

Liquid membrane phenomena: Steady state energy conversion for composite membranes generated by cholesterol

Abhay K Jain*, Rajesh K Srivastava, Manoj K Gupta & Suresh K Das

Chemistry Department, St. Andrew's College, Gorakhpur 273 001, U.P., India

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The efficiencies of electro-kinetic energy conversion across composite liquid membranes generated by cholesterol on one side and both sides of the supporting membrane have been evaluated for both electroosmosis and streaming potential. The efficiencies of energy conversion have also been calculated across cholesterol liquid membranes alone in the absence of supporting membrane. The results thus obtained have been found to be consistent with the linear theories of steady state thermodynamics. An attempt has been made to relate the maximum conversion efficiency characterizing the series composite membrane as a whole with the maximum conversion efficiency for its constituent membrane elements. Substitution of the values of various experimentally evaluated parameters into the relationship developed for series membrane yields results in fair agreement for the situation when cholesterol liquid membrane is generated on one side of the supporting membrane interface.

An important phenomenon common to energy conversion devices is the direct coupling between the spontaneous processes, which serve as the energy source and the output. The formal expression for entropy production in irreversible thermodynamics leads to a clear definition of energy conversion¹⁻³. Based on the formalism developed earlier¹⁻³, Srivastava and Jain^{4,5} have experimentally determined the efficiency of electrokinetic energy conversion for both modes, viz., electroosmosis and streaming potential. The results thus obtained have been shown to be consistent with the steady-state thermodynamics.

The primary objectives of the studies reported in this paper are: (a) to investigate the relationship between the maximum conversion efficiency characterizing the composite series membrane as a whole and that of its constituent membrane elements; and (b) to check the validity of the derived relationship from the experimentally evaluated parameters. We report here conversion efficiencies for the composite series membrane systems generated by cholesterol on one and both sides of the supporting membrane as well as for the constituent membrane elements from electroosmotic transport data.

The membranes composed of different elements arranged in series array are of special interest not only because they occur frequently in living systems but also because of their remarkable physical properties.

Theory

The explicit phenomenological relations for the simultaneous transport of matter and electricity in the linear range can be written as^{6,7},

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

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

which follow from the following dissipation equation,

$$T \frac{dis}{dt} = J_v \Delta P + I \Delta \phi \quad \dots (3)$$

In Eqs (1), (2) and (3), J_v and I represent volume flux and flow of electricity respectively in presence of both pressure difference, ΔP , and electrical potential difference, $\Delta \phi$. The coefficients L_{ik} are called the phenomenological coefficients. In accordance with Onsager's reciprocal relation (ORR), we have

$$L_{12} = L_{21} \quad \dots (4)$$

Since in irreversible processes $dis/dt \geq 0$, it follows that L_{11} and L_{22} are always positive and L_{12} (or L_{21}) is subject to the restriction^{6,7},

$$L_{12}^2 \leq L_{11} L_{22} \quad \dots (5)$$

The phenomenological description of two coupled flows¹ leads to the definition of 'degree of coupling', q , which is limited by the Eq. (5). The quantity q is related to the phenomenological coefficients in the following manner^{1,8}:

For electroosmosis,

$$q_e = L_{12}/\sqrt{L_{11}L_{22}} \quad \dots (6)$$

For streaming potential,

$$q_s = L_{21}/\sqrt{L_{11}L_{22}} \quad \dots (7)$$

where subscripts e and s stand for phenomena of electroosmosis and streaming potential, respectively.

In view of Eqs (1) and (2), the conversion efficiency for the two reciprocal phenomena of electroosmosis and streaming potential would be given by^{4,5} Eqs (8) and (9) respectively.

$$\eta_e = -J_v \Delta P / I \Delta \phi \quad \dots (8)$$

$$\eta_s = -I \Delta \phi / J_v \Delta P \quad \dots (9)$$

In a coupled system the maximum conversion efficiency is uniquely determined by the degree of coupling¹ (Eq. 10).

$$\eta_{\max} = \frac{q^2}{(1 + \sqrt{1 - q^2})^2} \quad \dots (10)$$

For very low values of q, the term q² becomes negligible in comparison to unity and Eq. (10) reduces to,

$$\eta_{\max} = \frac{q^2}{4} \quad \dots (11)$$

Efficiency of energy conversion for series membranes

In dealing with composite series membranes, it is more convenient to utilize inverse phenomenological relations⁷ between thermodynamic forces, X, and fluxes, J, i.e.,

$$X_i = \sum_k R_{ik} J_k \quad \dots (12)$$

Here the resistance coefficients (R_{ik}) are connected to the coefficients (L_{ik}) (cf. Eqs 1 and 2) by Eq. (13),

$$R_{ik} = \frac{A_{ik}}{|L|} \quad \dots (13)$$

A_{ik} being the minor of L_{ik} and |L| the determinant of L_{ik}. Since for a symmetrical matrix L_{ik} the complements A_{ik} are symmetrical too, the R_{ik}'s obey the Onsager's reciprocal relation,

$$R_{ik} = R_{ki} \quad \dots (14)$$

The relationship between various transport coefficients characterizing the series membrane as a

whole and the coefficients for its constituent membrane elements in terms of R_{ik} coefficients can be written for two membrane elements as⁹⁻¹²:

$$R_{ik}^B = R_{ik}^h + R_{ik}^k$$

or in general

$$R_{ik}^B = \sum_r R_{ik}^r \quad \dots (15)$$

In Eq. (15), superscript B stands for total series system and superscripts h, k and r stand for constituent membrane elements.

If the degree of coupling for the rth membrane element is q^r, Eq. (6) in terms of R_{ik} coefficients can be written as,

$$q^r = -\frac{R_{12}^r}{\sqrt{R_{11}^r R_{22}^r}} \quad \dots (16)$$

On the basis of similar considerations the degree of coupling for the total series membrane can be written as,

$$q^B = -\frac{R_{12}^B}{\sqrt{R_{11}^B R_{22}^B}} \quad \dots (17)$$

Making use of Eqs (15), (16) and (17), we can arrive at the following relationship,

$$q^B = \sum_r q^r b_{ik}^r \quad \dots (18)$$

in which

$$b_{ik}^r = \left(\frac{R_{11}^r R_{22}^r}{R_{11}^B R_{22}^B} \right)^{1/2}$$

Eq. (18) represents the relationship between degree of coupling characterising the composite series system as a whole and its constituent membrane elements. Now, substituting Eq. (18) in Eq. (11), we can derive the following relation,

$$\sqrt{\eta_{\max}^B} = \sum_r \sqrt{\eta_{\max}^r} b_{ik}^r \quad \dots (19)$$

Eq. (19) express the relationship between the maximum conversion efficiency characterizing the total series membrane and that for its constituent membrane elements.

Materials and Methods

Cholesterol (Sigma Chemicals) was recrystallized from absolute ethanol before use. Water was

distilled once over potassium permanganate and ethanol was purified by the method described in the literature¹³. Aqueous solutions of cholesterol were prepared by the method adopted by Srivastava and Jakhar¹⁴. The CMC of the aqueous solution of cholesterol was found to be ~ 3.0 nM.

The electroosmotic cell used in the present studies and the procedure followed for the measurements of ordinary permeability, electroosmotic velocity, streaming potential and streaming current were similar to those already described by Srivastava and Yadav¹⁵. The electroosmotic cell was kept in a thermostat maintained at 38 ± 0.1°C.

Results and Discussion

From Eqs (1) and (2), it is obvious that the $[(J_v)_{\Delta\phi=0}, \Delta P]$, $[(J_v)_{\Delta P=0}, \Delta\phi]$, $[(\Delta\phi)_{I=0}, \Delta P]$ and $[(I)_{\Delta\phi=0}, \Delta P]$ plots should be linear and pass through the origin. The values of various phenomenological coefficients (L_{11} , L_{12} , L_{21} and L_{22}) for various concentrations of aqueous solutions of cholesterol which were used to generate liquid membranes on one and both sides of the supporting membrane were estimated from the slopes of the above mentioned linear plots and are recorded in Table 1. The validity of the relation $L_{12} = L_{21}$ is also obvious from the data in Table 1. These results are in conformity with the earlier findings¹⁴.

In the present experimental studies, two types of the series membranes can be visualized: the

type (i) in which liquid membranes were generated on one side of the supporting membrane and the type (ii) in which supporting membrane was sandwiched between liquid membranes. Evidently, in situation (i) we consider two membrane elements, i.e., sintered glass membrane and one unit of cholesterol liquid membrane and in situation (ii) we consider three membrane elements, i.e. sintered glass membrane and two units of cholesterol liquid membranes. With these considerations we can recast Eq. (15) for situation (i) as,

$$R_{ik}^T = R_{ik}^G + R_{ik}^C \quad \dots (20)$$

and for situation (ii) as,

$$R_{ik}^* = R_{ik}^G + 2R_{ik}^C \quad \dots (21)$$

In Eqs (20) and (21) superscripts G, C, T and * denote the sintered glass membrane, cholesterol liquid membrane, series membrane in situation (i) and series membrane in situation (ii) respectively. Before making use of Eqs (20) and (21) for estimation of the R_{ik}^C values, it is necessary to transform L_{ik} coefficients given in Table 1 into R_{ik} coefficients. Using the values of L_{ik} coefficients in Eq. (13), we have estimated the values of R_{ik} coefficients for various systems and these are recorded in Table 2. The values of R_{ik}^C in Table 3(a) were calculated using Eq. (20) whereas the values of R_{ik}^C in Table 3(b) were obtained using Eq. (21). Then the data in Table 3 were utilized to draw the graphs between $(J_v)_{\Delta\phi=0}$ and ΔP , $(J_v)_{\Delta P=0}$ and $\Delta\phi$, $(\Delta\phi)_{I=0}$ and ΔP , and $(I)_{\Delta\phi=0}$ and ΔP for eval-

Table 1 – Values of various phenomenological coefficients, β , η_{max} and q for series systems

| [Cholesterol] (nM) | $L_{11} \times 10^{12}$ ($ni^2N^{-1}s^{-1}$) | $L_{12} \times 10^{10}$ (m^3AJ^{-1}) | $L_{21} \times 10^{10}$ (m^3AJ^{-1}) | $L_{22} \times 10^4$ (ohm^{-1}) | $\beta_c \times 10^3$ | $\beta_s \times 10^3$ | $\eta_{\epsilon_{max}} \times 10^3$ from β_c | $\eta_{s_{max}} \times 10^3$ from β_s | $\eta_{\epsilon_{max}} \times 10^3$ from plot of η_c vs ΔP | $\eta_{s_{max}} \times 10^3$ from plot of η_s vs $\Delta\phi$ | $q \times 10^2$ |
|-----------------------|---|---|---|--|-----------------------|-----------------------|--|---|--|---|-----------------|
| (a) Situation (i) | | | | | | | | | | | |
| 0.0 | 1.355 | 2.750 | 2.750 | 0.268 | 2.082 | 2.082 | 0.520 | 0.520 | 0.49 | 0.49 | 4.563 |
| 10.0 | 1.216 | 2.310 | 2.300 | 0.252 | 1.741 | 1.726 | 0.435 | 0.431 | 0.43 | 0.43 | 4.163 |
| 15.0 | 1.153 | 1.810 | 1.800 | 0.198 | 1.435 | 1.419 | 0.358 | 0.354 | 0.36 | 0.33 | 3.778 |
| 20.0 | 1.130 | 1.640 | 1.640 | 0.189 | 1.259 | 1.259 | 0.314 | 0.314 | 0.31 | 0.31 | 3.548 |
| 25.0 | 1.038 | 1.140 | 1.150 | 0.143 | 0.875 | 0.890 | 0.218 | 0.222 | 0.22 | 0.22 | 2.972 |
| 30.0 | 0.869 | 0.916 | 0.920 | 0.129 | 0.748 | 0.755 | 0.187 | 0.188 | 0.18 | 0.18 | 2.742 |
| 35.0 | 0.822 | 0.846 | 0.841 | 0.129 | 0.675 | 0.667 | 0.168 | 0.166 | 0.16 | 0.17 | 2.590 |
| 40.0 | 0.775 | 0.714 | 0.714 | 0.117 | 0.562 | 0.562 | 0.140 | 0.140 | 0.14 | 0.14 | 2.354 |
| 45.0 | 0.747 | 0.572 | 0.569 | 0.095 | 0.461 | 0.456 | 0.115 | 0.114 | 0.12 | 0.11 | 2.142 |
| (b) Situation (ii) | | | | | | | | | | | |
| 15.0 | 0.619 | 0.485 | 0.444 | 0.090 | 0.422 | 0.354 | 0.105 | 0.088 | 0.103 | 0.087 | 1.968 |
| 20.0 | 0.466 | 0.357 | 0.340 | 0.070 | 0.391 | 0.354 | 0.098 | 0.088 | 0.094 | 0.078 | 1.929 |
| 30.0 | 0.346 | 0.275 | 0.272 | 0.063 | 0.347 | 0.332 | 0.087 | 0.107 | 0.087 | 0.088 | 1.852 |
| 35.0 | 0.307 | 0.237 | 0.241 | 0.061 | 0.299 | 0.310 | 0.075 | 0.077 | 0.078 | 0.084 | 1.746 |

Table 2 – Values of various resistance coefficients; q, and η_{\max} for series system

| [Cholesterol] (nM) | $R_{11} \times 10^{-12}$ ($m^{-5} NS$) | $-R_{12} \times 10^{-6}$ ($m^{-3} A^{-1} J$) | $-R_{21} \times 10^{-6}$ ($m^{-3} A^{-1} J$) | $R_{22} \times 10^{-4}$ (ohm) | $q \times 10^3$ | $\eta_{\max} \times 10^3$ computed from q |
|-----------------------|---|---|---|----------------------------------|-----------------|---|
| (a) Situation (i) | | | | | | |
| 0 | 0.738 | 7.575 | 7.575 | 3.732 | 4.563 | 0.520 |
| 15 | 0.868 | 7.938 | 7.894 | 5.057 | 3.788 | 0.358 |
| 20 | 0.884 | 7.679 | 7.679 | 5.291 | 3.551 | 0.315 |
| 30 | 1.150 | 8.170 | 8.206 | 7.751 | 2.736 | 0.187 |
| 35 | 1.216 | 7.978 | 7.931 | 7.751 | 2.598 | 0.168 |
| (b) Situation (ii) | | | | | | |
| 15 | 1.615 | 8.705 | 7.969 | 11.110 | 2.055 | 0.105 |
| 20 | 2.146 | 10.944 | 10.423 | 14.285 | 1.976 | 0.097 |
| 30 | 2.890 | 12.615 | 12.478 | 15.870 | 1.862 | 0.086 |
| 35 | 3.257 | 12.655 | 12.869 | 16.390 | 1.732 | 0.075 |

Table 3 – Values of various resistance coefficients, q and η_{\max} for cholesterol liquid membranes

| [Cholesterol] (nM) | $R_{11}^c \times 10^{-12}$ ($m^{-5} NS$) | $-R_{12}^c \times 10^{-6}$ ($m^{-3} A^{-1} J$) | $-R_{21}^c \times 10^{-6}$ ($m^{-3} A^{-1} J$) | $R_{22}^c \times 10^{-4}$ (ohm) | $q \times 10^2$ | $\eta_{\max} \times 10^4$ computed from q |
|-----------------------|---|---|---|------------------------------------|-----------------|---|
|-----------------------|---|---|---|------------------------------------|-----------------|---|

(a) R_{ik}^c values evaluated considering unit layer of liquid membrane generated on one side of the supporting membranes

| | | | | | | |
|----|-------|-------|-------|-------|-------|-------|
| 15 | 0.130 | 0.363 | 0.319 | 1.325 | 0.822 | 0.168 |
| 20 | 0.146 | 0.104 | 0.104 | 1.559 | 0.217 | 0.017 |
| 30 | 0.412 | 0.595 | 0.631 | 4.019 | 0.476 | 0.056 |
| 35 | 0.478 | 0.403 | 0.356 | 4.019 | 0.273 | 0.018 |

(b) R_{ik}^c values evaluated considering two unit layers of liquid membranes, i.e., one unit liquid membrane on each side of the supporting membrane

| | | | | | | |
|----|-------|-------|-------|-------|-------|-------|
| 15 | 0.438 | 0.565 | 0.197 | 3.689 | 0.299 | 0.022 |
| 20 | 0.704 | 1.684 | 1.424 | 5.276 | 0.805 | 0.162 |
| 30 | 1.076 | 2.520 | 2.450 | 6.069 | 0.972 | 0.236 |
| 35 | 1.259 | 2.540 | 2.647 | 6.325 | 0.919 | 0.211 |

uating the efficiency of energy conversion across liquid membrane alone.

Steady state energy conversion

On the basis of theoretical considerations¹⁻⁵ and experimental findings¹⁶⁻²⁰ of the efficiency of energy conversion as defined by Eqs (8) and (9), the following general conclusions have been reached:

(1) The maximum conversion efficiency for a fixed value of input force always occurs when output force equals half its steady state value.

(2) The value of maximum conversion efficiency is independent of applied input force.

(3) The values of maximum conversion efficiency for both modes of conversion, i.e., electroosmosis and streaming potential, are equal as a consequence of Onsager's reciprocal relation.

Utilizing Eqs (8) and (9), we calculated the values of η_e and η_s for sintered glass membrane, series membranes in situation (i), series membranes in situation (ii) and also for cholesterol li-

quid membranes alone corresponding to two fixed values of input forces using the method described earlier^{4,8} from the transport data on ordinary permeability, electroosmotic velocity, streaming potential and streaming current at several values of output forces ranging between zero and their steady state values. Some typical results are shown in Figs 1 and 2. These figures clearly demonstrate the validity of all the three conclusions listed above. The values of $\eta_{e \cdot \max}$ and $\eta_{s \cdot \max}$ for all the systems and at various concentrations of cholesterol obtained from the curves of the type shown in Figs 1 and 2 are given in Table 1.

In order to ascertain the consistency of the results, the values of maximum conversion efficiency, $\eta_{e \cdot \max}$ and $\eta_{s \cdot \max}$, have been evaluated from the respective values of the figure of merit, β (Eq. 22)^{3,16-20},

$$\eta_{e \cdot \max} = \frac{(1 + \beta_e)^{1/2} - 1}{(1 + \beta_e)^{1/2} + 1}; \eta_{s \cdot \max} = \frac{(1 + \beta_s)^{1/2} - 1}{(1 + \beta_s)^{1/2} + 1} \dots (22)$$

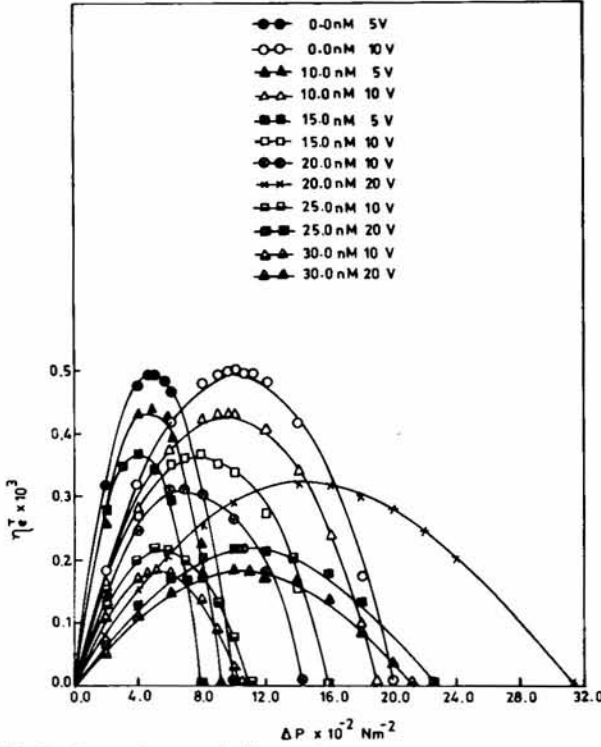


Fig.1 – Dependence of η_c^T on ΔP at two fixed values of input force ($\Delta\phi$) when cholesterol liquid membranes are generated in series with supporting membrane on one side

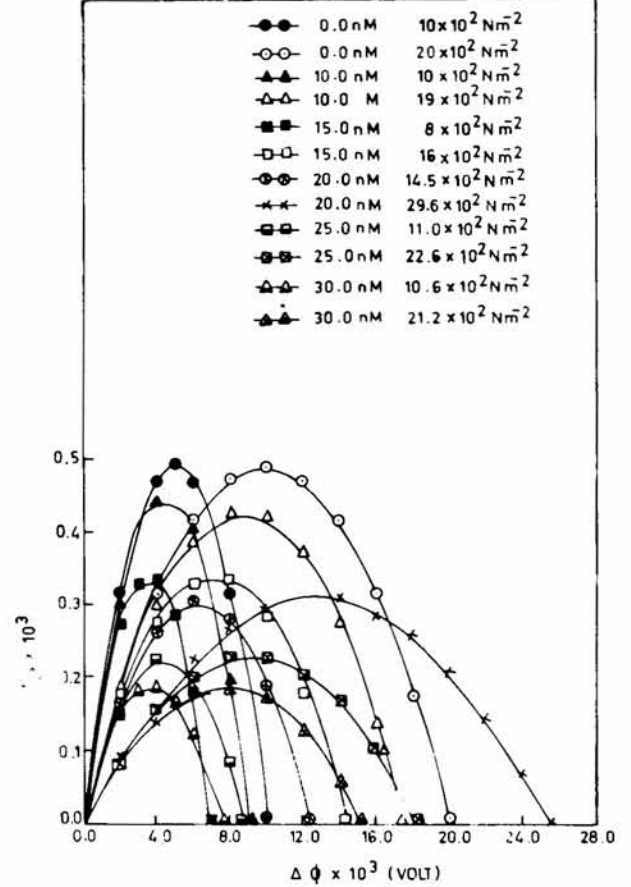


Fig. 2 – Dependence of η_s^T on $\Delta\phi$ at two fixed values of input force (ΔP) when cholesterol liquid membranes are generated in series with supporting membrane on one side

where β_c and β_s are related to the phenomenological coefficients in the following manner,

$$\beta_c = \left(\frac{L_{11}L_{22}}{L_{12}^2} - 1 \right)^{-1}, \quad \beta_s = \left(\frac{L_{11}L_{22}}{L_{21}^2} - 1 \right)^{-1} \quad \dots (23)$$

The values of β_c and β_s calculated from Eq. (23) are given in Table 1 for all the series systems which satisfy the relationship $\beta_c = \beta_s$ as a consequence of validity of Eq. (4). The values of maximum conversion efficiencies evaluated from Eq. (22) were found to be in fair agreement with the values predicted from the maxima of the curves plotted between η_c and ΔP and η_s and $\Delta\phi$ (Table 1). Alternatively, the consistency of the results can be checked from Eq. (10) using the values of q_c and q_s defined by Eqs (6) and (7) for L_{ik} coefficients and Eqs (16) and (17) for R_{ik} coefficients. The values of degree of coupling obtained from the mean of two cross phenomena, $(q_c + q_s/2)$ (Tables 1 and 2) show that the values of q and η_{max} calculated using the values of L_{ik} coefficients are in fair agreement with those evaluated from R_{ik} coefficients. This further corroborates the consistency of the results.

Test of equation (19)

Eq. (19) for the two membrane elements can be rewritten as,

$$\sqrt{\eta_{max}^T} = \sqrt{\eta_{max}^G} \left(\frac{R_{11}^G R_{22}^G}{R_{11}^T R_{22}^T} \right)^{1/2} + \sqrt{\eta_{max}^C} \left(\frac{R_{11}^C R_{22}^C}{R_{11}^T R_{22}^T} \right)^{1/2} \quad \dots (24)$$

Eq. (24) was tested for the electroosmotic conversion efficiency in the following manner. For a particular concentration of cholesterol (say 15.0 nM) the value of $\eta_{c,max}^i$ (i.e., at 0.0 nM) was noted from Table 1(a), the value of $\eta_{c,max}^c$ was noted from Table 3(a), the values of $R_{11}^G, R_{22}^G, R_{11}^T$ and R_{22}^T were noted from Table 2(a) and the values of R_{11}^C and R_{22}^C were noted from Table 3(a). Substituting these values in Eq. (24), we calculated the value of $\eta_{c,max}^T$. The value of $\eta_{c,max}^T$ thus predicted was found to agree with the values read from the plot between η_c^T and ΔP for all concentrations. A comparison of these values is given in Table 4. Similarly, Eq. (24) can be tested for the phenomenon of streaming potential.

For the series system in situation (ii), Eq. (19) can be recasted as,

Table 4 – Comparison of the values of η_{\max}^T and η_{\max}^* calculated from Eqs (24) and (25) respectively with those predicted from the maxima of the curves

| [Cholesterol] (nM) | $\eta_{\max}^T \times 10^4$ | | $\eta_{\max}^* \times 10^4$ | |
|-----------------------|-----------------------------|--|-----------------------------|--|
| | Calc. from Eq. (24) | Predicted from plot of η_e^T and ΔP | Calc. from Eq. (25) | Predicted from plot of η_e^* and ΔP |
| 15 | 3.56 | 3.65 | 0.872 | 1.03 |
| 20 | 3.16 | 3.15 | 0.482 | 0.94 |
| 30 | 1.87 | 1.85 | 0.364 | 0.83 |
| 35 | 1.67 | 1.65 | 0.295 | 0.78 |

$$\sqrt{\eta_{\max}^*} = \sqrt{\eta_{\max}^G} \left(\frac{R_{11}^G R_{22}^G}{R_{11}^* R_{22}^*} \right)^{1/2} + 2 \sqrt{\eta_{\max}^C} \left(\frac{R_{11}^C R_{22}^C}{R_{11}^* R_{22}^*} \right)^{1/2} \dots (25)$$

To test Eq. (25), R_{11}^C and R_{22}^C values were noted from Table 3(b) and R_{11}^* and R_{22}^* values were noted from Table 2(b) at 15.0 nM concentration. The values of $\eta_{e\text{-max}}^*$ predicted from Eq. (25) were found to agree with the values obtained from the plots between η_e^* and ΔP . However, when the values of R_{11}^C and R_{22}^C were used from Table 3(a), the values of $\eta_{e\text{-max}}^*$ obtained from Eq. (25) were not found to agree with the values predicted from the plots between η_e^* and ΔP (Table 4).

This discrepancy can be rationalized by taking into consideration polarity of flow which leads to a correlation between macroscopic observables and membrane structure⁹⁻¹¹. The polarity of flow is expected to arise from the transition layers which may be considered as additional membrane elements⁹⁻¹¹. This situation is likely to occur in the present series system because of any specific orientation²¹ of the surfactant molecules at the interface and interactions between the surfactant molecules themselves either by lipid-lipid interaction²² or through hydrogen bonding²³ between the hydroxyl group of cholesterol molecules.

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References

- 1 Kedem O & Caplan S R, *Trans Faraday Soc*, 61 (1965) 1897.
- 2 Rottenberg H, Caplan S R & Essing A, *Membrane and ion transport*, Vol I, edited by E Edward Bitter (Wiley Interscience, NY) 1970, 165.
- 3 Osterle J F, *Appl Sci Res*, 12 (1964) 425.
- 4 Srivastava R C & Jain A K, *J Hydrol*, 25 (1975) 339.
- 5 Srivastava R C & Jain A K, *J polymer Sci (Polymer Phys Ed)*, 13 (1975) 1603.
- 6 Prigogine I, *Introduction to the thermodynamics of irreversible processes* (Wiley, New York) 1968.
- 7 Katchalsky A & Curran P F, *Non-equilibrium thermodynamics in bio-physics*, (Harvard University Press, Cambridge) 1965.
- 8 Jain A K, Tewari R K & Srivastava R K, *J membrane Sci*, 31 (1987) 195.
- 9 Kedem O & Katchalsky A, *Trans Faraday Soc*, 59 (1963) 1918.
- 10 Kedem O & Katchalsky A, *Trans Faraday Soc*, 59 (1963) 1931.
- 11 Kedem O & Katchalsky A, *Trans Faraday Soc*, 59 (1963) 1941.
- 12 Srivastava R C & Jain A K, *J Hydrol*, 25 (1975) 325.
- 13 Vogel AI, *A text book of practical organic chemistry*, 3rd edn (Longmans Green, London), 1956.
- 14 Srivastava R C & Jakhar R P S, *J phys Chem*, 85 (1981) 1457.
- 15 Srivastava R C & Yadav S, *J non-equilib Thermodyn*, 4 (1979) 219.
- 16 Srivastava R C & Abraham M G, *J Colloid Interface Sci*, 57 (1976) 58.
- 17 Srivastava R C, Abraham M G & Jain A K, *J phys Chem*, 81 (1977) 906.
- 18 Jain A K, Tewari R K & Mishra R K, *Indian J Chem*, 18A (1979) 112.
- 19 Jain A K, Tewari R K & Mishra R K, *J non-equilib Thermodyn*, 5 (1980) 275.
- 20 Jain A K & Tewari R K, *Indian J Chem*, 24A (1985) 923.
- 21 Haydon D A & Taylor J, *J theor Biol*, 4 (1963) 281.
- 22 Gershfeld N L & Pagano R E, *J phys Chem*, 76 (1972) 1231.
- 23 Parker P S & Bhaskar K P, *Biochemistry*, 7 (1968) 1286.