

Studies of Cellulose Acetate Supported Ergosterol Liquid Membrane

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Abstract

Supported liquid membrane on cellulose acetate matrix has been formed by using ergosterol, a fungal product as a surfactant. The behaviour of this membrane has been simulated with biological membranes by its electrochemical characterization. For this purpose membrane potential has been measured using NaCl and CaCl₂ solutions of different concentrations. Ionic transport numbers have been used to estimate fixed charge density and permselectivity. The variation of membrane potential has also been examined as a function of concentration and pH values of NaCl & CaCl₂ solutions.

Keywords: Ergosterol; Liquid membrane

Introduction

Liquid membrane technology has attracted attention recently because of its numerous applications which include gas transport, metal ion recovery, waste water treatment, reverse osmosis, desalination, biotechnology and biomedical engineering [1-6]. Liquid membranes are usually formed at every interface encountered by a surfactant solution. Permeation through liquids is orders of magnitude faster than that through solid polymers of comparable thickness. Among various studies on surfactant generated liquid membranes [7], the studies with surfactants of fungal origin are rare. Ergosterol is a fungal product and a biologically important material known as provitamin D which can be converted to vitamin D₂ on exposure to ultraviolet radiation. The epidermal cells of the skin of man and animal contain large amount of ergosterol, which is converted to vit D₂ by exposure of the skin to sunlight. Vitamin D₂ is a powerful antirachitic compound for man and rat. It helps in maintaining the levels of calcium and phosphorus in the body and is involved in resorption of calcium from calcified bones by osteolytic cells. Vitamin D₂ is necessary for proper growth of bone and teeth.

Ergosterol has therefore been used in the present investigation as a surfactant for the formation of liquid membrane supported on the cellulose acetate matrix. Ergosterol is a white crystalline compound. There is a hydroxyl group present in ergosterol. Three double bonds are also present in its nucleus. Ergosterol is non ionic as such. The liquid membrane has been electrochemically characterized by measuring membrane potentials by the use of NaCl, and CaCl₂ solutions of various concentrations. Structure of ergosterol is given in Figure 1.

Materials and Methods

The film of cellulose acetate was prepared as already reported [8]. The thickness of cellulose acetate film used was 7.3×10^{-5} m and its cross sectional area was 1.78×10^{-4} m². Liquid membrane generation was accomplished [9,10] following the method suggested by Gershfeld and Pagano [11]. A large amount of water was added to a known amount of ergosterol (ACROS ORGANICS) dissolved in ethanol. The mixture was constantly stirred. Dispersions of ergosterol of different known concentrations were thus prepared. Generation of liquid membrane was carried out by first equilibrating the film with water and then keeping it in contact with ergosterol solution of lowest concentration. To ascertain the minimum concentration needed for liquid membrane formation, Ergosterol suspension of different concentrations were prepared and used. The minimum ergosterol concentration needed

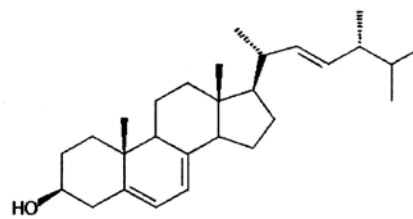


Figure 1: Ergosterol.

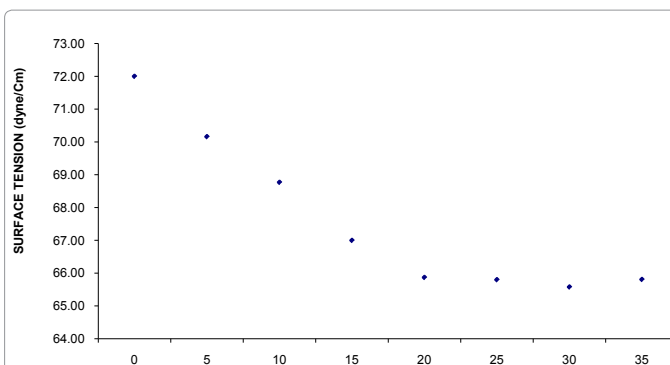


Figure 2: Critical Micelle Concentration Determination by Surface Tension Measurements.

for complete liquid membrane formation was found to be 20 µM. It is believed that liquid membrane formation occurs when the critical micelle concentration (CMC) is exceeded. The CMC was determined by measuring surface tension and it was found to be 20 µM. Membrane resistance was measured. Ergosterol dispersions of higher concentration (35 µM) were used in the present study.

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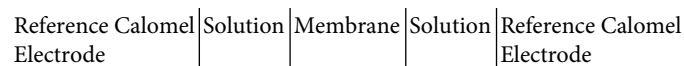
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Membrane potential was measured as usual [12] with the help of digital multimeter (MAS 830) using calomel electrodes. Sodium chloride and calcium chloride solutions of unequal concentrations with and without ergosterol were kept on either side of the supported matrix to allow equilibration and liquid membrane formation. Membrane potentials were also measured in the same manner using sodium chloride and calcium chloride solutions of different pH values.

Results and Discussion

The formation of liquid membrane was ascertained by measuring membrane resistance using ergosterol suspensions of different concentrations. Due to accumulation of ergosterol in the interfacial region, the resistivity changed and approached a constant value after 3-4 h. This was attributable to the accumulation of ergosterol in the interfacial region. The plot of surface tension against concentrations of ergosterol solutions is given in Figure 2. The trend shows that upto the CMC (20 μM) of ergosterol and thereafter the values of surface tension become constant. This is in consonance with Kesting's hypothesis. With increasing concentration of ergosterol, the surface tension of water is lowered showing that the interface is being progressively covered. The critical micelle concentration must be exceeded for the occurrence of complete liquid membrane formation. Surface tension was also measured when the surfactant solution contained different concentrations of electrolytes (NaCl and CaCl₂). The value of CMC in presence of all the electrolytes remains almost constant (Figure 3,4). A curve almost parallel to concentration axis ensures that the interface is completely covered. Membrane potential was measured using the following type of experimental cell:



The condition I=0 is fulfilled by short circuiting electrodes and then taking measurements.

The formation of liquid membrane is indicated by lowering of membrane potential and it is clear from the membrane potential values, given in Table 1,2.

Since cellulose acetate is practically uncharged its selectivity is considerably low. Permselectivity was estimated using the equation [13]

$$P_s = \frac{t_+ - t_-}{t_+ - (2t_+ - 1)t_-} \quad (1)$$

The transport number on the basis of TMS theory may be given as [14], for 1:1 electrolyte i.e. for NaCl and KCl.

$$\bar{t}_+ = \frac{E}{2E_{\max}} + 0.5 \quad (2)$$

Where the symbols have their usual meaning. A simplification of TMS theory gives:

$$E = \frac{RT}{F} (2\bar{t}_+ - 1) \ln \frac{a_1}{a_2} \quad (3)$$

and if the membrane is ideally selective,

$$E_{\max} = \frac{RT}{F} \ln \frac{a_1}{a_2} \quad (4)$$

Permselectivity is related to fixed charge density as [15]

$$\bar{\phi} = \frac{2\bar{c}P_s}{\sqrt{1 - P_s^2}} \quad (5)$$

Where \bar{c} is the mean concentration.

For CaCl₂, which is 2:1 electrolyte, the membrane potential which is in fact the liquid junction potential is given as [16]

$$E_L = \left[1 - \frac{3}{2} \bar{t}_+ \right] \frac{RT}{F} \ln \frac{a_1}{a_2} \quad (6)$$

Where the activities are the geometric mean activities. For an ideally selective membrane this potential is given as

$$E_{\max} = \frac{-RT}{2F} \ln \frac{a_1}{a_2} \quad (7)$$

Teorell-Meyer-Sievers theory gives the following expression for membrane potential for 2:1 electrolyte [17]

$$E = \left[1 - \frac{3}{2} \bar{t}_+ \right] \frac{RT}{F} \ln \frac{a_1}{a_2} \quad (8)$$

Solving Eqs (6) and (8) the transport number \bar{t}_+ , may be given as :

$$\bar{t}_+ = \frac{E}{E_L} \left[\bar{t}_+ - \frac{2}{3} \right] + \frac{2}{3} \quad (9)$$

For calculating \bar{t}_+ the experimentally measured values of membrane potential E, have been used.

In Table 3 the values of transport numbers for CaCl₂ are given which are calculated using eqn. 9. E_L and E_{max} values, calculated by using eqs (6) and (7) are also recorded in this table.

C (mol-dm ⁻³)	C ₁ (mol-dm ⁻³)		C ₂ (mol-dm ⁻³)	E (mV)	
	f ₁	f ₂		Without ergosterol	With ergosterol
0.15	0.2	0.6949	0.1	14.9	12.5
0.30	0.4	0.5976	0.2	13.6	11.1
0.45	0.6	0.5263	0.3	12.3	10.3
0.60	0.8	0.4828	0.4	11.6	9.7
0.75	1.0	0.4430	0.5	10.3	9.1

Table 1: Membrane potential data at different mean concentration of NaCl with and without ergosterol.

C (mol-dm ⁻³)	C ₁ (mol-dm ⁻³)		C ₂ (mol-dm ⁻³)		E (mV)	
	f ₁	f ₂	f ₁	f ₂	Without ergosterol	With ergosterol
0.075	0.1	0.5322	0.05	0.6402	14.5	13.6
0.15	0.2	0.4828	0.1	0.5322	13.1	12.3
0.30	0.4	0.2833	0.2	0.4828	12.8	11.4
0.60	0.8	0.1680	0.4	0.2833	11.9	10.1
0.75	1.0	0.1361	0.5	0.2441	7.5	6.4

Table 2: Membrane potential data at different mean concentration of CaCl₂ with and without ergosterol at 25° ± 0.1°C.

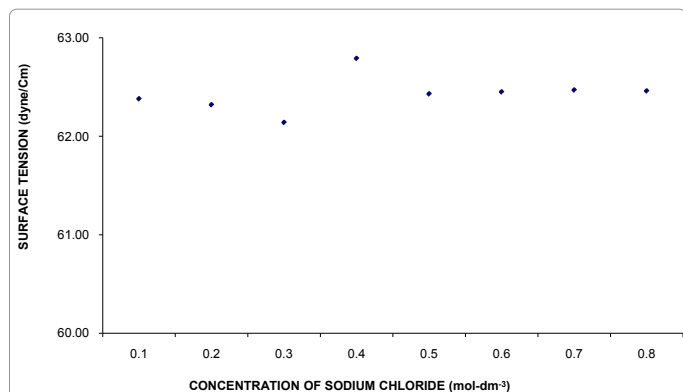


Figure 3: Variation of Surface Tension with Different Concentration of Sodium Chloride.

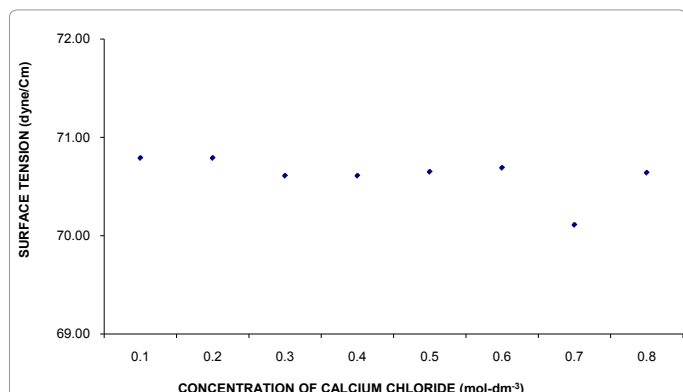


Figure 4: Variation of Surface Tension with Different Concentration of Calcium Chloride.

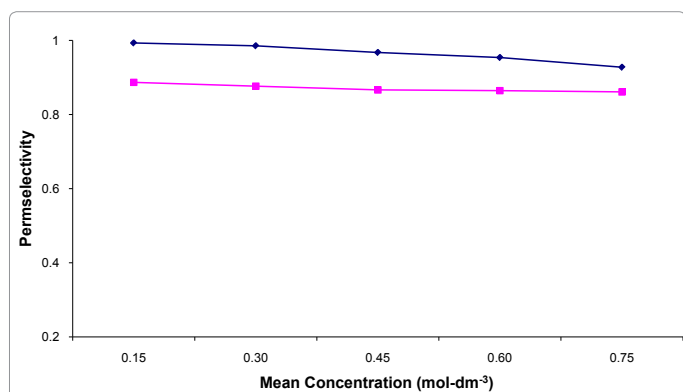


Figure 5: Variation of permselectivity with mean concentration for cellulose acetate sodium chloride system.

Activity coefficient values needed for the estimation of activity were calculated using the equation [18]

$$\log f = -AZ_+Z_- \sqrt{I}$$

Where f = activity coefficient of the electrolyte Z_+ and Z_- are ionic charges of the cation and anion respectively and A is a constant.

In Table 3, the transport number values for calcium chloride system are given. The results show that cellulose acetate film exhibits

change in selectivity i.e. at lower mean concentration, E is greater than E_L even when cellulose acetate supports ergosterol liquid membrane, it indicates towards anion acceleration, but as the mean concentration increases, E_L becomes greater than E either with or without ergosterol liquid membrane. Thus at higher mean concentration cation is accelerated, since $t_+ > t_-$ transport number is found to increase with increasing mean concentration.

In case of NaCl, the transport number increases with decreasing pH values showing that the anion selectivity increases with lowering of pH however a decrease in transport number with increasing concentration indicates the decrease of selectivity of the film with increasing mean concentration.

For NaCl, the permselectivity and fixed charge density, both increase with decreasing pH (Table 4) but a decrease in permselectivity and increase in fixed charge density with increasing mean concentration is observed in the case of sodium chloride (Figure 5,6) as well as potassium chloride systems. It is known that cellulose acetate undergoes swelling when kept in aqueous solutions and the swelling decreases with increase in concentration. The deswelling of the cellulose acetate membrane is likely to enhance openness of its matrix

C (mol-dm ⁻³)	t_+		t_-
	Without ergosterol	With ergosterol	
0.075	0.0142	0.0251	0.4041
0.15	0.1050	0.1392	0.3980
0.30	0.4601	0.4830	0.3842
0.60	0.4861	0.5060	0.3650
0.75	0.4900	0.5162	0.3520

Table 3: Transport number values at different mean concentration of CaCl₂ derived using eqn. (9).

pH	P_s	$\bar{\varphi X}$ (mol dm ⁻³)	
		Without ergosterol	With ergosterol
6.5	0.4683	0.3879	0.3580
5.5	0.5572	0.4439	0.4458
4.5	0.6477	0.5339	0.5474
3.5	0.6806	0.5802	0.6223
2.5	0.7342	0.6532	0.6789
1.5	0.7499	0.7022	0.6803

Table 4: Permselectivity and fixed charge density values at different pH for NaCl: C = 0.30, C₁ = 0.40, C₂ = 0.20 (mol dm⁻³).

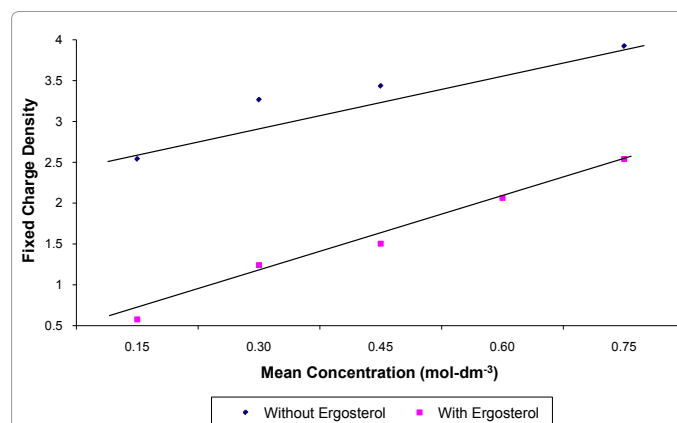
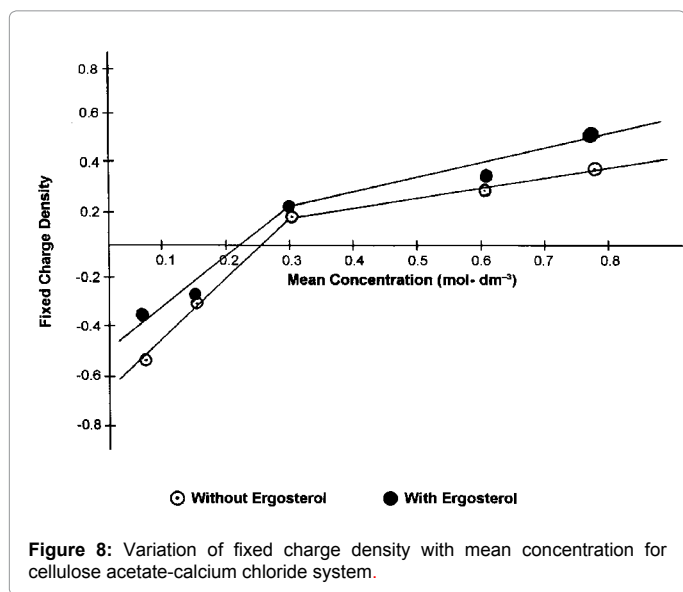
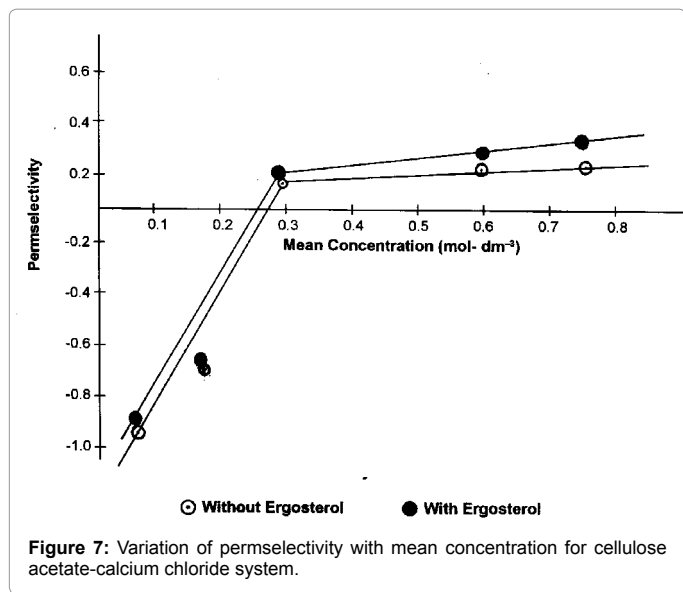


Figure 6: Variation of fixed charge density for cellulose acetate-sodium chloride system at different mean concentrations.



leading to reduction in permselectivity inspite of increased fixed charge density with concentrations of NaCl.

For CaCl₂ system, at lower mean concentration, the permselectivity values are negative and with increasing concentration the values become positive (Figure 7). These values indicate that the selectivity of the cellulose acetate membrane is changing from anion to cation. The same trend is obtained for fixed charge density (Figure 8). An increasing tendency of both the parameters ensures an increase in selectivity of cellulose acetate membrane. An increase in permselectivity and fixed charge density with increasing pH values justifies the increase in selectivity.

When a surfactant is added to a membrane, the transmission characteristics of membrane is modified due to formation of immobilized structure [19,20]. Surfactants are amphipathic compounds. They consist of both hydrophilic and hydrophobic portions in the same molecule. In the case of ergosterol, only -OH group is hydrophilic and the rest part is hydrophobic. When dispersed in aqueous solution at

low concentration, the surfactant migrates towards any available hydrophobic interface and orients its hydrophobic segment towards the interface and its hydrophilic portion in the aqueous phase [21-23]. During studies, it has been found that immobilization of the surfactant depends on many factors like pH, ionic strength, temperature and surfactant structure.

The values for various parameters in the case of ergosterol liquid membrane supported on cellulose acetate film are larger than those obtained earlier [24]. This may be attributed to the structural feature of ergosterol which contains three double bonds in its structure resulting in the presence of electron rich environment. It is also responsible for enhanced surface activity.

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