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Electrokinetic Energy Conversion Studies Across Bio Membranes

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Electrokinetic studies of different permeants across interfaces of urinary bladder membrane, testosterone membrane, liquid membrane generated by cholesterol and some inorganic membranes have been reviewed. Electrokinetic energy conversion maxima and degree of coupling have been analysed for different systems. It has been found that energy conversion maxima and degree of coupling differ significantly even for the same permeant using different membranes. The interaction of the membrane with permeating material seems to be a decisive factor in such situations. Generally it has been observed that degree of coupling and energy conversion maxima decrease with increase in concentration except for urinary bladder membranes which responds to some of the living characteristics. The behaviour of the membrane-permeant system has been explained in terms of electrokinetic (zeta) potential and various other factors related with interfaces.

INTRODUCTION

Electrokinetic studies[1–5] across biomembranes are of immense importance due to the fact that stable and metastable states[6] existing in biological systems are the outcome of coupling of different forces operating in them. The efficiency of electrokinetic energy conversion for both modes namely electro-osmosis and streaming potential acquires special significance as the two phenomena are closely related with mobilization[7–10] of fluids in biological systems. The membranes chosen are of diverse nature *i.e.* liquid membrane generated by cholesterol, testosterone a hormonal membrane, urinary bladder membrane, which responds to some of the living properties and some of the inorganic membranes but the common characteristics is the validity of Onsager's reciprocal relationship in all the cases chosen. Some of the membranes behave non-linearly only with respect to pressure while a few demonstrate non-linearity with respect to electrical potential but urinary bladder membrane produces non-linearity with respect to both these forces. Since non-linearity is an essential criterion[11] of biological behaviour, attempts have been made to search out the elements common in all of them. Since efficiency of energy conversion[12,13] depends both on the degree of coupling and the operating conditions, evaluation of degree of coupling indicates a fair measure of dependence of one force with the other one. Thus the present paper attempts to correlate structural relationship of the membrane with permeating material.

THEORETICAL

Using methodology of non-equilibrium thermodynamics, volume flow J_v and current flow (I), across a membrane in a non-linear range may be expressed as[14-15].

$$J_v = L_{11}\Delta P + L_{12}\Delta\phi + L_{112}\Delta P\Delta\phi + \ldots \quad (1)$$

and

$$I = L_{21}\Delta P + L_{22}\Delta\phi + L_{212}\Delta P\Delta\phi + \ldots \quad (2)$$

where L_{ij}, L_{ijk} (i, j, k = 1, 2) are phenomenological coefficients.

Conversion efficiency[12, 13] for two reciprocal phenomena of electro-osmosis and streaming potential would be given as

$$\eta_o = -\frac{J_v\Delta P}{I\Delta\phi} \quad (3)$$

and

$$\eta_s = -\frac{I\Delta\phi}{J_v\Delta P} \quad (4)$$

where subscript o and s denote the phenomena of electro-osmosis and streaming potential.

Conversion efficiency is related with degree of coupling (q) in the following manner

$$\eta_{max} = \frac{q^2}{(1+\sqrt{(1-q^2)})^2} \quad (5)$$

EXPERIMENTAL

Membrane Chosen and Its Interaction with Permeant

(i) *Urinary Bladder Membrane and Urea as Permeant*

Urinary bladder stores urine, the major proportion of which is urea. The presence of aqueous urea solution (0.01M) renders *longevity* to the membrane behaviour. The concentrated urea solution is known to be a better solvent[16] both for polar and non-polar compounds. Increase of concentration is also known to be protein *denaturant*[17]. As far as its structural behaviour is concerned, it is known to be structure *maker*. The -CO- group and the two $-NH_2-$ groups of urea molecule are very much similar to those of -CO-NH group of the peptide bond of the proteins. Excretion of urea in the urine depends on many factors but mainly on proteins diet. The effect of glucose in the urine may be masked considerably[18] by the use of diet whose end product ultimately excretes urea in the urine. Thus urinary bladder/urea interface studies bear special significance.

(ii) *Testosterone-urea Interface*

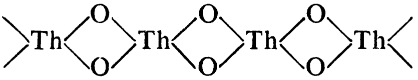
Testosterone is a male sex hormone which is responsible for distinguishing characteristics of masculine body. Besides, muscular development[19], it affects bone growth and calcium retention. Its effect on electrolyte and water balance of the body and also on red blood cells is quite obvious. The testosterone, that does not become fixed to the tissues, undergoes degradation and is excreted either into the gut in the bile or into the urine. Aqueous solution of urea has been used as permeant on account of its active role in many metabolic actions in the body and its enormous medicinal applications[20].

(iii) *Cholesterol-solution Interface*

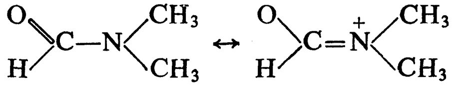
Cholesterol membrane is a model membrane which has certain dimensional, electrical permeability and excitable characteristcs that closely resemble those of biological membranes[21, 22]. It creates some circulatory problems such as hardening of arteries and high blood pressure. For deposition in arteries, and as stones in the gall bladder, the first stage is coagulation which is influenced by properties of cholesterol-solution interface[23]. In this case, liquid membrane[2] has been generated when the concentration on both sides of supporting membrane is filled with cholesterol solution of concentration equal to critical micelle concentration (CMC).

(iv) *Thorium oxide/dimethyl formamide systems*[24] (DMF)

Thorium oxide has following representative network structure



The oxygen atom lying in the matrix of the membrane causes it to have a negative charge. The dimethyl formamide permeant is coplanar and has the following resonating structures.



I II

The structure (II) is the major contributing structure. Thorium oxide membrane has been used in the form of a plug by mechanical compression.

(v) *Pyrex-etectrolyte system*[25] *and pyrex impregnated with cellulose acetate-electrolyte system*[26]

G_4 pyrex sintered disc has been chosen as a membrane and the electrolytes considered NaCl, $BaCl_2$ and $AlCl_3$ in aqueous medium. The concentration of these permeants has been changed from 10^{-4} m to 10^{-3} m. In the other case, pyrex sintered disc has been impregnated with cellulose acetate. The electrolytes chosen for studies are ammonium chloride, ammonium nitrate and mixtures of these permeants in aqueous medium.

RESULTS AND DISCUSSION

Degree of coupling and energy conversion maxima for different membranes and their permeants are given in Table 1.

Following inferences can be drawn from the values of Table 1.

(i) Energy conversion maxima and degree of coupling decrease with increase in concentration except in the case of urinary bladder membranes.

(ii) Energy conversion maxima and degree of coupling differ significantly for the same permeant using different membranes.

(iii) Degree of coupling is generally very low which shows that membrane-permeant systems considered are not tightly coupled.

TABLE 1

ELECTROKINETIC ENERGY CONVERSION STUDIES ACROSS MEMBRANES

Since η_e^{max} and η_e^{max} are approximately equal, only one value has been given

(a) Urinary bladder/urea interface

Conc. of urea (moles)	Energy conversion maxima $\eta_{max} \times 10^{-5}$	Degree of coupling $(q \times 10^{-2})$
0.02	1.83	0.8584
0.04	2.06	0.9106
0.06	2.26	0.9534
0.08	2.82	1.0634
0.10	3.22	1.1198

(b) Testo sterone/urea interface

Conc. of urea $(M \times 10^{-4})$	Energy conversion maxima $\eta_{max} \times 10^{-6}$	Degree of coupling $(q \times 10^{-3})$
1.0	0.40	1.2600
2.0	0.20	0.8944
4.0	0.30	1.0953
6.0	2.20	0.0143
10.0	0.10	0.6323

Table 1 (cond.)

(c) Cholesterol solution interface

Conc. of cholesterol nM	Energy conversion maxima $\eta_{max} \times 10^{-5}$	Degree of coupling $(q \times 10^{-2})$
0.00	66.0	5.12
9.40	65.0	5.22
15.04	62.0	4.94
28.20	51.0	4.50
30.08(CMC)	50.5	4.46
37.60	52.0	4.54
56.40	54.5	4.59

(d) Thorium oxide/dimethyl formamide system

Conc/set	Energy conversion maxima $\eta_{max} \times 10^{-5}$	Degree of coupling $(q \times 10^{-2})$
I	0.686	0.262
II	0.676	0.260
III	0.667	0.258

(e) Pyrex/Electrolyte system

Conc.	NaCl solution		$BaCl_2$ solution		$AlCl_3$ solution	
	$\eta_{max} \times 10^{-5}$	$q \times 10^{-2}$	$\eta_{max} \times 10^{-5}$	$q \times 10^{-2}$	$\eta_{max} \times 10^{-5}$	$q \times 10^{-2}$
0.0000	1.20	0.70	0.30	0.35	0.50	0.30
0.0001	0.80	0.57	0.10	0.20	0.20	0.14
0.0005	0.50	0.44	0.03	0.12	0.02	0.10
0.0010	0.34	0.34	0.02	0.08	—	—

(f) Pyrex-cellulose acetate/electrolyte system

System (Moles) NH_4Cl	$\eta_{max} \times 10^{-5}$ (Energy conversion maxima)	Degree of coupling $(q \times 10^{-2})$
1×15^{-4}	8.57	1.84×10^{-2}
1×10^{-3}	2.21	0.94×10^{-2}
1×10^{-2}	0.50	0.44×10^{-2}

Energy conversion maxima and degree of coupling are derived from the values of electro-osmosis and streaming potential respectively. The two phenomena are of opposite nature but they represent the same conclusions. Since Onsager's reciprocal relationship holds good in all the cases studied, coupling of fluxes and forces and their interdependence is quite obvious. Very low values of degree of coupling suggests that these membranes cannot be used as a source of energy. However, individual results carry useful informations:

(a) Urinary bladder stores urine, the major constituent of which is urea. Its role is passive collection and active expulsion of urine. The expulsion of urine is carried out by conversion of electrical energy into mechanical work. Such an action is the combined effect of pressure and electrical potential gradients acting on the membrane. In this process, urinary bladder membrane undergoes depolarization and repolarization. Although urine has highest polarizing[27] power, the role of individual constituents of urine cannot be underestimated. Since urea is a major constituent of urine it also interacts with urinary bladder membranes. Its polarizing power is less than urine but as far as other constituents are concerned, its contribution is significant. Increasing trend of degree of coupling indicates tightness of coupling.

(b) Testosterone-urea interface indicates very poor coupling. In other words, interaction of the two is quite weak.

(c) *Cholesterol-solution Interface.* Degree of coupling decreases with increase in concentration of cholesterol. Thus it may be inferred that efficiency of energy conversion decreases with increase in concentration of cholesterol. That is why, cholesterol deposit hampers the movement of fluid from one part to the other.

(d) *Thorium oxide/dimethyl formamide system.* In this case, degree of coupling for different sets practically remains the same.

(e) *Pyrex/electrolyte system and pyrex-cellulose acetate/electrolyte system.* It may be generallized for these membranes that degree of coupling decreases with increase in concentration of the electrolytes whether the electrolyte is monovalent, divalent or trivalent.

The conversion efficiency and degree of coupling may be explained in terms of electrokinetic behaviour of the membrane interfaces with permeating liquid. Electro-osmosis and streaming potential depend upon zeta potential in the following way:

$$J_v = \frac{i\epsilon\zeta}{4\pi K_{sp}\eta} \quad (6)$$

$$\Delta\phi_{\text{streaming}} = \frac{\Delta P \cdot \epsilon\zeta}{4\pi\eta K_{sp}} \quad (7)$$

where K_{sp} is the surface conductance, i is the current, ϵ is dielectric constant of the medium and ζ is the electrokinetic potential (zeta) developed across the membrane respectively.

Electrokinetic potential (ζ) decreases with increase in concentration in all the cases studied except in urinary bladder/urea system. Variations in the values of zeta potential are explained in terms of ionic concentrations in Inner Helmholtz Plane (IHP) and Outer Helmholtz Plane (OHP). Thus decrease of energy conversion and degree of coupling may be explained in terms of zeta potentials developed across the membranes.

Since degrees of coupling for the membranes are quite low, more of the membranes can be used as energy converter.

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REFERENCES

1. R. P. Rastogi, K. Singh, Ram Shabd and B. M. Upadhyaya, *J. Colloid Interface Sci.*, **80**, 402 (1981).
2. R. C. Srivastava and R. P. S. Jakhar, *J. Phys. Chem.*, **86**, 1941 (1982).
3. M. L. Srivastava and Bali Ram, *Carbohydrate Research*, **132**, 209 (1984).
4. P. C. Shukla and G. Misra, *J. Membrane Sci.*, **31**, 157 (1987).
5. P. C. Shukla, G. Misra and J. P. Misra, *J. Colloid. and Interface Sci.*, **129**, 53 (1989).
6. M. V. Volkenstein, Bio-Physics, MIR Publications, Moscow (1983).
7. E. Schoffeniels, Cellular Aspects of Membrane Permeability, Pergamon Press (1967).
8. S. G. Schultz, *J. Gen. Physiol.*, **59**, 794 (1972).
9. A. N. Hill, Proc. Roy. Soc. London, 190, 1 (1975).
10. E. N. Lightfoot, Transport Phenomena in Living Systems: Bio-medical aspects of momentum and mass transfer, Wiley, New York, NY (1974).
11. P. C. Shukla, O. Misra and J. P. Misra, *Bio-Phys. Chem.*, **33**, 31 (1989).
12. O. Kedem and S. R. Caplan, *Trans. Faraday Soc.*, **61**, 1897 (1965).
13. R. J. Gross and J. F. Osterle, *J. Chem. Phys.*, **49**, 228 (1968).
14. N. Lakshminarayaih, Equations of Membrane Bio-physics, Academic Press (1984).
15. J. B. Lorimer, *J. Membrane Sci.*, **25**, 181 (1985).
16. O. Enea and C. Jollcoeur, *J. Phys. Chem.*, **86**, 3870 (1982).
17. D. W. James and R. L. Frost, *J. Phys. Chem.*, **78**, 1754 (1974).
18. P. C. Shukla, G. M. Misra, J. P. Misra and Rahul Tewari, *Indian J. Exptl. Biol.* (in press).

19. A. C. Guyton, Text-book of Medical Physiology, W. B. Saunders Co., Philadeiphia, p. 998 (1981).
20. O. O. Wilson, O, Gisvold and R. P. Doerge, Text-book of Organic, Medical and Pharamaceutical Chemistry, J. B. Lippincott Co., Philadelphia, Toronto, 6th Ed., p. 795 (1971).
21. H. T. Tien, Bilayer Lipid Membranes, Marcel Dekker, New York (1974).
22. K. Singh and A. K. Tewari, *J. Colloid and Interface Sci.*, **116**, 42 (1987).
23. Ram Shabd and B. M. Upadhyaya, *Carbohydrate Research*, **93**, 191 (1981).
24. M. L. Srivastava and S. N. Lal, *J. Membrane Sci.*, **7**, 21 (1980).
25. M. L. Srivastava, Raj Kumar and S. N. Lal *Indian, J. Techn.*, **16**, 50 (1978).
26. R. L. Blokhra, M. L. Parmer and S. S. Thakur, *J. Membrane Sci.*, **21**, 123 (1984).
27. P. C. Shukla and G. Misra, *Indian J. Biochem. and Bio-phys.*, **24**, 287 (1987).

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