^n z_i F \, dn_i^1/dt \qquad (I.28)$$

The corresponding forces are hydraulic pressure difference, ΔP, and electrical potential difference $\Delta\phi$. Transport equations in the linear range would be written as

$$J = L_{11}\Delta P + L_{12}\Delta\phi \qquad (I.29)$$

$$I = L_{21}\Delta P + L_{22}\Delta\phi \qquad (I.30)$$

where L's are phenomenological coefficients governed by the following conditions

i) $L_{12} = L_{21}$ (Onsager's reciprocity relations)

ii) $L_{11}L_{22} > L_{21}L_{12}$ (On account of the positive definite character of entropy production).

Equations (I.29) and (I.30) yield the following expressions for the various steady states.

Electro-osmosis

$$(J)_{\Delta P=0} = L_{12}\Delta\phi; \quad (J/I)_{\Delta P=0} = L_{12}/L_{22} \tag{I.31}$$

Electro-osmotic pressure

$$(\Delta P)_{J=0} = - (L_{12}/L_{11})\ \Delta\phi \tag{I.32}$$

Streaming potential

$$(\Delta\phi)_{I=0} = - (L_{21}/L_{22})\ \Delta P \tag{I.33}$$

Streaming current

$$(I)_{\Delta\phi=0} = L_{21}\Delta P; \ (I/J)_{\Delta\phi=0} = L_{21}/L_{11} \tag{I.34}$$

These phenomena are interrelated on account of Onsager relations. Thus

$$(\Delta P/\Delta\phi)_{J=0} = - (I/J)_{\Delta\phi=0} \tag{I.35}$$

$$(\Delta\phi/\Delta P)_{I=0} = - (J/I)_{\Delta P=0} \tag{I.36}$$

which are well known Saxen's relations for the coupled flow processes.

B. Degree of Coupling

Since the electro-kinetic effects namely electro-osmotic pressure and streaming potential are a consequence of the coupling between flow of matter and flow of electricity, it is profitable to summarise here a generalised discussion of degree of coupling which quantitatively measures the tightness of coupling and the efficiency of Energy Conversion. A brief account of the discussion of the degree of coupling which is being presented in the subsequent lines is based on the important papers by Kedem and Caplan (1965), Morrison and Osterle (1965) and Osterle (1964a,b).

The phenomenological description of two coupled flows leads to a definition of their 'degree of coupling.' This diamensionless parameter, the absolute value of which lies between zero and unity is a generalization of the coefficient of coupling used in the theory of electrical networks. It should serve as a basis of comparison between systems in which the nature of the flows and the forces are different. The efficiency of energy conversion, which is defined by means of entropy production function of the system, depends on both the degree of coupling and the conditions of operation; but the maximum efficiency and the efficiency at maximum output are uniquely determined by the degree of coupling. The requirement for optimal matching of the load to the converter is essentially dictated by the degree of coupling. Reversible energy conversion (when the efficiency is unity) is a limit towards which only fully coupled systems can tend at infinitesimal rates of flow.

No energy conversion occurs when a non-equilibrium state is maintained against its tendency to relax, without net flow taking place. The energy required for this is derived from a spontaneous coupled process. Nor does energy conversion occur when matter (or heat etc.) is transferred in the absence of a gradient of concentration (or temperature etc.). The energy expended is determined by the degree of coupling and the internal resistance of the system.

Consider any system in which two irreversible processes take place; the entropy production per unit time d_iS/dt has the form of a sum of two products,

$$d_iS/dt = J_1 X_1 + J_2 X_2 \tag{I.37}$$

Here J_1, J_2 are the two flows and X_1, X_2 the two conjugate forces. This sum must always be positive while $J_1 X_1$ or $J_2 X_2$ separately may be positive or negative. The meaning of $J_1X_1 > 0$ is that flow 1 is itself a spontaneous process and would take place in the same direction (although its magnitude might differ) even if flow 2 were absent. $J_1X_1 < 0$ indicates that the direction of J_1 is opposite to the spontaneous one and is made possible only by coupling to the spontaneous process 2.

In the thermodynamics of irreversible processes, each flow is assumed to be a linear function of both forces

$$J_1 = L_{11}X_1 + L_{12}X_2; \quad J_2 = L_{21}X_1 + L_{22}X_2 \tag{I.38}$$

with the Onsager symmetry relation $L_{12} = L_{21}$. From the thermodynamic condition $d_i S/dt \geqslant 0$ it follows that L_{11} and L_{22} are always positive and L_{12} is subject to restriction,

$$L_{12}^2 \leqslant L_{11}L_{22} \qquad (I.39)$$

Alternatively,

$$X_1 = R_{11}J_1 + R_{12}J_2; \; X_2 = R_{21}J_1 + R_{22}J_2 \qquad (I.40)$$

with the additional relations

$$R_{12} = R_{21}; \quad R_{12}^2 \leqslant R_{11}R_{22}$$

From equation (I.38) we derive the ratio between the two flows as a function of X_1/X_2. Defining the quantities

$$x = X_1/X_2, \; j = J_1/J_2, \quad z = \sqrt{L_{11}/L_{22}}$$

one obtains

$$j/z = \left(\frac{L_{12}}{\sqrt{L_{11}L_{22}}} + zx\right) \Bigg/ \left(1 + \frac{L_{12}}{\sqrt{L_{11}L_{22}}} \; zx\right) \qquad (I.41)$$

It is assumed that both processes can take place at measurable rates so that both L_{11} and L_{22} are different from zero. The coefficient z then reduces both the flow and force ratios to diamensionless numbers.

The value of the ratio $L_{12}/\sqrt{L_{11}L_{22}}$, denoted by q, is limited by restriction (I.39);

$$q = L_{12} / \sqrt{L_{11}\,L_{22}} \quad (-1 \leqslant q \leqslant 1) \qquad (I.42)$$

The nearer the absolute value of q is to unity the slighter the dependence of j on x, i.e., a high value of of q indicates tight coupling between the two processes. For $q=0$, j is proportional to x; then the two processes are independent of each other and each flow is proportional to the conjugate force without any influence by the other force.

Thus q is a measure of the degree of coupling, and a basis of comparison for different processes. From equation (I.38) and (I.40)

$$q = - R_{12}/\sqrt{R_{11}\ R_{12}}$$

and

$$z = \sqrt{R_{22}/R_{11}} \qquad (I.43)$$

So far we have considered only the absolute value of q. The physical significance of the sign is clearest if both flows and forces are vectors. The flow of a solute through a membrane may drag another solute along in the same direction ($L_{12} > 0$) or tend to push it back ($L_{12} < 0$). Heat flow through a wire circuit may create electric current in the same or in the opposite direction. We refer to these interactions as 'positive' or 'negative' coupling respectively.

The importance of q as a measure of coupling may also be seen by comparing the relative magnitudes of one flow under different conditions. Let X_2 be constant and J_2

measured for two different values of X_1; (a) $X_1=0$, (b) X_1 adjusted so that $J_1=0$. The ratio between the values of J_2 in these two measurements is, from equations (I.38) and (I.42);

$$(J_2)_{J_1=0} / (J_2)_{X_1=0} = 1 - q^2 \ (X_2 \text{ constant}) \qquad (I.44)$$

From equation (I.44), process 2 cannot take place when J_1 is stopped if $q^2=1$. It will make no difference whether J_1 flows freely or is stopped entirely if $q^2=0$. By analogy

$$(J_1)_{J_2=0} / (J_1)_{X_2=0} = 1 - q^2 \ (X_1 \text{ constant}) \qquad (I.45)$$

The symmetry shown by equations (I.44) and (I.45) does not depend on Onsager relation but is a consequence of the linear dependence between flows and forces. The definition of q in the asymmetric case is

$$q_{12} = L_{12} / \sqrt{L_{11}L_{22}} \quad \text{and} \quad q_{21} = L_{21} / \sqrt{L_{11}L_{22}}$$

C. Thermo-osmosis

The phenomenon of thermo-osmosis through a barrier or a membrane is a classical non-equilibrium phenomenon which can be satisfactorily interpreted by using methods of irreversible thermodynamics (Alexander, 1954a,b, 1955; De Groot, 1966; Denbigh and Rauman, 1951b; Haase, 1959a,b, 1969; Prigogine, 1968; Spanner, 1964). The great utility of non-equilibrium thermodynamics is in spotting out fluxes and forces appropriate to the phenomena which are otherwise not obvious. In a system consisting of two compartments containing a single fluid (say water) maintained at different temperatures T and T+ΔT respectively and separated by a porous barrier, migration of fluid takes place across the barrier as a result of which pressure difference ΔP sets up in the steady state corresponding to the temperature difference ΔT. For such a system equation for entropy production σ is given by (De Groot, 1966; Denbigh, 1951a; Haase, 1969; Prigogine, 1968)

$$\sigma = J_w \left(-\frac{\bar{V}\Delta P}{T}\right) + J_q \left(-\frac{\Delta T}{T^2}\right) \tag{I.46}$$

where J_w is the water flow and J_q is the heat flow and $\bar{V}$ is the specific volume. When the departure from the equilibrium is small, the fluxes and the forces are related by the equations

$$J_w = L_{11} \left(-\frac{\bar{V}\Delta P}{T}\right) + L_{12} \left(-\frac{\Delta T}{T^2}\right) \tag{I.47}$$

$$J_q = L_{21} \left(-\frac{\bar{V}\Delta P}{T}\right) + L_{22} \left(-\frac{\Delta T}{T^2}\right) \tag{I.48}$$

where L_{ik} are the phenomenological coefficients and are independent of the thermodynamic forces. On account of Onsager's reciprocal relation, we have

$$L_{12} = L_{21}$$

From equations (I.47) and (I.48) it follows that

$$(J_q/J_w)_{\Delta T=0} = \frac{L_{21}}{L_{11}} = Q^* \qquad (I.49)$$

The quantity Q^* which is known as the heat of transport is defined as, the heat transported per unit mass transport when there is no temperature difference across the barrier (Denbigh 1952b). In the steady state when mass flow ceases, i.e., $J_w = 0$ equation (I.47) yields

$$(\Delta P/\Delta T)_{J_w=0} = - \frac{L_{12}}{L_{11}\bar{v}T} \qquad (I.50)$$

or

$$(\Delta P/\Delta T)_{J_w=0} = - Q^*/\bar{v}T \qquad (I.51)$$

The equation (I.50) represents the thermo-osmotic pressure difference and equation (I.51) represents the relationship between thermo-osmotic pressure difference and heat of transport on account of Onsager's reciprocal relations. If in the given system pressure is not allowed to develop across the barrier, i.e. $\Delta P=0$ we can write from eqn.(I.47)

$$(-J_w)_{\Delta P=0} = L_{12}\frac{\Delta T}{T^2} = L'_{12}\,\Delta T \qquad (I.52)$$

which is the expression for the thermo-osmotic velocity. The negative sign in equation (I.52) indicates that thermo-osmotic movement takes place from warmer to the cooler side. The equation

$$(-J_w/\Delta T) = L'_{12} = \frac{L_{12}}{T^2} \qquad (I.53)$$

is obvious from equation (I.52).

Some of the notable experimental studies on thermo-osmosis through porous barriers (Eg. rubber membrane, cellophane, unglazed porcelain, copper ferrocyanide, clays and soil systems etc.) are by Bearman (1957,1966); Dariel and Kedem (1975); Denbigh and Raumann (1951b), Hanley (1965, 1966), Rastogi et al (1964,1966), Srivastava and Avasthi (1975). These attempts confirmed the validity of linear and homogeneous equations (I.47) and (I.48) in a variety of cases and also lead to the interpretation of the heat of transport in terms of the mechanism of flow. It may be pointed out that the direct experimental measurement of J_q is difficult and, therefore, not many attempts have been made for its measurements. A consolidated review of such attempts is available in the monographs by Haase (1969) and Lakshminarayaniah (1969).

I.4 REFERENCES

Abrahamson, H.A. (1934): Electrokinetic phenomena and their application to biology and medicine (c.f. Colloid Science Vol. I. Irreversible systems, Kruyt, H.R. ed.) Elsevier Pub. Co. Amsterdam.

Adam, N.K. (1941): The physics and chemistry of surfaces, 3rd ed. Oxford Univ. Press, London.

Alexander, K.F. (1954a): Theory of thermal diffusion in liquids I. Connection between kinetic and phenomenological theories of transport processes in continuous systems. Z. Physik Chem (Leipzig). 203, 181.

Alexander, K.F. (1954b): Theory of chemical diffusion V. Kinetic theory of self diffusion and self thermo diffusion in water. Z. Physik Chem (Leipzig). 203, 357.

Alexander, K.F. (1955): Recent theories of thermal diffusion in liquids. Physica 21, 446.

Bearman, R.J. (1957): The thermo-osmosis of the rare gases through a rubber membrane. J. Phys. Chem. 61, 708.

Bearman, Y.M., and Bearman, R.J.(1966): Heats of transport of the rare gases in a rubber membrane. J. Phys. Chem. 70, 3010.

Carman, P.C. (1956): The flow of gases through porous media. Academic Press, New York.

Casimir, H.B.G.(1954): On Onsager's principle of microscopic reversibility. Rev. Mod. Phys. 17, 343.

Dariel, M.S., and Kedem, O. (1975): Thermo-osmosis in semi-permeable membranes. J. Phys. Chem. 79, 336.

De Groot, S.R. (1966): Thermodynamics of irreversible processes. (10th reprint) North-Holland Pub. Co., Amsterdam.

De Groot, S.R. and Mazur, P. (1962): Non equilibrium thermodynamics, North Holland Pub. Co., Amsterdam.

Denbigh, K.G. (1915a): The thermo-dynamics of the steady state. Methuen, London.

Denbigh, K.G., and Rauman, G. (1951b): The thermo-osmosis of gases through a membrane. Part II, Experimental. Proc. Roy. Soc. A210, 518.

Denbigh, K.G. (1952a): Entropy creation in open reaction systems. Trans. Faraday Soc. 48, 389.

Denbigh, K.G. (1952b): The heat of transport in binary regular solutions. Trans. Faraday Soc. 48, 1.

Engelund, F. (1953): On the laminar and turbulent flows of ground water through homogeneous sand. Trans. Danish Acad. Sci. No. 3.

Esienman, G. (ed.) (1972): Membranes, Vol. I. Macroscopic system and models. Marcel Dekker, New York.

Fitts, D.D. (1962): Non-equilibrium thermodynamics. McGraw-Hill, New York.

Haase, R. (1959a): Thermo-osmosis of liquids I. Fundamental Z. Physik Chem. (Frankfurt). 21, 244.

Haase, R. (1959b): Thermo-osmosis of liquids II. Measurements Z. Physik. Chem. (Frankfurt). 21, 270.

Haase, R. (1969): Thermodynamics of Irreversible processes. Addison-Wesley, New York.

Hanely, H.J.M., and Steele, W.A. (1965): Thermal transpiration in the unsteady state. Trans. Faraday Soc. 61, 2661.

Hanely, H.J.M. (1966): Thermal transpiration measurements on a porous cermaic Trans. Faraday Soc. 62, 2395.

Helfferich, F. (1962): Ion exchange. McGraw-Hill, New York.

Houpeurt, A. (1957): Elements de mecanique des fluides dans les milieux poreux. Inst. France de Petrole, Paris.

Hwang, S.T., and Kammermeyer, K. (1975): Techniques of Chemistry Vol. 7. Membranes in separations. John Wiley and Sons Inc., New York.

Katchalsky, A., and Curran, P.F. (1965): Non-equilibrium Thermodynamics in Biophysics. Harvard University Press, Cambridge.

Kedem, O., and Caplan, S.R. (1965): Degree of coupling and its relation to efficiency of energy conversion. Trans. Faraday Soc. 61, 1897.

Kelin, M. (1960): Thermodinamica dei processi Irreversibili. Nicola Zanichelli, Editore, Bologna.

Lacey, E.R., and Loeb, S.(eds.) (1972): Industrial processing with membranes. John Wiley and Sons. Inc., New York.

Lakshminarayanaih, N. (1969): Transport phenomena in membranes. Academic Press, New York.

Mazur, P., and Overbeek, J.Th.G.(1951): Electro-osmosis and streaming potentials in diaphragms II. Quantitative relation between electrokinetic effects. Rec. trav. chim. 70, 83.

Mears, P. (ed) (1976): Membrane separation processes.Elsiver scientific publishing Co., Amsterdam.

Meixner, J. and Reik, H.G.(1959): Handbook der Physik. Vol. III/2. Berlin Goettingen, Heidelberg.

Meixner, J. (1963): Thermodynamics of electrical networks and the Onsager-Casimir reciprocal relations. J. Math. Phys. 4, 153.

Morrison, F.A., and Osterle, J.F. (1965): Electrokinetic energy conversion in ultrafine capillaries. J. Chem. Phys., 43, 2111.

Muskat, M. (1946): The flow of homogeneous fluids through porous media. 2nd print. Edwards, Ann Arbor, Michigan.

Muskat, M. (1949): Physical principles of oil production. McGraw-Hill Book Co., New York.

Oster, G., Perelson, A. and Katchalsky, A. (1971): Network thermodynamics. Nature, 234, 393.

Oster, G., Perelson, A., and Katchalsky, A. (1973a): Network thermodynamic modelling of biophysical systems. Q. Rev. Biophys., 6, 1.

Oster, G., and Perelson, A. (1973b): Systems, circuits, and thermodynamics. Israel J. Chem. 11, 445.

Osterle, J.F. (1964a): A unified treatment of the thermodynamics of steady state energy conversion. Appl. Sci. Res., 12, 425.

Osterle, J.F. (1964b): Electrokinetic energy conversion. J. Appl. Mech., 31, 161.

Overbeek, J.Th.G. (1952): Colloid Science. Vol. 1. Irreversible Systems (Kruyt, H.R. ed.). Elsevier Pub. Co., Amsterdam.

Prigogine, I. (1947): Etude thermodynamique des phenomenes Irreversibles. Dunod, Paris and Desoer, Liege.

Prigogine, I. (1968): An introduction to the thermodynamics of irreversible processes. Wiley, New York.

Rattee, I.D., and Breuer, M.M. (1974): The physical chemistry of dye adsorption. Academic press Inc. (London) Ltd.

Rastogi, R.P., Balokhra, R.L., and Agarwal, R.K.(1964): Cross phenomenological coefficients. Part 1. Studies on Thermo-osmosis. Trans. Faraday Soc. 60, 1386.

Rastogi, R.P., and Kher Singh (1966): Cross Phenomenological coefficients. Part-5. Thermo-osmosis of liquids through a cellophane membrane. Trans. Faraday Soc., 1754.

Scatchard, G. (1964): The encyclopedia of electrochemistry (Hampel, C.A. ed.) Reinhold, New York.

Scheidegger, A.E. (1960): Hydrodynamics in porous media. Encyclopedia of Physics. Vol. 9. Springer, Berlin.

Scheidegger, A.E. (1963): The physics of flow through porous media (2nd ed. 2nd Prtg) Oxford University Press, London.

Schlogl, R. (1956): The significance of convection in transport processes across porous membranes. Dis. Faraday Soc. 21, 46.

Sollner, K. (1964): The encyclopedia of electro chemistry (Hampel, C.A. ed.) Reinhold, New York.

Speigler, K.S. (1962): Salt water purification. Wiley, New York.

Speigler, K.S. (ed.) (1966): Principles of desalination. Academic Press, New York.

Srivastava, R.C., and Avasthi, P.K. (1975): Non-equilibrium thermodynamics of thermo-osmosis of water through bentonite. J. Hydrol. 24, 111.

Staverman, A.J. (1952): Non-equilibrium thermodynamics of membrane processes. Trans. Faraday Soc. 48, 176.

Todd, D.K. (1959): Ground water hydrology. J. Wiley and Sons, New York.

Tuwiner, S.B. (1962): Diffusion and membrane technology. American chemical society monograph series No. 156. Reinhold, Chapman and Hall, Ltd., London.

CHAPTER II

ELECTRO-OSMOSIS OF LIQUID MIXTURES[*]

---

[*] Based on the work reported in this chapter, the following three papers one each in

1. J. Chem. Soc. Faraday Trans.I, 72, 2631 (1976)
2. J. Colloid Interface Sci. 57, 58 (1976)
3. J. Phys. Chem. 81, 906 (1977)

have been published.

ELECTRO OSMOSIS OF LIQUID MIXTURES

II.1 INTRODUCTION

Electro-kinetic phenomena are of considerable interest from the stand point of biological transport, which has been stimulated by the need to understand permeability phenomena and suction processes. By electrokinetic phenomena we mean phenomena involving electricity and connected with a tangential movement of two phases along each other. They may arise either from an external electric field directed along the phase boundary and resulting in a movement or from a movement of the phases along each other, resulting in a transport of electricity. Examples of the first kind are electro-osmosis and electrophoresis, of the second kind; streaming potential and migration potential (Abrahamson, 1934; Adam, 1941; Lakshminarayaniah, 1969; Mazur and Overbeek, 1951; Overbeek, 1952). These processes received much attention because of their technical importance in separation processes (Hwang and Kammermeyer, 1975; Lacey and Loeb, 1972; Marinsky, 1966; Mears, 1976; Speigler, 1962).

Electrokinetic phenomena are of intrinsic interest since they give rise to a number of steady states which can be conveniently studied experimentally. This affords an example where the power of non-equilibrium thermodynamics (De Groot and Mazur, 1962; Katchalsky and Curran, 1965; Prigogine, 1968) can be easily demonstrated. This is one of the few phenomena where non-linear transport processes have been experimentally observed (Rastogi, 1969b,c) and studied. In this chapter we report our studies on the phenomena of electro-osmosis and streaming current. The theory has been discussed in Chapter I (Section 2.A) and can be found in greater detail in a review article of Rastogi (1969a).

Studies on the electro-osmosis of various liquids and binary liquid mixtures through pyrex sintered glass membrane have been conducted in the linear and non-linear region in the recent past (Rastogi, 1966, 1970; Balokhra, et al., 1973, 1974). Analysis of the data in the light of the thermodynamic theory of irreversible processes has confirmed the validity of the linear phenomenological relations and Onsager's reciprocity relations.

The non-equilibrium thermodynamic approach to the transport processes through membranes, as discussed in Chapter I, is purely phenomenological in nature and makes no reference to the nature of membranes. In fact the membrane is treated very much like a black box and one may deduce its mechanism and function from observations of input and output data. This no doubt makes the equations completely general but the price that one has to pay for this generality is that not much can be learnt about the mechanism of the transport processes inside the membrane. It is for this reason that several mechanistic models have been proposed. The Speigler's frictional model which relates the various phenomenological coefficients with the coefficients of friction between the permeating species themselves and between the permeating species and the membranes, is the one that has attracted attention in recent years (Manning, 1972; Smit,etal. 1975).

Experiments reported in this chapter, on the electro-osmosis of liquid mixtures, have been designed with the intention of throwing light on the validity of the Speigler's model and for this variation of the various phenomenological coefficients with the composition of the mixtures have been studied. For the study of electro-osmosis of liquid mixtures through a pyrex sintered glass membrane (porosity G-4) the binary liquid mixtures selected are acetone-methanol, acetone-water, and methanol-water in ascending order of their interactions. The experiments have been carried out at various compositions of the liquid mixtures. The data in addition to studying the concentration dependence of the phenomenological coefficients and verifying the Onsager's formalism have also been used to study the efficiencies of electrokinetic energy conversion, for both modes of conversion namely electro-osmosis and streaming potential. The results thus obtained have shown to lend support to the non-equilibrium thermodynamic theories of electrokinetic energy conversion.

II.2 EXPERIMENTAL

A! Material

a) Acetone

Acetone (BDH : LR) was purified using methods described in literature (Vogel, 1956). It was refluxed for 3 hours with a small amount of $KMnO_4$ and was subsequently distilled. The distillate was subjected to fractional distillation. The purity was checked from density and boiling point measurements . The density of the purified sample was 0.7742g/cm^3 at 35°C and boiling point 58°C which matches with the literature values (Hodgmann, 1964).

b) Methanol

Methanol (BDH : LR) was also purified using the methods described in literature (Vogel, 1956). It was refluxed with magnesium and iodine for 3 hours and distilled in the absence of moisture. The purity of the sample was checked from density and boiling point measurements. The density of the sample was 0.7772 gm/cm^3 at 35°C and boiling point was 64.9°C in agreement with the literature values (Hodgmann, 1964).

c) Water

Triple distilled water was used in preparing mixtures of acetone-water and methanol-water

B. The Electro-osmotic cell

The electro-osmotic cell has been depicted in Fig.[II.1]. It consisted of glass tube of length 25 cm and 2.5 cm diameter with a sintered glass membrane M (Porosity G-4) at the middle. The tube AA^1 was fused with B.24 female joints at each end. The spiral platinum electrodes P_1 and P_2 were so adjusted that they just pressed the sides of the membrane. The electrodes P_1 and P_2 were fused to the glass tubes T_1 and T_2 which in turn were fused to B-24 male joints S_1 and S_2. The electrical contact between the electrodes and the terminals of power supply was made through mercury filled in the tubes T_1 and T_2. The two vertical tubes Q_1 and Q_2 of length 10 cm and diameter 1.5 cm emerging from the tube AA^1, were provided with a B-14 female joint in order that the portions G L_2L_1 and G_2K could be connected with and detached from the tube AA^1. The purpose of the stopcock R_1 in the portion $G_1L_2L_1$ was simply to adjust the meniscus of liquid in the capillary L_2L_1 (diameter 0.2084 cm) at any

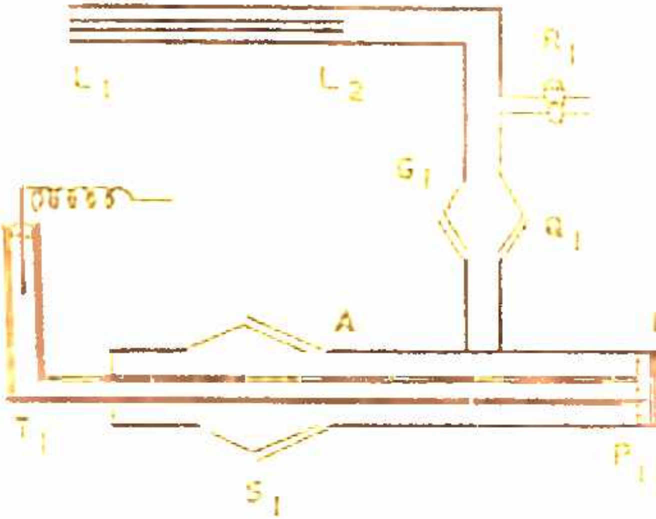
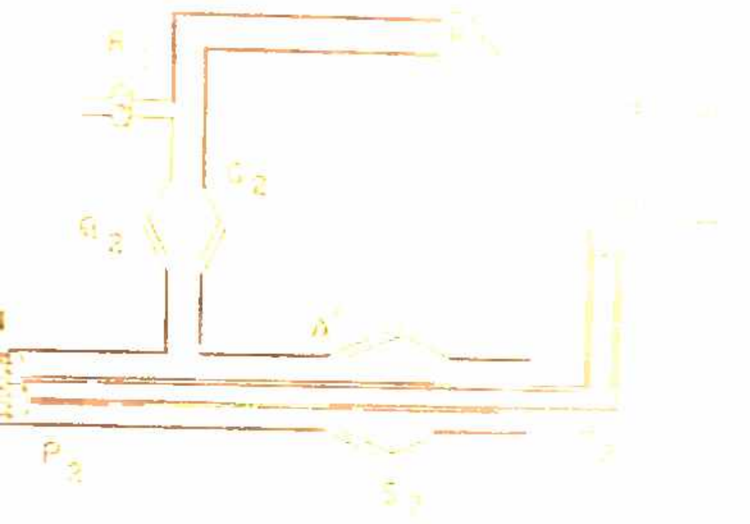


FIG. II.1 ELECTR



OSMOTIC CELL

desired distance to note the liquid flow. The portion G_2K is at the same level as $G_1L_2L_1$ and was connected to the pressure head. The stopcock R_2 was to fill the apparatus without any air bubles.

C. Procedure

The pyrex sintered glass membrane M (porosity G-4) fixed at the middle of the glass tube AA^1 in the electro-osmotic cell was treated with 1:1 nitric acid (AR) and washed repeatedly with triple distilled water to remove traces of nitric acid. Finally it was dried in an electrically operated oven at 120-140°C and was allowed to cool slowly. This treatment has been recommended in literature (Rastogi, 1966) in order to avoid fluctuations in the permeability of glass membrane. The cell was then filled with the liquid mixture.

Permeability measurement were made by applying known pressure differences across the glass membrane. The consequent volume flux was measured by noting the rate of advancement of the liquid meniscus in the capillary L_1L_2 with a cathetometer of least count 0.001 cm and a stop watch of least count 0.1 sec.

For measuring the electro-osmotic velocity known electrical potential differences were applied across the membrane by connecting the electrodes to the terminals of an electronically operated power supply (Beltronix, Model ED-101). The volume flow of the liquid induced by the applied potential difference was observed by noting the rate of advancement of the liquid meniscus in the capillary L_1L_2. The uncertainty in the applied potential was ± 0.05V. During electro-osmotic velocity measurements the condition $\Delta P=0$ was enforced on the system.

The streaming potentials across the sintered glass membrane were measured using a V.T.V.M. (Philips GM 6020/90). Known pressure differences were applied across the membrane and when the flow in the capillary L_1L_2 became steady, the streaming potential was measured by connecting the electrodes to the terminals of the V.T.V.M. through proper keys. The assymetry potential of the platinum electrodes were taken into account in these measurements. The electrical resistance of the system was measured with a Leitfahigkertsmesses conductivity meter and the values of streaming current were calculated from the streaming potential and resistance of the system using Ohm's Law.

All measurements were made under constant temperature condition by placing the electro-osmotic cell in an air thermostat maintained at 40°C with the help of Jumo relay and Jumo contact thermometer with an accuracy of ± 0.1°C.

II.3 RESULTS

The permeability data for various compositions of acetone-methanol, acetone-water, and methanol-water mixture have been plotted in Figs. [II.2], [II.6] and [II.10] respectively. The electro-osmotic velocity data are given in Figs. [II.3], [II.7] and [II.11]. Streaming potential and streaming current data are given in Figs. [II.4], [II.8], [II.12] and [II.5], [II.9], [II.13] respectively.

II.4 DISCUSSION

The linear phenomenological relations for the simultaneous transport of matter and electricity as obtained from the non-equilibrium thermodynamic treatment (DeGroot and Mazur, 1962; Haase, 1969; Katchalsky and Curran 1965) for the electro-osmotic effects, discussed in Chapter I (Section I.2.A) are

$$J = L_{11}\Delta P + L_{12}\Delta\phi \qquad \text{(II.1)}$$

$$I = L_{21}\Delta P + L_{22}\Delta\phi \qquad \text{(II.2)}$$

In equations (II.1) and (II.2) J represents the volume flux I for the flow of electricity, ΔP and $\Delta\phi$ for the pressure difference and potential difference across the membrane. L_{ik}'s are the phenomenological coefficients. On account of Onsager's reciprocal relation we have

$$L_{12} = L_{21} \qquad \text{(II.3)}$$

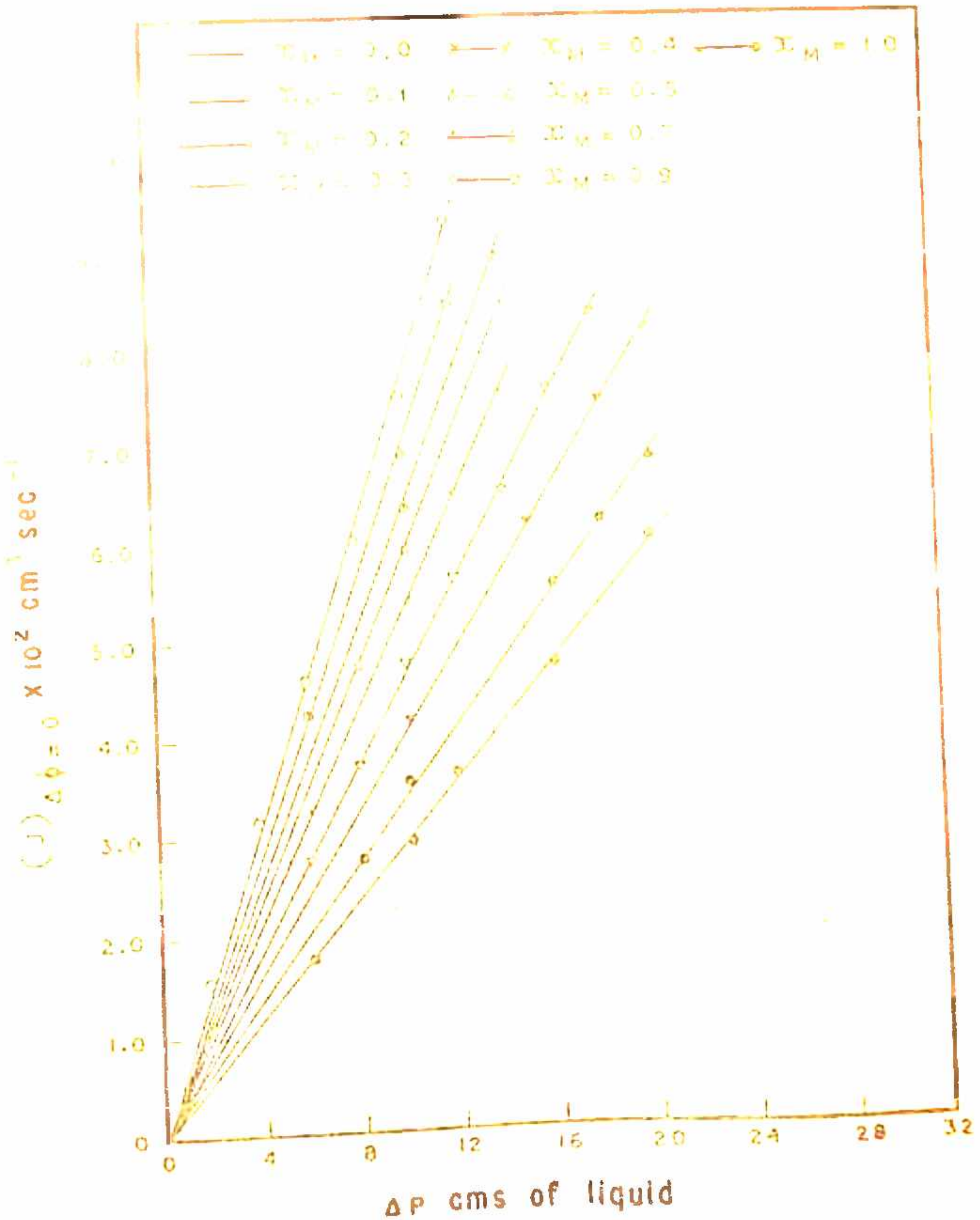


FIG. II. 2 PERMEABILITY DATA FOR ACETONE – METHANOL MIXTURES.

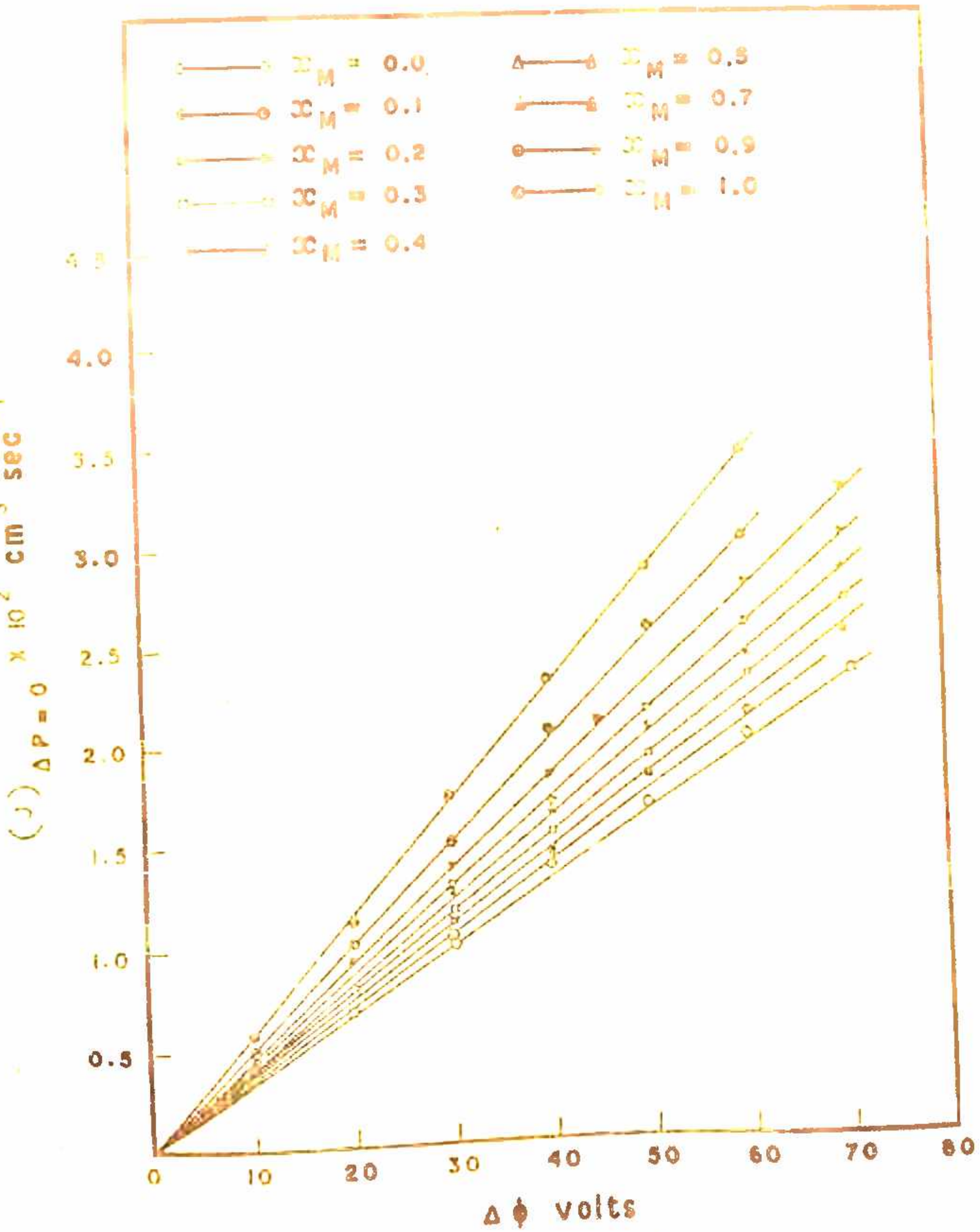


FIG. II.3 ELECTRO OSMOTIC VELOCITY DATA FOR ACETONE – METHANOL MIXTURES.

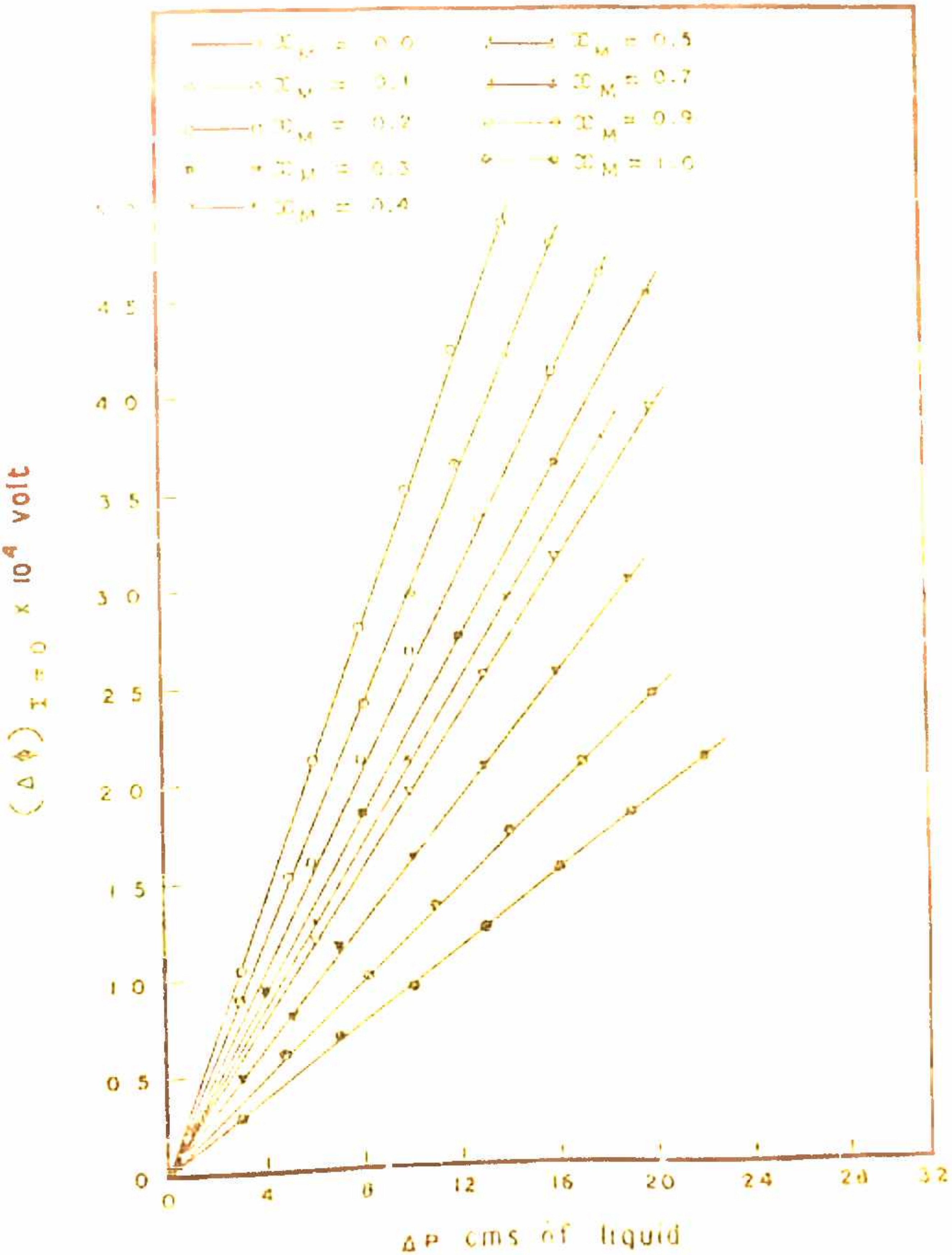


FIG. II.4 STREAMING POTENTIAL DATA FOR ACETONE – METHANOL MIXTURES.

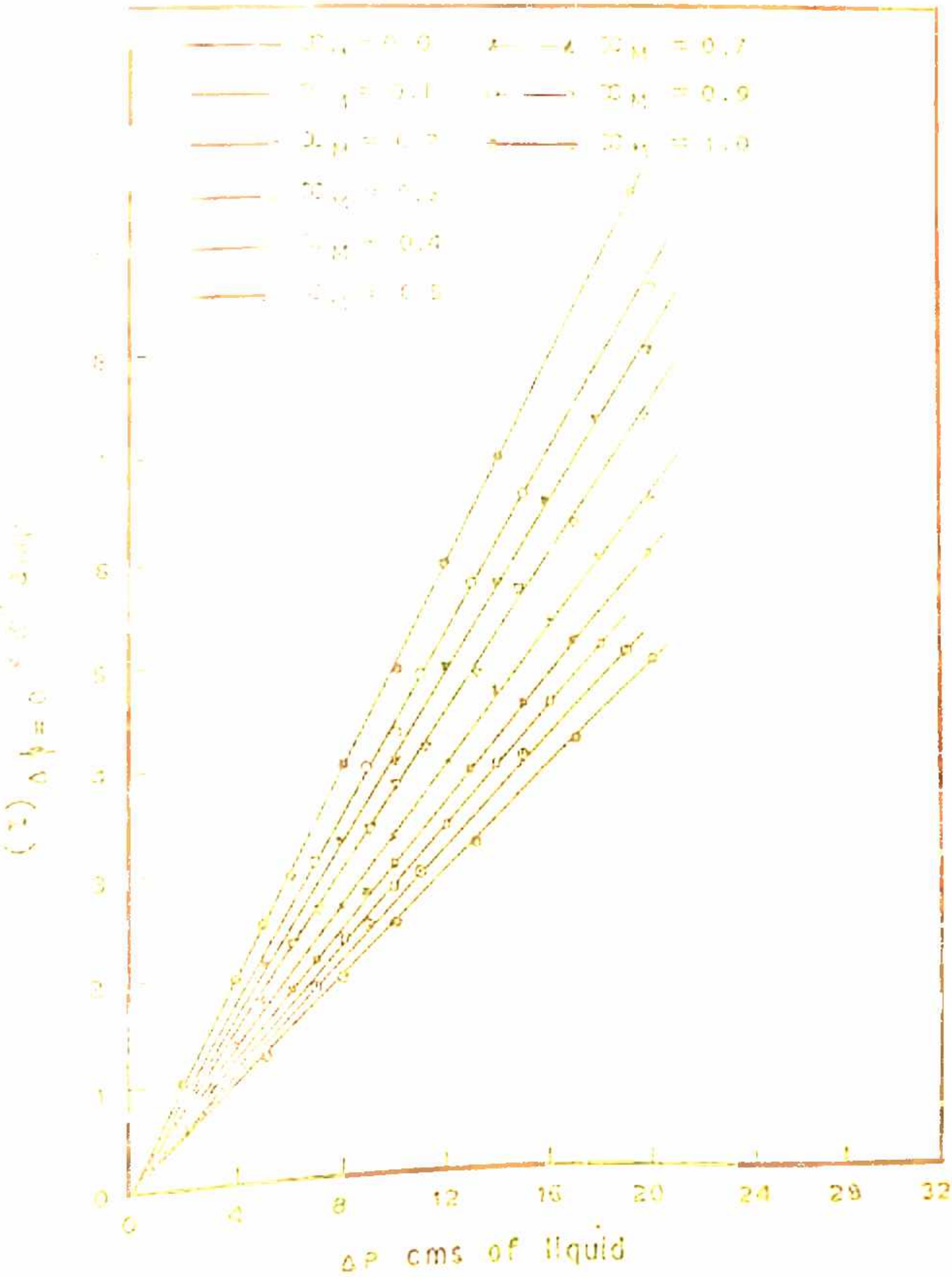


FIG. II.5 STREAMING CURRENT DATA FOR ACETONE-METHANOL MIXTURES.

FIG. II 5. PERMEABILITY DATA FOR ACETONE - WATER MIXTURES.

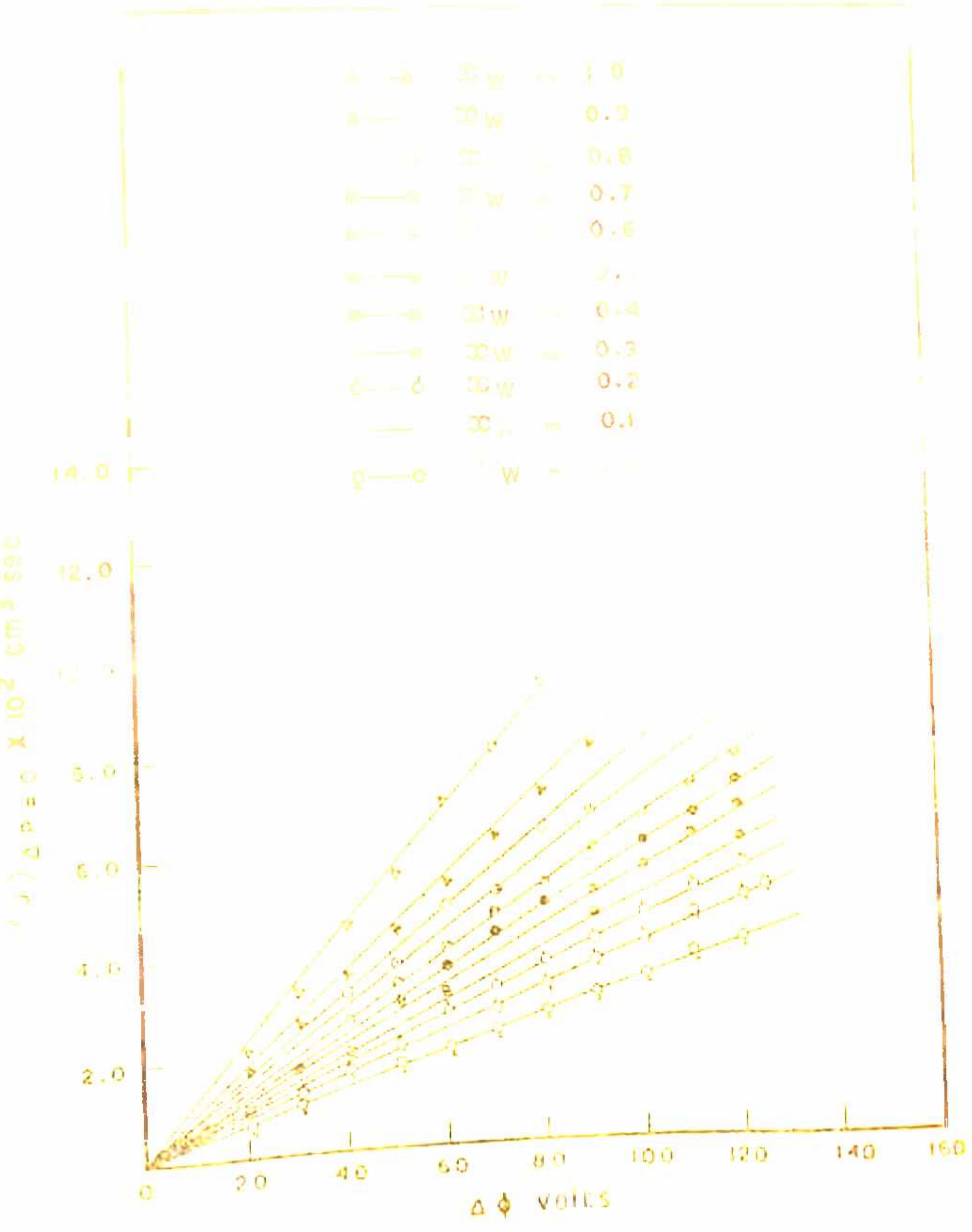


FIG. II.7 ELECTRO OSMOTIC VELOCITY DATA FOR ACETONE – WATER MIXTURE.

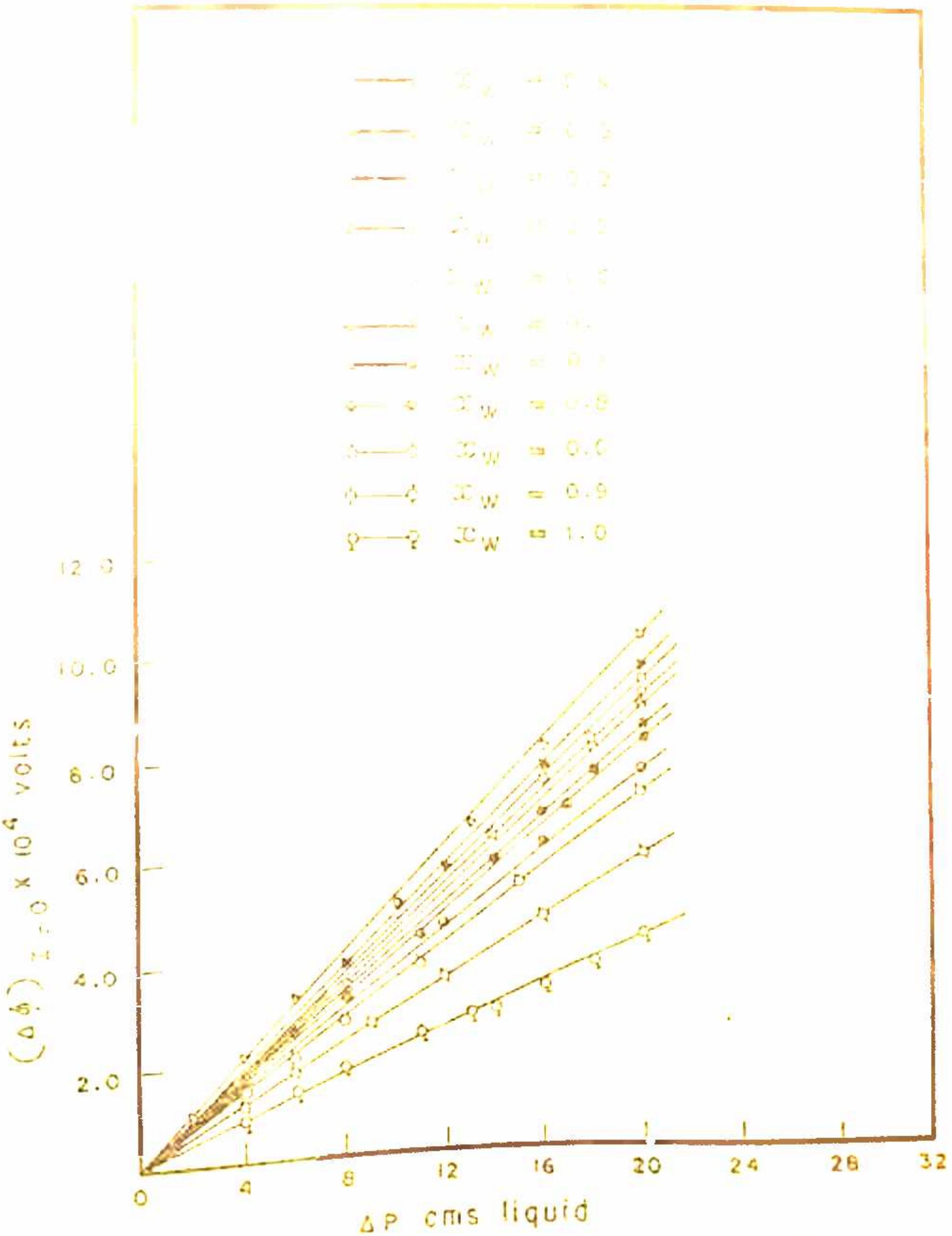


FIG. II. 8 STREAMING POTENTIAL DATA FOR ACETONE – WATER MIXTURES.

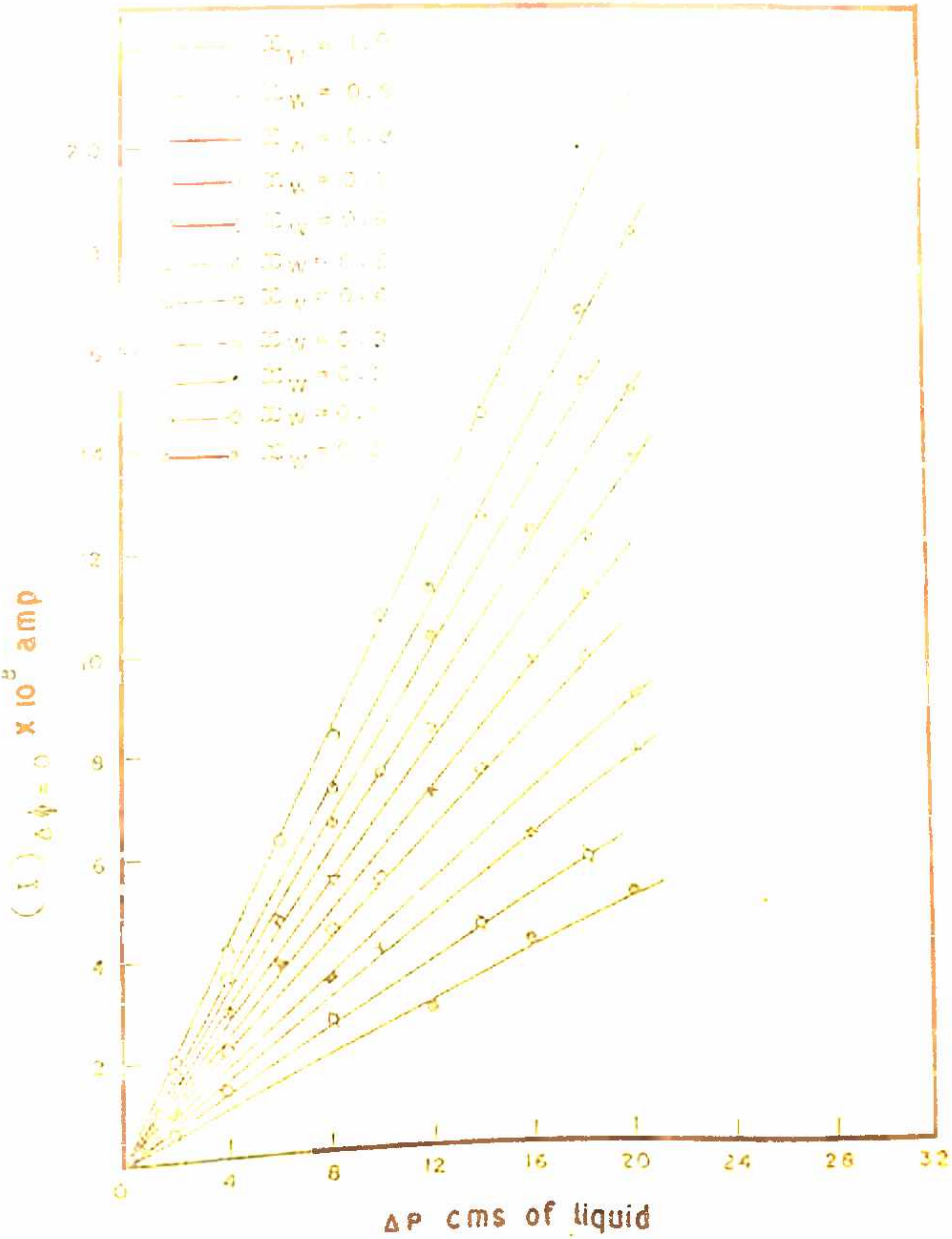


FIG. II.9 STREAMING CURRENT DATA FOR ACETONE - WATER MIXTURES.

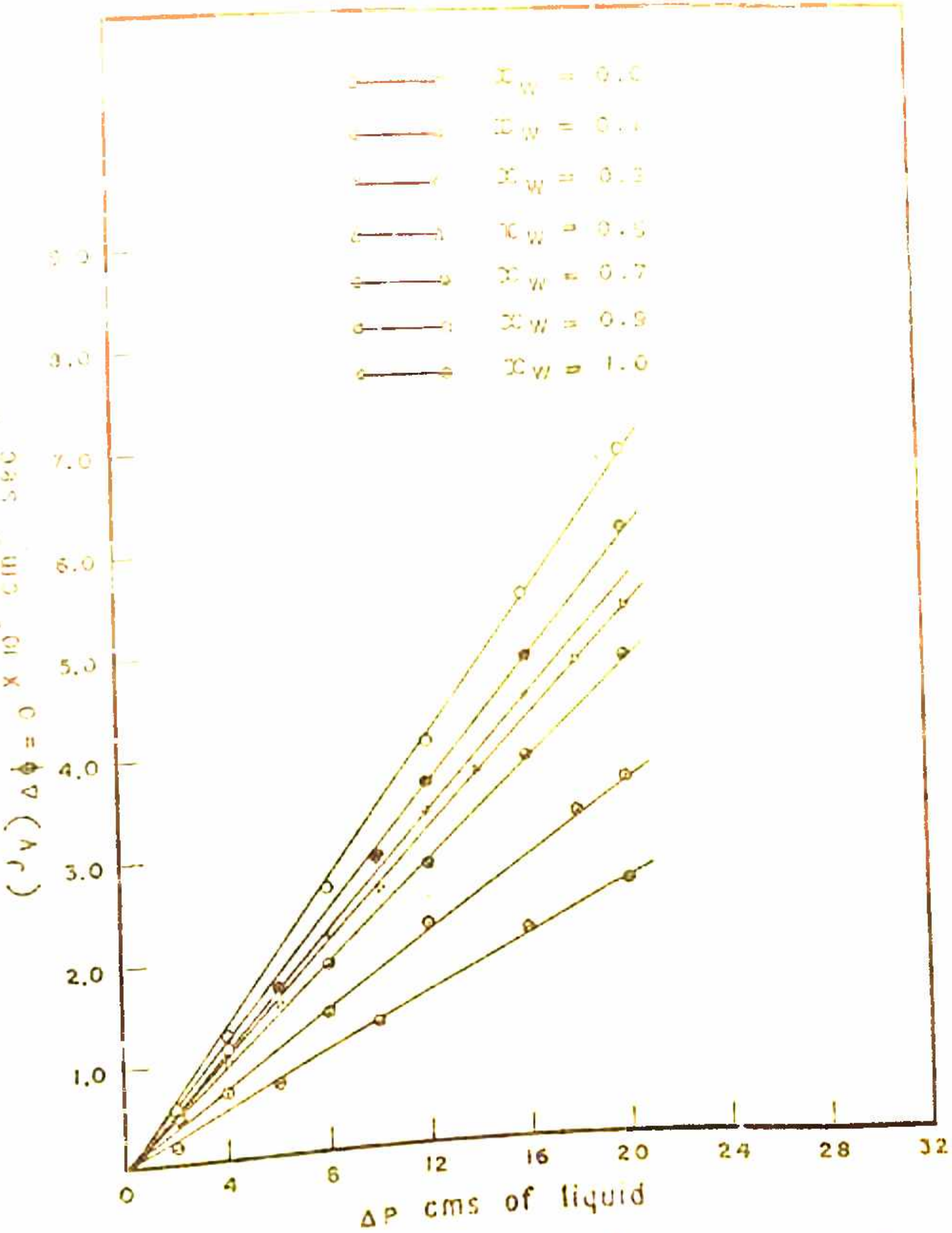


FIG. II.10 PERMEABILITY DATA FOR METHANOL WATER MIXTURES.

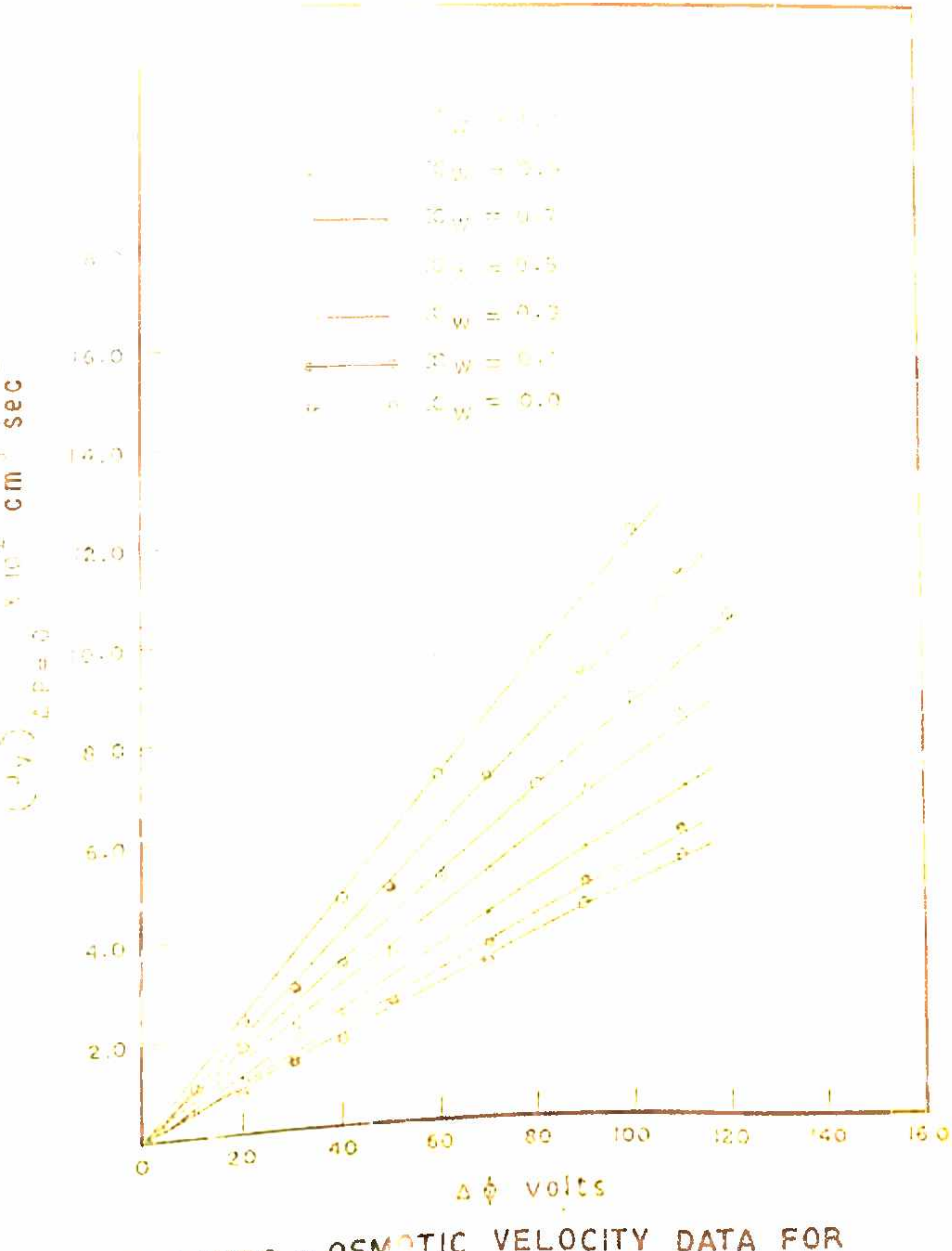


FIG. II.11 ELECTRO-OSMOTIC VELOCITY DATA FOR METHANOL-WATER MIXTURES.

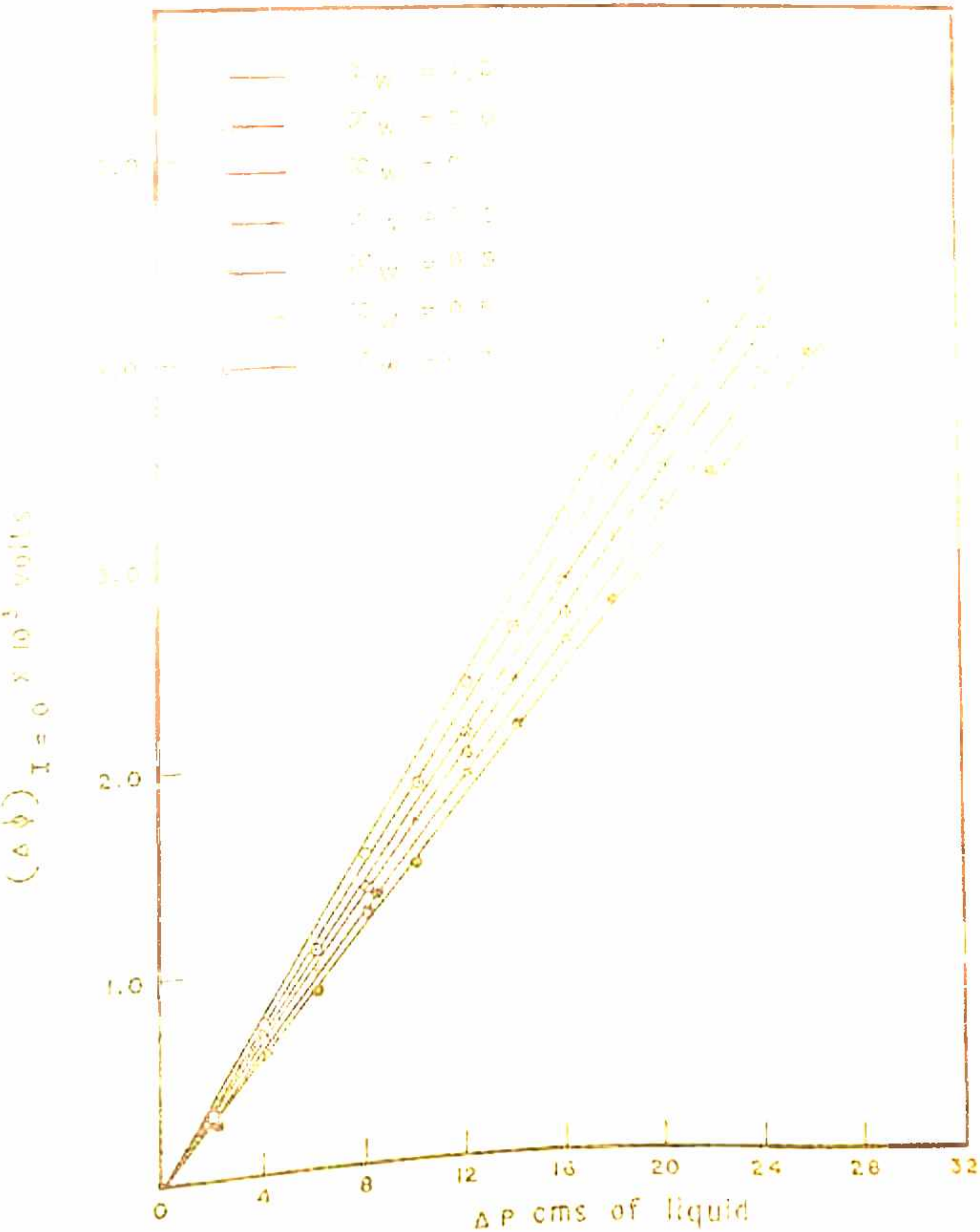


FIG. II.12 STREAMING POTENTIAL DATA FOR METHANOL – WATER MIXTURES.

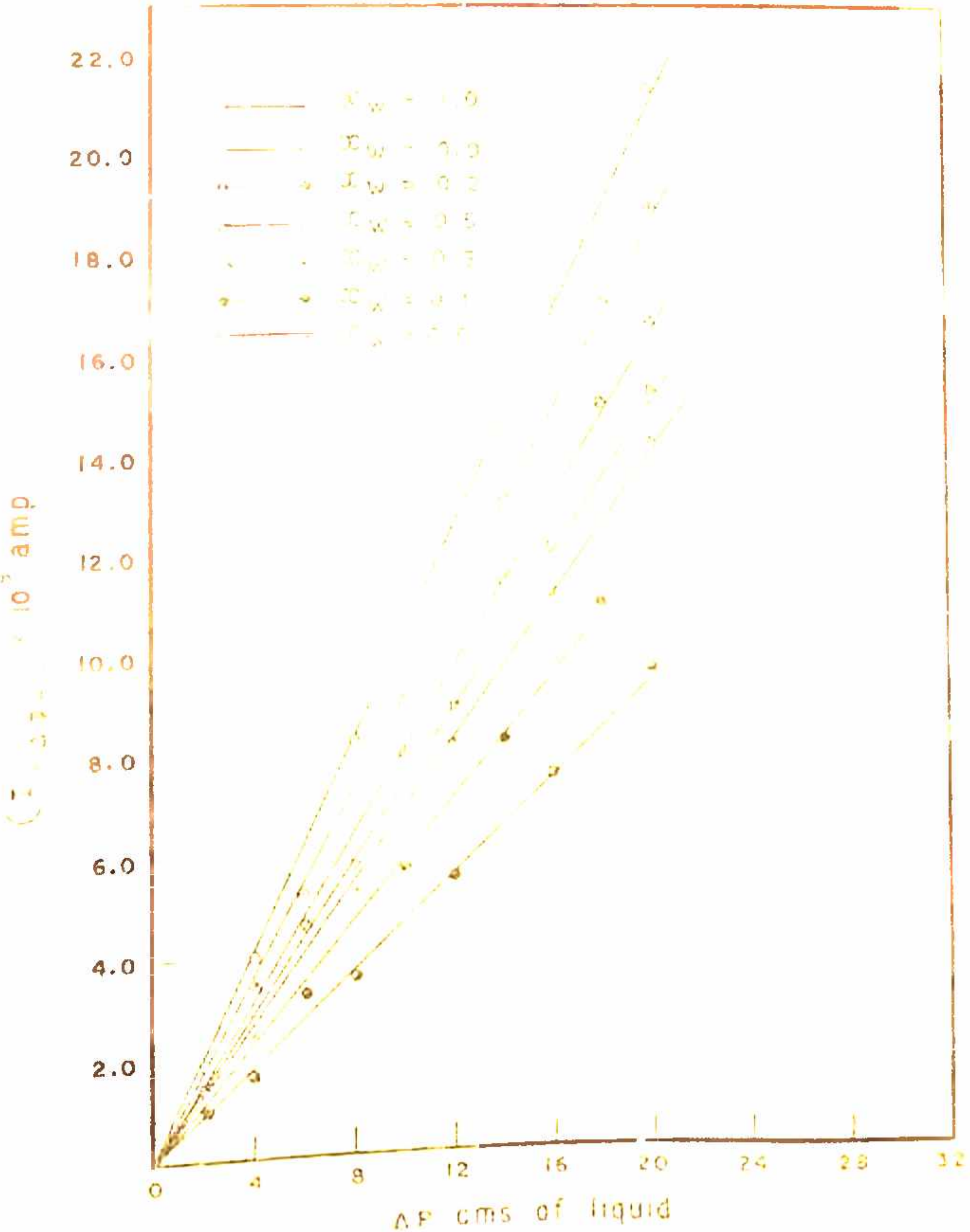


FIG. II.13 STREAMING CURRENT DATA FOR METHANOL-WATER MIXTURES.

If equations (II.1) and (II.2) are obeyed the following relationships would follow:

For ordinary permeability

$$(J)_{\Delta\phi=0} = L_{11}\Delta P \qquad \text{(II.4)}$$

For electro-osmotic velocity

$$(J)_{\Delta P=0} = L_{12}\Delta\phi \qquad \text{(II.5)}$$

For streaming potential

$$(\Delta\phi/\Delta P)_{I=0} = -L_{21}/L_{22} \qquad \text{(II.6)}$$

And for streaming current

$$(I)_{\Delta\phi=0} = L_{21}\Delta P \qquad \text{(II.7)}$$

The data plotted in Figs.|II.2| to |II.13| for various compositions of the three mixtures, viz. acetone-methanol, acetone-water, and methanol-water, demonstrate the validity of equations (II.4) to (II.7). This in turn implies the validity of the linear phenomenological relations (II.1) and (II.2) for various compositions of the mixtures.

The phenomenological coefficients L_{11}, L_{12}, L_{21} and L_{22} for various compositions of the three mixtures were estimated from the slopes of the straightline plots in Figs. |II.2| to |II.13|. The values obtained are given in tables II.1, II.2 and II.3. The validity of Onsager's reciprocal relations (II.3) for various compositions of the three mixtures is apparent from the values of phenomenological

TABLE II.1

Values of the Phenomenological Coefficients for various compositions of acetone-methanol mixtures

Mass fraction of methanol x_M	$L_{11} \times 10^6$ cm^3 dyn^{-1} sec^{-1}	$L_{22} \times 10^6$ Ohm^{-1}	$L_{12} \times 10^4$ cm^{3}AJ^{-1}	$L_{21} \times 10^4$ cm^{3}AJ^{-1}
0.0	9.331	7.14	3.130	3.302
0.1	9.181	8.72	3.571	3.403
0.2	8.722	10.31	3.845	3.665
0.3	7.929	12.74	4.166	3.924
0.4	7.474	15.73	4.545	4.325
0.5	7.168	19.38	4.750	5.000
0.7	6.305	25.09	5.550	5.234
0.9	5.508	36.50	5.871	5.750
1.0	5.081	52.40	6.450	6.250

TABLE II.2

Values of the phenomenological Coefficients for various compositions of acetone-water mixtures

Mass fraction of water x_w	$L_{11} \times 10^6$ $cm^3\ dyn^{-1}\ sec^{-1}$	$L_{22} \times 10^6$ Ohm^{-1}	$L_{12} \times 10^4$ $cm^3 AJ^{-1}$	$L_{21} \times 10^4$ $cm^3\ AJ^{-1}$
0.0	9.33	7.14	3.303	3.280
0.1	8.50	7.75	3.961	3.989
0.2	7.70	8.54	4.674	4.773
0.3	6.92	9.52	5.200	5.289
0.4	6.15	10.94	6.028	6.160
0.5	5.35	12.48	6.790	6.696
0.6	4.55	14.99	7.520	7.511
0.7	3.75	18.09	8.164	8.160
0.8	2.95	21.87	8.770	8.920
0.9	2.30	31.46	9.434	9.567
1.0	1.41	50.00	10.180	10.350

TABLE II.3

Values of the Phenomenological Coefficients for various Compositions of methanol-water mixtures

Mass fraction of water x_w	$L_{11} \times 10^6$ $cm^5\ dyn^{-1}\ sec^{-1}$	$L_{22} \times 10^5$ Ohm^{-1}	$L_{12} \times 10^4$ $cm^3\ AJ^{-1}$	$L_{21} \times 10^4$ $cm^3\ AJ^{-1}$
0.0	5.08	2.50	6.34	6.29
0.1	4.73	3.12	7.02	7.39
0.3	4.06	4.00	7.66	7.78
0.5	3.30	4.54	8.33	8.19
0.7	2.55	5.26	9.09	8.81
0.9	1.83	5.40	9.75	9.80
1.0	1.41	5.50	10.52	11.03

coefficients L_{12} and L_{21} given in tables II.1 to II.3.

A. Concentration Dependence of the Phenomenological Coefficients

The concentration dependence of the phenomenological coefficients L_{11} and L_{12} or L_{21} for all the three mixtures, viz. acetone-methanol, acetone-water, and methanol-water are shown in Figs. [II.14] to [II.19]. From Figs. [II.14] to [II.16] it can be concluded that the variation of L_{11} with composition of the various mixtures can be quantitatively expressed as follows:

For acetone-methanol

$$L_{11} = x_A (L_{11})_A + x_M (L_{11})_M \tag{II.8a}$$

For acetone-water

$$L_{11} = x_A (L_{11})_A + x_W (L_{11})_W \tag{II.8b}$$

For methanol-water

$$L_{11} = x_M (L_{11})_M + x_W (L_{11})_W \tag{II.8c}$$

Similarly from Fig. [II.17] to [II.19] the concentration dependence of the coefficient L_{12} or L_{21} can be quantitatively expressed as follows:

For acetone-methanol mixture

$$L_{12} = x_A (L_{12})_A + x_M (L_{12})_M \tag{II9a}$$

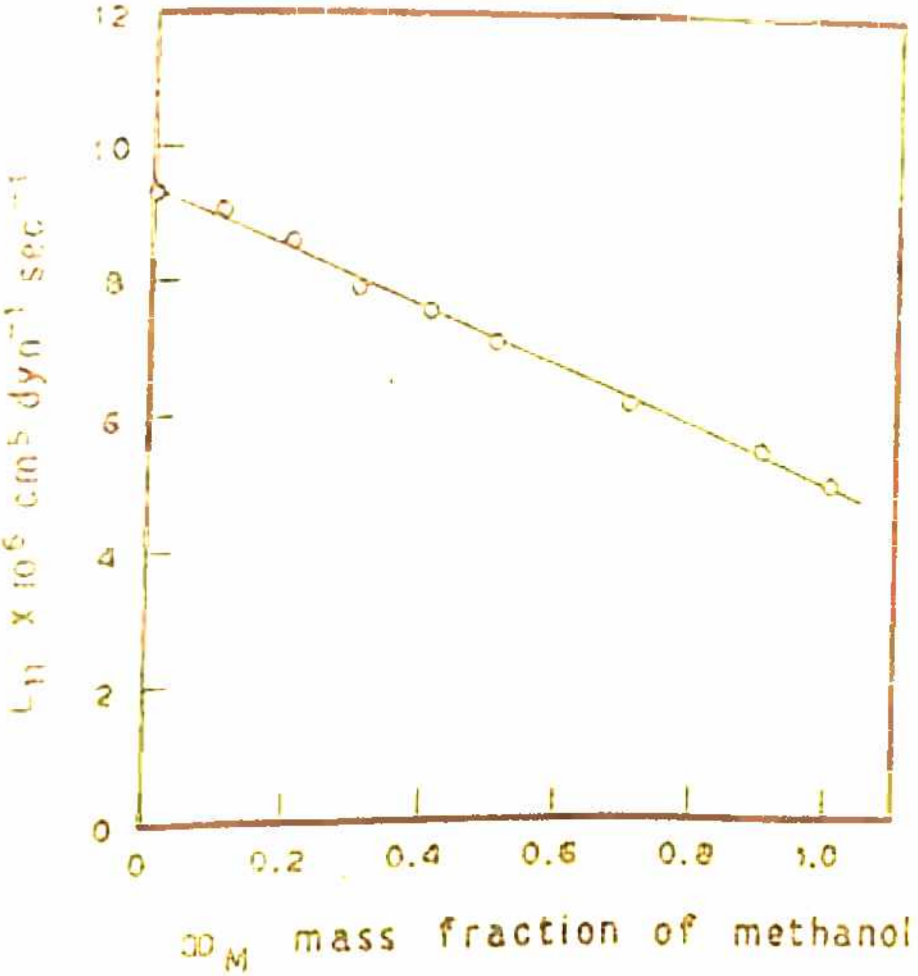


FIG. II.14 CONCENTRATION DEPENDENCE OF L_{11} FOR ACETONE – METHANOL MIXTURE.

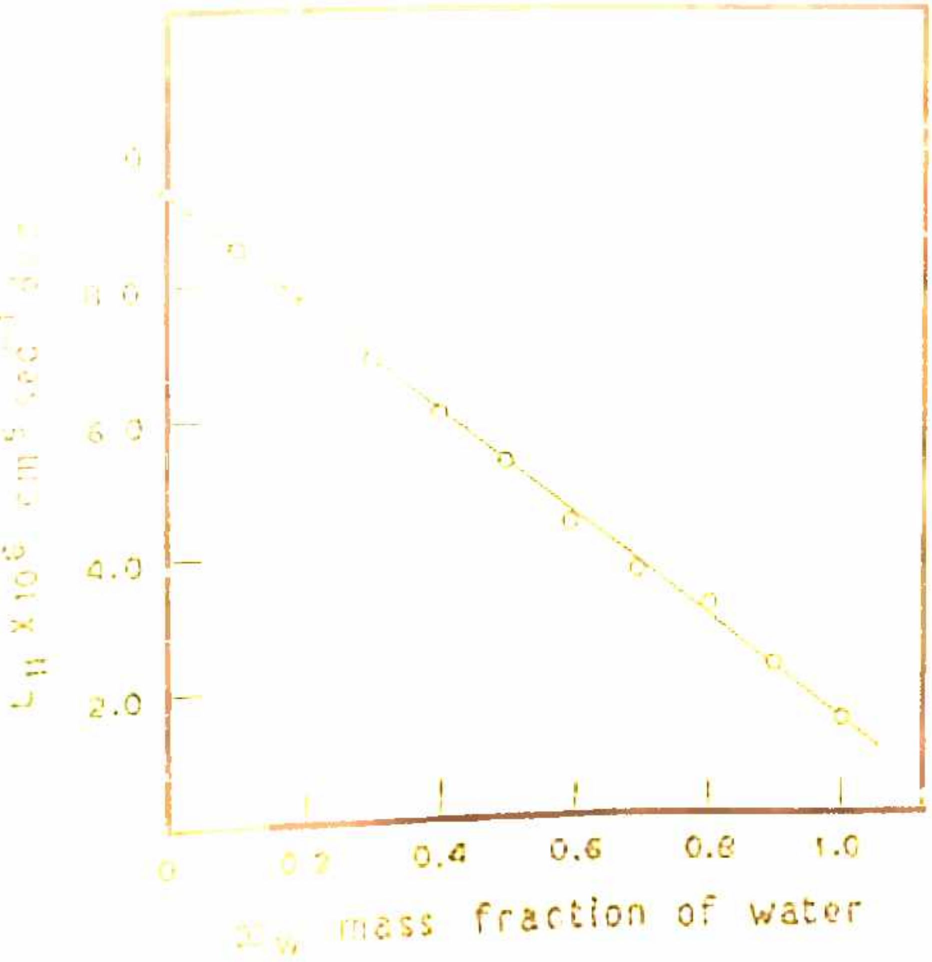


FIG. II.15 CONCENTRATION DEPENDENCE OF L_{11} FOR ACETONE – WATER MIXTURES.

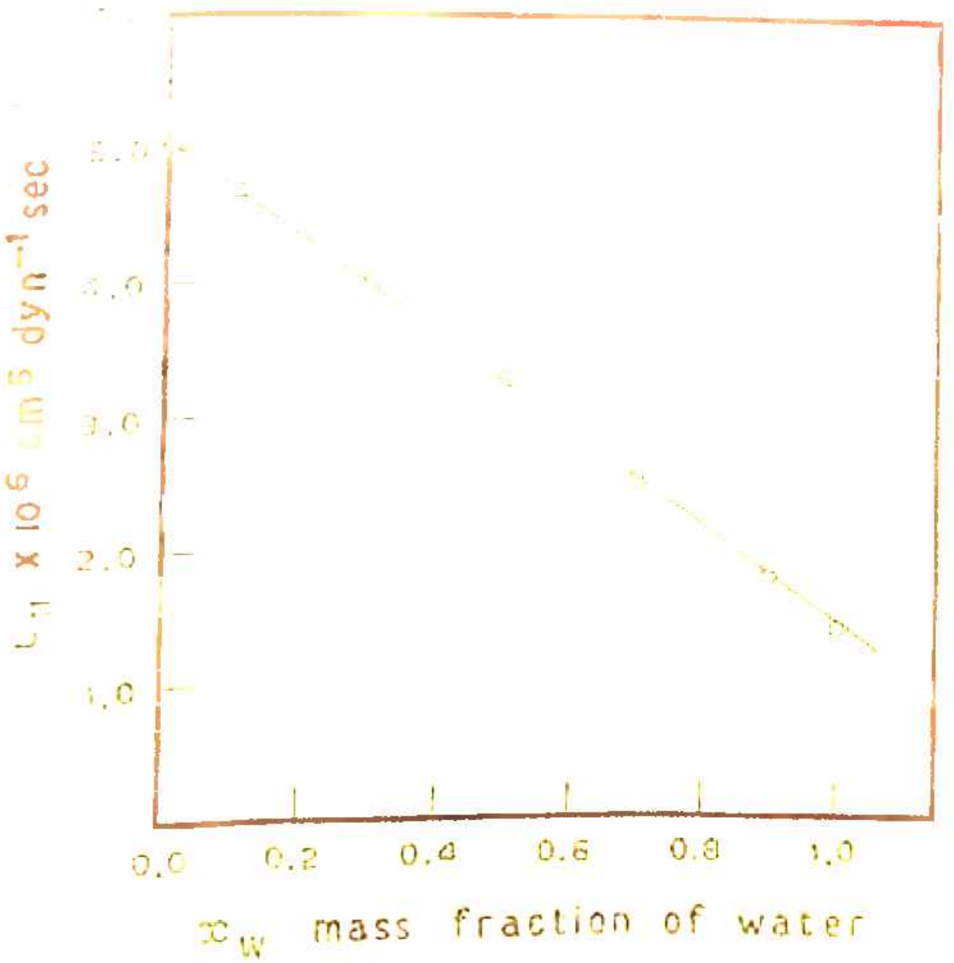


FIG. II.16 CONCENTRATION DEPENDENCE OF L_{11} FOR METHANOL - WATER MIXTURE.

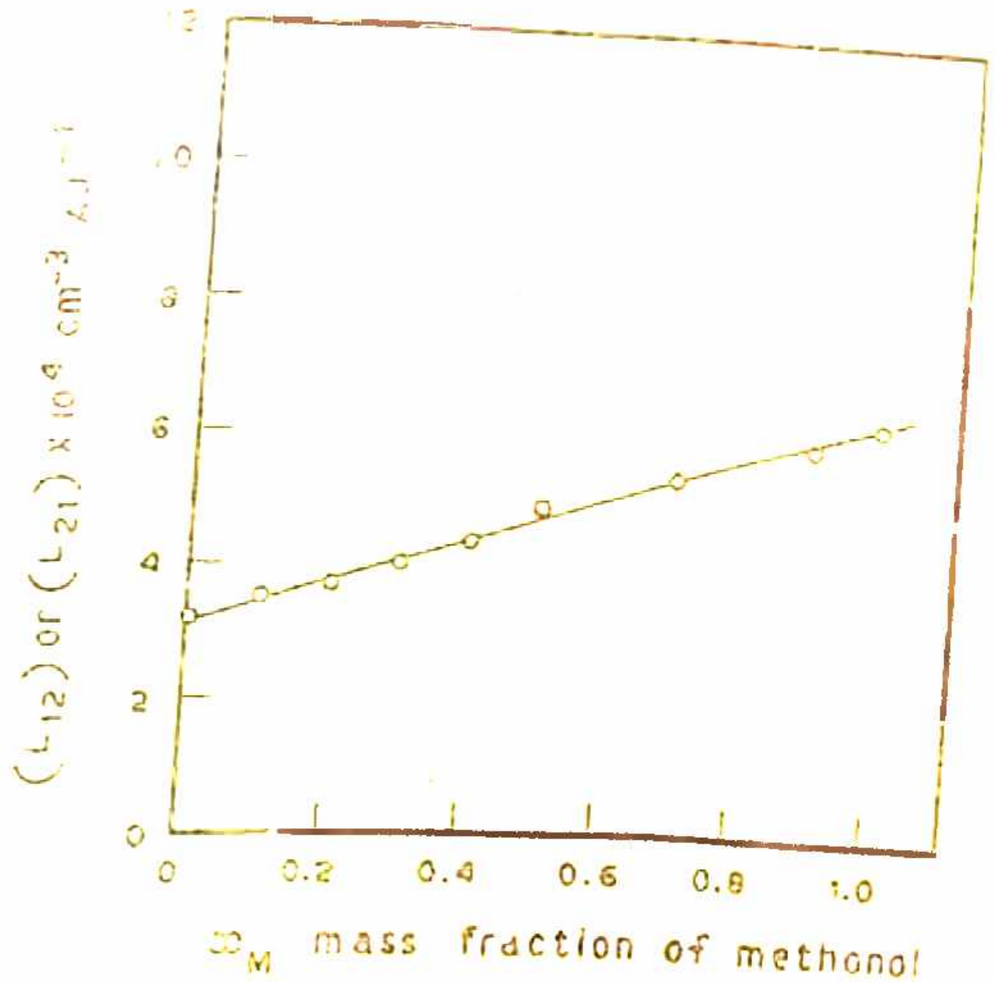


FIG. II.17 CONCENTRATION DEPENDENCE OF L_{12} FOR ACETONE – METHANOL MIXTURES.

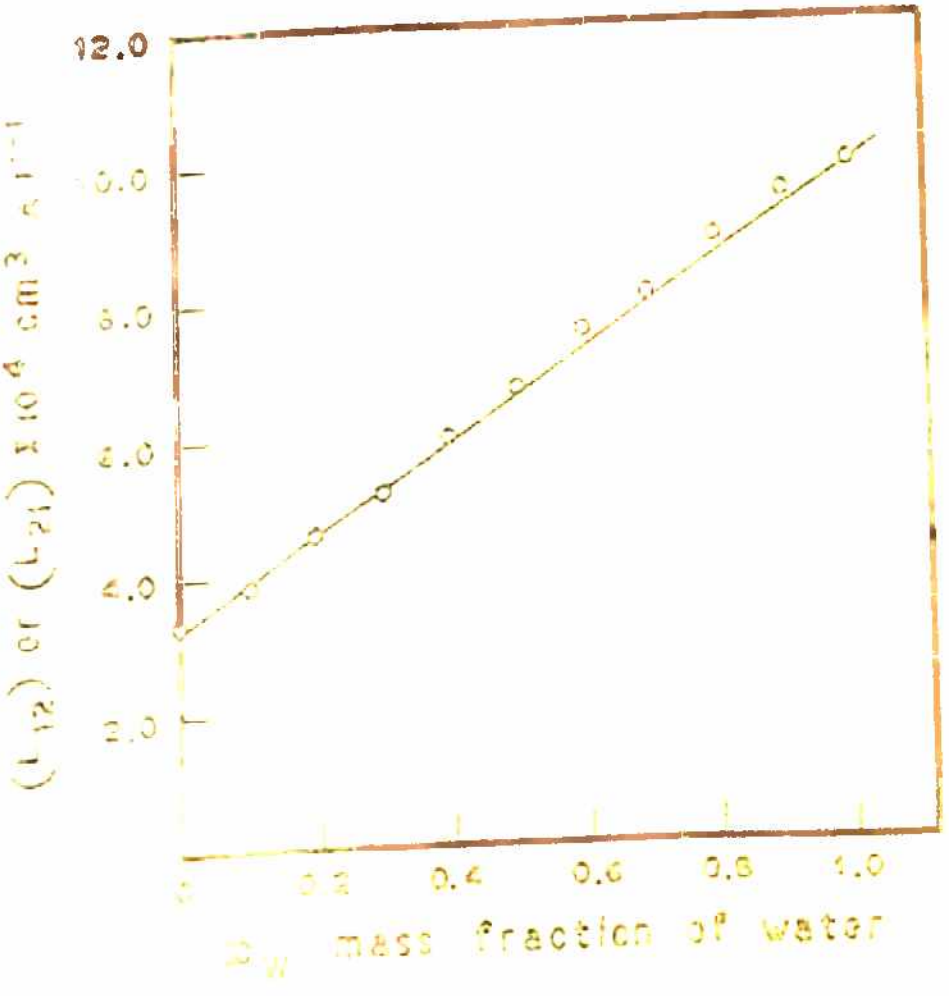


FIG. II.18 CONCENTRATION DEPENDENCE OF L_{12} FOR ACETONE – WATER MIXTURES.

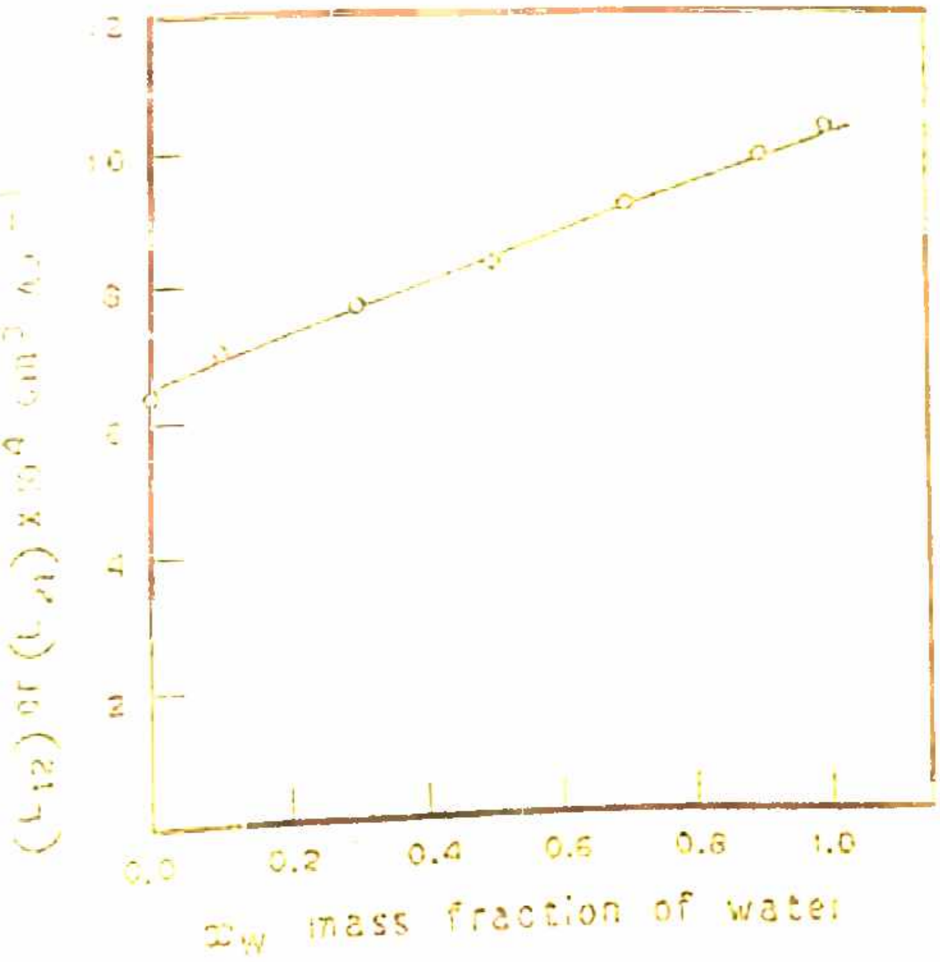


FIG. II.19 CONCENTRATION DEPENDENCE OF L_{12} FOR METHANOL – WATER MIXTURES.

For acetone-water

$$L_{12} = x_A (L_{12})_A + x_W (L_{12})_W \qquad \text{(II.9b)}$$

For methanol-water

$$L_{12} = x_M (L_{12})_M + x_W (L_{12})_W \qquad \text{(II.9c)}$$

In equations (II.8a) to (II.9c) the subscripts A, M and W stand for acetone, methanol and water. And x represents the mass fraction of the species denoted by the subscript.

The concentration dependence of the coefficients shown by (II.8a) to II.9c) can be shown to be consistent with the Spiegler's frictional model (Katchalsky and Curran, 1965; Smit, 1975; Speigler, 1958). To discuss this let us consider as an example, the concentration dependence of L_{11} in the case of acetone-methanol mixtures.

The general treatment of Speigler (1958) assumes the additivity of the frictional forces that counterbalance the thermodynamic forces. In order to discuss the concentration dependence of L_{11} let us consider the situation where $\Delta\phi=0$. In such a situation the equation for entropy production for a binary mixture (acetone-methanol) would reduce to (Katchalsky and Curran, 1965)

$$\sigma = v_A x_A (dm_A/dt) \Delta P + v_M x_M (dm_M/dt) \Delta P \qquad \text{(II.10)}$$

In equation (II.10) 'v' represents the specific volume and 'm' represents the mass . Identifying v(dm/dt) with the volume flux of the species denoted by the subscripts, the two conjugate thermodynamic forces are $x_A \Delta P$ and $x_M \Delta P$. If X_{AM}, X_{AS} and X_{MS} represent the frictional forces between the species denoted by the subscripts, the formal hydrodynamic description of these forces is

$$\begin{aligned} X_{MA} &= f_{MA}\,(V_M - V_A) \\ X_{AM} &= f_{AM}\,(V_A - V_M) \\ X_{AS} &= f_{AS}\,(V_A - V_S) \\ X_{MS} &= f_{MS}\,(V_M - V_S) \end{aligned} \qquad \text{(II.11)}$$

In (II.11) the subscript 'S' stands for the sintered glass membrane, f stands for the frictional coefficients between the species denoted by the subscripts, and V represents the velocities of the various species indicated by the subscripts. Considering the membrane velocity V_S as reference and taking $V_S=0$, Speigler's assumption of additivity of frictional forces will lead to the relationships

$$x_A \Delta P = X_{AM} + X_{AS} = V_A(f_{AM}+f_{AS}) - V_M\, f_{AM} \qquad \text{(II.12)}$$

and

$$x_M \Delta P = X_{MA} + X_{MS} = V_M(f_{MA}+f_{MS}) - V_A\, f_{MA} \qquad \text{(II.13)}$$

Solving (II.12) and (II.13) for V_A and V_M and identifying the total volume flux $(J\,)_{\Delta\phi=0}$ with $(V_M + V_A)$ the coefficient

L_{11} can be identified with the quantity

$$x_A \left[\frac{(f_{MA} + f_{MS}) + f_{MA}}{(f_{AM} + f_{AS})(f_{MA} + f_{MS}) - f_{AM}\, f_{MA}} \right] +$$

$$x_M \left[\frac{f_{AM} + (f_{AM} + f_{AS})}{(f_{AM} + f_{AS})\,(f_{MA} + f_{MS}) - f_{MA}\, f_{AM}} \right]$$

Thus it is apparent that the variation of the phenomenological coefficient L_{11} with the composition of the mixture, as given by equation II.8a is consistent with the Speigler's fractional model. Further from comparison with equation II.8a the following correspondence between the phenomenological coefficient and frictional coefficient becomes apparent. That is

$$(L_{11})_A = \frac{(f_{MA} + f_{MS}) + f_{MA}}{(f_{AM} + f_{AS})(f_{MA} + f_{MS}) - f_{AM}\, f_{MA}} \qquad \text{(II.14)}$$

and

$$(L_{11})_M = \frac{(f_{AM} + f_{AS}) + f_{AM}}{(f_{AM} + f_{AS})(f_{MA} + f_{MS}) - f_{AM}\, f_{MA}} \qquad \text{(II.15)}$$

Similar considerations would apply for L_{12} or L_{21} also.

The concentration dependence of the phenomenological L_{22}, however, was found to be different from the concentration dependence of L_{11} and L_{12} and hence does not appear to be consistent with the Speigler's frictional model. The data on concentration dependence of L_{22} for the three mixtures, viz. acetone-methanol, acetone-water, and methanol-water, are plotted in Figs. [II.20], [II.21], and [II.22] respectively. From Figs. [II.20] to [II.22] the concentration dependence of the coefficient L_{22} in the three cases can be quantitatively expressed as follows:

For acetone-methanol

$$L_{22} = (L_{22})_A + 1.428 \times 10^{-5} x_M + 3.10 \times 10^{-6} x_M^2 \qquad (II.16)$$

For acetone-water

$$1/L_{22} = x_M \, 1/(L_{22})_W + x_A \, 1/(L_{22})_A \qquad (II.17)$$

And for methanol-water

$$L_{22} = (L_{22})_W - 0.75 \; 10^{-6} x_M - 2.1 \; 10^{-5} x_M^2 \qquad (II.18)$$

A perusal of Figs. [II.13] to [II.15] shows that the coefficient L_{11} decreases as we increase the mass fraction of the hydrogen bonded species in the three mixtures. These trends can be shown to be consistent with the structural modifications that are likely to occur in the respective mixtures.

For flow through a single capillary it can be shown that (Overbeek, 1953a; Rastogi, 1969)

$$L_{11} = \pi r^4 / 8 \mu l. \qquad (II.19)$$

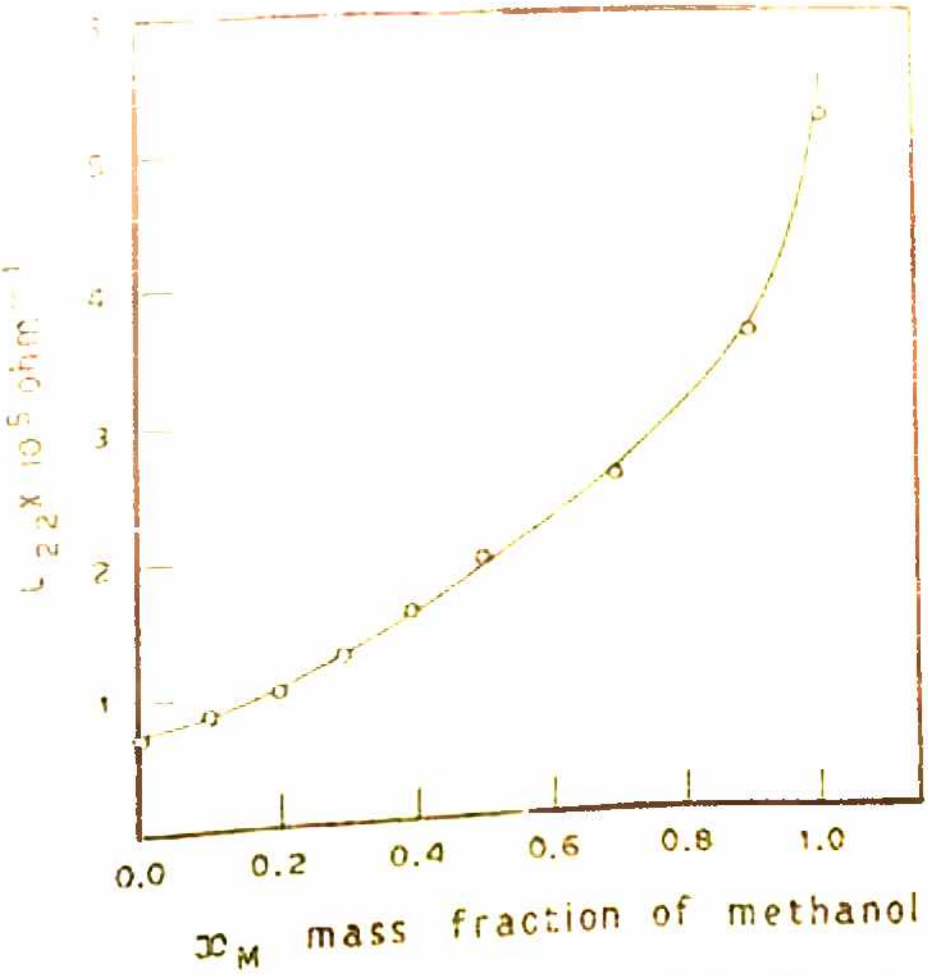


FIG. II.20 CONCENTRATION DEPENDENCE OF L_{22} FOR ACETONE – METHANOL MIXTURES.

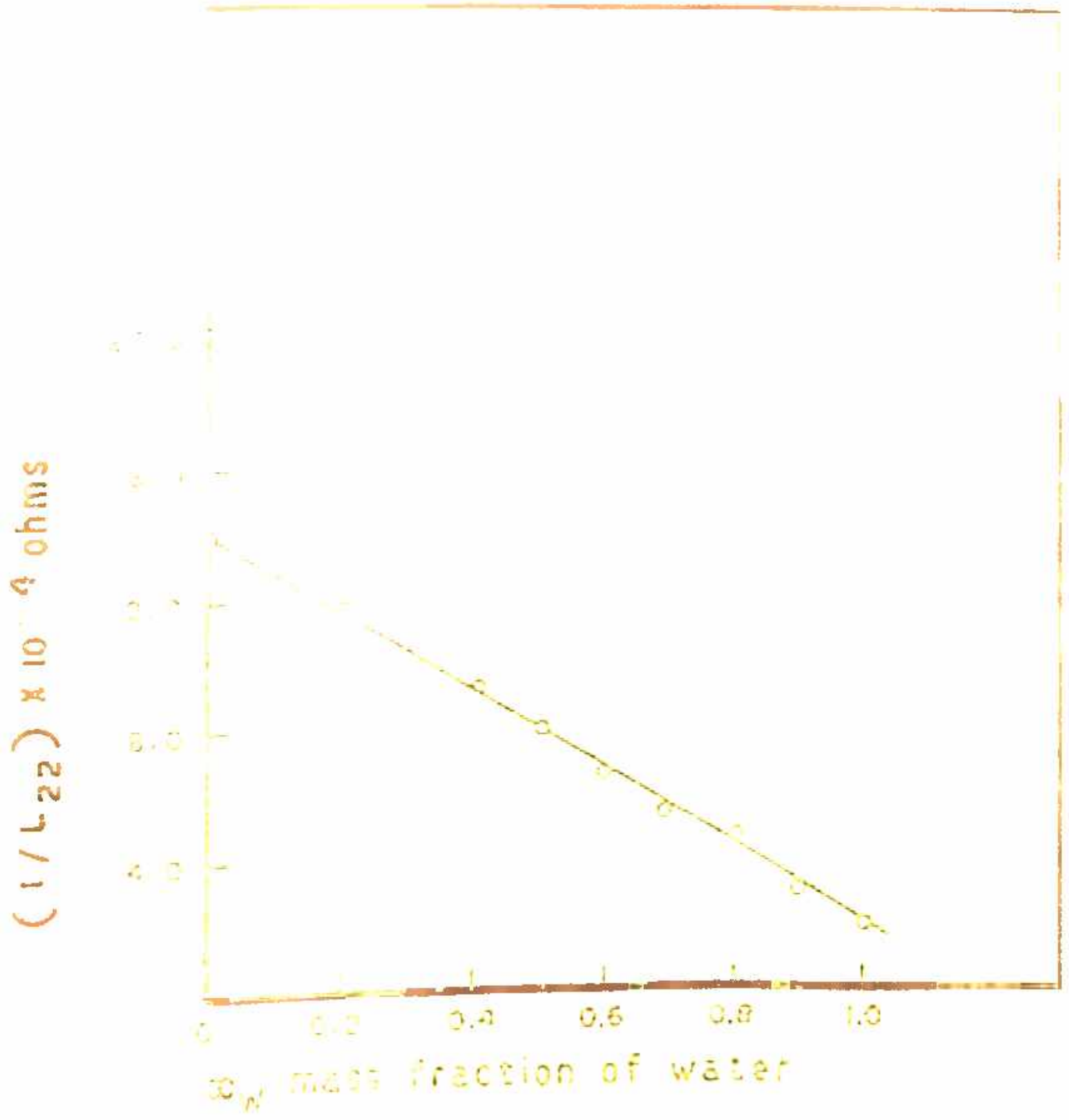


FIG. II-21 CONCENTRATION DEPENDENCE OF L_{22} FOR ACETONE - WATER MIXTURES.

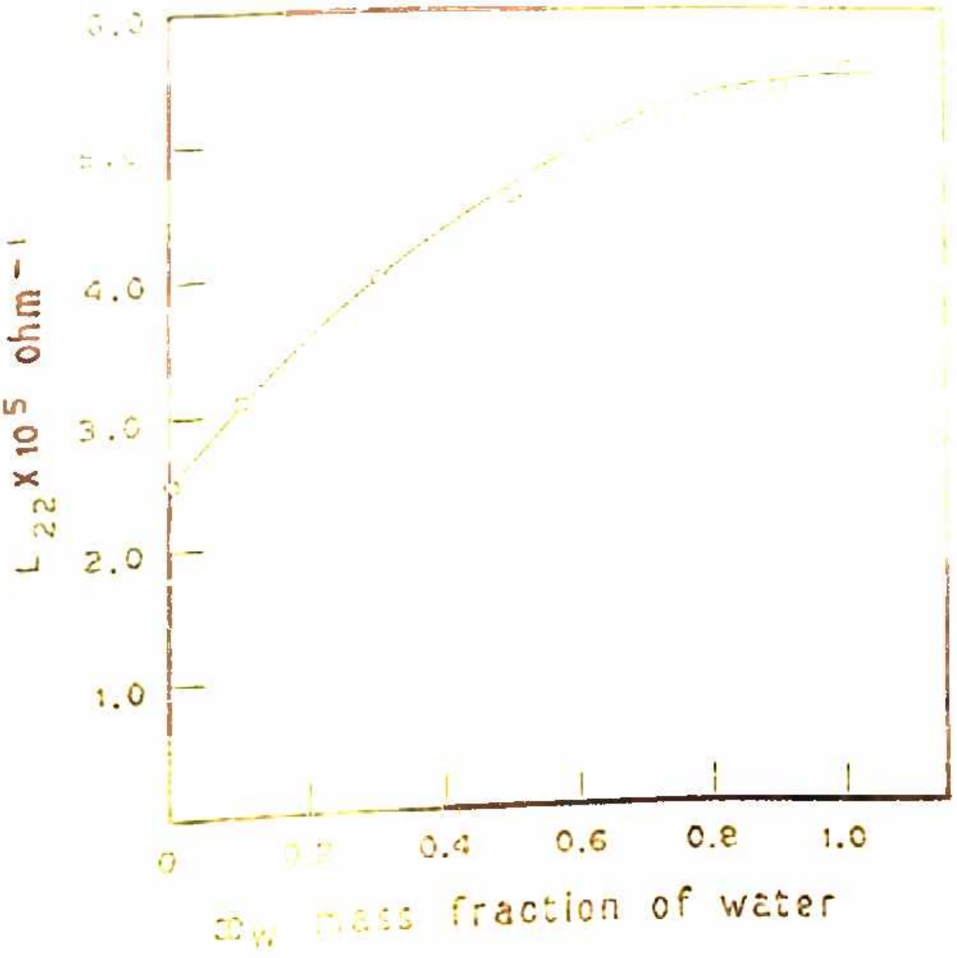


FIG. II. 22 CONCENTRATION DEPENDENCE OF L_{22} FOR METHANOL – WATER MIXTURES.

In equation (II.19), 'r' is the radius of the capillary 'l' is the length of the capillary and 'μ' is the viscosity of the medium. If the single capillary is replaced by a parallel array of 'n' capillaries (here the sintered glass membrane) the right hand side of equation (II.19) has to be multiplied by 'n'. The increased molecular interactions in the hydrogen bonded system decrease the freedom of molecular motion and therefore tend to increase the viscosity of the system (Vinogradov and Linnel, 1971). Thus the viscosity increases as we go from pure acetone to pure methanol in acetone-methanol system or from pure acetone or pure methanol to 100% water in acetone-water or methanol-water systems. This accounts the descreasing trend of L_{11} with increase in the mass fraction of the hydrogen bonded species.

From Figs. [II.17], [II.18], and [II.19] it is apparent that the coefficient L_{12} increases as we increase the concentration of the hydrogen bonded species in the mixtures. This trend can be explained on the basis of the double layer model. For flow through a single capillary we can write (Overbeek 1953a; Rastogi, 1969)

$$L_{12} = \varepsilon r^4 \xi / 4 \mu l \qquad \text{(II.20)}$$

In equation (II.20), r, l, ε, μ, and ξ stand for radius of the capillary, length of the capillary, dielectric constant, viscosity, and zeta potential of the medium respectively. For a system consisting of a bundle of 'n' parallel capillaries (here the sintered glass membrane) the right hand side of equation (II.20) also has to be multiplied by n. It is clear from the above equation that L_{12} varies directly proportional to ϵ and ζ and inversely proportional to μ. Although both ϵ and μ increase with the increase in the concentration of the hydrogen bonded species in the mixture (Hasted, 1973; Vinogradov and Linnel, 1971) the increase in viscosity is not expected to be as pronounced as the increase in dielectric constant because during the process of flow through the restricted barrier (sintered glass membrane) the frictional forces are likely to break some of the hydrogen bonds. Moreover from double layer considerations (Overbeek, 1953b; Rastogi, 1969) it can be seen that the quantity ($\epsilon\zeta$) is likely to increase with the increase of the hydrogen bonded species due to the possible increase in the thickness of the double layer.

B. Degree of Coupling and Efficiency of Energy Conversion

The phenomena of electro-osmotic flow and streaming potential are examples where energy conversion from one form to another takes place. In the former electrical energy is converted into mechanical work while in the latter case reverse conversion of mechanical energy into electrical work takes place. Osterle (1964a,b), Morrison and Osterle (1965), Gross and Osterle (1968) and Kedem and Caplan (1965) have discussed (see also Section 2.C, Chapter I) the efficiency of electrokinetic energy conversion utilizing the formalism of non-equilibrium thermodynamics. The generalised definition of the energy conversion efficiency η in terms of the thermodynamic fluxes J and forces F can be written as

$$\eta = - \frac{J_o F_o}{J_i F_i} \qquad \text{(II.21)}$$

In equation (II.21) the subscripts o and i indicate the output and input quantities. The negative sign indicates that the direction of output fluxes and forces are opposite to that of the input quantities. In the light of equation (II.21) the efficiency of energy conversion for the two reciprocal phenomena, i.e. electro-osmosis and streaming potential can be written as

$$\eta_e = - \frac{J \Delta P}{I \Delta \phi} = \frac{J \Delta P}{(\Delta \phi)^2 / R} \qquad \text{(II.22)}$$

$$\eta_\psi = - \frac{I \Delta \phi}{J \Delta P} = \frac{(\Delta \phi)^2 / R}{J \Delta P} \qquad \text{(II.23)}$$

In equations (II.22) and (II.23) the subscript e and ψ represents the phenomena of electro-osmosis and streaming potential and R is the electrical resistance of the system.

In an electro-osmosis experiment, the applied potential difference is used to drive the liquid uphill. This liquid, if allowed to accumulate, exerts a pressure difference ΔP across the membrane causing a black flow of the liquid. When ΔP equals electro-osmotic pressure difference, the net water flux J becomes zero. Thus it is clear from equation (II.22) that (η_e) would be zero when either $\Delta P = 0$ or ΔP equals electro-osmotic pressure and therefore the graph between (η_e) and ΔP for a fixed value of input force $\Delta\phi$ would pass through a maximum as ΔP is varied from zero to the electro-osmotic pressure and it has been shown earlier (Srivastava and Jain, 1975a,b) that the value of (η_e) would attain a maximum when ΔP equals half the value of electro-osmotic pressure, i.e., when

$$\Delta P = (1/2)(\Delta P)_{J=0} \tag{II.24}$$

Similar considerations would apply to ($_{\psi}$).

The values of (η_e) and (η_ψ) corresponding to several fixed values of input forces were calculated for output forces ranging from zero to their steady state value, for various compositions of acetone-methanol, acetone-water, and methanol-water mixtures, using the transport data in Figs. [II.2] to [II.13]. The procedure adopted for the calculation of η was the same as laid out by Srivastava and Jain (1975b). It is summarised below for a particular composition of acetone-methanol mixture.

For a fixed value of $\Delta\phi$, say 20 volts, the electro-osmotic flow was read from Fig. [II.3]. The pressure difference ΔP, i.e., the electro-osmotic pressure difference which induces a flow equal to that induced by $\Delta\phi = 20$ volts but in opposite direction was noted from Fig. [II.2]. Now having known the value of the electro-osmotic pressure difference various values of ΔP ranging from zero to the electro-osmotic pressure difference were chosen and the flux corresponding to them was read from Fig. [II.2]. These values of flux were subtracted from the flux corresponding to 20 volts read from Fg .[II.2]. This gave the net flux corresponding to various pressure differences ranging from zero to the electro-osmotic pressure for the fixed value of input force ($\Delta\phi = 20$ volts). With this data at hand (η_e) was calculated using equation (II.22). An identical procedure was adopted for the calculation of (η_ϕ) for different fixed input forces, ΔP.

(η_e) and (η_ϕ) values thus calculated for various compositions of all the three mixtures, viz. acetone-methanol acetone-water, and methanol-water at two fixed values of input forces and at various values of output forces ranging from zero and their stationary state values, using the transport data in Figs. |II.2| to |II.13| were plotted against the output forces. From the plots of (η_e) vs ΔP and (η_ϕ) vs $\Delta\phi$ thus obtained, the values of $(\eta)_{max}$ were read. These are given in Tables II.4 to II.6. Representative plots of (η_e) vs ΔP and (η_ψ) vs $\Delta\phi$ for three mass fractions of acetone-methanol, acetone-water, and methanol-water are given in Figs. [II.23] to [II.28]. From these data (tables II.4 to II.6 and figs. [II.23] to [II.28]) the following conclusions can be drawn for the various compositions of all the three mixtures.

i) The maximum value of energy conversion efficiency $(\eta)_{max}$ for a fixed value of the input force for both modes of conversion, viz. electro-osmosis and streaming potential, in all cases occurs when the output forces equal half its stationary state value.

ii) The values of $(\eta)_{max}$ in all cases was found to be independent of the input forces.

iii) The maximum value of (η_e), i.e., $(\eta_e)_{max}$ was always found to be equal to the maximum value of (η_ψ) i.e., $(\eta_\psi)_{max}$, i.e., $(\eta_e)_{max} = (\eta_\psi)_{max}$ for the various compositions of all the three mixtures.

The first conclusion is in agreement with the theoretical deductions (Srivastava and Jain, 1975a). The theoretically deduced condition for electro-osmosis is given by equation (II.24). The other two conclusions are also in accordance with the theory.

TABLE II.4

Values of β and $(\eta)_{max}$ for various compositions of acetone-methanol mixtures.

Mass fraction of methanol x_M	$\beta_{1o} \times 10^4$	$\beta_{o1} \times 10^4$	$(\eta_e)_{max} \times 10^5$ *	$(\eta_\psi)_{max} \times 10^5$ **	$(\eta_e)_{max} \times 10^5$ +	$(\eta_\psi)_{max} \times 10^5$ ++
0.0	1.454	1.469	3.45	3.63	3.43	3.67
0.1	1.504	1.617	3.65	3.74	3.75	4.04
0.2	1.566	1.650	3.80	3.87	3.92	4.13
0.3	1.537	1.739	4.05	4.00	3.84	4.34
0.4	1.592	1.678	4.20	4.33	3.98	4.19
0.5	1.708	1.698	4.50	4.48	4.27	4.24
0.7	1.840	1.711	4.58	4.75	4.60	4.28
0.9	1.928	1.841	4.87	4.85	4.82	4.60
1.0	1.982	1.926	5.09	4.95	4.96	4.83

* From η_e vs ΔP plots

** From η_ψ vs $\Delta\phi$ plots

+ From β_{o1} (equation II.28)

++ From β_{o1} (equation II.29)

TABLE II.5

Values of β and $(\eta)_{max}$ for various compositions of acetone-water mixtures

Mass fraction of water x_w	$\beta_{io} \times 10^4$	$\beta\beta_{oi} \times 10^4$	$(\eta_e)_{max} \times 10^5$ *	$(\eta_\psi)_{max} \times 10^5$ **	$(\eta_e)_{max} \times 10^5$ +	$(\eta_\psi)_{max} \times 10^5$ ++
0.0	1.82	1.89	4.56	4.72	4.20	4.52
0.1	2.38	2.41	5.94	6.05	6.00	6.17
0.2	3.31	3.45	8.28	8.63	8.19	8.40
0.3	4.12	4.26	10.28	10.64	10.10	10.35
0.4	5.48	5.80	13.69	14.49	13.20	13.97
0.5	6.94	6.73	17.26	16.81	17.20	16.50
0.6	8.30	8.26	20.26	20.64	20.10	21.00
0.7	10.11	9.81	25.27	24.54	24.80	23.95
0.8	11.87	11.90	29.65	29.75	28.90	29.80
0.9	12.27	12.75	30.68	31.87	30.12	32.00
1.0	14.75	15.19	36.84	37.97	37.00	37.60

* From η_e vs ΔP plots

** From η_ψ vs $\Delta\phi$ plots

\+ From β_{io} (equation 2.II.28)

++ From β_{oi} (equation II.29)

TABLE II.6

Values of β and $(\eta)_{max}$ for various compositions of methanol-water mixtures

Mass fraction of water x_w	$\beta_{io} \times 10^4$	$\beta_{oi} \times 10^4$	$(\eta_e)_{max} \times 10^5$ *	$(\eta_\phi)_{max} \times 10^5$ **	$(\eta_e)_{max} \times 10^5$ +	$(\eta_\phi)_{max} \times 10^5$ ++
0.0	3.17	3.12	7.91	7.80	7.88	7.60
0.1	3.30	3.60	8.25	9.00	8.50	8.80
0.3	3.61	3.73	9.02	9.32	9.10	9.40
0.5	4.60	4.40	12.50	11.00	13.00	11.50
0.7	6.10	5.70	15.20	14.25	15.50	14.00
0.9	9.50	9.70	23.70	24.25	23.90	24.00
1.0	14.20	16.75	35.00	41.60	35.60	40.00

* From η_e vs ΔP plots

** From η_ϕ vs $\Delta\phi$ plots

\+ From β_{io} (equation II.28)

++ From β_{oi} (equation II.29)

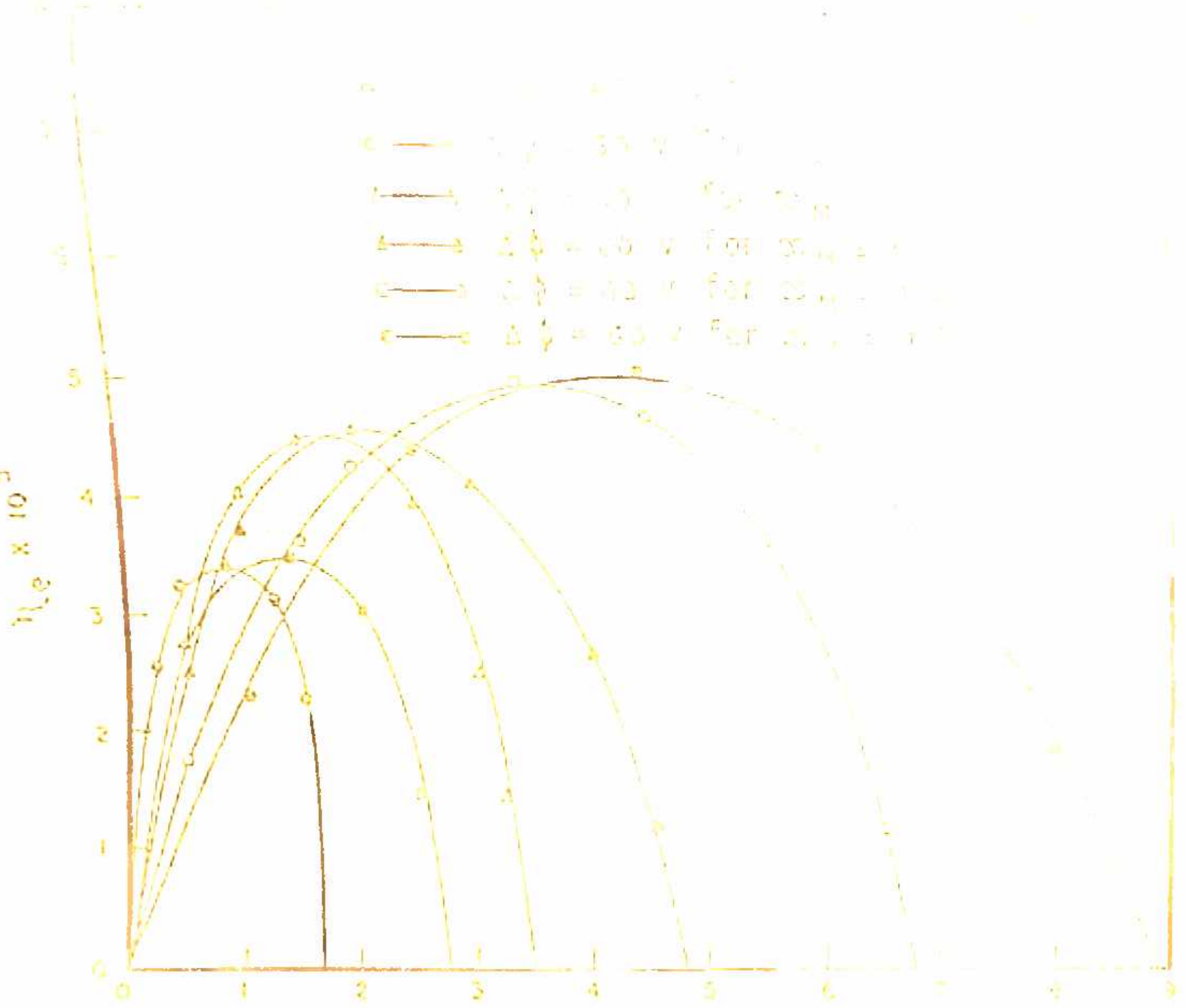


FIG. II.23 VARIATION OF η_e WITH PRESSURE DIFFERENCE FOR ACETONE –METHANOL MIXTURES.

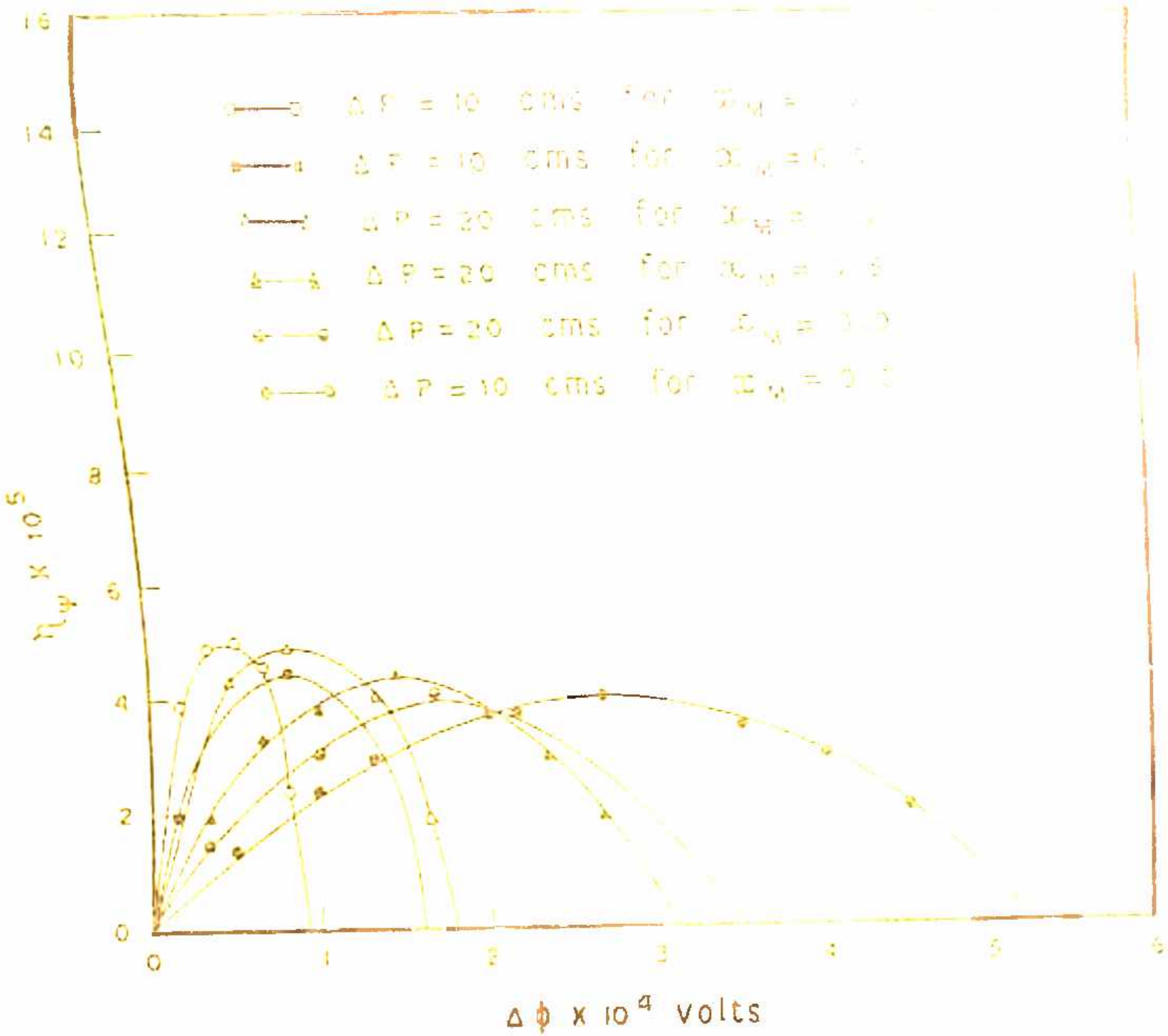


FIG. II.24 VARIATION OF η_{ψ} WITH POTENTIAL DIFFERENCE FOR ACETONE – METHANOL MIXTURES.

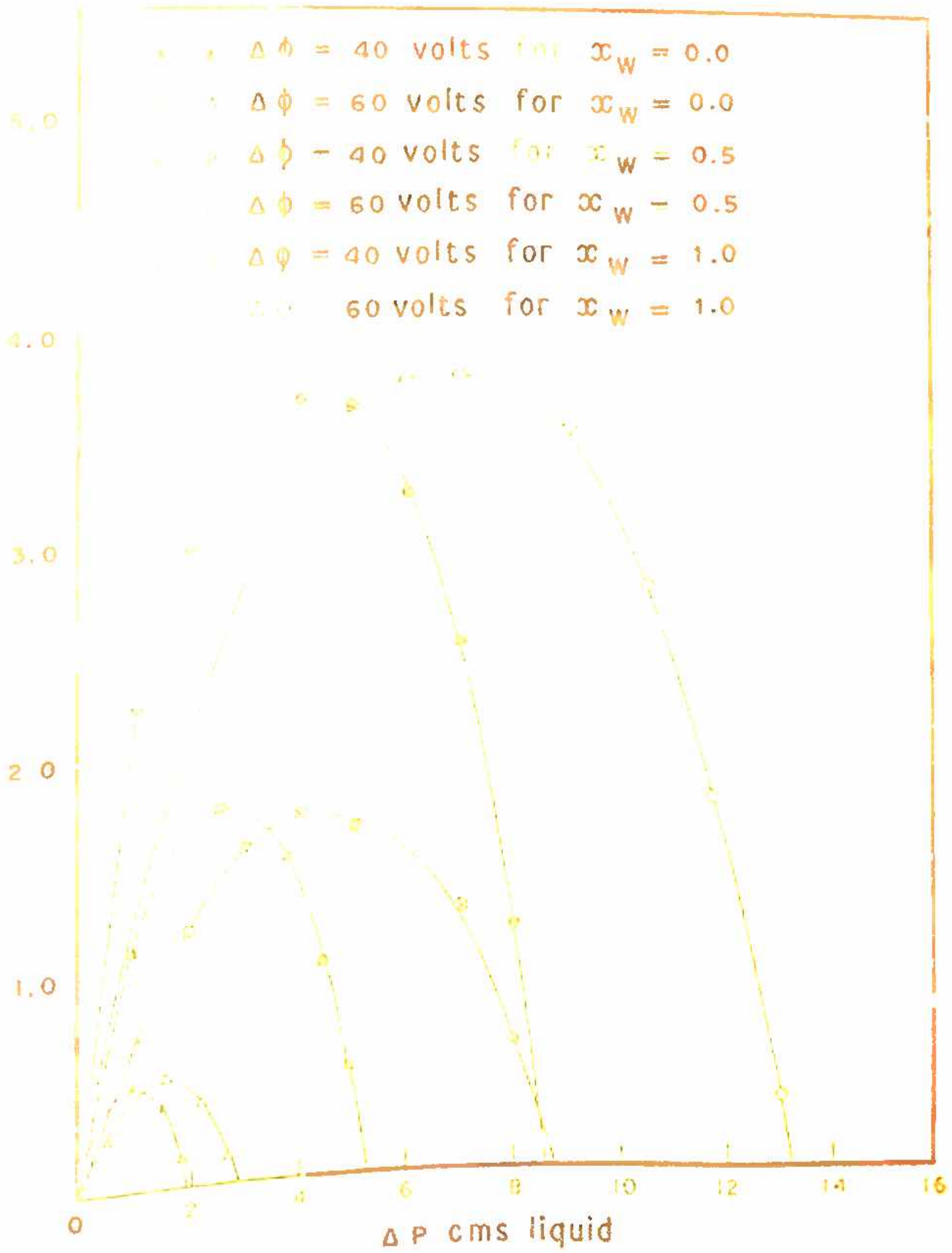


FIG. II 25 VARIATION OF η_e WITH PRESSURE DIFFERENCE FOR ACETONE – WATER MIXTURES.

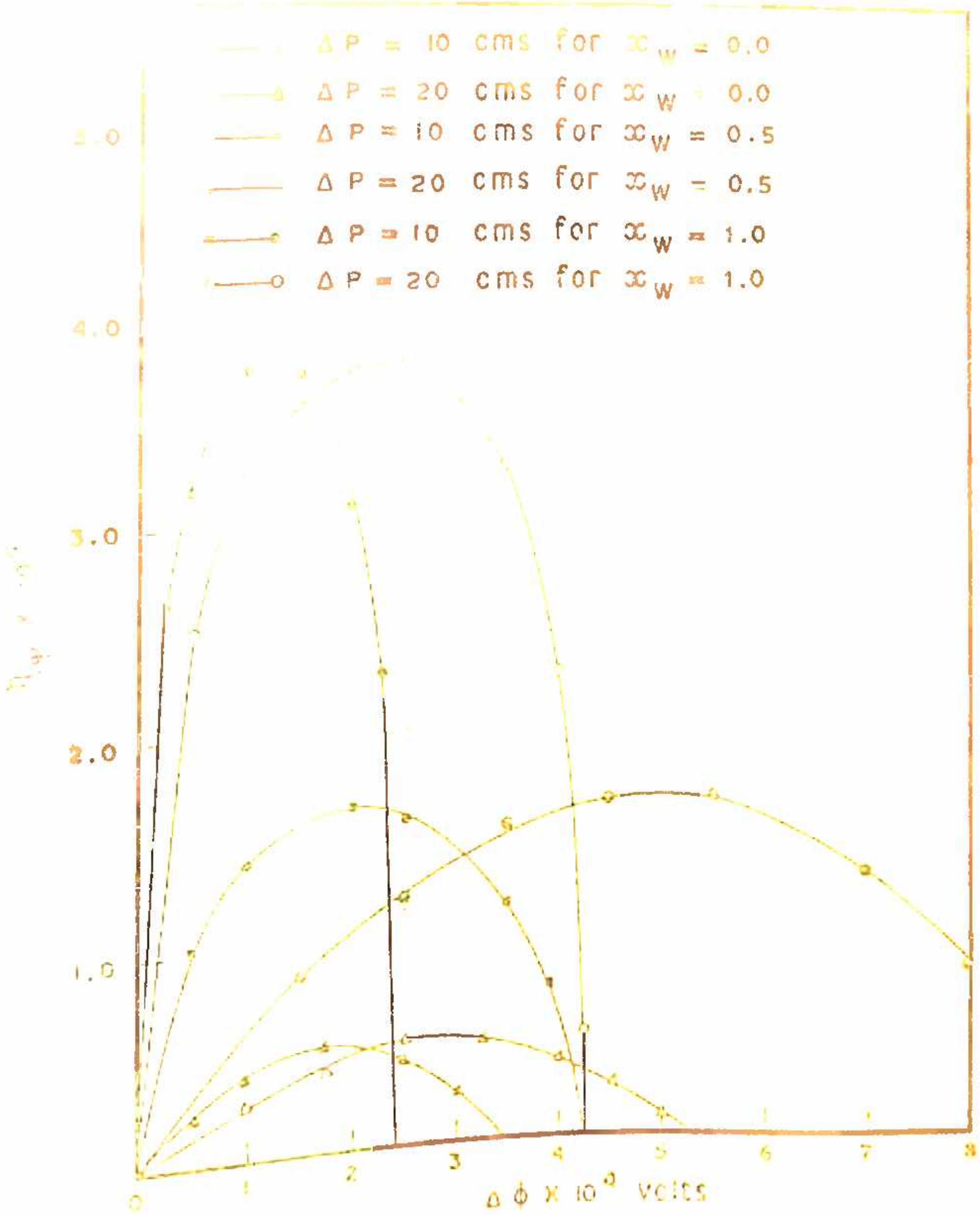


FIG.II.26 VARIATION OF η_ψ WITH POTENTIAL DIFFERENCE FOR ACETONE-WATER MIXTURES.

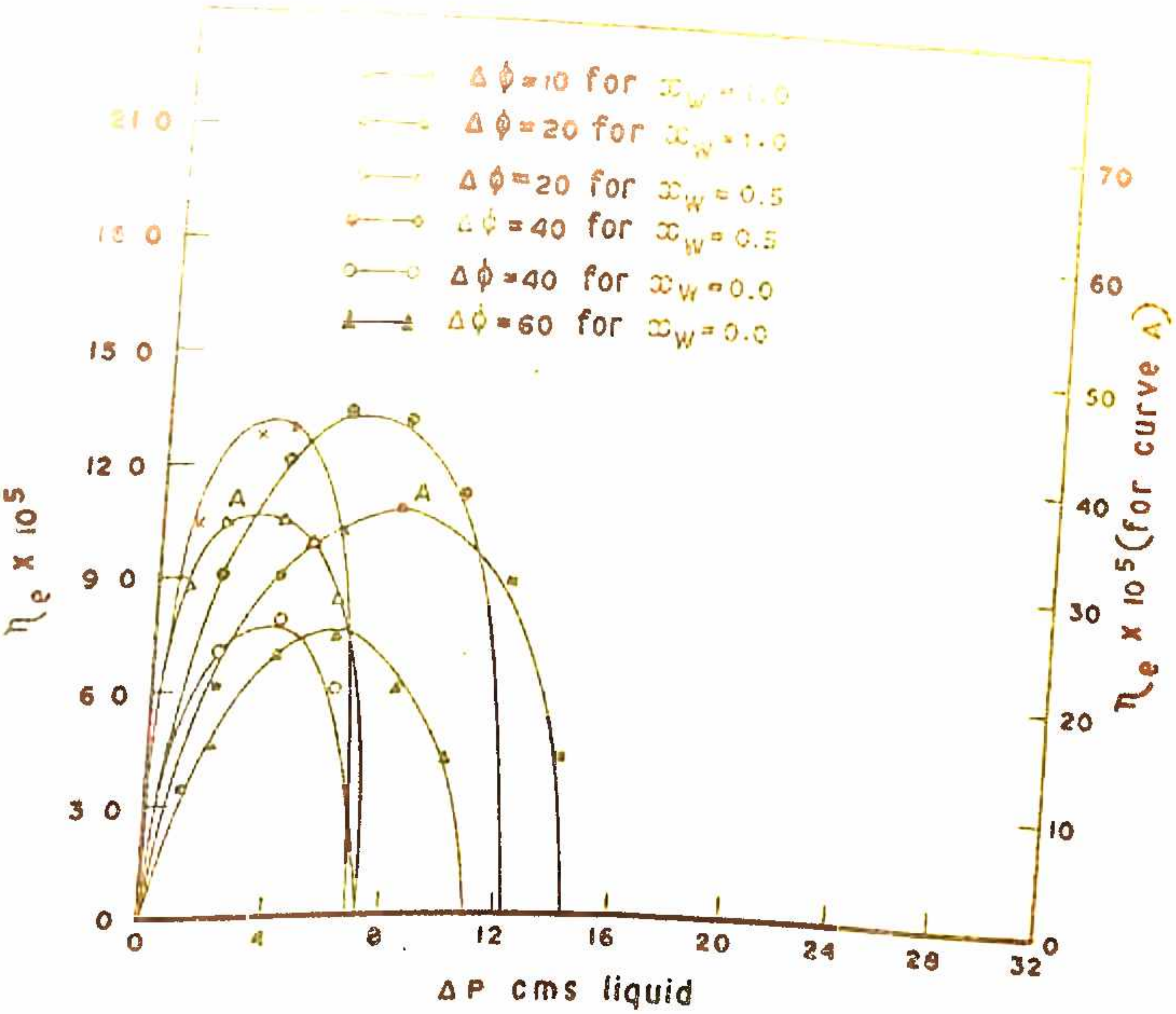


FIG. II.27 VARIATION OF η_e WITH PRESSURE DIFFERENCE FOR METHANOL – WATER MIXTURES.

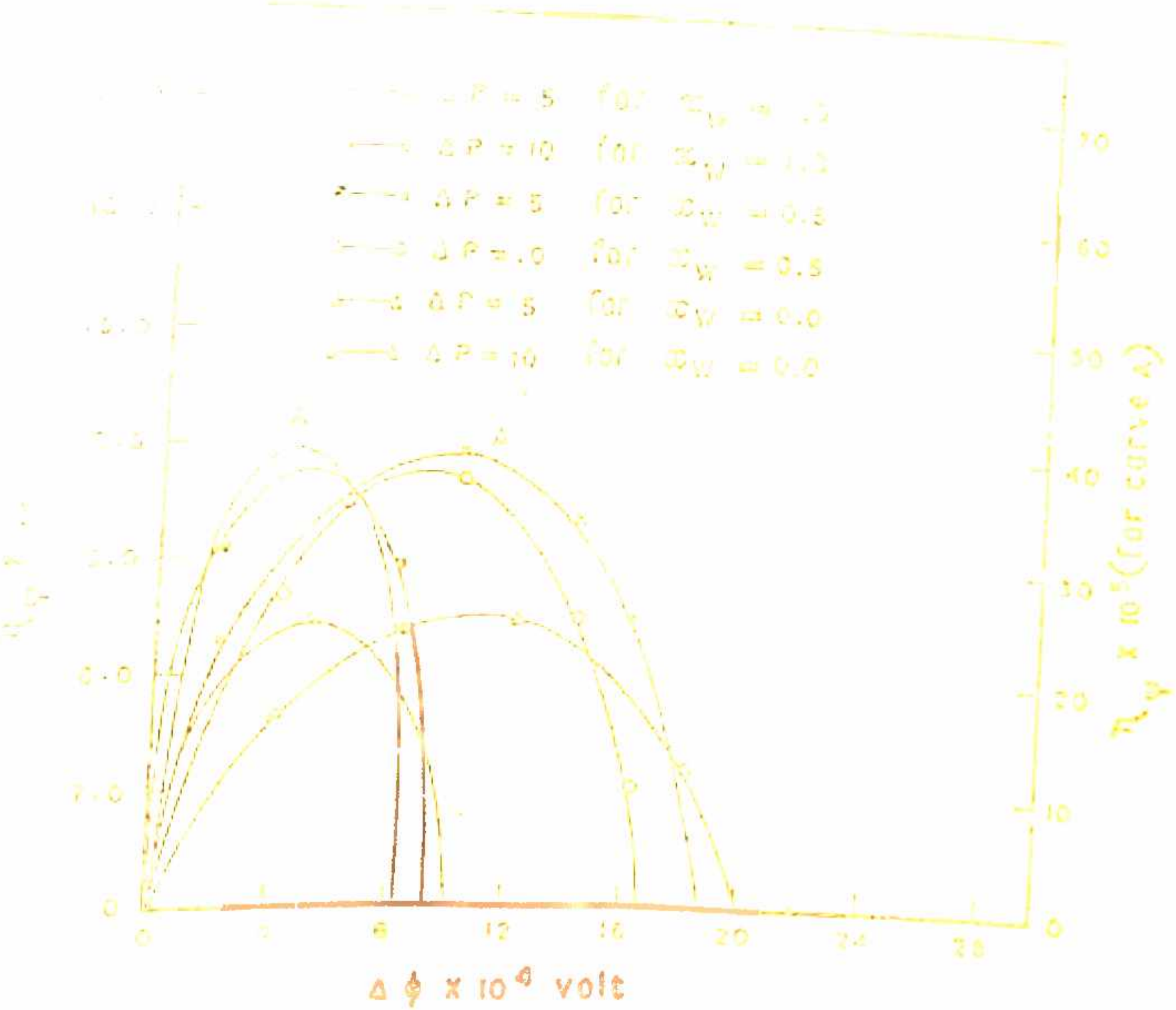


FIG. II.28 VARIATION OF η_ψ WITH POTENTIAL DIFFERENCE FOR METHANOL — WATER MIXTURES.

It has been shown by Gross and Osterle (1968) that $(\eta)_{max}$ is related to the phenomenological coefficients. That is

$$(\eta)_{max} = \frac{(1+\beta)^{\frac{1}{2}} - 1}{(1+\beta)^{\frac{1}{2}} + 1} \tag{II.25}$$

where β is called the figure of merit and is given by

$$\beta_{1o} = \left(\frac{L_{11}\ L_{oo}}{L_{1o}^{2}} - 1\right)^{-1} \tag{II.26}$$

The term $(L_{11}L_{oo}/\ L_{1o}^{2})$ in equation (II.26) is the reciprocal of the square of the degree of coupling defined by Kedem and Caplan (1965). Since β is much smaller in comparison to unity equation (II.25) approximates to

$$(\eta)_{max} \approx \beta/4 \tag{II.27}$$

The figure of merit β in the specific cases of electro-osmosis and streaming potential can be written as

$$\beta_{e} = \left(\frac{L_{22}\ L_{11}}{L_{12}^{2}} - 1\right)^{-1} \tag{II.28}$$

and

$$\beta_{\psi} = \left(\frac{L_{22}\ L_{11}}{L_{21}^{2}} - 1\right)^{-1} \tag{II.29}$$

Because of Onsager's reciprocal relation $L_{io} = L_{oi}$ it is obvious from equation (II.26) that

$$\beta_{io} = \beta_{oi} \quad \text{or} \quad \beta_e = \beta_\psi \qquad \text{(II.30)}$$

which implies that values of $(\eta)_{max}$ given by eqn. (II.25) or (II.27) would remain the same for either direction of conversion, i.e.,

$$(\eta_e)_{max} = (\eta_\psi)_{max} \qquad \text{(II.31)}$$

The values of β and $(\eta)_{max}$ calculated from the values of the phenomenological coefficients (table II.1 to II.3) are given in tables II.4 to II.6. The validity of the relations (II.30) and (II.31) can be seen from these tables in all cases i.e., for the various compositions of all the three mixtures.

Since $(\eta)_{max}$ is a function of β only which in turn is a function of the phenomenological coefficients only, $(\eta)_{max}$ has to be independent of the input thermodynamic forces because in the linear region the phenomenological coefficients are constant and do not depend upon thermodynamic forces.

II.5 REFERENCES

Abrahamson, H.A. (1934): Electrokinetic phenomena and their application to biology and medicine (cf. Colloid Science, I. Irreversible systems; Kruyt, H.R. ed.). Elsevier Pub. Co ., Amsterdam.

Adam, N.K.(1941): The physics and chemistry of surfaces, 3rd edition. Oxford Univ. Press, Oxford.

Blokhra, R.L., and Singhal, T.C. (1973): Non equilibrium thermodynamic studies of electrokinetic effects III - Amides. Electroana. Chem. Inter. Electro Chem. 48, 353.

Blokhra, R.L., and Singhal, T.C. (1974): Non equilibrium thermodynamic studies of electrokinetic effects IV. Acqueous methanol. Electroana. Chem. Inter. Electro. Chem. 57, 19.

De Groot, S.R., and Mazur, P. (1962): Non equilibrium thermodynamics. North Holland Pub. Co., Amsterdam.

Gross, R.J., and Osterle, J.F. (1968): Membrane transport characteristics of ultra fine capillaries. J. Chem. Phys. 49, 228.

Haase, R. (1969): Thermodynamics of irreversible processes. Addition-Wesley, New York.

Hasted, J.B. (1973): In Water - A comprehensive treatise. (Franks, F.ed) Plenum Press, New York.

Hodgmann, C.D.(ed.) (1964): Handbook of chemistry and physics. Chemical Rubber Co., Cleveland, Ohio.

Hwang, S.T., and Kammermeyer, K. (1975): Techniques of chemistry. Vol. 7. Membranes in separations. John Wiley and Sons Inc., New York.

Katchalsky, A., and Curran, P.F.(1965): Non-equilibrium thermodynamics in biophysics. Harvard University Press, Cambridge.

Kedem, O., and Caplan, S.R. (1965): Degree of coupling and its relation to efficiency of energy conversion. Trans. Faraday Soc. 61, 1897.

Lacey, E.R., and Loeb, S.(ed) (1972): Industrial processing with membranes. John Wiley and Sons Inc., New York.

Lakshminarayanaiah, N.(1969): Transport phenomena in membrane. Academic press, New York.

Manning, G.S.(1972): On the correlation of solute permeability and reflection coefficient for rigid membranes with high solvent content. J. Phys. Chem. 76, 393.

Marinsky, J.A.(ed) (1966): Ion exchange Vol. 1. Marcel Dekker Inc., New York.

Mazur, P., and Overbeek, J.Th.G.(1951): Electro-osmosis and streaming potentials in diaphragms, II. Quantitative relation between electrokinetic effects. Rec. Trav. Chem. 70, 83.

Meares, P.(ed) (1976): Membrane separation processes. Elsiver Scientific Pub. Co. Amsterdam.

Morrison, F.S., and Osterle, J.F.(1965): Electrokinetic energy conversion in ultrafine capillaries. J.Chem. Phys. 43, 2111.

Osterle, J.F.(1964a): A unified treatment of the thermodynamics of steady state energy conversion. Appl. Sci. Res. 12, 425.

Osterle, J.F.(1964b): Electrokinetic energy conversion. J. Appl. Mecha. 31, 161.

Overbeek, J.Th.G.(1952): Colloid Science. Vol. I. Irreversible Systems (Kruyt, H.R. ed.). Elsevier Publishing Co., London.

Overbeek, J.Th.G.(1953a): Thermodynamics of electrokinetic phenomena. J. Colloid Sci. 8, 420.

Overbeek, J.Th.G.(1953b): Significance of constants involved in electrochemical double layers. Natl. Bur. Standards Circ. No. 524, 213.

Prigogine, I. (1968): An introduction to the thermodynamics of irreversible processes. Wiley, New York.

Rastogi, R.P., and Jha, K.M. (1966): Cross-phenomenological coefficients. 4. Electro-osmosis of acetone. Trans. Faraday Soc. 62, 585.

Rastogi, R.P. (1969a): Irreversible thermodynamics of electro-osmotic effects. J. Scint. Ind. Research 28, 284.

Rastogi, R.P., Kehar Singh, and Sri Nath Singh (1969b): Non linear phenomenological equation for electro-osmosis. J. Phys. Chem. 73, 1593.

Rastogi, R.P., Kehar Singh, and Srivastava, M.L. (1969c): Cross phenomenological coefficients XI. Non linear transport equations. J. Phys. Chem. 73, 46.

Rastogi, R.P., Srivastava, M.L. and Sri Nath Singh (1970): Cross phenomenological coefficients 13. Electro-osmotic transport in membranes. J.Phys.Chem. 74, 1960.

Smit, J.A.M., Eijsermans, J.C., and Staverman, A.J.(1975): Friction and partion in membranes, J. Phys. Chem. 79, 2168.

Speigler, K.S. (1958): Transport processes in ionic membranes. Trans. Faraday Soc. 54, 1408.

Speigler, K.S. (1962): Salt water purification. Wiley, New York.

Srivastava, R.C., and Jain, A.K. (1975a): Non-equilibrium thermodynamics of electro-osmosis of water through composite clay membranes, 3. The electrokinetic energy conversion. J. Hydrol. 25, 339.

Srivastava, R.C. and Jain, A.K. (1975b): Electro-osmosis of water through cellulose acetate membrane. J. Polymer Sci., Polymer Phys. ed. 13, 1603.

Vinogradov, S.N., and Linnel, R.H. (1971): Hydrogen bonding Van Nostrand Reinhold, London.

Vogel, A.I. (1956): A text book of practical organic chemistry 3rd ed. Longmans, London.

CHAPTER III

ELECTRO-OSMOTIC PERMEABILITY OF COMPOSITE CLAY MEMBRANES

ELECTRO-OSMOTIC PERMEABILITY OF COMPOSITE CLAY MEMBRANES

III.1 INTRODUCTION

The water content in soil is rarely static, water additions from snow melt, rainfall, irrigation or condensation and water loses from evaporation transpiration or drainage occur most of the time. Thus the distribution and migration of water in soils are dependent on may fluxes such as those arising from the internal energy of the water itself, and from external and surficial mechanisms and driving forces due to thermal, ionic, osmotic, gravitational, hydraulic and other gradients. The rate of movement or migration of water will depend on the magnitude of the forces and gradients and also on the factors determining the transmission coefficient or hydraulic conductivity of the soil. Again water movement in soils can be broadly classified into two as saturated flow and unsaturated flow (Baver, 1956; Childs, 1969; Hadas, etal., 1973; Hillel, 1971; Low, 1961; Young and Warkentin, 1975). The importance of soil-water system in nature evolved studies in various directions. The most important among them is the soil physics which is becoming increasingly an exact and quantitative science in the study of soil-water phenomena (Babcock and Overstreet, 1955; Bolt and Frissel, 1960; de Jong, 1968; Edlefsen and Anderson, 1943; Miller and Miller, 1955,1956; Philip, 1960).

The application of non-equilibrium thermodynamics to soil water phenomena is a new exploration in the field of soil physics (Cary, 1964; Groenevelt and Bolt, 1969; Srivastava and Rajpal, 1973; Taylor and Cary, 1960; Winterken, 1958).

In the present chapter we report our studies on the coupled flow processes through composite clay membranes consisting of two different clay membranes arranged in a parallel array and in a series array.

The theory for the permeability of the composite membranes, on the basis of non-equilibrium thermodynamics, has been developed by Kedem and Katchalsky (1963a,b,c). This theory was primarily intended for biological membranes. It is therefore worthwhile to explore, to what extent the theory of Kedem and Katchalsky can be helpful in analysing the data on flow through composite porous media that one comes across in geo-systems, e.g. porous soils or rocks having layered structure. It was with this object in view that studies on the electro-osmosis of water through composite clay membranes were undertaken recently (Srivastava and Jain, 1975a,b,c). The composite clay membranes chosen for these studies were of two types - (i) Kaolinite and bentonite clay membrane elements arranged in a parallel array, and (ii) kaolinite and bentonite clay membrane elements arranged in a series array. These studies revealed that the combination rules for the phenomenological coefficients as predicted by the theory of Kedem and Katchalsky (1963a,b,c,) cannot be taken to be valid in toto and need modifications in the case of composite clay membrane consisting of kaolinite and bentonite clay membrane elements arranged in both parallel and series arrays. This is because, in the treatment of Kedem and Katchalsky the validity of linear phenomenological relations in the constituent membrane elements of the composite system as well as in the composite membrane is presupposed, while in the composite clay systems studied by Srivastava and Jain (1975a,b,c,), the bentonite clay membrane element does not obey the usual linear and homogeneous form of phenomenological equation for the mass flux in presence of both pressure difference and electrical potential difference (Srivastava and Avasthi, 1973; Srivastava and Jain, 1975a, Swartsendruber, 1962).

In the present studies, therefore, the bentonite clay membrane element has been replaced by the crysotile clay membrane element. That is to say the two composite clay membrane systems presently chosen are (i) kaolinite clay membrane elements arranged ina a parallel and crysotile clay membrane array, and (ii) kaolinite and crysotile clay membrane elements arranged in a series array. Since both the constituents (i.e. kaolinite and crysotile) of the composite clay systems are expected to obey linear laws, we can expect greater correspondence between experimental data and the theory of Kedem and Katchalsky.

III.2 EXPERIMENTAL

A. Materials

Kaolinite and crysotile clays supplied by M/s Impex Chemical Corporation Bombay and triple distilled water were used in the studies.

B. Apparatus

The all glass electro-osmotic cell (Fig. [III.1]) used in the earlier studies by Srivastava and Jain (1975a,b) was used in the present studies also. It consisted of four parts. Part I of the apparatus consisted of a glass tube AA^1 of 35 cm length with a B-24 socket at each end and one B-29 joint in the middle at X_1. The electrodes S_1 and S_2 were fused to the glass tubes Q and R, which in turn were fused to B-24 cones. Mercury was filled in Q and R to provide electrical contacts. All electrodes (S_1, S_2, S_3 and S_4) were made from coiled platinum wire of 0.1 cm in diameter. The

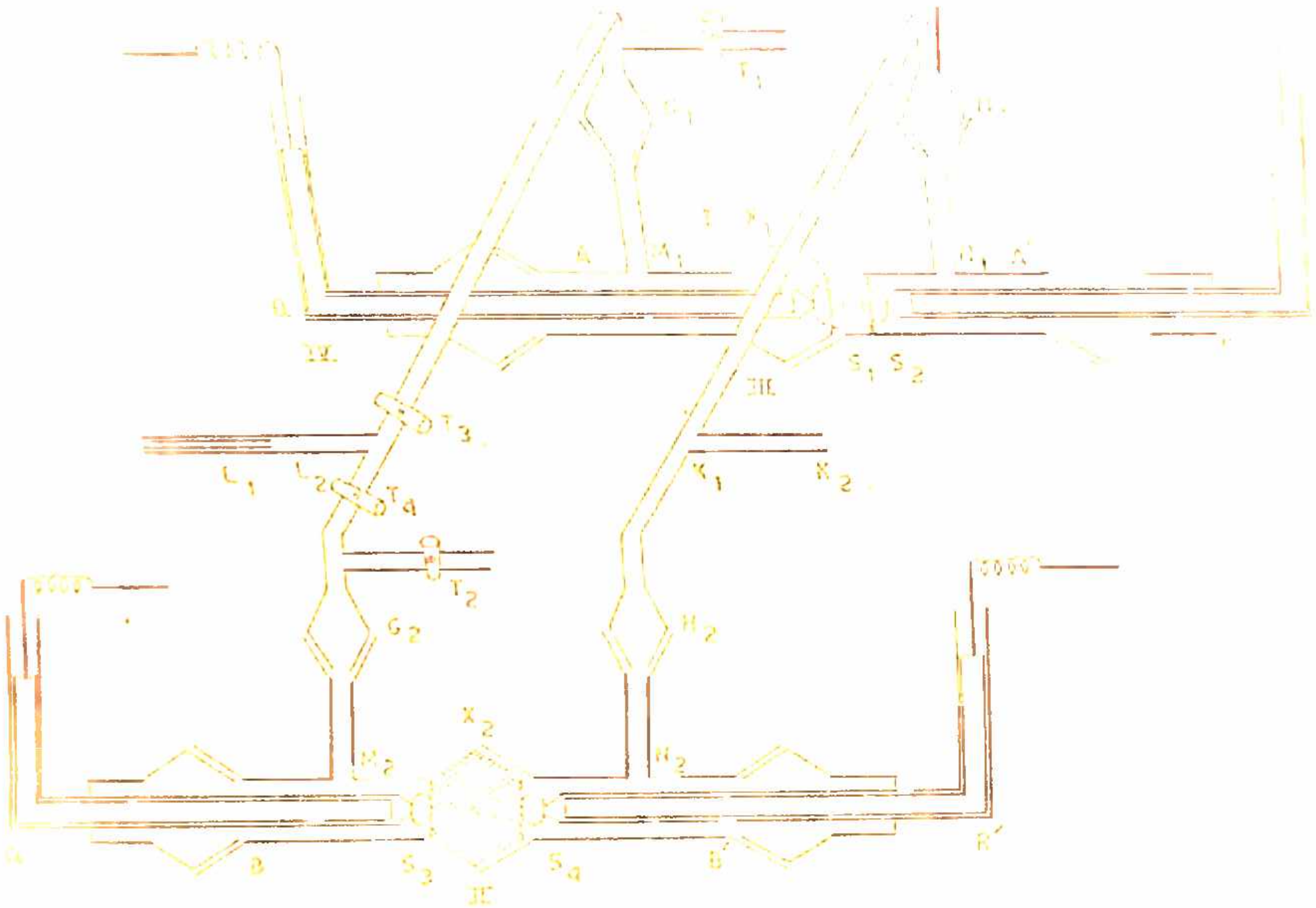


FIG.III.1 ELCTRO OSMOTIC CELL

electrodes were so adjusted that they just pressed the two sides of the clay plugs. The two vertical tubes M_1 and N_1 of 10 cm length emerging from the tube AA^1 were each provided with a B-14 socket at G_1 and H_1. Part II of the apparatus was exactly similar to part I. Part III was a glass tube bent twice at right angles, with B-14 cones, at the ends H_1 and H_2. The tube K_1K_2 provided in part III of the apparatus could be connected to the pressure head. Part IV of the apparatus was also a glass tube bent twice at right angles and having B-14 cones at the ends G_1 and G_2. The purpose of the capillary L_1L_2 of 20 cms length and a diameter of 0.285 cm was to measure the water flux. The stopcocks T_1 and T_2 were helpful in filling water in the electro-osmotic cell and also for adjusting the water meniscus in the capillary L_1L_2. The purpose of the stopcocks T_3 and T_4 was to isolate part I and part II of the apparatus from each other, as and when desired. As is obvious from Fig. |III.1| part I and II of the apparatus could be joined and detached from each other through parts III and IV.

C. Procedure

After thorough cleaning of the electro-osmotic cell, highly compressed kaolinite and crysotile clay plugs were placed in the cell (represented in Fig. [III.1] as K and C) by means of filter paper and tight rubber washers. The cell was filled with triple distilled water and allowed to stand for several days, so that the clay plugs were completely wet with water. Hydraulic permeability measurements were then made and when reproducible values were obtained it was concluded that the clay plugs were completely wet with water. As shown in Fig. [III.1], the crysotile plug was placed in the vicinity of the socket B-29 at X_1 of part I and the kaolinite plug was placed within the B-29 cone at X_2 of part II. This was purposely done, because, for the measurement of permeabilities through the series array, portion RX_1 of part I with the B-29 socket and portion Q^1X_2 of part II with B-29 cone could be taken out and joined together whenever desired, to give an electro-osmotic cell with the series clay membrane (Fig. [III.2]).

For the measurement of hydraulic permeabilities through kaolinite, crysotile, and composite parallel array of membrane systems, known pressure differences were applied across the clay plugs by connecting the tube K_1K_2 to a pressure head and the movement of water in capillary L_1L_2 was noted with time using a cathetometer with a least count of 0.001 cm, and a stop watch with a least count of 0.1 sec.

For the measurements of electro-osmotic velocities through kaolinite, crysotile, and composite parallel array of membrane systems, known potential differences were applied across the various clay plugs by connecting the

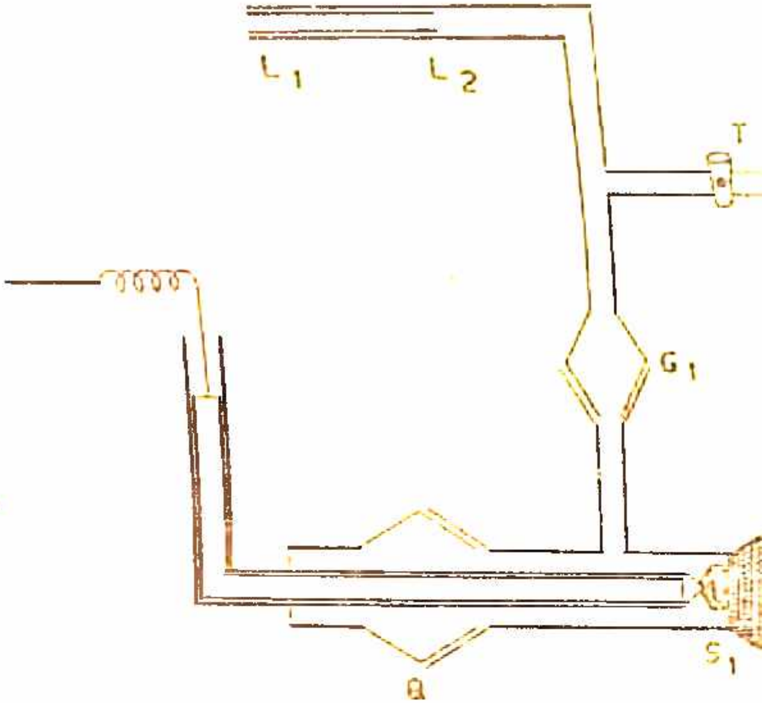
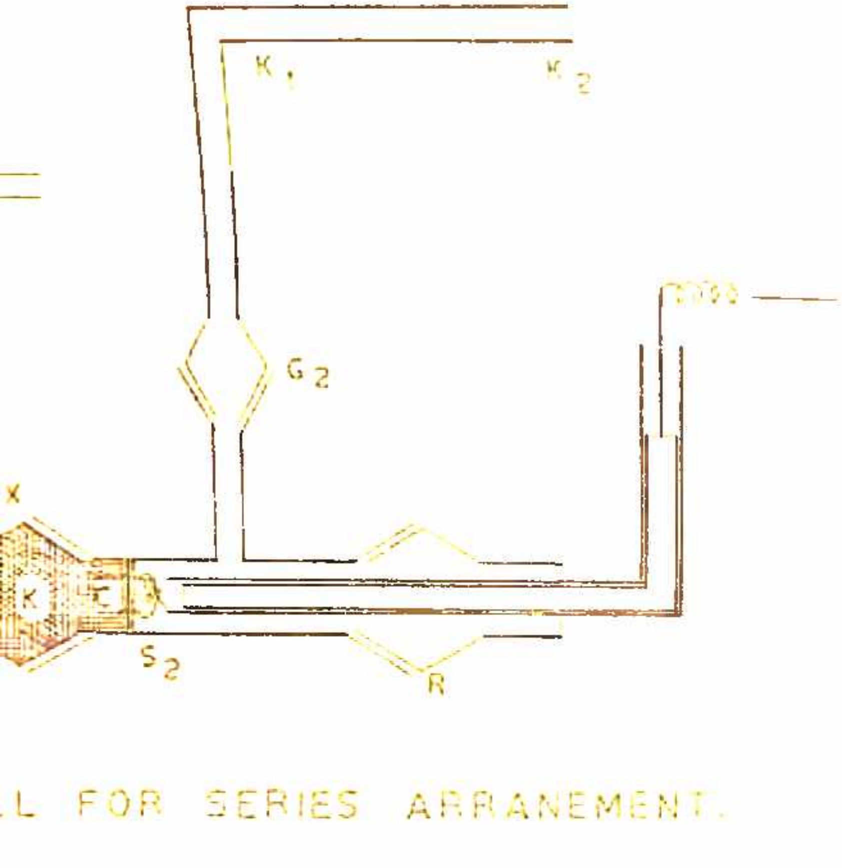


FIG. III.2 ELECTRO OSMOLIC CEL



LL FOR SERIES ARRANEMENT.

respective electrodes to the terminals of an electronically operated power supply (Systronics, Type 612) and the water flow induced by the various potential differences applied was observed in the capillary L_1L_2. Obviously, for the measurement of electro-osmotic permeability through the parallel composite array membrane the electrodes S_1 and S_3 were connected to one terminal of the power supply and the electrodes S_2 and S_4 were connected to the other. The uncertainty in the applied potential difference was ± 0.05 V. In all the measurements of electro-osmotic velocity the condition $\Delta P = 0$ was enforced on the system. The current strength in the system was not allowed to exceed 5 mA. For this, water in the electro-osmotic cell was changed several times during the experiment because it was expected that the conductivity of the water would increase due to electrolysis near the electrodes.

The streaming potentials across kaolinite, crysotile and parallel composite array of membrane systems were measured with the help of a V.T.V.M. (Philips microvoltmeter 6020/90). Known pressure differences were applied across the clay plugs and when the flow in the capillary L_1L_2 became steady, the streaming potential was measured by connecting the electrodes across the various clay plugs to the terminals of the V.T.V.M. The asymmetry potential of the electrodes, which was measured before and after the experimental run, was taken into account while recording the values of the streaming potentials. The electrical resistances across kaolinite, crysotile, and parallel composite array of membrane systems were measured with the help of a conductivity meter (Toshniwal, Type CL01/02A), and the values of the streaming current were estimated using the values of the resistances thus obtained. It may be pointed out that for measurements of all the three quantities, viz. hydraulic permeability, electro-osmotic velocity and streaming potential through kaolinite, stop cock T_3 was closed and T_4 was kept open. Similarly for the measurements in the case of crysotile stop-cock T_4 was closed and T_3 was kept open, whereas, for all measurements through the parallel composite membrane both the stop-cocks T_3 and T_4 were kept open. Stop-cocks T_1 and T_2 were kept closed throughout all measurements.

After all measurements through the composite clay membrane consisting of kaolinite and crysotile in parallel array and its constituent membrane elements were completed portion RX_1 with the socket of the B-29 joint of part I and portion Q^1X_2 with the cone of the B-29 joint of part II of the apparatus (Fig. [III.1]) were taken out and joined together. This gave an electro-osmotic cell for the series arrangement. The electro-osmotic cell thus formed is depicted in Fig. [III.2]. The methods for the measurement of hydraulic permeability, electro-osmotic velocity and streaming potentials have already been described.

All measurements in case of both parallel and series composite array membrane systems were made under constant temperature condition by placing the electro-osmotic cell in a thermostat set at 40 ± 0.1°C.

III.3 RESULTS AND DISCUSSION

The data on hydraulic permeability, electro-osmotic velocity, streaming potential, and streaming current for the Kaolinite-water, crysotile-water and the composite membranes consisting of kaolinite and crysotile clay membrane elements in parallel and series arrangements are plotted in Figs. [III.3] to [III.6]. The straight line plots passing through the origin in Figs. [III.3] to [III.6] confirm the validity of the linear and homogeneous form of the phenomenological equations (De Groot, 1966)

$$J_v = L_{11} \Delta P + L_{12} \Delta\phi \qquad (III.1)$$

$$I = L_{21} \Delta P + L_{22} \Delta\phi \qquad (III.2)$$

for the simultaneous transport of water and electricity through the constituent clay membrane elements as well as the composite membranes consisting of their parallel and series arrangement. In equations (III.1) and (III.2) J_v stands for the volume flux of water, I stands for the flow of electricity,

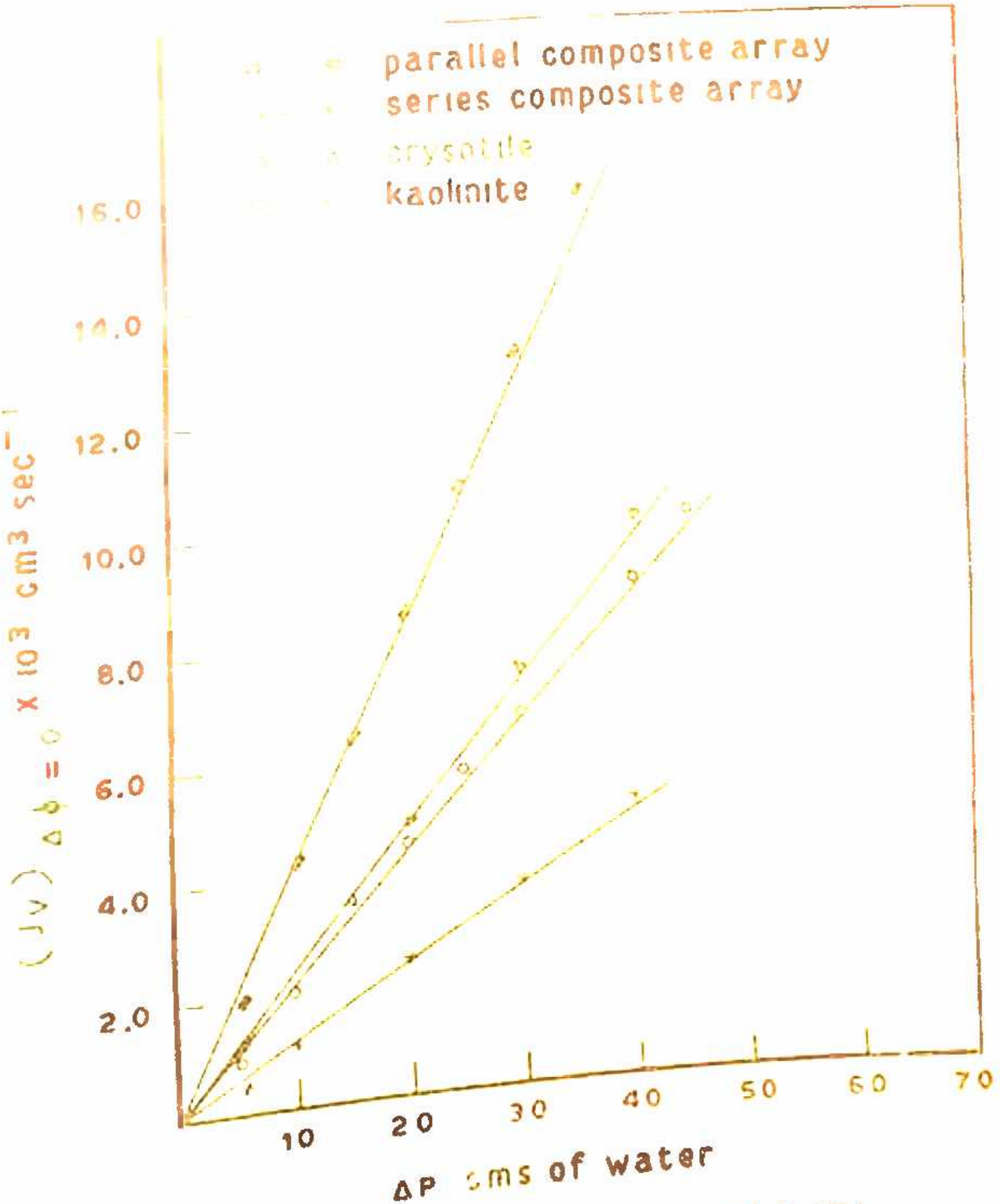


FIG. III. 3 HYDRAULIC PERMEABILITY DATA.

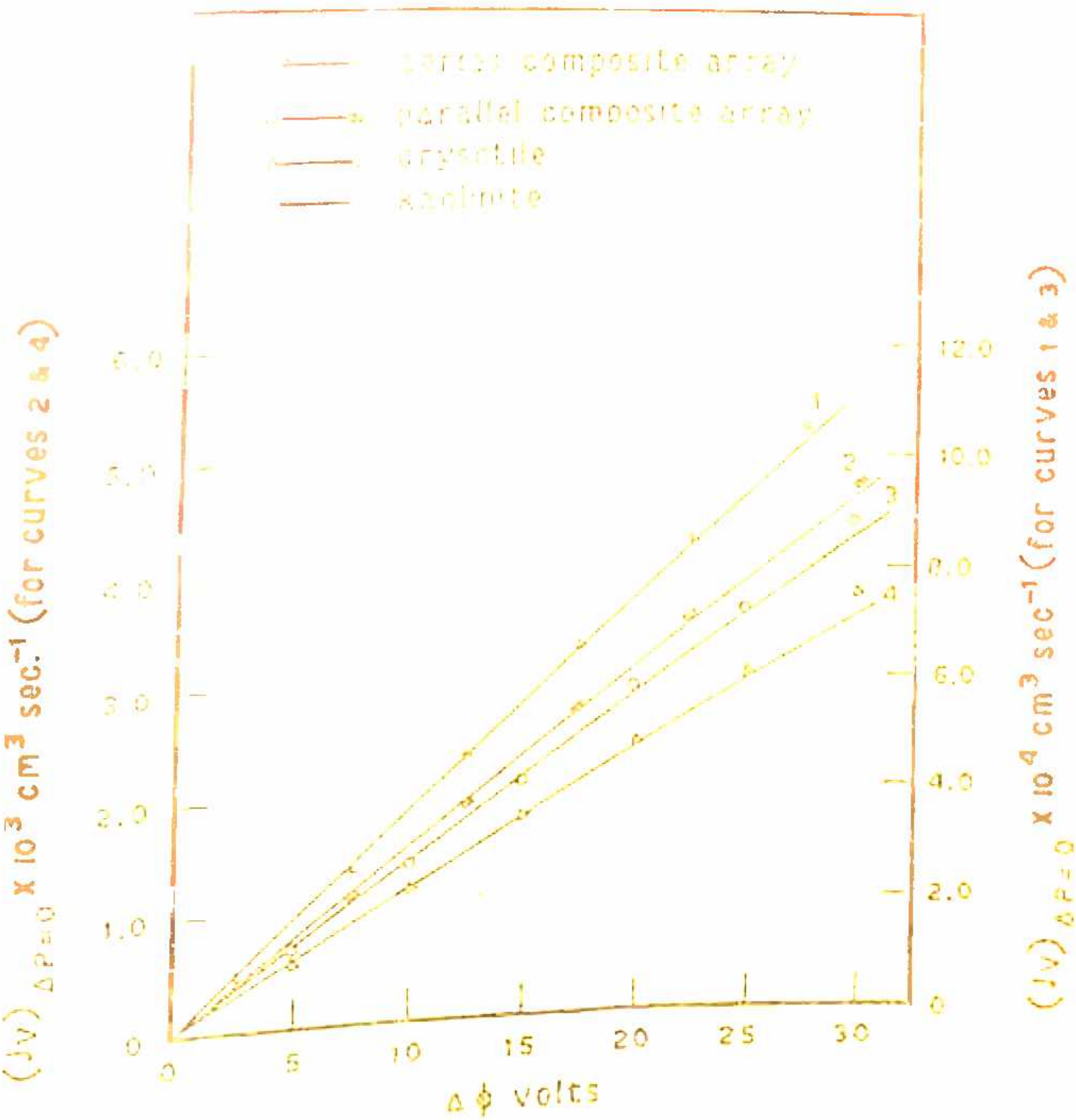
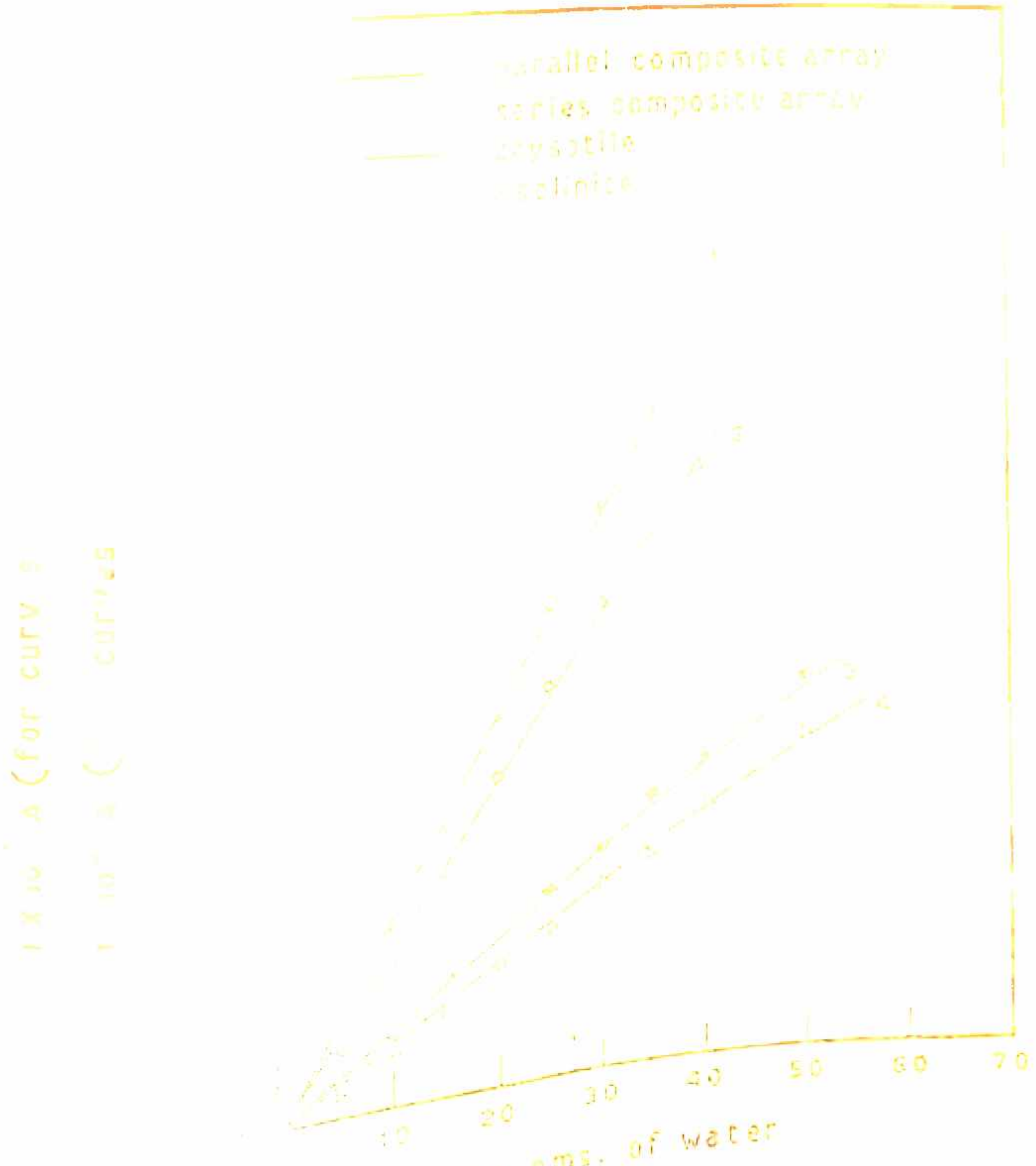


FIG. III.4 ELECTRO-OSMOTIC VELOCITY DATA.



F STREAMING CURRENT DATA.

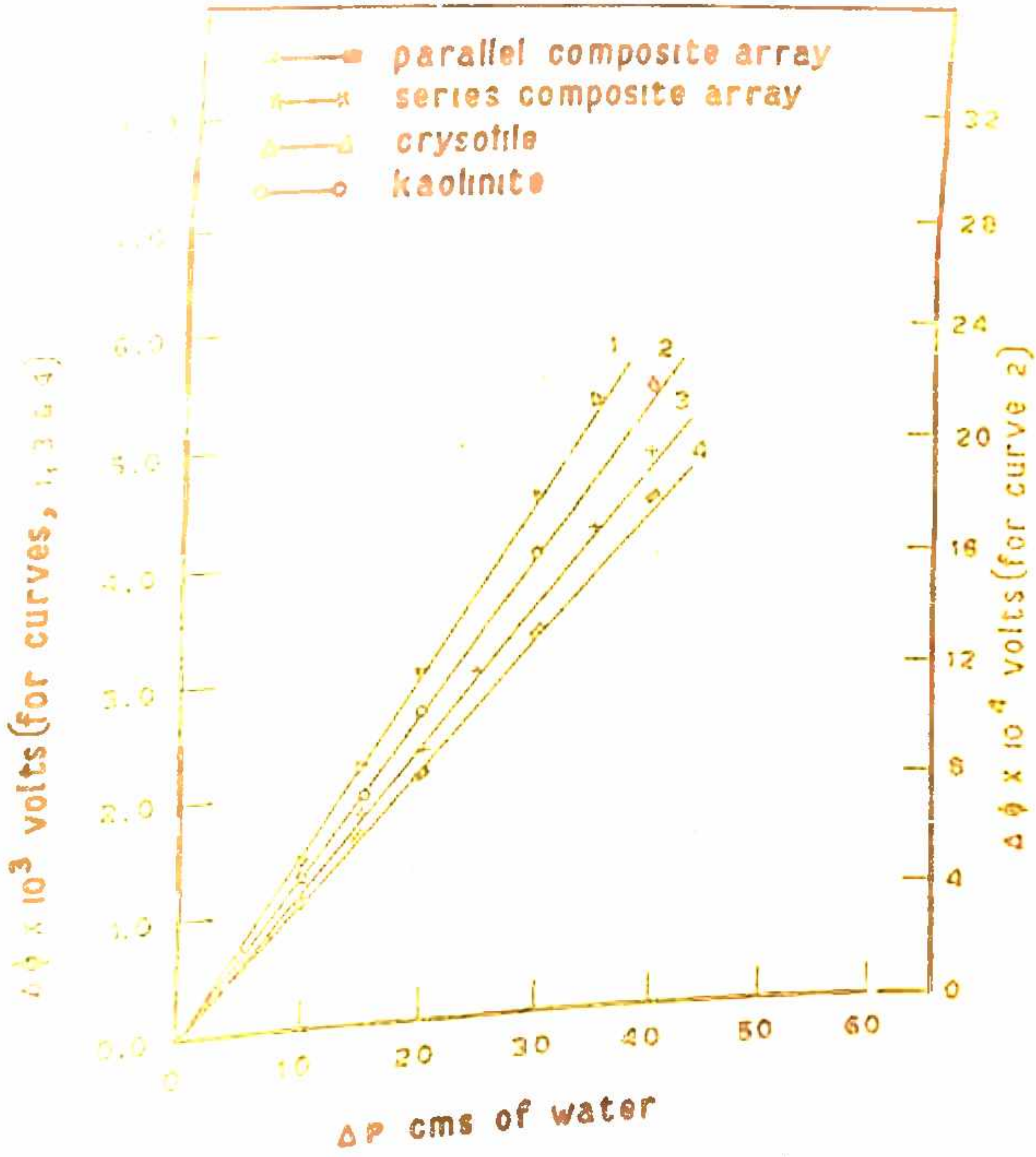


FIG. III.6 STREAMING POTENTIAL DATA

ΔP and $\Delta\phi$ are the pressure difference and the electrical potential difference respectively. The coefficients L_{ik} are called the phenomenological coefficients. The values of the various phenomenological coefficients estimated from the slopes of the straight lines plots in Figs. [III.3] to [III.6] are given in Table III.1. From the values of the phenomenological coefficients given in Table III.1 the validity of the Onsager's reciprocal relations i.e.

$$L_{12} = L_{21} \tag{III.3}$$

is obvious for the constituent clay membrane elements i.e. kaolinite and crysotile and also for the parallel and series composite clay membrane systems.

A. The Parallel Composite Membrane

The data can be utilised to relate the phenomenological coefficients characterising the composite parallel membrane as a whole to the coefficients for the constituent clay membrane elements. In the theory of Kedem and Katchalsky (1963b) for the parallel composite membrane the linear phenomenological relations between fluxes and forces are assumed to be valid for the composite parallel membrane as well as for the constituent membrane elements. It is further assumed that the flows are parallel to the x-coordinate axis, normal to membrane surface and are

TABLE III.1

Phenomenological Coefficients for Kaolinite,Crysotile,parallel composite and series composite clay systems.

Phenomenological coefficients.	Kaolinite	Crysotile	Parallel composite	Series composite
$L_{11} \times 10^7$ $(cm^5\ sec^{-1}\ dyn^{-1})$	2.245	2.449	4.762	1.173
$L_{12} \times 10^5$ $(cm^3\ AJ^{-1})$	2.857	12.000	15.00	3.70
$L_{21} \times 10^5$ $(cm^3\ AJ^{-1})$	3.175	14.83	15.66	3.402
$L_{22} \times 10^5$ (Ohm^{-1})	5.55	7.693	12.33	3.031

independent of x. The force considered are differences of the potential acting across the membrane. Since the same compartment maintains contact with all elements on each side of the membrane, the same force which operates on the parallel composite membrane is also operative on all the constituent membrane elements. This means that the forces are perpendicular to the membrane surface and that no lateral forces have to be considered and hence no lateral flows creating internal circulation need to be considered and all lines of flows may be assumed to be parallel. Thus the total flow through the parallel composite membrane is assumed to be the sum of the total flows through the constituent membrane elements. This in the present case of parallel composite clay membrane would mean

$$(J_v)^p_{\Delta\phi=0} = (J_v)^k_{\Delta\phi=0} + (J_v)^c_{\Delta\phi=0} \qquad \text{(III.4a)}$$

$$(J_v)^p_{\Delta P=0} = (J_v)^k_{\Delta P=0} + (J_v)^c_{\Delta P=0} \qquad \text{(III.4b)}$$

$$(I)^p_{\Delta\phi=0} = (I)^k_{\Delta\phi=0} + (I)^c_{\Delta P=0} \qquad \text{(III.4c)}$$

$$(I)^p_{\Delta P=0} = (I)^k_{\Delta P=0} + (I)^c_{\Delta P=0} \qquad \text{(III.4d)}$$

The superscripts p, k and c stand for the parallel composite membrane, kaolinite clay membrane and the crysotile clay membrane respectively. The data on hydraulic permeability and electro-osmotic velocity, given in Tables III.2 and III.3, confirms the validity of equations (III.4a) and (III.4b). Equations (III.4c) and (III.4d) represent the well established combination rules for the flow of electrical current through conductors arranged in parallel to each other. The streaming current data in Table III.4 confirm the validity of equation (III.4c). In view of the validity of the linear phenomenological equations (III.1) and (III.2) for the composite parallel membrane and its constituent membrane elements and the fact that the same force which operates across the parallel composite membrane is also operative on the constituent clay membrane elements, the equations (III.4a) to (III.4d) would in turn imply

$$\left(\frac{J_v}{\Delta P}\right)^{p}_{\Delta\phi=0} = \left(\frac{J_v}{\Delta P}\right)^{k}_{\Delta\phi=0} + \left(\frac{J_v}{\Delta P}\right)^{c}_{\Delta\phi=0} \qquad \text{(III.5a)}$$

or $$L^{p}_{11} = L^{k}_{11} + L^{c}_{11}$$

$$\left(\frac{J_v}{\Delta \phi}\right)^{p}_{\Delta P=0} = \left(\frac{J_v}{\Delta \phi}\right)^{k}_{\Delta P=0} + \left(\frac{J_v}{\Delta \phi}\right)^{c}_{\Delta P=0} \qquad \text{(III.5b)}$$

or $$L^{p}_{12} = L^{k}_{12} + L^{c}_{12}$$

TABLE III.2

Hydraulic Permeability data for Kaolinite, Crysotile, parallel composite and series composite clay systems.

ΔP cms of water	$(J_v)^{k}_{\Delta\phi=0} \times 10^{3}$ ($cm^3 sec^{-1}$) (1)	$(J_v)^{c}_{\Delta\phi=0} \times 10^{3}$ ($cm^3 sec^{-1}$) (2)	Sum of the quantities in colmns. 1 and 2. $\times 10^{3}$ (3)	$(J_v)^{p}_{\Delta\phi=0} \times 10^{3}$ ($cm^3 sec^{-1}$) (observed value) (4)	Deviation (in %) between (3) and (4)	$(J_v)^{s}_{\Delta\phi=0} \times 10^{3}$ (cm^3 sec^{-1}) (observed value)
5	1.02	1.15	2.17	2.07	5.00	0.5879
10	2.10	2.35	4.45	4.20	6.26	1.196
15	3.20	3.60	6.80	6.60	2.80	1.734
20	4.30	4.80	9.10	9.00	1.10	2.317
25	5.35	6.00	11.35	11.15	1.80	2.90
30	6.47	7.25	13.75	13.60	0.90	3.48
35	7.55	8.70	16.25	16.00	1.50	4.05

TABLE III.3

Electro-osmotic velocity data for Kaolinite, Crysotile, Parallel Composite and series composite clay Systems.

$\Delta\phi$ Volts	$(J_v)^k_{\Delta P=0} \times 10^4$ ($cm^3 sec^{-1}$) (1)	$(J_v)^c_{\Delta P=0} \times 10^3$ ($cm^3 sec^{-1}$) (2)	Sum of the quantities in columns (1) and (2) $\times 10^3$ (3)	$(J_v)^P_{\Delta P=0} \times 10^3$ ($cm^3 sec^{-1}$) (observed value) (4)	Deviation (in %) between columns (3) and (4)	$(J_v)^s_{\Delta P=0} \times 10^4$ ($cm^3 sec^{-1}$) (observed value)
5.0	1.35	0.550	0.685	0.70	3.00	1.75
10.0	2.80	1.175	1.455	1.50	3.03	3.10
15.0	4.35	1.800	2.235	2.30	2.80	5.60
20.0	6.75	2.400	3.075	3.10	0.80	7.40
25.0	7.30	3.65	3.780	3.75	1.00	9.50
30.00	8.80	3.70	4.580	4.70	2.50	11.50

TABLE III.4

Streaming current data for Kaolinite, Crysotile, Composite parallel and composite series clay systems.[*]

ΔP cms of water.	$(I)^k_{\Delta\phi=0} \times 10^8$ (A) (1)	$(I)^c_{\Delta\phi=0} \times 10^7$ (A) (2)	Sum of the quantities in columns (1) and (2) $\times 10^7$ (3)	$(I)^p_{\Delta\phi=0} \times 10^7$ (A) (observed value) (4)	Deviation (in %) between colmn. (3) and (4).	$(I)^s_{\Delta\phi=0} \times 10^8$ (A) (observed value)
5.0	1.30	0.461	0.591	0.048	7.60	1.516
10.0	2.70	1.039	1.309	1.433	8.00	3.334
15.0	4.30	1.654	2.084	2.280	8.50	5.304
20.0	5.90	2.308	2.898	3.00	3.33	7.122
25.0	7.40	2.846	3.580	3.600	0.55	8.939
30.0	8.90	3.461	4.350	4.390	0.90	10.910
35.0	9.70	4.078	5.048	5.134	1.60	12.880
40.0	11.30	4.692	5.820	5.990	2.90	14.70

[*] Resistance of the systems : Kaolinite = 1.80 x 10^4 Ohms Composite Parallel = 7.5 x 10^3 Ohms
Crysotile = 1.30 x 10^4 Ohms Composite series = 3.3 x 10^4 Ohms

$$\left(\frac{I}{\Delta P}\right)^{p}_{\Delta\phi=0} = \left(\frac{I}{\Delta P}\right)^{k}_{\Delta\phi=0} + \left(\frac{I}{\Delta P}\right)^{e}_{\Delta\phi=0}$$

$$\text{or} \quad L^{p}_{21} = L^{k}_{21} + L^{e}_{21} \qquad \text{(III.5c)}$$

and

$$\left(\frac{I}{\Delta\phi}\right)^{p}_{\Delta P=0} = \left(\frac{I}{\Delta\phi}\right)^{k}_{\Delta P=0} + \left(\frac{I}{\Delta\phi}\right)^{e}_{\Delta P=0}$$

$$\text{or} \quad L^{p}_{22} = L^{k}_{22} + L^{e}_{22} \qquad \text{(III.5d)}$$

The validity of the combination rules (III.5a) to (III.5d) is obvious from the values of the phenomenological coefficients given in Table-III.1.

In view of the validity of the combination rules (III.5a) to (III.5d) the electro-osmotic pressure for the parallel composite clay membrane can be shown to be related to the electro-osmotic pressures for the constituent clay membrane elements by the following equation

$$\left(\frac{\Delta P}{\Delta\phi}\right)^{p}_{J_v=0} = \left(\frac{\Delta P}{\Delta\phi}\right)^{k}_{J_v=0}\left(\frac{L^{k}_{11}}{L^{k}_{11}+L^{e}_{11}}\right) + \left(\frac{\Delta P}{\Delta\phi}\right)^{e}_{J_v=0}\left(\frac{L^{e}_{11}}{L^{k}_{11}+L^{e}_{11}}\right) \qquad \text{(III.6)}$$

Similarly for the streaming potential

$$\left(\frac{\Delta\phi}{\Delta P}\right)^{p}_{I=0} = \left(\frac{\Delta\phi}{\Delta P}\right)^{k}_{I=0}\left(\frac{L^{k}_{22}}{L^{k}_{22}+L^{e}_{22}}\right) + \left(\frac{\Delta\phi}{\Delta P}\right)^{e}_{I=0}\left(\frac{L^{e}_{22}}{L^{k}_{22}+L^{e}_{22}}\right) \qquad \text{(III.7)}$$

B. Series Composite Membrane

In this section we will try to check the valdity of the combination rules for the various phenomenological coefficients in the case of the series composite membrane.

The assumptions made in the treatment of Kedem and Katchalsky (1963c) for the permeability of a series composite membrane are summarised below:

(a) In series array the same flow passes all the elements and the partial elementary flow equals the observable external flow. All the flows passing through the system are assumed to be stationary.

(b) The potentials of the thermodynamic driving forces are assumed to be continuous across all boundaries in the system (Kedem and Katchalsky, 1963c; Kirkwood, 1954). The condition of continuity in the present case is equivalent to the statement that the forces are additive across the system, that is the thermodynamic forces acting across the series membrane are equal to the sum of the forces acting across the constituent membrane elements.

The above condition of stationarity of flows, in the present case of composite series clay membrane would mean

$$(J_v)^{s}_{\Delta\phi=0} = (J_v)^{k}_{\Delta\phi=0} = (J_v)^{c}_{\Delta\phi=0} \qquad \text{(III.8a)}$$

$$(J_v)^s_{\Delta P=0} = (J_v)^k_{\Delta P=0} = (J_v)^c_{\Delta P=0} \qquad \text{(III.8b)}$$

$$(I)^s_{\Delta\phi=0} = (I)^k_{\Delta\phi=0} = (I)^c_{\Delta\phi=0} \qquad \text{(III.8c)}$$

$$(I)^s_{\Delta P=0} = (I)^k_{\Delta P=0} = (I)^c_{\Delta P=0} \qquad \text{(III.8d)}$$

Similarly the condition (b) of the additivity of forces in the present case would mean

$$(\Delta P)^s = (\Delta P)^k + (\Delta P)^c \qquad \text{(III.9)}$$

$$(\Delta\phi)^s = (\Delta\phi)^k + (\Delta\phi)^c \qquad \text{(III.10)}$$

where the superscript s stands for the series composite membrane. If the coupled flow processes in the series composite membrane and in the constituent membrane elements are adequately described by the linear phenomenological relations, one gets from equations (III.9), (III.10), and (III.8a) to (III.8d) the following combination rules for the various phenomenological coefficients.

$$\frac{1}{L^s_{11}} = \frac{1}{L^k_{11}} + \frac{1}{L^c_{11}} \qquad \text{(III.11a)}$$

$$\frac{1}{L^s_{12}} = \frac{1}{L^k_{12}} + \frac{1}{L^c_{12}} \qquad \text{(III.11b)}$$

$$\frac{1}{L^s_{21}} = \frac{1}{L^k_{21}} + \frac{1}{L^c_{21}} \qquad \text{(III.11c)}$$

$$\frac{1}{L_{22}^{s}} = \frac{1}{L_{22}^{k}} + \frac{1}{L_{22}^{c}} \qquad \text{(III.41d)}$$

In order to test the postulate of additivity of forces given by equations (III.9) and (III.10) the pressure drops and electrical potential drops across the constituent clay membrane elements corresponding to certain fixed values of total applied ΔP and $\Delta\phi$ across the composite series clay membrane were estimated from the data on hydraulic permeability and electro-osmotic velocity for the composite clay membrane and for the constituent clay membrane elements, using the method adopted by Srivastava and Jain (1975b) in earlier studies. In doing this the condition of stationarity of flows given by equations (III.8a) to (III.8d) was presupposed. The detailed procedure adopted for estimation of the pressure drops and electrical potential drops across the constituent clay membrane elements, is described below.

Known pressure differences were applied across the series clay membrane and water flow $(J_v)_{\Delta\phi=0}$ was noted. If one assumes the condition (III.8a) of stationarity of flow to be valid, the value of water flux thus noted will also be the value of water-flow through constituent membrane elements i.e., kaolinite and crysotile. This being so, the pressure drops across the constituent membrane elements can be read from the plot of $(J_v)_{\Delta\phi=0}$ vs ΔP for kaolinite and crysotile elements (Fig. [III.3]). The values of various pressure differences, acting across the constituent membrane elements $(\Delta P)^k$ and $(\Delta P)^c$ calculated in this manner are recorded in Table III.5.

For checking the additivity relation (III.10) a similar procedure was adopted. Known electrical potential differences were applied across the series membrane and the values of the electro-osmotic velocity measured. Using the condition (III.8b), the values of electrical potential drops across the constituent membrane elements, i.e., $(\Delta\phi)^k$ and $(\Delta\phi)^c$ were evaluated from the electro-osmotic velocity data (Fig. [III.4]). The values are recorded in Table III.6. A perusal of Tables III.5 and III.6 reveals that the additivity postulate of forces holds good for ΔP (equation III.9) but not for $\Delta\phi$ (equation III.10). Form this it can be concluded that the character of J_v induced by $\Delta\phi$ alone is much different from the character of flow induced by ΔP alone. Since equation (III.9) has been found to be valid and equation (III.10) has not been found to be valid, the obvious conclusion would be that combination rule, equation (III.11a) for L_{11} is obeyed while the combination rule, equation (III.11b) does not hold good. On account of the validity of the Onsager's reciprocal relations for the series clay system the combination rule (III.11c) for the cross coefficient L_{21} would also not hold good. The combination rule (III.11d)

TABLE III.5

Values of the total applied apressure difference across the series membrane $(\Delta P)^s$ and the consequent pressure drops across the constituent membrane elements calculated from the hydraulic flow data.

$(J_v)_{\Delta\phi=0} \times 10^3$ ($cm^3 \ sec^{-1}$)	$(\Delta P)^k$ (in cms of water) (1)	$(\Delta P)^c$ (in cms of water) (2)	Sume of the quantities of colms.1 and 2 (3)	$(\Delta P)^s$ (in cms of water) (4)	Deviation in % between (3) and (4)
1.0	4.80	4.30	9.10	9.80	7.20
2.0	9.05	8.50	17.55	18.60	6.00
3.0	12.50	14.50	27.00	28.60	5.50
4.0	18.75	17.00	35.75	37.50	4.40
5.0	23.50	21.00	44.50	46.20	3.80
6.0	28.50	25.00	53.50	55.00	2.72

TABLE III.6

Values of the total applied electrical potential difference across the series membrane $(\Delta\phi)^s$ and the consequent electrical potential drops across the constituent membrane elements calculated from the electro-osmotic velocity data.

$(J_v)_{\Delta P=0} \times 10^4$ cm^3 sec^{-1}	$(\Delta\phi)^k$ (V)	$(\Delta\phi)^c$ (V)	$(\Delta\phi)^s$ (V)
2.50	8.50	2.50	6.75
5.00	17.50	4.50	13.25
7.50	26.25	6.75	20.75
10.00	35.00	8.75	26.00

for the coefficient L_{22}, which represents the well known Kirchoff's law for the additivity of electrical resistances was, however, found to be valid.

C. Efficiency of Energy Conversion

The non-equilibrium thermodynamic theory of the electro-kinetic energy conversion based on linear phenomenological laws and Onsager's relations, has been worked out by Gross and Osterle (1968), Morrison and Osterle (1965) and Osterle (1964a,b). According to their definition, the efficiency of energy conversion for the two reciprocal phenomena of electro-osmosis and streaming potential can be written

$$\eta_e = -\frac{J_v \, \Delta P}{I \Delta\phi} = -\frac{J_v \Delta P}{(\Delta\phi)^2/R} \qquad \text{(III.12)}$$

and
$$\eta_\phi = -\frac{I\Delta\phi}{J_v \Delta P} = -\frac{(\Delta\phi)^2/R}{J_v \Delta P} \qquad \text{(III.13)}$$

respectively. The subscript e stands for the phenomena of electro-osmosis and ϕ stands for the phenomenon of streaming potential. The negative sign in equations (III.12) and (III.13) indicates that the output fluxes and forces are in the direction opposite to that of the input fluxes and forces. From the discussion of the efficiency of the electro-kinetic energy conversion defined by equations (III.12) and (III.13), as outlined in the previous chapter the following conclusions can be drawn (Srivastava and Jain, 1975c)

(i) The maximum value of the energy conversion efficiency $(\eta)_{max}$ for a fixed value of input force, always occurs when the output force equals half its steady state value.

(ii) The values of $(\eta)_{max}$ are independent of applied input forces.

(iii) $(\eta_e)_{max} = (\eta_\psi)_{max}$ which is a consequence of the validity of Onsager's reciprocal relations.

The values of η_e and η_ψ, at various values of the output forces ranging between zero and their steady state values for the constituent clay membrane elements and the parallel and series composite membranes, corresponding to two fixed values of input forces were calculated from the transport data given in Figs. [III.3] to [III.6]. The method of calculation has been described in the previous chapter (chapter II, section 3.B). From the results which have been plotted in Figs. [III.7] and [III.8] the validity of all the three conclusions listed above is obvious.

From the theory of Gross and Osterle (1968), Morrison and Osterle (1965), and Osterle (1964a,b) which is based on

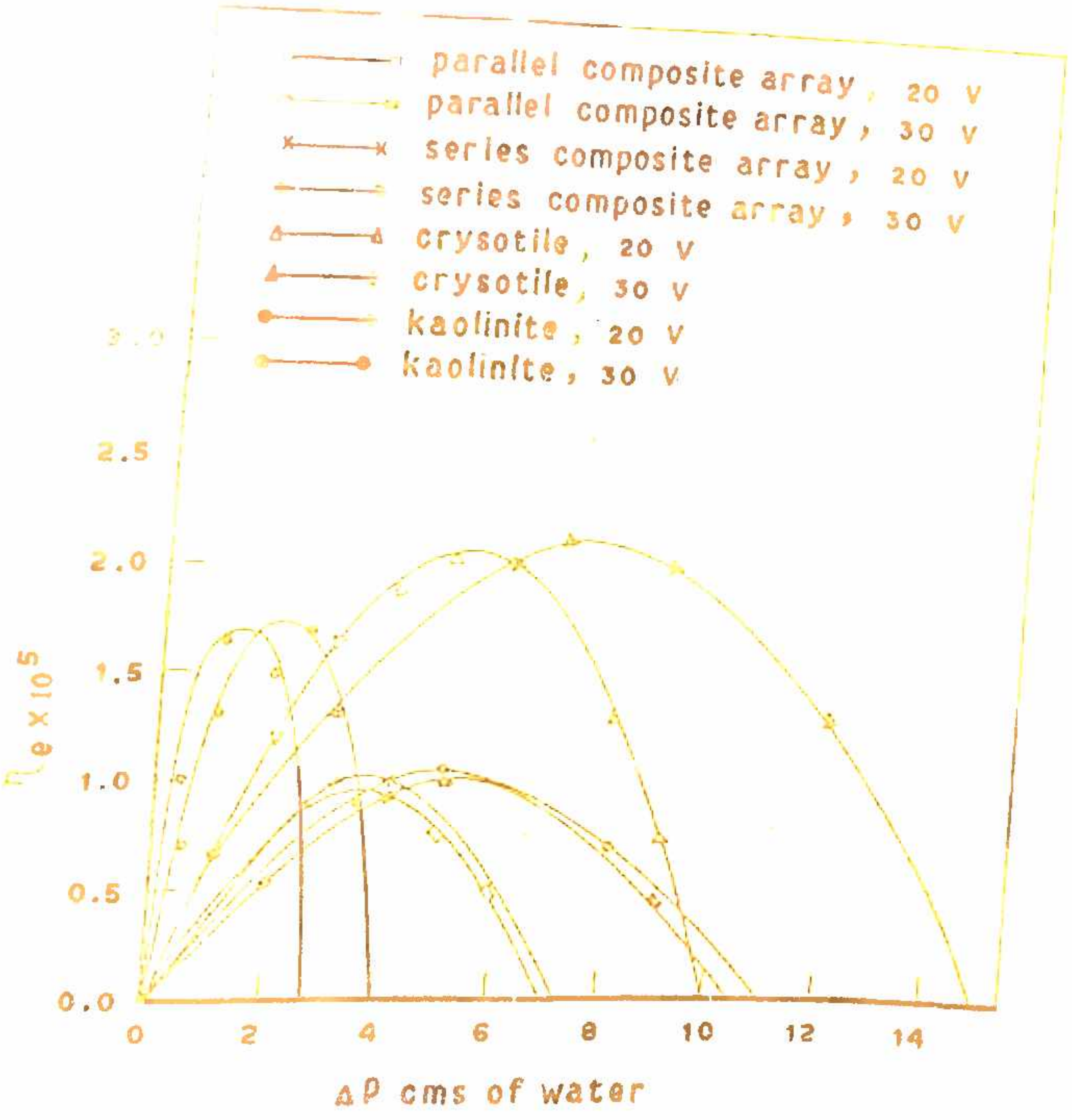


FIG. III.7 VARIATION OF η_e WITH PRESSURE DIFFERENCE

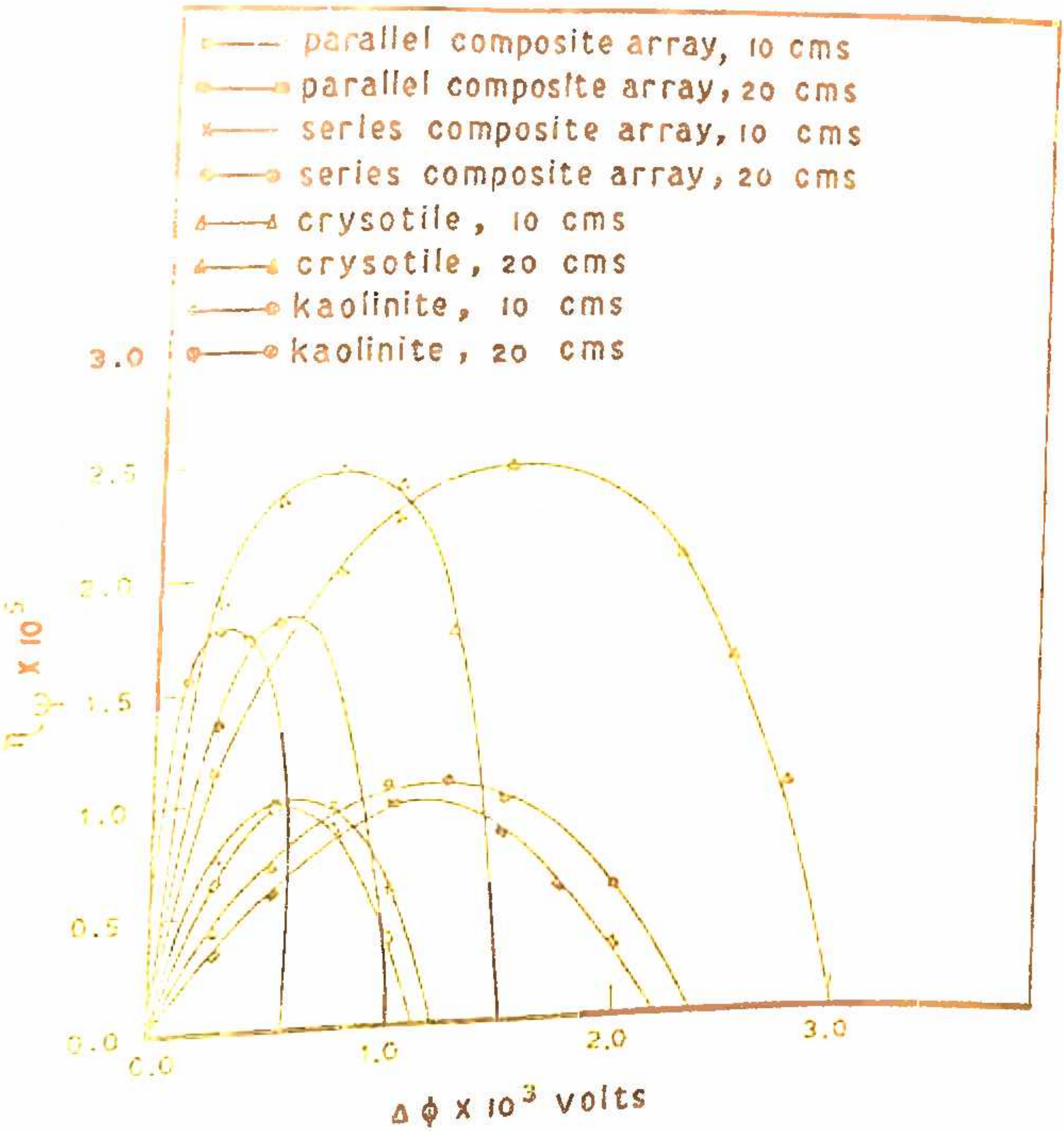


FIG. III. 8 VARIATION OF η_ψ WITH POTENTIAL DIFFERENCE the validity of linear phenomenological relations and Onsager's reciprocal relations, as has been shown in the previous chapter, the relationship between $(\eta)_{max}$ and the figure of merit β is given by the equation

$$(\eta)_{max} = \frac{(1+\beta)^{\frac{1}{2}} - 1}{(1+\beta)^{\frac{1}{2}} + 1} \qquad \text{(III.14)}$$

where β is related to the degree of coupling q in the following manner

$$\beta_{io} = \left(\frac{1}{q_{io}^2} - 1\right)^{-1} \qquad \text{(III.15)}$$

The subscripts o and i represent the output and input quantities. The degree of coupling as defined by Kedem and Caplan (1965) is related to the phenomenological coefficients by the equation

$$\frac{1}{q_{io}^2} = \frac{L_{ii}\,L_{oo}}{L_{io}^2} \qquad \text{(III.16)}$$

On account of Onsager's theorem follows the equality

$$\beta_{io} = \beta_{oi} \qquad \text{(III.17)}$$

which in turn implies the relationship

$$(\eta_e)_{max} = (\eta_\phi)_{max} \qquad \text{(III.18)}$$

The values of β and $(\eta)_{max}$ for both the modes of conversion have been calculated from the values of phenomenological coefficients (Table III.1) using equations (III.14) and (III.15) and are given in Table III.7. From the data in Table III.7 the agreement between the values $(\ )_{max}$ thus calculated and those obtained from Figs. [III.7] and [III.8] is obvious in all the cases. The data in Table III.7 also confirm the validity of equations (III.17) and (III.18) for all cases, i.e., constituent clay membrane elements and the parallel and series composite clay membranes.

The degree of coupling q for the parallel composite clay membrane, which is intimately related to $(\eta)_{max}$ through equations (III.14) and (III.15) can be shown to be related to the degree of coupling for the constituent clay membrane elements by the following equation

$$q^p = q^k\sqrt{\frac{L^k_{11}\cdot L^k_{22}}{(L^k_{11}+L^e_{11})(L^k_{22}+L^e_{22})}} + q^e\sqrt{\frac{L^e_{11}\cdot L^e_{22}}{(L^k_{11}+L^e_{11})(L^k_{22}+L^e_{22})}} \qquad \text{(III.19)}$$

on account of the validity of the combination rules given by equations (III.5a) to (III.5d) for the parallel composite membrane. The equation (III.19) is a useful relationship because it enables us to predict the values of q^p from knowledge of the values of phenomenological coefficients for the constituent membrane elements. Since the combination

TABLE III.7

The values of $(\eta)_{max}$ for Kaolinite, Crysotile and the Composite clay Systems

	Kaolinite	Crysotile	Composite parallel	Composite Series
Values from fig.[III.7] $(\eta_e)_{max} \times 10^5$	1.700	2.050	0.980	1.050
Values from β_{io} $(\eta_e)_{max} \times 10^5$	1.530	2.140	0.958	0.964
Values from fig.[III.8] $(\eta_\phi)_{max} \times 10^5$	1.800	2.480	0.980	1.075
Values from β_{oi} $(\eta_\phi)_{max} \times 10^5$	1.870	2.350	1.034	0.814
$\beta_{io} \times 10^5$	6.124	8.572	3.830	3.857
$\beta_{oi} \times 10^5$	7.460	9.400	4.140	3.256

rules for the cross coefficients given by equation (III.11b) and (III.11c) were not found to be valid in the case of series composite membrane it is futile to look for a relationship similar to equation (III.19) for the series composite membrane.

III.4 REFERENCES

Babcock, K.L., and Overstreet, R. (1955): The thermodynamics of soil moisture : a new approach. Soil Sci. 80, 257.

Baver, L.D. (1956): Soil Physics. Wiley, New York.

Bolt, G.H., and Frissel, M.J. (1960): Thermodynamics of soils moisture. Neth. J. Agr. Sci. 8, 57.

Cary, J.W. (1964): An evaporation experiment and its irreversible thermodynamics. Intern. J. heat and mass transfer 7, 531.

Childs, E.C. (1969): An introduction to the physical basis of soil water phenomena. Wiley (Interscience), New York.

De Groot, S.R. (1966): Thermodynamics of irreversible processes 10th reprint. North-Holland, Amsterdam.

De Jong, E. (1968): Applications of thermodynamics to soil moisture. Proc. Hydrology Symp. 6th National Research Council of Canada.

Edlefsen, N.E., and Anderson, A.B.C. (1943): Thermodynamics of soil moisture. Hilgardia 15, 31.

Groenevelt, P.H., and Bolt, G.H. (1969): Non-equilibrium thermodynamics of the soil water system. J. Hydrol. 7, 358.

Gross, R.J., and Osterle, J.F. (1968): Membrane transport characteristics of ultrafine capillaries. J. Chem. Phys. 49, 228.

Hadas, A., Swartzendruber, D., Rijtema, P.E., Fuchs, M. and Yaron, B. (eds.) (1973): Ecological studies - 4 - Physics of soil water and salts. Springer-Verlag.

Hillel, D. (1971): Soil and water-Physical principles and processes. Academic Press, New York.

Kedem, O., and Caplan, S.R. (1965): Degree of coupling and its relation to efficiency of energy conversion. Trans. Faraday Soc. 61, 1897.

Kedem, O., and Katchalsky, A.(1963a): Permeabilities of composite membranes.1. Electrical current, volume flow and flow ofsolute through membranes. Trans. Faraday Soc., 59, 1918.

Kedem, O. and Katchalsky, A. (1963a): Permeabilities of composite membranes, 2. Parallel Elements. Trans. Faraday Soc. 59, 1931.

Kedem, O. and Katchalsky, A. (1963c): Permeabilities of composite membranes, 3. Series array of elements Trans. Faraday Soc. 59, 1941.

Kirkwood, J.G. (1954): In ion transport across membranes. (Clarke ed.) Academic Press, New York.

Low, P.F. (1961): Physical chemistry of clay-water interactions. Advan. Agron. 13, 269.

Miller, E.E., and Miller, R.D. (1955): Theory of capillary flow: 1. Practical implications. Soil Sci. Soc. Amer. Proc. 19, 267.

Miller, E.E., and Miller, R.D. (1956): Physical theory for capillary flow phenomena. J. Appl. Phys. 27, 324.

Morrison, F.A. and Osterle, J.F. (1965): Electrokinetic energy conversion in ultrafine capillaries. J. Chem. Phys. 43, 2111.

Osterle, J.F. (1964a): A unified treatment of the thermodynamics of steady state energy conversion. Appl. Sci. Res. 12, 425.

Osterle, J.F. (1964b): Electrokinetic energy conversion. J. Appl. Mech. 31, 161.

Philip, J.R. (1960): Absolute thermodynamic functions in soil water studies. Soil Sci. 89, 111.

Srivastava, R.C., and Avasthi, P.K. (1973): Electro-osmotic effects in a bentonite-water system. J. Hydrol. 20, 37.

Srivastava, R.C., and Jain, A.K. (1975a): Non-equilibrium thermodynamics of electro-osmosis of water through composite clay membrane, 1. The parallel arrangement. J. Hydrol. 25, 307.

Srivastava, R.C. and Jain, A.K. (1975): Non-equilibrium thermodynamics of electro-osmosis of water through composite membrane, 2. The series arrangement. J. Hydrol. 25, 325.

Srivastava, R.C. and Jain, A.K. (1975c): Non-equilibrium thermodynamics of electro-osmosis of water through composite clay membrane, 3. The electrokinetic energy conversion. J. Hydrol. 25, 339.

Srivastava, R.C., and Rajpal (1973): Non-equilibrium thermodynamics in soil physics. Oxford and IBH, New Delhi.

Swartzendruber, D. (1962): Modification of darcy's law for the flow of water in soils. Soil Sci. 93, 22.

Taylor, S.A., and Cary, J.W. (1960): Analysis of the simultaneous flow of water and heat of electricity with the thermodynamics of irreversible processes. Trans. Intern. Cong. Soil Sci., Madison, 7th 1, 80.

Winterkon, H.F. (1958): Mass transport phenomena in moist porous systems as viewed from the thermo-dynamics of irreversible processes. Highway Res. Board, Sepc. Rep. 40, 324.

Yong, R.N. and Warkentin, B.P. (1975): Developments in Geotechnical engineering, 5. Soil properties and behavior, Elsevier Scientific Pub. Co. Amsterdam.

CHAPTER IV

THERMO-OSMOSIS THROUGH COMPOSITE CLAY MEMBRANES

THERMO-OSMOSIS THROUGH COMPOSITE CLAY MEMBRANES

IV.1 INTRODUCTION

The fact that temperature gradients can induce water movements in soils has been known for over the last 60 years. (Bouyoucons, 1915). Studies on the relative importance and the interaction of thermal and suction gradients in transporting soil moisture were carried out by Hutchison, etal., (1948), Philip and DecVries (1957), Taylor and Cary (1960), Cary and Taylor (1965, 1966). Taylor and Cary in their analysis of the simultaneous transport of water and heat through soil systems made use of the formalism of irreversible thermodynamics. A brief but consolidated acount of the utility of non-equilibrium thermodynamics in the study of simultaneous transport of matter and energy in soil systems is available in the recent monograph by Srivastava and Rajpal (1973).

As already stated in the previous chapter, Kedem and Katchalsky's non-equilibrium thermodynamic theory for the permeability of composite membranes was primarily intended for biological membranes. Experiments exploring the extent to which this theory can be useful in analysing the data on flow through composite porous media that one comes across in geosystems, e.g. porous soils or rocks having layered structure, have been described in the previous chapter (chapter III). Since migration of water under thermal gradients is an important phenomenon with practical consequences especially in agriculture, the studies reported in the previous chapter (Chapter III) have been extended in this chapter to the case of thermo-osmosis of water through composite clay membranes.

The hydraulic permeability and thermo-osmotic permeability measurements for parallel and series composite clay membranes and also for their constituent clay membrane elements have been made. The data has been utilised to test the validity of the combination rules as deduced by Kedem and Katchalsky (1963a,b,c) connecting the various phenomenological coefficients, for the total composite clay membranes and the corresponding phenomenological coefficients for their constituent clay membrane elements. The composite clay membrane systems chosen for the present studies also were (1) Kaolinite and crysotile clay membrane elements arranged in a parallel array and (2) Kaolinite and crysotile clay membrane elements arranged in a series array.

IV.2 PHENOMENOLOGICAL RELATIONS

Although the phenomenological relations for the simultaneous transport of water and heat have been described in

Chapter I (section I.3.C), these will be repeated here again for the sake of the continuity and readability of the chapter. When two chambers containing a single fluid (say water) are separated by a porous barrier, the pore size of which is comparable to the mean free path of the permeating fluid and a difference of temperature is maintained on the two sides of the porous plug, migration of fluid occurs and a pressure difference ΔP sets up in the steady state corresponding to the temperature difference ΔT. For such a situation the equation for entropy production σ can be written as (De Groot, 1966; Prigogine, 1968) -

$$\sigma = J_w \left(- \frac{\bar{V}\Delta P}{T} \right) + J_q \left(- \frac{\Delta T}{T^2} \right) \qquad (IV.1)$$

where J_w and J_q represent the mass flow of water and the heat flow respectively, $\bar{V}$ is the spcific volume of water. The linear phenomenological relations for the simultaneous transport of water and heat across the porous plug can be written as

$$J_w = L_{11} \left(- \frac{\bar{V}\Delta P}{T} \right) + L_{12} \left(- \frac{\Delta T}{T^2} \right) \qquad (IV.2)$$

and

$$J_q = L_{21} \left(- \frac{\bar{V}\Delta P}{T} \right) + L_{22} \left(- \frac{\Delta T}{T^2} \right) \qquad (IV.3)$$

In equations (IV.2) and (IV.3) L_{ik}'s are the phenomenological coefficients and the equality

$$L_{12} = L_{21} \tag{IV.4}$$

holds among them on account of Onsager's reciprocity theorem. From equations (IV.2) and (IV.3) it follows that

$$(J_q/J_w)_{\Delta T=0} = \frac{L_{21}}{L_{11}} = Q^* \tag{IV.5}$$

The quantity Q^* is known as heat of transport and is defined as the heat transported per unit mass transport when there is no temperature difference across the porous plug. In the steady state when $J_w = 0$, the equation

$$(\Delta P/\Delta T)_{J_w=0} = -\frac{L_{12}}{L_{11}\bar{V}T} \tag{IV.6}$$

for thermo-osmotic pressure difference can be deduced from equation (IV.2). The relationship

$$(\Delta P/\Delta T)_{J_w=0} = -\frac{Q^*}{\bar{V}T} \tag{IV.7}$$

between thermo-osmotic pressure difference and the heat of transport follows as a consequence of Onsager's reciprocal relation (IV.4). If in the given system pressure is not allowed to develop the equation

$$(-J_w)_{\Delta P=0} = \frac{L_{12}}{T^2}\Delta T = L'_{12}\,\Delta T \tag{IV.8}$$

for thermo-osmotic velocity can be deduced from equation (IV.2) by imposing the restriction $\Delta P=0$.

IV.3 EXPERIMENTAL

A. Apparatus

The thermo-osmotic cell used in the present studies has been depicted in Fig. [IV.1]. It consisted of six parts. Part I, II, III and IV consisted individually of glass tubes A_1A_2, B_1B_2, C_1C_2 and D_1D_2 of length 12 cms and diameter 1 cm. Each of the tubes A_1A_2, B_1B_2, C_1C_2 and D_1D_2 contained an outer jacket, through which water at desired temperature could be circulated, and each of them were fitted with a B-14 socket at one end and a sliding standard ground glass joint at the other end. The part I and part III or the part II and part IV could be joined or detached from each other through these sliding ground glass joints. The part V of the apparatus consisted of a glass tube bent twice at right angles with B-14 cones at the ends E_1 and E_2. The tube G_1G_2 provided in part V could be connected the pressure head. Part VI of the apparatus was also a glass tube bent twice at right angles with B-14 cones at the ends F_1 and F_2 and a capillary L_1L_2 of length 20 cm and diameter 0.232 cm. The water flux was measured by noting the rate of advancement of water miniscus in the capillary L_1L_2. The purpose of the two step-cocks T_1 and T_2 in part VI of the apparatus was to connect or

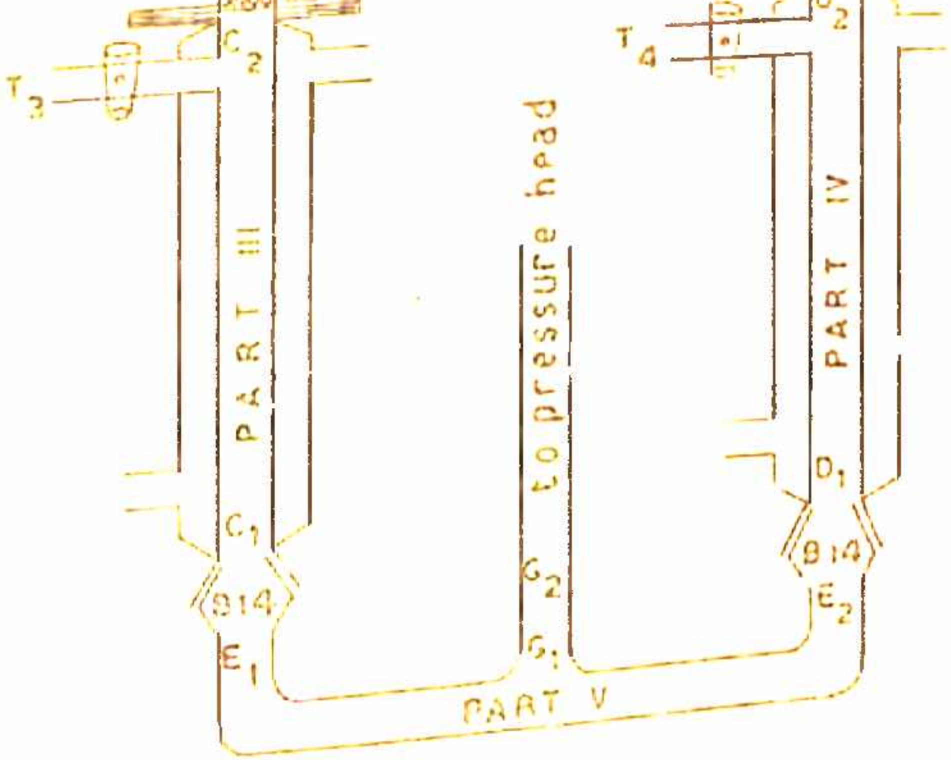
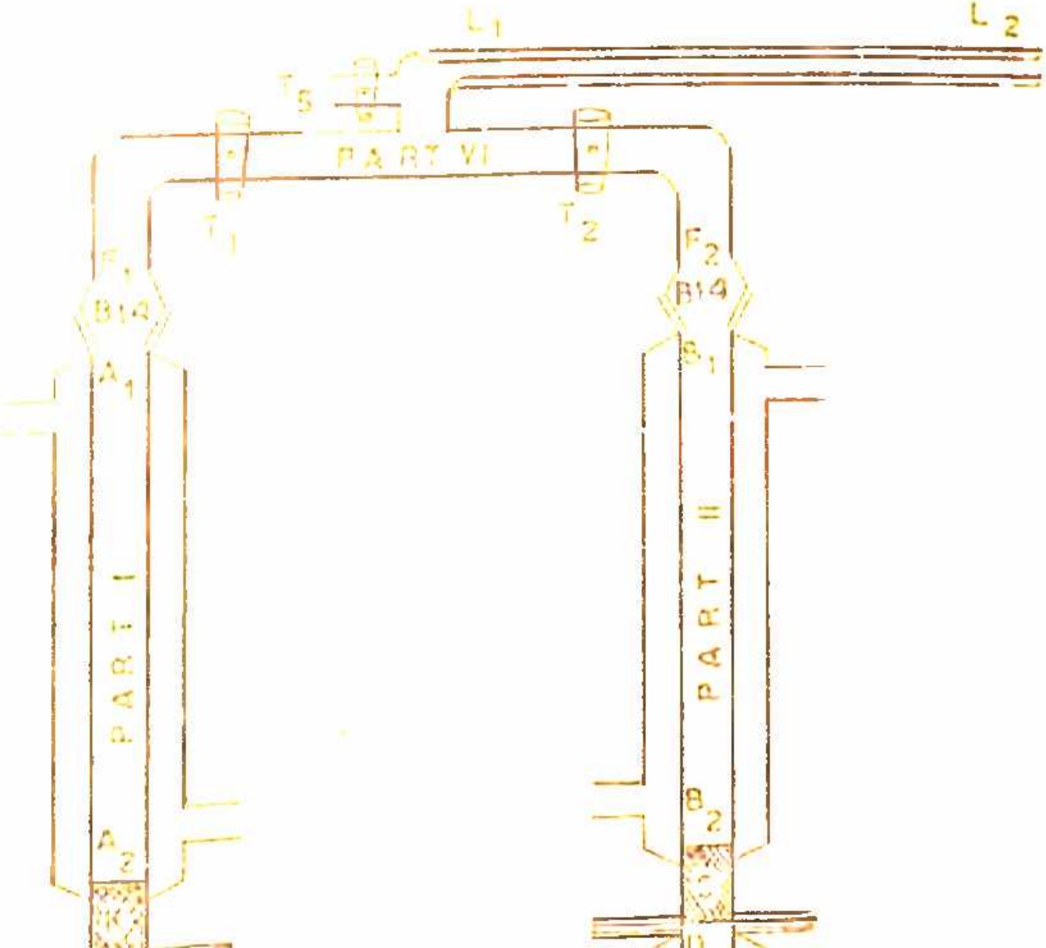


FIG. IV.1 THERMO OSMOTIC CELL


L1
L2
T5
PART VI
T1
T2
F1
B14
F2
B14
A1
B1
PART I
PART II
A2
B2

disconnect the two halves of the thermo-osmotic cell (i.e. parts (I+III) and (II+IV)) with each other as and when required. The purpose of the other stopcocks T_3, T_4 and T_5 was simply to remove the air bubbles if any while filling the apparatus with water.

B. Procedure

After a thorough cleaning of the apparatus, compressed kaolinite and crysotile clay plugs were placed at the ends A_2 and B_2 of the tubes A_1A_2 and B_1B_2. The part I was then joined with part III and part II was joined with part IV through the sliding ground glass joints. These two portions i.e. parts (I+III) and (II+IV) were then joined together through parts V and VI. The arrangement thus obtained (Fig. [IV.1]) was used for measurements on the parallel composite membrane. The thermo-osmotic cell (Fig. [IV.1]) was then filled with triple distilled water and was allowed to stand for several days so that the clay plugs were completely wet with water. In order to test whether the clay plugs were completely saturated with water or not hydraulic permeability measurements were made. When reproducible values were obtained, it was concluded that the clay plugs were completely wet with water.

For the measurements of hydraulic permeabilities through kaolinite, crysotile and the parallel composite clay membrane system known pressure differences were applied across the clay plugs by connecting the tubes G_1G_2 to a pressure head and the movement of water in the capillary L_1L_2 was noted with time using a cathetometer with a least count of 0.001 cm and a stop watch reading upto 0.1 secs.

For the measurement of thermo-osmotic velocities, temperature difference ΔT across the clay plugs was created by circulating water at different temperatures in the outer jackets of parts I, II, III and IV of the apparatus and water flux induced by the temperature difference thus created was measured by noting the movement of water miniscus in the capillary L_1L_2. In all measurements of thermo-osmotic velocity the condition $\Delta P=0$ was enforced by adjusting the pressure head. The temperature differences in the measurements of thermo-osmotic velocity were so adjusted that mean temperature did not vary. The mean temperature was kept constant at 45°C. The hydraulic permeability measurements were also made at 45°C. For this the entire thermo-osmotic cell was placed in an air thermostat set at 45°C.

It may be pointed out that for the measurement of both hydraulic permeability and thermo-osmotic velocity through kaolinite plug the stopcock T_1 was closed and T_2 was kept open. Similarly for the measurements through crysotile plug the stopcock T_2 was closed and T_1 was kept open whereas for the measurements through the parallel composite clay membrane both stopcocks T_1 and T_2 were kept open. The stopcocks T_3, T_4 and T_5 were kept closed throughout all measurements.

After all measurements through the parallel composite clay membrane were completed, the part I of the apparatus was joined with the part II through the sliding ground glass joint. This gave the thermo-osmotic cell for the measurements on the series clay membrane and has been shown in Fig.|IV.2|. The method for the measurements of hydraulic permeability and thermo-osmotic velocity in the case of series membrane also were similar to those described for the parallel composite membrane. While measuring the thermo-osmotic velocity for the series composite membrane also, the temperature differences across the series composite clay plug were so adjusted that the mean temperature was always 45°C. The hydraulic permeability measurements, in this case also, were made at 45°C.

IV.4 RESULTS

The data on hydraulic permeability and thermo-osmotic velocity for the parallel composite clay membrane, the series composite clay membrane and their constituent clay membrane elements are plotted in Figs. [IV.3] and [IV.4]. It may be mentioned that the thermo-osmotic movement of water as observed in the present studies was always from warmer to the colder side.

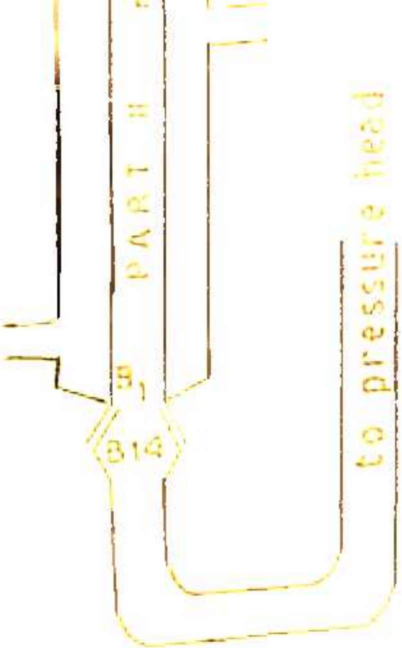
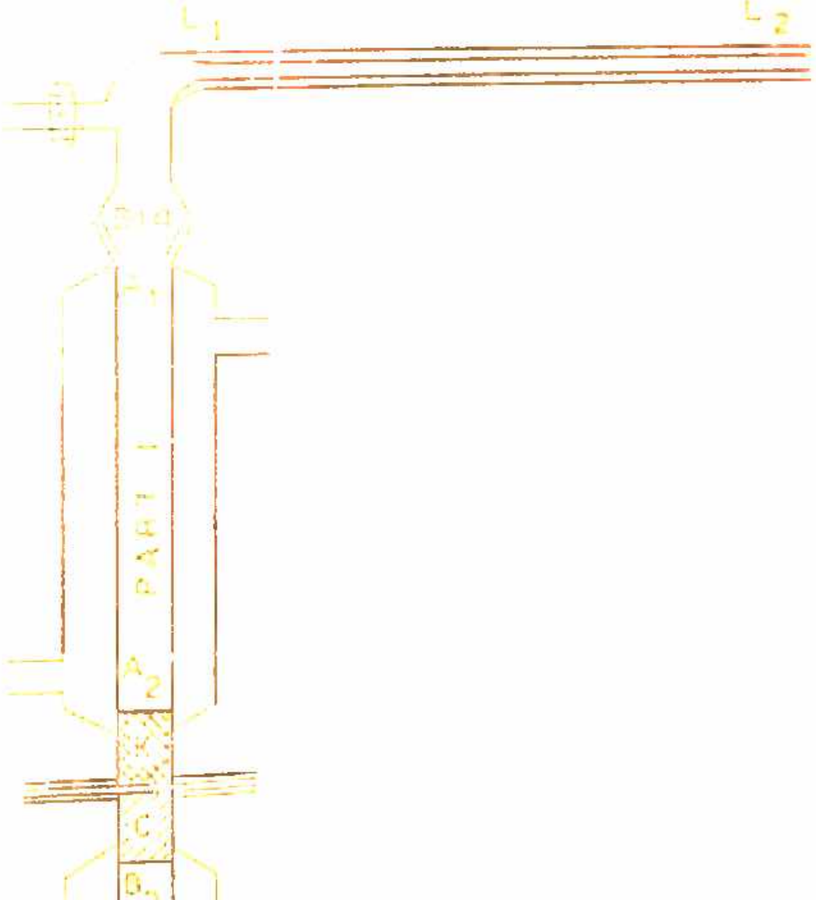


FIG. IV-2 THERMO OSMOTIC CELL FOR SERIES ARRANGEMENT.


L_1
L_2
A_1
PART I
A_2
K
C

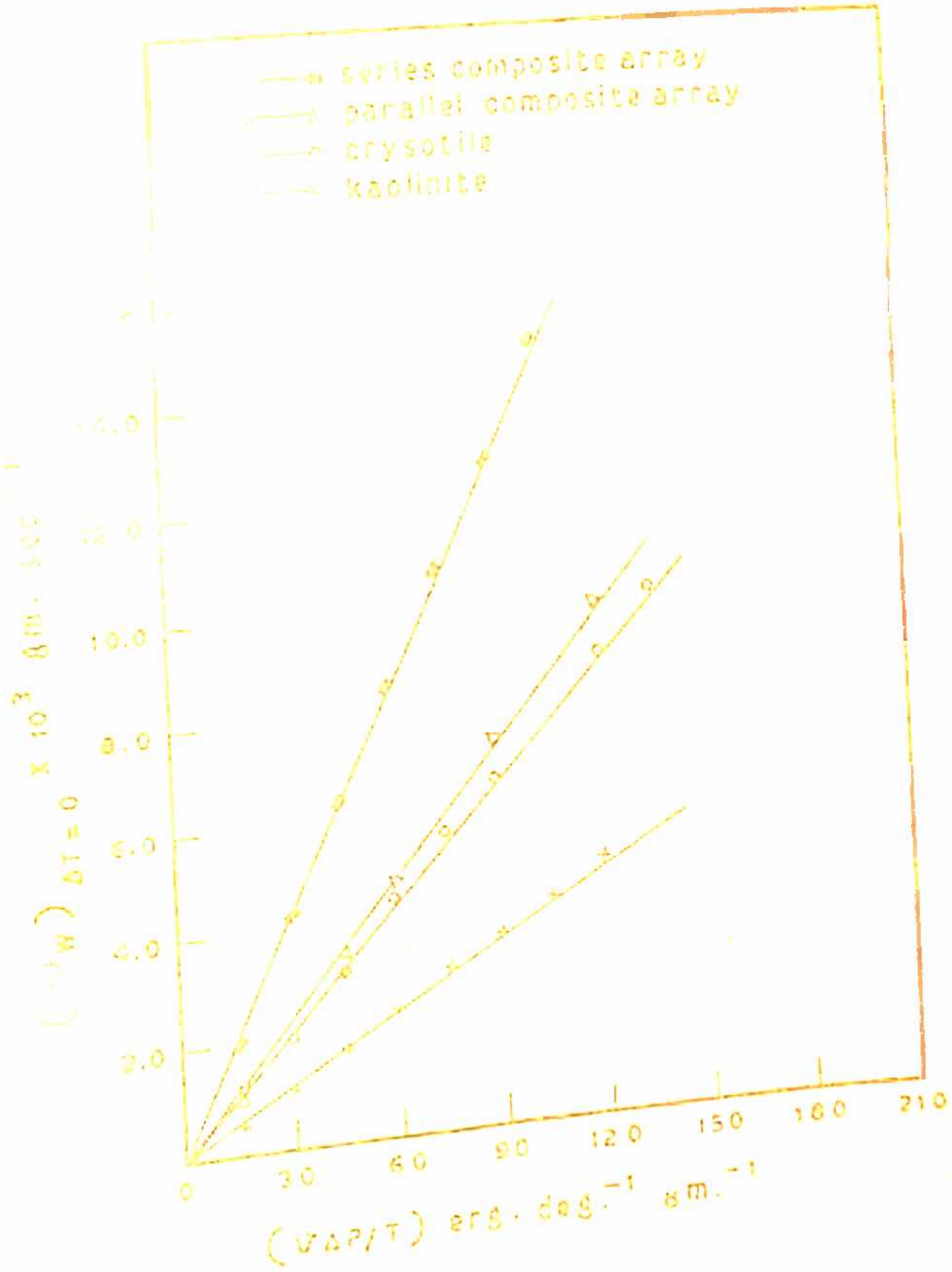


FIG. IV.3 HYDRUALIC PERMEABILITY DATA

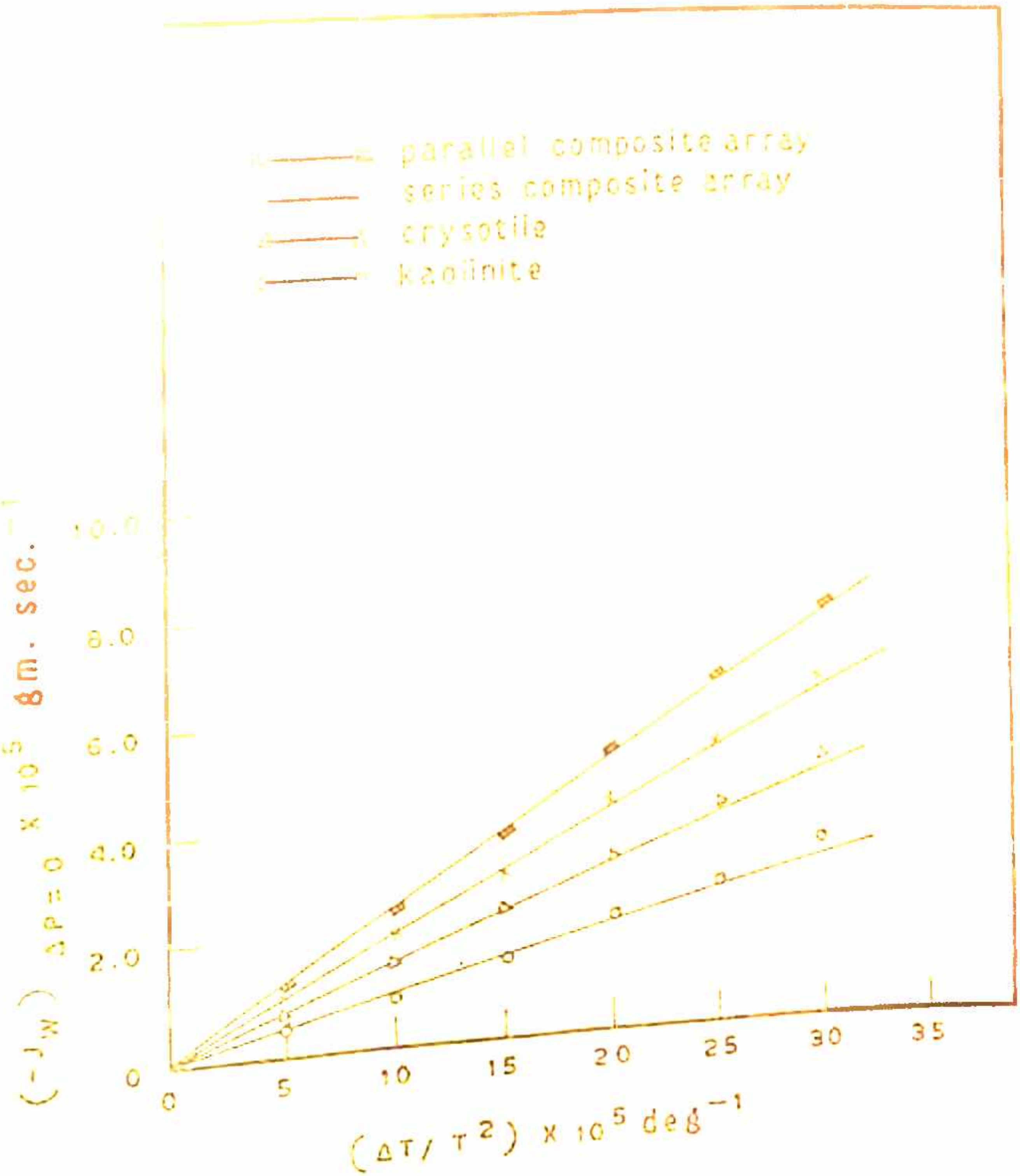


FIG. IV.4 THERMO OSMOTIC VELOCITY DATA

IV.5 DISCUSSION

The straight line plots in Fig. [IV.3] and [IV.4] confirm the validity of the linear phenomenological equation (IV.2) for both the parallel composite clay membrane and the series composite clay membrane and also for their constituent clay membrane elements. The values of the phenomenological coefficients L_{11} and L_{12} obtained from the slope of the straight line plots shown in Figs. [IV.3] and [IV.4], for the various systems studied are recorded in Table IV.1.

A. The Parallel Composite Membrane

The treatment of Kedem and Katchalsky (1963b) for the parallel composite membrane assumes that linear phenomenological relations between fluxes and forces are valid for the parallel composite membrane and also for the constituent clay membrane elements. It is also assumed that flows are normal to the membrane surface, parallel to the x-axis and independent of x. The forces considered are differences of the potentials acting across the membrane. Since the same compartment maintains contact with all elements on each side of the membrane, the same force which acts on the parallel composite membrane also operates on the constituent

TABLE IV.1

Values of the Phenomenological Coefficients

Membrane System	$L_{11} \times 10^5$ gm^{2}deg erg^{-1}sec^{-1}	$L_{12} \times 10$ gm deg sec^{-1}
Kaolinite	7.33	1.00
Crysotile	8.33	1.55
Composite series array	4.00	2.05
Composite parallel array	13.63	2.60

membrane elements. This implies that the forces are perpendicular to the membrane surface and no lateral forces creating internal circulation need be considered. Thus the total flow through the parallel composite membrane is assumed to be sum of the total flows through the constituent membrane elements. This in the present would mean

$$(J_w)^{p}_{\Delta T=0} = (J_w)^{k}_{\Delta T=0} + (J_w)^{c}_{\Delta T=0} \qquad \text{(IV.9)}$$

$$(J_w)^{p}_{\Delta P=0} = (J_w)^{k}_{\Delta P=0} + (J_w)^{c}_{\Delta P=0} \qquad \text{(IV.10)}$$

where the superscripts p, k and c represent the parallel composite membrane, kaolinite clay membrane elements and crysotile clay membrane elements. The data on hydraulic permeability and thermo-osmotic velocity given in Tables IV.2 and IV.3 confirms the validity of equations (IV.9) and (IV.10). In view of the validity of the linear phenomenological equation (IV.2) for the parallel composite clay membrane and its constituent clay membrane elements (Figs. [IV.3] and [IV.4]) and the fact that same force which acts across the parallel composite membrane also acts across constituent clay membrane elements, the equations (IV.9) and (IV.10) would in turn imply

$$L_{11}^{p} = L_{11}^{k} + L_{11}^{c} \qquad \text{(IV.11)}$$

TABLE IV.2

Hydraulic Permeability data for Kaolinite, Crysotile, parallel composite and series composite clay systems.

$(\overline{V}\Delta P/T)$ (erg gm^{-1} deg^{-1})	$(J_w)^k_{\Delta T=0} \times 10^3$ ($gm\ sec^{-1}$) (1)	$(J_w)^c_{\Delta T=0} \times 10^3$ ($gm\ sec^{-1}$) (2)	Sum of quantities in colmns (1) and (2) $\times 10^3$ (3)	$(J_w)^p_{\Delta T=0} \times 10^3$ ($gm\ sec^{-1}$) (observed value) (4)	Deviation(in %. between colm. (3) and (4)	$(J_w)^s_{\Delta T=0} \times 10^3$ ($gm\ sec^{-1}$) (observed value)
15.0	1.02	1.15	2.17	2.07	5.00	0.588
30.0	2.10	2.35	4.45	4.20	6.26	1.196
45.0	3.20	3.60	6.80	6.60	2.80	1.734
60.0	4.30	4.80	9.10	9.00	1.10	2.317
75.0	5.35	6.00	11.35	11.15	1.80	2.90
90.0	6.47	7.25	13.75	13.60	0.90	3.48
105.0	7.55	8.70	16.25	16.00	0.15	4.05

TABLE IV.3

Thermo-osmotic data for Kaolinite, Crysotile, Parallel composite and series composite clay systems.

$(\Delta T/T^2) \times 10^5$ (deg^{-1})	$(J_w)^k_{\Delta P=0} \times 10^5$ (gm sec^{-1}) (1)	$(J_w)^c_{\Delta P=0} \times 10^5$ (gm sec^{-1}) (2)	(Sume of colms. 1 and 2) $\times 10^5$ (3)	$(J_w)^p_{\Delta P=0} \times 10^5$ (gm sec^{-1}) (observed value) (4)	Deviation(in %.) between columns (3) and (4)	$(J_w)^s_{\Delta P=0} \times 10^5$ (gm sec^{-1}) (observed value)
5.0	0.50	0.75	1.25	1.15	8.09	1.00
10.0	1.00	1.50	2.50	2.45	2.00	1.90
15.0	1.38	2.30	3.68	3.60	2.20	3.05
20.0	2.05	3.10	3.15	5.10	1.00	4.15
25.0	2.50	3.85	6.35	6.40	0.78	5.20
30.0	3.10	4.68	7.78	7.80	0.32	6.35

and

$$L_{12}^{p} = L_{12}^{k} + L_{12}^{c} \qquad (IV.12)$$

Values of the phenomenological coefficients given in Table IV.1 confirm the validity of the combination rules given by equation (IV.11) and (IV.12). In view of the validity of the combination rules given by equation (IV.11) and (IV.12) the thermo-osmotic pressure difference for the composite parallel membrane can be shown to be related to the thermo-osmotic pressure differences for the constituent clay membrane elements by the equation

$$(\Delta P/\Delta T)^{p}_{J_w=0} = \left(\frac{\Delta P}{\Delta T}\right)^{k}_{J_w=0} \left(\frac{L_{11}^{k}}{L_{11}^{c}+L_{11}^{k}}\right) + \left(\frac{\Delta P}{\Delta T}\right)^{c}_{J_w=0} \left(\frac{L_{11}^{c}}{L_{11}^{c}+L_{11}^{k}}\right) \qquad (IV.13)$$

The equation (IV.13) on account of equation (IV.7) can be rewritten as

$$(Q^{*}) = (Q^{*})^{k} \left(\frac{L_{11}^{k}}{L_{11}^{k}+L_{11}^{c}}\right) + (Q^{*})^{c} \left(\frac{L_{11}^{c}}{L_{11}^{c}+L_{11}^{k}}\right) \qquad (IV.14)$$

which gives a relationship between the heat of transport for composite parallel clay membrane and the heats of transport for the constituent clay membrane elements.

B. The Series Composite Membrane

The assumptions made in treatment of Kedem and Katchalsky (1963c), for the series composite membrane are summarised below:

(1) In the series array the same flow passes all the elements and the partial elementary flow equals the observable external flow. All the flows passing through the system are assumed to be stationary.

(2) The potentials of the thermodynamic driving forces are assumed to be continuous across all boundaries in the system (Kedem and Katchalsky, 1963c; Kirkwood, 1954). This in the present case implies that the thermodynamic forces acting across the series composite membrane are equal to the sum of the forces acting across the constituent membrane elements.

The condition (1) of stationarity of flows, in the present case, would mean

$$(J_w)^s_{\Delta T=0} = (J_w)^k_{\Delta T=0} = (J_w)^e_{\Delta T=0} \qquad (IV.15)$$

$$(J_w)^s_{\Delta P=0} = (J_w)^k_{\Delta P=0} = (J_w)^e_{\Delta P=0} \qquad (IV.16)$$

where the superscript s stands for the series membrane.

Similarly the requirement of condition (IV.2) of the continuity of potentials or additivity of thermodynamic forces, in the present case, would mean

$$(\bar{\nabla}\,\Delta P/T)^{s} = (\bar{\nabla}\,\Delta P/T)^{k} + (\bar{\nabla}\,\Delta P/T)^{c} \qquad \text{(IV.17)}$$

and

$$(\Delta T/T^{2})^{s} = (\Delta T/T^{2})^{k} + (\Delta T/T^{2})^{c} \qquad \text{(IV.18)}$$

Equations (IV.17) and (IV.18) in view of the validity of the linear phenomenological relations (IV.2), for the series membrane as well as for the constituent clay membrane elements (Figs. [IV.3] and [IV.4]), and the condition of stationarity of the flows given by equations (IV.15) and (IV.16), would lead to the following combination rules for the phenomenological coefficient.

$$1/L_{11}^{s} = 1/L_{11}^{k} + 1/L_{11}^{c} \qquad \text{(IV.19)}$$

$$1/L_{12}^{s} = 1/L_{12}^{k} + 1/L_{12}^{c} \qquad \text{(IV.20)}$$

In order to test the validity of the postulate of additivity of thermodynamic forces given by equations (IV.17) and (IV.18) the components of the total thermodynamic force $(\bar{\nabla}\Delta P/T)$ or $(\Delta T/T^{2})$ acting across the series composite membrane,

TABLE IV.4

Values of the total thermodynamic force $(\frac{\bar{V}\Delta P}{T})$ acting across the series array of clay membrane system and its components across the constituent membrane elements calculated from hydraulic flow data.

$(J_w)_{\Delta T=0} \times 10^3$ gm sec^{-1}	$(\frac{\bar{V}\Delta P}{T})^s$ erg gm^{-1}deg^{-1} (1)	$(\frac{\bar{V}\Delta P}{T})^k$ erg gm^{-1}deg^{-1} (2)	$(\frac{\bar{V}\Delta P}{T})^e$ erg gm^{-1}deg^{-1} (3)	Sum of the quantities in columns (2) and (3) (4)	Deviation (in %.) between (1) and (4).
1.00	29.80	16.40	12.90	29.30	1.75
2.00	53.50	27.15	25.50	52.65	1.50
3.00	81.30	37.50	43.50	81.00	1.02
4.00	107.45	56.25	51.00	107.25	0.70
5.00	133.35	70.50	63.00	133.50	0.50

TABLE IV.5

Values of the total thermodynamic force ($\Delta T/T^2$) acting across the series array of clay membrane system and its components across the constituent membrane elements calculated from thermo-osmotic velocity data.

$(J_w)_{\Delta P=0} \times 10^5$ gm sec^{-1}	$(\Delta T/T^2)^s \times 10^5$ deg^{-1}	$(\Delta T/T^2)^m \times 10^5$ deg^{-1}	$(\Delta T/T^2)^c \times 10^5$ deg^{-1}
0.5	2.5	5.0	3.75
1.0	5.0	10.5	6.50
1.5	7.43	14.85	10.52
2.0	9.85	19.50	13.00
2.5	12.00	25.60	16.05
3.0	15.35	28.85	20.75

which act across the constituent membrane elements, were estimated from the transport data in Figs. [IV.3] and [IV.4]. In doing this condition of stationarity of flows given by equations (IV.15) and (IV.16) was assumed. The detailed procedure adopted was similar to the one described in the previous chapter (Chapter III section 3.B). The values thus obtained are recorded in Tables IV.4 and IV.5 from which it is apparent that the postulate of additivity of forces holds good for $\bar{V}\Delta P/_T$ (equation IV.17) but not for $\Delta T/_{T^2}$ (equation IV.18). Consequently the combination rule given by equation (IV.19) for the straight coefficient L_{11} would be obeyed while the combination rule given by equation (IV.20) for the cross coefficient L_{12} would not be obeyed. This is also apparent from the values of the phenomenological coefficients L_{11} and L_{12} given in Table IV.1.

IV.6 REFERENCES

Bouyoncous, G.J. (1915): Effect of temperature on the movement of water vapor in soils. J. Agr. Res. 5, 141.

Cary, J.W. (1965): Water flux in moist soil: Thermal versus suction gradients. Soil Sci. 100, 168.

Cary, J.W. (1966): Soil moisture transport due to thermal gradients: practical aspects. Soil Sci. Soc. Amer. Proc. 30, 428.

Cary, J.W., and Taylor, S.A. (1962): The interaction of the simultaneous diffusions of heat and water vapour Soil Sci. Soc. Amer. Proc. 26, 413.

De Groot, S.R., 1966. Thermodynamics of Irreversible Processes. North Holland, Amsterdam.

Hutchinson, H.P., Dinon, I.S., and Denbigh, K.G. (1948): The Thermo-osmosis of liquids through porous materials. Discuss. Faraday Soc. 3, 86.

Kedem, O. and Katchalsky, A. (1963a): Permeabilities of Composite Membranes, 1. Electrical current, Volume flow and Flow of Solute through Membranes. Trans. Faraday Soc. 59: 1918

Kedem, O., and Katchalsky, A. (1963b): Permeabilities of Composite Membranes, 2. Parallel elements. Trans. Faraday Soc. 59: 1931.

Kedem, O., and Katchalsky, A.; (1963c): Permeabilities of composite membranes, 3. Series Array of Elements. Trans . Faraday Soc. 59: 1941.

Kirkwood, J.G. (1954): In Ion Transport Across Membranes. (Clarke ed.)! Academic Press, New York.

Philip, J.R., and deVries, D.A. (1957): Moisture movement in porous materials under thermal gradients. Trans. Amer. Geophys. Union 38, 222.

Prigogine, I. (1968): Introduction to Thermodynamics of Irreversible Processes. Wiley, New York.

Srivastava, R.C. and Rajpal. (1973): Non-equilibrium thermodynamics in soil physics. Oxford and IBH Publishing Co., New Delhi.

Taylor, S.A., and Cary, J.W. (1960): Analysis of the simultaneous flow of water and heat or electricity with the thermodynamics of irreversible processes. Trans. Itern. Cong. Soil Sci., Madison, 7th I, 394.

SUMMARY

SUMMARY

This thesis embodies the work done by the author on 'Non-equilibrium thermodynamics of coupled flow processes through porous media'. The thesis contains four chapters. A brief summary of each chapter is given below.

Chapter I

This chapter gives a brief introduction to thermodynamics of irreversible processes. Introduction has also been made to the formalism of Network thermodynamics which is relatively a more recent development. While discussing the postulates and methodology of Thermodynamics of Irreversible processes, attention has been focused on electrokinetic phenomena, thermo-osmotic phenomena and degree of coupling, because the work reported in the subsequent chapters are concerned with these.

Chapter II

This chapter describes the studies conducted on electro-osmosis of binary liquid mixtures through a sintered glass membrane (Porosity G-4). The three binary liquid mixtures chosen for the study are acetone-methanol, acetone-water, and methanol-water. The data demonstrate the validity of the linear and homogeneous forms of phenomenological relations for the simultaneous transport of matter and electricity and Onsager's reciprocal relations for the various mass fractions of all the three binary liquid mixtures, viz., acetone-methanol, acetone-water and methanol-water. Concentration dependence of the phenomenological coefficients for all the three binary mixtures has been studied. It has been revealed that in all cases concentration dependence of the phenomenological coefficient L_{11} representing the volume flow per unit pressure difference and the coefficients L_{12} or L_{21} representing the electro-osmotic velocity or streaming current conforms to the Speigler's frictional model while the concentration dependence of the coefficient L_{22} representing electrical conductivity does not. The data have been further utilised to calculate the efficiencies of electrokinetic energy conversion (η) for both the modes of conversion, viz. electro-osmotic flow and streaming potential for all the three binary mixtures. The results thus obtained have been shown in all cases, to be in accordance with the non-equilibrium thermodynamic theories by Gross and Osterle, Kedem and Caplan, Morrision and Osterle, and Osterle.

Chapter III

Theory for the permeability of composite membranes has been developed by Kedem and Katchalsky. This theory was primarily intended for biological membranes which are composite structures consisting of several layers of substances differing in composition and permeability characteristics. Since such composite porous media eg. porous soils or rocks having layered structure are of interest in geosciences as well it is worthwhile to explore the extent to which the theory of Kedem and Katchalsky can be made applicable to them. Studies reported in this chapter have been conducted with this object in view.

Electro-osmosis of water through composite clay membranes considting of kaolinite and crysotile clay membrane elements in parallel and in series arrangement has been studied. The linear phenomenological relations and Onsager's reciprocal relations have been shown to be valid for both parallel and series array of composite clay membranes and also for the constituent clay membrane elements. The combination rules for the various phenomenological coefficients as deduced from the theory of Kedem and Katchalsky have been found to be valid for the parallel composite clay membrane. However, in the case of the series composite clay membrane the combination rules have been found to be valid only for the straight phenomenological coefficients and not for the cross coefficients. This suggests that, in the case of series composite clay membrane the nature of flow induced by electrical potential difference alone is entirely different from the nature of flow induced by pressure difference alone. The efficiencies of electro-kinetic energy conversions have been calculated for both composite clay membrane and also for their constituent clay membrane elements. The results thus obtained have been shown to be in accordance with the non-equilibrium thermodynamic theories of energy conversion in all the cases. The validity of the combination rules in the case of parallel composite clay membrane has yielded the following relationship between the degree of coupling 'q' for the parallel composite clay membrane and the degree of coupling for the constituent clay membrane elements

$$q^{p} = q^{k}\sqrt{\frac{L_{11}^{k}\cdot L_{22}^{k}}{(L_{11}^{k}+L_{11}^{c})(L_{22}^{k}+L_{22}^{2})}} + q^{c}\sqrt{\frac{L_{11}^{c}\cdot L_{22}^{c}}{(L_{11}^{k}+L_{11}^{c})(L_{22}^{k}+L_{22}^{c})}} \qquad (1)$$

where the subscript p, k, and c represent the parallel composite membrane, kaolinite clay membrane, and crysotile clay membrane respectively. Similarly from the validity of the combination rules for the parallel composite membrane, following correlations have been deduced for electro-osmotic pressure $(\Delta P/\Delta\phi)_{J_v=0}$ and streaming potential $(\Delta\phi/\Delta P)_{I=0}$.

$$\left(\frac{\Delta P}{\Delta \phi}\right)^{p}_{J_v=0} = \left(\frac{\Delta P}{\Delta \phi}\right)^{k}_{J_v=0} \left(\frac{L^{k}_{11}}{L^{k}_{11}+L^{e}_{11}}\right) + \left(\frac{\Delta P}{\Delta \phi}\right)^{e}_{J_v=0} \left(\frac{L^{e}_{11}}{L^{k}_{11}+L^{e}_{11}}\right) \qquad (2)$$

$$\left(\frac{\Delta \phi}{\Delta P}\right)^{p}_{I=0} = \left(\frac{\Delta \phi}{\Delta P}\right)^{k}_{I=0} \left(\frac{L^{k}_{22}}{L^{k}_{22}+L^{e}_{22}}\right) + \left(\frac{\Delta \phi}{\Delta P}\right)^{e}_{I=0} \left(\frac{L^{e}_{22}}{L^{k}_{22}+L^{e}_{22}}\right) \qquad (3)$$

These correlations (equations 1,2 and 3) are helpful in predicting the values of the respective quantities for the parallel composite membrane from the knowledge of the phenomenological coefficients of the constituent membrane elements.

Chapter IV

Since the movement of water through porous barriers induced by thermal gradients is an important phenomenon with practical consequences, studies reported in the previous chapter (Ch. III) have been extended in this chapter to the phenomenon of thermo-osmosis. The object of these studies also is to assess the extent to which Kedem and Katchalsky's theory for the permeability of composite membranes, which was primarily intended for biological membranes can be helpful in analysing the flow data through composite porous media that one comes across in geo-systems e.g. porous soils or rocks having layered structure.

With this object in view thermo-osmosis of water through composite clay membranes consisting of kaolinite and crysotile clay membrane elements in parallel and in series arrangement has been studied. Water flux in presence of both pressure difference and temperature difference for both parallel and series composite clay membranes and also for the constituent clay membrane elements has been shown to be adequately described by the usual linear and homogeneous phenomenological equation . The combination rules for the phenomenological coefficients L_{11} and L_{12} representing hydraulic permeability and thermo-osmotic permeability as deduced from the theory of Kedem and Katchalsky, have been found to be valid for the parallel composite clay membrane. In the case of the series composite clay membrane, however, the combination rules have been found to be valid only for the straight coefficient L_{11} and not for the cross phenomenological coefficient L_{12}. This again suggests that in the case of series composite membrane, the nature of flow induced by pressure difference alone is much different from the nature of flow induced by temperature difference alone.

Validity of the combination rules for L_{11} and L_{12}, in the case of parallel composite membrane has led to the following relationship between the heat of transport of water (Q^*) for the parallel composite membrane and the heat of transport of water through the constituent clay membrane elements.

$$(Q^*)^p = (Q^*)^k \left(\frac{L_{11}^k}{L_{11}^k + L_{11}^c} \right) + (Q^*)^c \left(\frac{L_{11}^c}{L_{11}^c + L_{11}^k} \right) \tag{4}$$

Where the subscripts p, k and c denote parallel composite membrane, kaolinite clay membrane element, and crysotile clay membrane element respectively. The above equation is a useful relationship on account of its predictive value.

****

LIST OF PUBLICATIONS

1. Non-equilibrium Thermodynamics of Electro-osmosis of Liquid Mixtures. Studies on Acetone-Methanol Mixtures., J. Colloid and Interface Sci., 57, 58 (1976).

2. Non-equilibrium Thermodynamics of Electro-osmosis of Liquid Mixtures. Studies on Acetone-Water Mixtures., J. Chem. Soc. Faraday Trans. I, 72, 2631 (1976).

3. Electro-osmosis of Liquid Mixtures - Studies on Aqueous Methanol., J. Phys. Chem., 81, 906 (1977).

4. Electro-osmotic Permeability of Composite Clay Membranes. (Communicated).

5. Thermo-osmosis of Water Through Composite Clay Membranes. (Communicated).