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ELECTROKINETIC STUDIES ON CARBOHYDRATES

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ABSTRACT

Measurements of hydrodynamic and electro-osmotic permeability through Pyrex sinter, using aqueous solutions of D-fructose, D-glucose, sucrose, and urea, have been made The data were analyzed by using the non-equilibrium thermodynamics of irreversible processes Electrokinetic potentials were calculated, in order to characterize the membrane–permeant interface.

INTRODUCTION

Studies of membrane transport have long been of interest to biologists, as well as to workers involved in other disciplines of experimental science, because transport across the boundaries of phases is commonly encountered in many fields of science[1]

Transport processes through membranes primarily depend on (*i*) the physicochemical characteristics of the membranes, (*ii*) such characteristics of the permeant species as size, shape, solubility in the membrane matrix, polar character, and hydrophobicity, and (*iii*) the driving force acting on the permeating molecules[2] In biological membranes, transport behavior is of the utmost importance, but it is difficult to study, due to its complex structure and functioning[3] Therefore, in view of the complexities of these membranes, considerable interest has developed in the study of transport behavior through model membranes[4] In the present communication, a comprehensive study of electrokinetic phenomena through Pyrex-sinter membranes has been made, using aqueous solutions of D-fructose, D-glucose, sucrose, and urea as the permeants The results have been analyzed on the basis of the non-equilibrium thermodynamics of irreversible processes, as well as on the basis of a kinetic model

EXPERIMENTAL

Pyrex-sinter (G_4 porosity) membrane, D-fructose, D-glucose, sucrose, urea (B D H , A R), and double-distilled water (having a specific conductance of the order of 1 μmho) were used in the present investigation

The membrane was thoroughly cleaned by a method described earlier[5] Measurements of hydrodynamic and electro-osmotic flux were made by using an experimental technique already described[6,7] Potential difference was applied with the help of an electronically operated, power supply, using Pt electrodes The conductance of the membrane equilibrated with the permeant was measured with the aid of a conductivity bridge (Toshniwal, India) at 50 Hz All measurements were made by use of an air thermostat maintained at 30 ±0 1°

RESULTS AND DISCUSSION

Electrokinetic phenomena are typically non-equilibrium, and are characterized by the positive, definite character of entropy production, σ, which may be written[8] as follows

$$\sigma = J_v \Delta P + I \Delta \phi \qquad (1)$$

The fluxes are the volume flow, J_v, and the current, I The forces are, respectively, the pressure difference, ΔP, and the potential difference, $\Delta\phi$ Within a linear domain, J_v and I are expressed as follows

$$J_v = L_{11}(\Delta P/T) + (L_{12}/T)\Delta\varphi \qquad (2)$$

$$I = L_{21}(\Delta P/T) + (L_{22}/T)\Delta\phi \qquad (3)$$

where L_{ik} $(i, k = 1, 2)$ are called the phenomenological coefficients When $\Delta\phi = 0$, Eq 2 reduces to

$$(J_v)_{\Delta\phi=0} = L_{11}(\Delta P/T) \qquad (4)$$

The plots of $(J_v)_{\Delta\phi=0}$ against ΔP, as shown in Fig 1 are straight lines, showing the validity of Eq 4 The values of L_{11}/T, estimated from the slopes of the straight lines in Fig. 1, are recorded in Table I When $\Delta P = 0$, Eq 2 reduces to

$$(J_v)_{\Delta P=0} = L_{12}(\Delta\phi/T) \qquad (5)$$

The plots of $(J_v)_{\Delta P=0}$ *versus* $\Delta\phi$ are all straight lines, as shown in Fig 2, and this

TABLE I

MEMBRANE PARAMETERS

System	$\frac{L_{11}}{T} \times 10^{14}$ $(m^5 N^{-1} s^{-1})$	$\frac{L_{22}}{T} \times 10^{6}$ (ohm^{-1})	$r \times 10^{7}$ (m)	$n \times 10^{-6}$
Pyrex–water	11 00	2 75	5 52	7 25
Pyrex–D-glucose	8 60	3 50	4 76	9 76
Pyrex–D-fructose	9 75	2 45	5 05	9 35
Pyrex–sucrose	7 50	3 05	4 51	11 08
Pyrex–urea	12 60	4 20	4 29	23 20

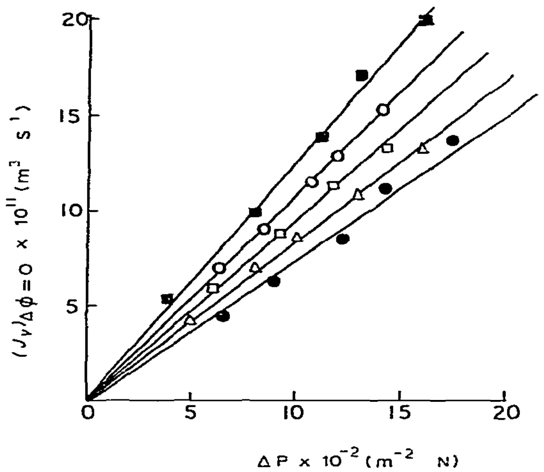

Fig 1 Dependence of volumetric flux $(J_v)_{\Delta\phi=0}$ on applied pressure difference ΔP, for Pyrex sinter–carbohydrate system (○) water, (□) D-fructose (△) D-glucose (●) sucrose, and (■) urea

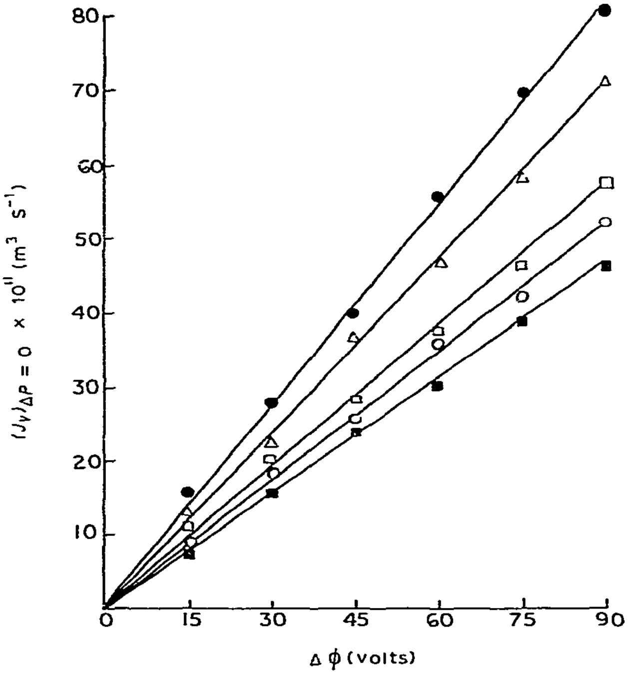

Fig 2 Dependence of electro-osmotic flux $(J_v)_{\Delta P=0}$ on applied potential difference, $\Delta\phi$, for Pyrex sinter–carbohydrate system (○) water, (□) D-fructose, (△) D-glucose, (●) sucrose, and (■) urea

TABLE II

PHENOMENOLOGICAL COEFFICIENTS AND ESTIMATED ZETA POTENTIALS

System	$\frac{L_{12}}{T} \times 10^{12}$ $(m^3 s^{-1} V^{-1})$	$\zeta \times 10^3$ (V)
Pyrex–water	5.80	2.84
Pyrex–D-glucose	6.80	4.35
Pyrex–D-fructose	6.50	3.16
Pyrex–sucrose	9.10	3.00
Pyrex–urea	5.00	1.28

confirms the validity of Eq. 5. The values of the phenomenological coefficients, L_{12}/T, estimated from the slopes of the straight lines in Fig. 2, are included in Table II.

The characterization of the membrane was achieved by measuring its thickness and cross-sectional area. From hydrodynamic-flux data and measurements of membrane conductance, average pore-radii, r, and number of capillary channels, n, could be estimated by using the relations[9]

$$r = \left[\frac{8\eta\left(\frac{L_{11}}{T}\right)k}{\frac{L_{22}}{T}}\right]^{\frac{1}{2}} \tag{6}$$

and $$n = \left[8\eta l\left(\frac{L_{11}}{T}\right)\right]/\pi r^4 \tag{7}$$

where η and k are the coefficient of viscosity and the specific conductance of the permeants, respectively, and L_{22} is the membrane conductance. The parameters characterizing the membrane are recorded in Table I.

An examination of Table I reveals that the magnitude of L_{11}/T decreases in the following way

$$(L_{11}/T)_{\text{urea}} > (L_{11}/T)_{H_2O} > (L_{11}/T)_{\text{D-fructose}} > (L_{11}/T)_{\text{D glucose}} > (L_{11}/T)_{\text{sucrose}}$$

The trend may be explained on the basis of the fluccuring, crystal model of water[10]. According to this model, water is open-structured and full of cavities (similar to those present in ice). The cavities are considered to contain a dense liquid composed of non-hydrogen-bonded molecules. Clusters and non-hydrogen-bonded water are in equilibrium with one another. When urea is added to the water, it disrupts the water

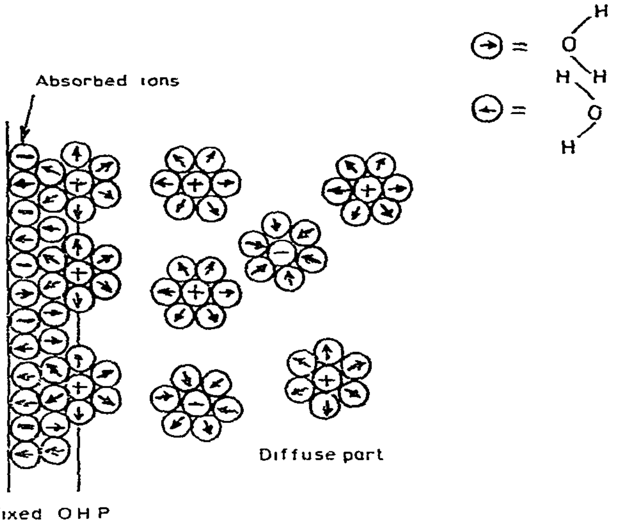

Fig 3 Structure of double layer for Pyrex sinter–carbohydrate system

clusters, because of its steric inability to fit into the tetrahedral water-structure[11] Thus, the permeability of urea increases with respect to water Furthermore D-fructose, D-glucose, and sucrose have structure-making properties, i e , the size of the water-molecule aggregates increases, and, hence, the rate of permeability decreases this is consistent with our experimental results It can be shown that the structure-making tendency decreases in the following order

Sucrose > D-glucose > D-fructose

Electro-osmotic flux always occurs towards the negative electrode in all of the cases studied, this can be explained on the basis of an electrical double-layer, formed at the membrane–permeant interface due to the adsorption of negative ions, as shown in Fig 3 Thus, the diffuse part of the double layer would contain an excess of positive ions which move towards the negative electrode, confirming the experimental results The double layer is endowed with an electrical potential, called electrokinetic, or zeta, potential, which is characteristic of the membrane material and the permeating species Within the linear range of electroosmosis, it is assumed that the zeta potential is independent of the applied potential difference, and it may be expressed[12] as

$$\zeta = \frac{4\pi\eta k}{L_{22} D}\left(\frac{L_{12}}{T}\right) \times 9 \times 10^{4} \text{ volts}, \qquad (8)$$

where k is the specific conductance of the permeant, L_{22} is the membrane conductance, and D is the dielectric constant of the permeants used The values of zeta potentials calculated by using Eq *8* are given in Table II

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