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Electroosmotic Transport of Urea and D-Glucose Solutions across Progesterone Plug Membrane

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Studies on hydrodynamic and electroosmotic permeation of water, aqueous solutions of D-glucose and urea in the concentration range 10^{-4} to 10^{-3} mol dm^{-3} across progesterone plug membrane have been carried out to characterize the electrical nature of interface. Phenomenological coefficients have been evaluated from the linear and nonlinear equations obtained. Membrane properties viz., pore radius and zeta potentials have been determined using these coefficients. The nonlinear variation of electroosmotic flow in case of aqueous solutions of urea has been explained on the basis of electrical double layer theory and the structural modifications that are likely to occur at membrane–solution interface because of solute–solvent, solvent–solvent, and membrane–permeant interactions.

Transport through membranes is important in many fields of technology and science[1] and in many biological systems of interest.[2] Recently considerable interest has developed in the transport through model biological membranes[3] because of their complex structure and functions.[4] In the present communication, progesterone, a female sex hormone responsible for normal development of female sex organs and for the maintenance of secondary sex characteristics[5] has been chosen as membrane material. A comprehensive physicochemical study with respect to progesterone interfaces in different types of electrolyte and nonelectrolyte solutions is expected to throw light on various facets of its functions.[6] Keeping this fact in view we have undertaken the measurement of hydrodynamic and electroosmotic permeation of aqueous solutions of urea and D-glucose across a progesterone plug membrane. The results obtained have been analysed from the view point of nonequilibrium thermodynamics.

Experimental

Materials and Methods: Progesterone obtained from Sigma Chemical Compnany, USA, was used to prepare membrane plug. Progesterone powder (95% weight fraction) was mixed with araldite (5% weight fraction) and it was cast in the form ofa plug by mechanical compression[7] in a pyrex glass cell. The thickness of the membrane plug was 0.502 cm and cross-sectional area 3.24 cm.[2]

D-Glucose and urea (AR, BDH, India) were used to prepare aqueous solutions employing conductivity water of specific conductance 10^{-6} S cm^{-1}.

Reversible silver–silver chloride electrodes used were prepared as reported[8] by anodic deposition of chloride on a silver disc attached to a silver rod from 0.1 M NaCl solution (1 M=1 mol dm^{-3}) at 0.4 mA cm^{-2}. The chloride layer on silver discs was very thin.

The experimental cell (Fig. 1) was used to measure electroosmotic permeability as reported earlier.[8] Potential difference upto 50 volt was applied through silver–silver chloride electrodes using an electronically operated power supply (HIL, India). Electroosmotic flux was observed to occur from negative to positive electrode.

Hydrodynamic permeability was measured applying constant hydrostatic pressure difference on the two faces of the membrane. Pressure difference was measured with a cathetometer reading upto ±0.001 cm. Correction was made for the residual flow.

An ac conductivity bridge (Toshniwal, India) at 50 Hz was used to measure conductance of the membrane equilibrated with the permeant before and after electroosmosis. All measurements were made at 25±0.5 °C in an air thermostat.

Results and Discussion

Nonequilibrium thermodynamic theory predicts that volume flux, J_v, and flow of electric current, I, under the simultaneous action of pressure difference, ΔP, and electrical potential difference, $\Delta\Phi$, across the membrane can be expressed by the following phenomenological equations.[9]

$$J_v = L_{11}(\frac{\Delta P}{T}) + L_{12}(\frac{\Delta \Phi}{T}), \tag{1}$$

$$I = L_{21}(\frac{\Delta P}{T}) + L_{22}(\frac{\Delta \Phi}{T}), \tag{2}$$

where L_{11} and L_{22} are straight coefficients and L_{12} and L_{21} are cross coefficients.

Hydrodynamic flux $(J_v)_{\Delta\Phi=0}$ was found to vary linearly with applied ΔP within the range of investigation (50 cm liquid column). L_{11} was evaluated from the slope of linear plot $(J_v)_{\Delta\Phi=0}$ vs. ΔP. The values are recorded in Table 1.

The electroosmotic flux $(J_v)_{\Delta P=0}$ has been found to vary linearly with $\Delta\Phi$ when aqueous solutions of D-glucose were used as permeants (Fig. 2). The linear phenomenological equation

$$(J_v)_{\Delta P=0} = L_{12}(\frac{\Delta \Phi}{T}), \tag{3}$$

satisfies the experimental data.

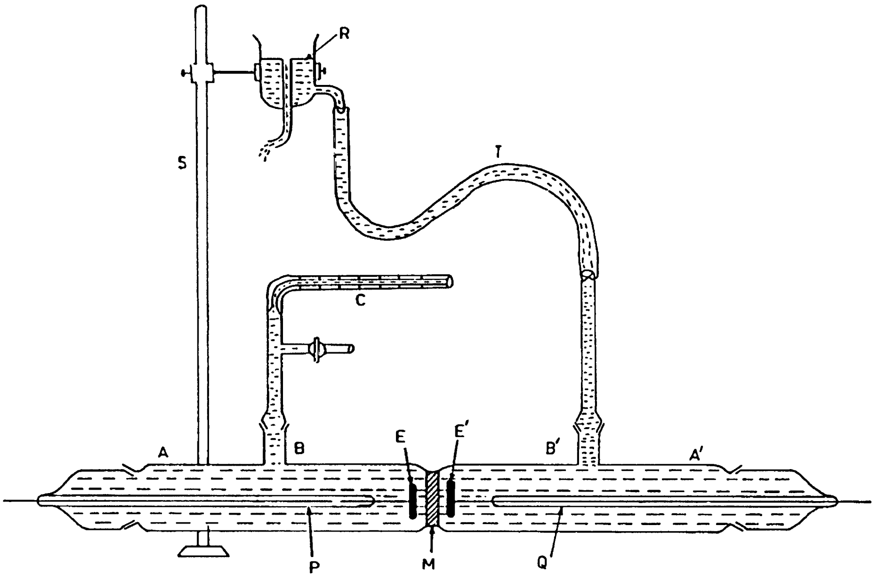


Fig. 1. Experimental set up for permeability measurement. T=Transparent polythene tube, R=Liquid reservoir, S=Stand, C=Graduated capillary, E & E'=Silver-silver chloride electrode, M=Membrane, P & O=Glass capillaries containing silver wires, A B A' B'=Glass cell assembly having constriction in the middle where membrane M is fixed.

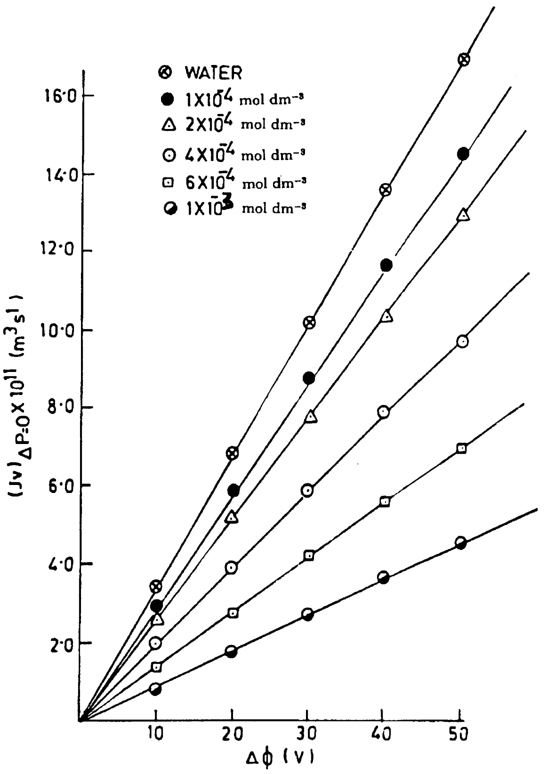


Fig. 2. Dependence of electroosmotic flux $(J_v)_{\Delta P=0}$ on applied potential difference, $\Delta\phi$, for progesterone aqueous D-glucose solution system.

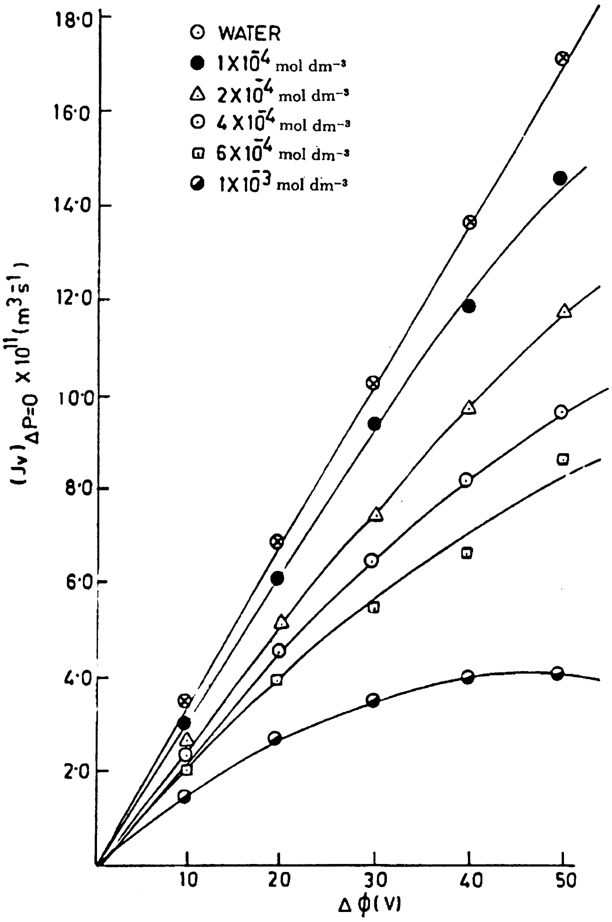


Fig. 3. Dependence of electroosmotic volume flux $(J_v)_{\Delta P=0}$ on applied potential difference, $\Delta\phi$, for progesterone aqueous urea system.

However, electroosmotic flux, $(J_v)_{\Delta P=0}$ has been found to vary nonlinearly with applied potential difference $\Delta\Phi$, when aqueous solutions of urea were used as permeants (Fig. 3). The following phenomenological equation[10] fits the experimental data.

$$(J_v)_{\Delta P=0} = L_{12}(\frac{\Delta \Phi}{T}) + 1/2L_{122}(\frac{\Delta \Phi}{T})^2, \quad (4)$$

where L_{12} and L_{122} are the first and second order electroosmotic transport coefficients. L_{12} and L_{122} were obtained from the intercept and slope of $\frac{(J_v)_{\Delta P=0}}{\Delta \Phi}$ vs. $\Delta \Phi$ plots (Fig. 4). The results are reproducible within the range of experimental error (5%).

Following the treatment of Overbeek[11] it can be shown that

$$\frac{L_{11}}{T} = \frac{n\pi r^4}{8\eta l} \quad (5)$$

and

$$\frac{L_{12}}{T} = \frac{n\varepsilon r^2}{4\eta l}\cdot\zeta_{l0}, \quad (6)$$

where L_{11} and L_{12} are hydrodynamic and electroosmotic transport coefficients, respectively, n is the number of pores, r is the average pore radius, l is the length of capillary channel in membrane, η and ε are the viscosity and dielectric constant of the permeating fluid, and ζ_{l0} is the electrokinetic potential at membrane–solution interface.

The conductivity of membrane equilibrated with permeant ($\frac{L_{22}}{T}$) is give by[8]

$$\frac{L_{22}}{T} = \frac{A_e k}{l} = \frac{n\pi r^2 k}{l}, \quad (7)$$

where $A_e = n\pi r^2$ is the effective cross sectional area of the membrane, l is the length of capillary channel, k is the conductivity of permeant in the membrane capillaries, n is the number of pores, and r is the average pore radius. The values of L_{22} are recorded in Table 1.

Electrical Double Layer and Electroosmotic Effect. The electroosmotic flux occurs towards the anode. This may be explained on the basis of electrical double layer formed at the progesterone–solution interface as follows. Progesterone has the following molecular structure (Chart 1).

The oxygen atom of $\rangle$C=O group attached to rings A and D and the π-electron density around the olefinic bond is completely responsible for generating an overall negative charge at the progesterone molecules present at the membrane matrix. D-Glucose shows negative excess heat, entropy, and volumes,[12] indicating that it is in a state of strong hydrogen bonding with surrounding water molecules. The possible mechanism for the formation of electrical double layer is now outlined. The water molecules dissociate as follows:

$$H_2O + H_2O \rightleftharpoons H_3^+O + OH^-.$$

The oxonium ions are adsorbed at the negatively charged membrane surface, as shown in Fig. 5 and form IHP. The H^+ ions at the IHP form strong bonds with the oxygen atoms at the hydroxyl groups present in the D-glucose molecule, forming the OHP. The OH^- ions are present in the bulk of the solution, and are also present in the diffused part of the electrical double layer. Thus, electroosmosis occurs from the negative to positive electrode when such a system is applied to an electrical potential difference.

Origin of Nonlinearity of Fluxes. It is worthwhile to discuss the various causes of nonlinearity.

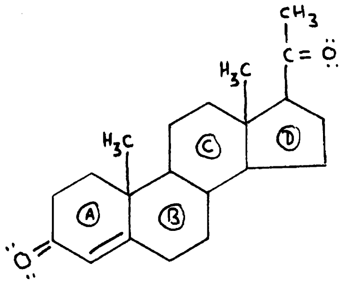


Chart 1.

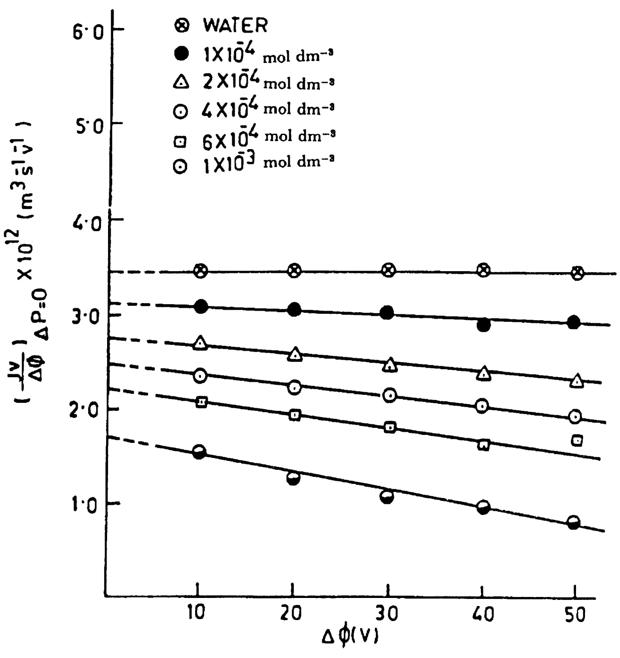


Fig. 4. Dependence of $(\frac{J_v}{\Delta \Phi})_{\Delta P=0}$ on applied potential difference, $\Delta \phi$, for progesterone aqueous urea system.

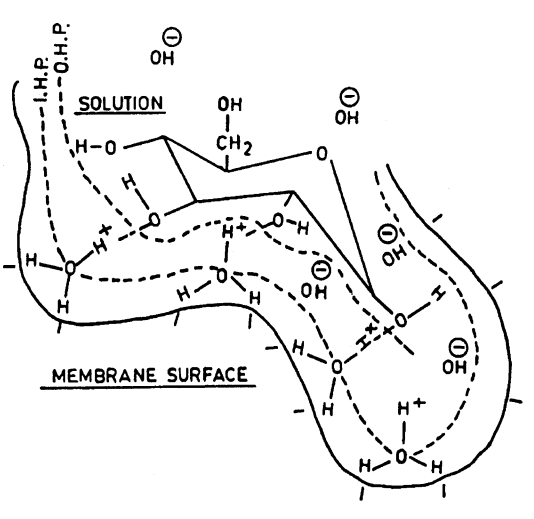


Fig. 5. Structure of the electrical double layer at the interface of progesterone–D-glucose solution.

Table 1. Phenomenological Coefficients for Progesterone/Aqueous-Urea and Progesterone/D-Glucose Systems

$C\times10^4$	$\frac{L_{11}}{T}\times10^{13}$ ($m^5 N^{-1} S^{-1}$)		$\frac{L_{22}}{T}\times10^{7}$ (S)		$\frac{L_{12}}{T}\times10^{12}$ ($m^3 S^{-1} V^{-1}$)		$\frac{L_{122}}{T^2}\times10^{10}$ ($m^3 s^{-1} V^{-2}$)
$mol\,dm^{-3}$	Glucose	Urea	Glucose	Urea	Glucose	Urea	Urea
0.0	—	—	0.80	1.12	3.42	3.40	0.0
1.0	4.18	7.51	0.85	1.21	2.92	3.16	−0.50
2.0	3.60	7.32	0.91	1.25	2.60	2.75	−0.81
4.0	2.90	6.80	0.94	1.38	1.95	2.45	−0.03
6.0	2.15	6.31	1.02	1.63	1.40	2.25	−1.52
10.0	1.10	5.40	1.15	1.95	0.90	1.70	−1.80

C=Concentration mol dm^{-3}. L_{11}=Hydrodynamic transport coefficient. L_{22}=Conductance of membrane equilibrated with permeant. L_{12}=First order electroosmotic transport coefficient. L_{122}=Second order electroosmotic transport coefficient.

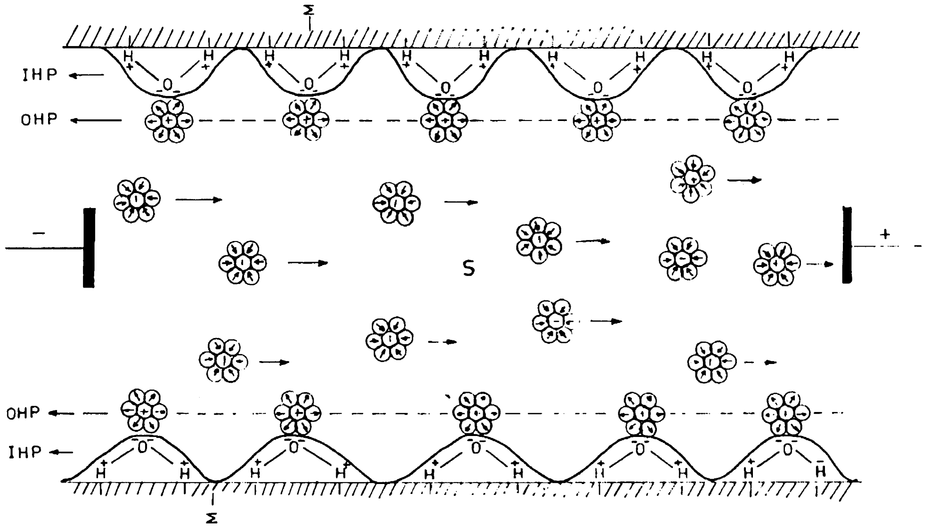


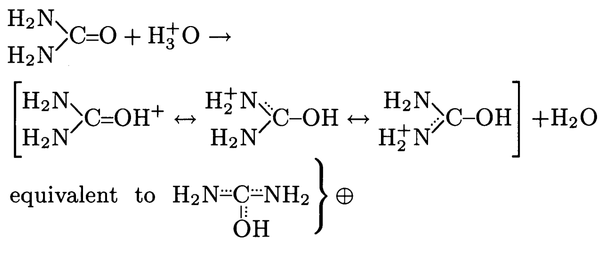
Fig. 6. Postulated picture of the electrical double layer at progesterone–aqueous urea interface. ⊕-Protonated urea molecules. ⊖-Indicates OH^-/HCO_3^-. $\ominus\text{-}\overset{H^+}{\underset{H^+}{>}}O^{2-}$. M - Membrane surface. S-Solution containing OH^-/HCO_3^- ions.

Bondarenko and Nerpin[13] studied electroosmosis in clays with various electric field intensities and found that on reaching a critical value, the electroosmosis increased sharply and then became constant again in the region of higher fields. Hadermann et al.[7] have invoked Onsager's dissociation field theory to explain departure from linearity. Y. Gur[14] attributed the nonlinearity to high surface potential in interpreting simultaneous measurements of streaming potential and electroosmotic counter pressure through a single capillary. Rastogi et al.[15—21] have suggested that nonlinearity arises due to the disturbance of the charge distribution near the interface and also argued that dipolar contributions towards the zeta potential arising from the adsorbed dipoles is also responsible for the appearance of L_{122} terms in the phenomenological transport equation.

The reasons for nonlinear electroosmotic transport observed when aqueous solutions of urea are used as permeants may be rationalized in various ways. Presence of dissolved CO_2 in conductivity water may lead to the following equilibria.

$$H_2O + H_2O \rightleftharpoons H_3^+O + OH^-,$$
$$H_2O + CO_2 \rightleftharpoons H_2CO_3,$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad (K_{a_1} = 4.3\times10^{-7}),$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad (K_{a_2} = 5.6\times10^{-11}).$$

Urea being a weak base (K_b=1.5×10^{-4}) will show a tendency to be protonated as follows.[10]



$$(H_2N)_2C{=}O + H_3^+O \rightarrow \left[(H_2N)_2C{=}OH^+ \leftrightarrow (H_2^+N)(H_2N)C{-}OH \leftrightarrow (H_2N)(H_2^+N)C{-}OH\right] + H_2O$$

$$\text{equivalent to } H_2N{\overset{\cdot\cdot}{-}}\underset{\overset{\vdots}{OH}}{C}{\overset{\cdot\cdot}{-}}NH_2 \Big\} \oplus$$

Now there will be a competition between water dipoles and protonated urea complex for adsorption at the progesterone surface and an electrical double layer will be formed as shown in Fig. 6. The electrical double layer structure shows that water dipoles get adsorbed at the membrane surface first to form the IHP of the double layer. The protonated urea complex accumulates at the OHP. The diffused part of the double layer

Table 2. Membrane Parameters (Pore radius r and zeta potentials)

$C\times 10^4$ (mol dm^{-3})	$r\times 10^6$ (m) Glucose	Urea	$\zeta_{\mathrm{e.o}}\times 10^3$ (V) Glucose	Urea
0.0	3.560	4.261	—	17.21
1.0	2.390	4.544	7.45	16.02
2.0	2.175	4.710	6.40	15.40
4.0	2.100	4.732	5.42	14.92
6.0	1.996	4.703	4.90	14.61
10.0	1.667	4.959	4.21	14.30

r = average pore radius. $\zeta_{\mathrm{e.o}}$ = zeta potential calculated using electroosmotic transport coefficient.

will have an excess of OH^-/HCO_3^- ions with the result that electroosmotic flux should occur towards the anode. The possible cause of nonlinearity in this case may be attributed to:

(i) change in the concentration of ions at the IHP and OHP of the double layer due to the applied electric field,

(ii) lateral interactions between water and urea dipoles leading to a change in the net number of water dipoles in one direction and affecting the value of dipole potential in other direction,

(iii) typical structural behavior of urea which is likely to be affected by lateral interactions between water and urea dipoles at increasing concentrations and field strength.

These points are substantiated from zeta potential values for urea recorded in Table 2.

Evaluation of Average Pore Radius and Zeta Potential. Using Eqs. 5 and 7, the average pore radius, r is give by

$$r=\sqrt{\frac{8\eta k L_{11}/T}{L_{22}/T}}. \tag{8}$$

The values of r recorded in Table 2 show that the electrical double layer theory is adequate to explain the observed results.

Zeta potential characterizes the electrical nature of membrane permeant interface. Equations 6 and 7 yield

$$\zeta_{10}=\frac{4\pi\eta k(L_{12}/T)}{(L_{22}/T)}\times 9\times 10^4 \text{ volts,}$$

where η and k are the viscosity and conductivity of permeants, respectively, and ε is the dielectric constant of the permeant.

The values of zeta potentials obtained from this equation are recorded in Table 2 and show unambiguously that the electrical double layer formed in the case of protonated urea is much pronounced than in the case of D-glucose.

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