NON-EQUILIBRIUM THERMODYNAMIC STUDIES ON MEMBRANE PENOMENA

Membrane parameters [Pore Radius and Zeta Potential]

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Abstract

Methods for estimation of some important membrane parameters viz., average pore radius and zeta potentials have been described, keeping in view the role of these parameters in explaining various membrane processes of industrial and chemical importance viz. in desalination and food processing industries and treatment of wastes.

The extent of separation is influenced by nature and characteristics of membrane itself. Therefore, average pore radii for progesterone plug membrane have been estimated using water and urea solutions from hydrodynamic permeability and membrane– permeant conductance data. Zeta potentials have been evaluated using electro- osmotic permeability and membrane-permeant conductance data.

Introduction

The use of membrane processes to achieve chosen purposes should come naturally to man since life depends on transfer of materials through many kinds of membranes in the body. However, the development of membrane processes to the point at which they can be used for industrial applications is relatively recent. The initial impetus to the development of membrane processes stemmed largely from the research on such processes for desalination. Now these processes are finding wide applications in various fields.

The extent of flow and nature of flow through a membrane is determined to a great extent by the characteristics of membrane itself. Hence, certain important parameters which provide an insight into the structural details viz. average pore radii and zeta potentials have been determined using fluid permeation measurements across progesterone plug membrane. Rastogi *et al.* [1] have used (i) electro-osmotic and hydrodynamic permeability and (ii) electro-osmotic pressure measurements, in the linear range to evaluate average pore radius for quartz plug membrane. We propose to show in this manuscript that average pore radius can also be conveniently estimated from hydrodynamic permeability and membrane-permeant conductance measurements. Zeta potentials may be evaluated from electro-osmotic permeability and membrane-permeant conductance measurements. For this purpose, measurements on hydrodynamic and electro-osmotic permeation of water and aqueous solution of urea in the concentration range 10^{-4} to 10^{-3} mol/l were carried out. Conductance of membrane equilibrated with water and various solutions of urea have also been measured [2].

Materials & Methods

Progesterone powder obtained from Sigma Chemicals Company Saint Louis U.S.A. was used as such for preparing plug membrane. Urea (A.R. grade, BDH, India) was used as such without further purification for preparing various aqueous solutions. Doubly distilled water (conductance 10^{-6} S) was used for preparing various solution.

Method for preparing plug membrane and for measurement of hydrodynamic permeability, electro-osmotic permeability and membrane-permeant conductance has been the same as described in an earlier publication [2].

Results and Discussion

According to the theory of non-equilibrium thermodynamics, the volume flux J_v and electric current 1, under the simultaneous action of pressure difference ΔP and electric potential difference $\Delta\phi$ across the membrane cane be expressed by the following phenomenological equations [3].

$$J_v = L_{11}\left(\frac{\Delta P}{T}\right) + L_{12}\left(\frac{\Delta\phi}{T}\right) \qquad (1)$$

$$I = L_{21}\left(\frac{\Delta P}{T}\right) + L_{22}\left(\frac{\Delta\phi}{T}\right) \qquad (2)$$

Where L_{11}/T and L_{22}/T are the straight coefficients and L_{12}/T and L_{21}/T are cross coefficients.

We restrict ourselves here to the use of equation (1) only. In case of the permeation of water an aqueous solution of urea through the membrane under the influence of only and hydrodynamic pressure difference ΔP equation (1) reduces to

$$\left(J_v\right)_{\Delta\phi=0} = \frac{L_{11}}{T}\left(\Delta P\right) \qquad\qquad (3)$$

The values of hydrodynamic permeability coefficient (L_{11}/T) obtained from the slope of linear plots of $(J_v)_{\Delta\phi=0}$ *vs* ΔP are recorded in Table1for Progesterone aqueous urea systems.

Within the range of investigation electro-osmotic flux $(J_v)_{\Delta P=0}$ was found to vary nonlinearly with applied potential difference $\Delta\phi$ and the following phenomenological equation [4] fits the experimentally observed results.

$$\left(J_v\right)_{\Delta P=0} = \frac{L_{12}}{T}\left(\Delta\phi\right) + \frac{1}{2}\frac{L_{122}}{T^2}\left(\Delta\phi\right)^2 \qquad\qquad (4)$$

which may also be written as

$$\frac{\left(J_v\right)_{\Delta P=0}}{\Delta\phi} = \frac{L_{12}}{T} + \frac{1}{2}\frac{L_{122}}{T^2}\left(\Delta\phi\right) \qquad\qquad (5)$$

Where L_{12}/T and L_{122}/T^2 are the first and second order electro-osmotic transport coefficients, respectively. The values of these coefficients have been determined from the intercept and slope of the linear plots of $\dfrac{\left(J_v\right)_{\Delta P=0}}{\Delta\phi}$ vs $\Delta\phi$.

The values of these coefficients are also recorded in Table 1.

Following the treatment of Overbeek [5] it can be shown that the rate of volume flux as a result of application of pressure difference ΔP and electrical potential difference $\Delta\phi$ across the membrane is given by

$$\left(J_v\right)_{\Delta\phi=0} = \frac{n\pi r^4}{8\eta\ell}\Delta P \qquad\qquad (6)$$

And $\quad\left(J_v\right)_{\Delta P=0} = \dfrac{n\in r^2}{8\eta\ell}\xi_{e.o.}\Delta\phi \qquad\qquad (7)$

Where n is the number of pores in the membrane, r is the average radius of the capillaries,ε is the dielectric constant of the permeant in the membrane pores, η is the coefficient of viscosity of the permeant, λ is the length of capillary channel and $\xi_{e.o.}$ is the zeta potential during electro-osmosis.

Comparison of equations (6) and (7) with equations (3) and (4) gives

$$\frac{L_{11}}{T} = \frac{n\pi r^4}{8\eta\ell} \qquad\qquad (8)$$

and $\quad \dfrac{L_{11}}{T} = \dfrac{n\in r^2}{4\eta\ell}.\xi_{e.o.} \qquad\qquad (9)$

The conductance of membrane-permeant system (L_{22}/T) is given by [6]

$$\frac{L_{22}}{T} = \frac{A_e k}{\ell} = \frac{n\pi r^2 k}{\ell} \qquad\qquad (10)$$

Where $A_e = \eta \pi r^2$ is the effective cross-sectional area of the membrane. The values of L_{22}/T were recorded with the help of an A.C. conductivity bridge (Toshniwal, India) at 50 Hz. Values of these coefficients are recorded in the Table1.

Evaluation of Pore Radius

Using equations (8) and (10) we have

$$r = \sqrt{\frac{8\eta k (L_{11}/T)}{(L_{11}/T)}} \qquad (11)$$

The value of r calculated using this equation is given in Table-1.

Determination of zeta potential

Electrical nature of the progesterone interfaces in various solutions of urea can be expressed in terms of zeta potential, which can be estimated by combining the electro-osmotic flux coefficient. (L_{12}/T) with the membrane permeant conductance, (L_{22}/T).

From equations (9) and (10) it follows that

$$\xi_{e.o.} = \frac{4\pi\eta k (L_{12}/T)}{\in (L_{12}/T)} e.s.u.$$

or $\quad \xi_{e.o.} = \frac{4\pi\eta k (L_{12}/T)}{\in (L_{22}/T)} \times 9 \times 10^4 \, volts.$ $\qquad (12)$

ε is the dielectric constant of the medium.

The value of zeta potentials estimated in this way is recorded in Table-1.

Acknowledgement

Table 1:   **Phenomenological coefficients and membrane parameters for progesterone-aqueous urea systems**

$C \times 10^4$ (mol/l)	$\dfrac{L_{11}}{T} \times 10^{13}$ ($m^5N^{-1}S^{-1}$)	$\dfrac{L_{22}}{T} \times 10^7$ (S)	$\dfrac{L_{12}}{T} \times 10^{12}$ ($m^3s^{-1}V^{-1}$)	$\dfrac{1}{2}\dfrac{L_{122}}{T^2} \times 10^{10}$ ($m^3s^{-1}V^{-2}$)	$R \times 10^6$ (m)	$\xi_{e.o} \times 10^3$ (V)
0.0	-	1.12	3.40	0.00	4.261	17.21
1.0	7.51	1.21	3.16	-0.50	4.544	16.02
2.0	7.32	1.25	2.75	-0.81	4.710	15.40
4.0	6.80	1.38	2.45	-0.93	4.732	14.92
6.0	6.31	1.63	2.25	-1.52	4.703	14.61
10.0	5.40	1.95	1.70	-1.80	4.959	14.30

Average value of r = (4.65±0.350)×10⁻⁶ m

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