Freundlich Adsorption Isotherm and Electrochemical Characterization of Cellulose acetate-Tween-20 supported liquid membrane

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Abstract

Cellulose acetate (CA) and Tween-20(T-20) are interacted and resulted as a supported liquid membrane system. The membrane potential was measured with uni-uni valent electrolyte, NaCl solutions using saturated calomel electrodes (SCEs).The effective fixed charge density of the membrane was determined by TMS method. Other important electrochemical parameters were calculated. Membrane adsorb-ability showed Freundlich type adsorption. Membrane water uptake with respect to time is observed. Membrane permselectivity (the ability of the membrane to discriminate between the anions (Cl^-) and cations (Na^+)) is estimated using effective fixed charge density of the membrane. The transport number which quantifies the fraction of the charge carried by certain ion is estimated by membrane potential values. Tween-20 surfactant is most frequently used for membrane surface modification. Electrochemical parameters are estimated under both conditions, i.e. without and with Tween-20 to investigate the effect on the membrane behavior.53% composite membrane of CA/T-20 is obtained as a liquid membrane.

Key Words: *Liquid membrane, Cellulose acetate, Tween-20, Transport number, Permselectivity, Effective fixed charge density.*

1.Introduction

Membrane processes are currently being studied for numerous applications of practical interest [1-4].Co-mixing is effective methods for modification in membrane activity [2]. To examine it, cellulose acetate (CA) membrane and aqueous Tween-20(T-20) were interacted and their characteristic properties were determined on the basis of water content and membrane potential studies. Membrane potential is determined by the combination of the properties of ions and of the membrane. There is, therefore, a possibility that the properties of ions can be reflected in the membrane potential more effectively by modifying the membrane properties. The transport number, reflecting the membrane selectivity, is determined by the product of the total ionic uptake and the average mobility, which contains the dissociation equilibria[2].It, follows that a membrane may be selectively permeable to ions either by preferential uptake or as a consequence of high mobility. The mobility ratio and the effective fixed charge density can be estimated from the membrane potential. These parameters are associated with the interactions between ions and membrane texture which is the key to understanding the salt separation mechanism [5].Membrane water content determines the presence of voids and hydrophilicity. It also reflects the presence of active sites in the membrane. Reported HLB value of T-20 is16.7.In the present study aqueous solution of T-20 is interacted with the CA membrane and a composite membrane system is generated having 53% cooperative. The resulting composite system is known as CA-T-20 liquid membrane.

2. Experimental

Chemicals and Membrane Materials

Cellulose acetate, CA, (CDH, India) and Tween-20(CDH, India) were used for liquid membrane formation. Sodium chloride (AR Grade, S.D.Fine Chemicals, India) and acetone (Qualigens Fine Chemicals, India) were used as received.

3. (A) Membrane Preparation Cellulose Acetate Membrane

4g of cellulose acetate polymer was dispersed in 48 ml of acetone. Uninterrupted stirring of the mixture was done on a magnetic stirrer for about 1 week to obtain homogeneous slurry. This slurry was uniformly spread on a clean, dried glass plate and allowed to dry at 70 degree Celsius in an incubator for one hour and then immersed in distilled water to detach the membrane from the glass plate [1].

4. Determination of Water Content of the Membrane

(i) Water content of the membrane with respect to time in distilled water

From the prepared cellulose acetate membrane, three equal pieces of size 2X2 cm^2 were cut. They were named M_1, M_2, and M_3 respectively. The constant dry weight of the membrane pieces was measured with analytical balance. Length and breadth under dry state was measured by scale and thickness was measured by screw gauge of least count 0.001cm.

The three pieces of the membrane were immersed in 25ml of distilled water for 0.5hr, 1hr, and 1.5hr respectively. After the completion of specified time, the membrane pieces were carefully taken out from water with help of a forceps. The excess water from the membrane surface was removed with filter paper. Length, breadth, weight and thickness of the membrane

pieces were again determined in wet state as done in dry state. Water content (Q_w) was calculated using the relation [6, 11] and shown in Fig.1.

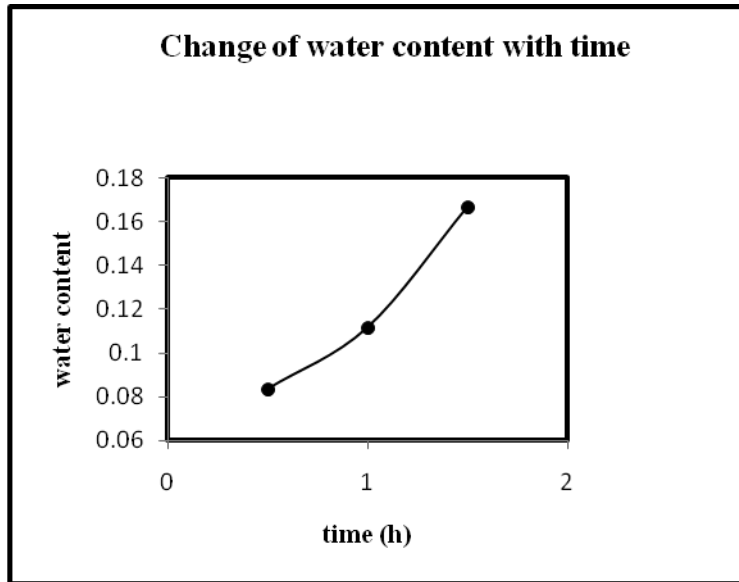$$Q_w = \frac{\text{wet weight of membrane} - \text{dry weight of membrane}}{\text{dry weight of membrane}} \tag{1}$$

Fig.1

5. Water content of the membrane in aqueous electrolyte solutions.

Cellulose acetate membrane of size 2X2cm^2 was immersed in aqueous solutions of NaCl of varying concentrations for 24 hours. Water content, was determined for every concentration as done in the case of distilled water.

6. Water content of the membrane in electrolyte solutions along with the presence of Surfactant.

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Cellulose acetate membrane of size 2X2cm^2 was immersed in aqueous solutions of electrolyte (NaCl) mixed with surfactant Tween-20. The membrane was immersed in each one of the solutions for 24 hours.

7. Membrane Potential Measurement

The electrochemical set up used for the measurement of membrane potential may schematically be shown as:

$$\text{SCE} \ \| \ \text{Solution (C}_1) \ | \ \text{Membrane} \ | \ \text{Solution (C}_2) \ \| \ \text{SCE} \qquad (2)$$

|| denote KCl salt bridge and SCE, the saturated calomel electrode. A piece of membrane was fixed in a glass cell. The experimental set up is shown elsewhere [2-4]. The membrane was equilibrated with 1 M NaCl or MgCl2 solution to convert it to appropriate ionic form. Solutions of unequal concentrations were then kept on the two sides of the membrane. The solutions were connected to saturated calomel electrodes through salt bridges. The solutions were renewed before measurement. The potential difference developed across the membrane was measured by a digital multimeter (Systronics, India.). To remove asymmetry, the salt bridges were interchanged and membrane potential measured again [4].Membrane potential of CA membrane was measured in the following: (i) Sodium chloride solution; (ii) Sodium chloride solution with presence of 0.1 mM Tween-20 (above CMC value).

8. Results and Discussion

Membrane Potential values of Cellulose Acetate/Sodium chloride system in the presence and absence of surfactant Tween-20 are shown in following Fig.2. According to the TMS theory [5-7], the membrane potential, E_m consists of the difference of the two Donnan potentials at the

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interfaces between membrane and solutions, E_{Don} and diffusion potential inside the membrane, E_d being obtained by the following equation
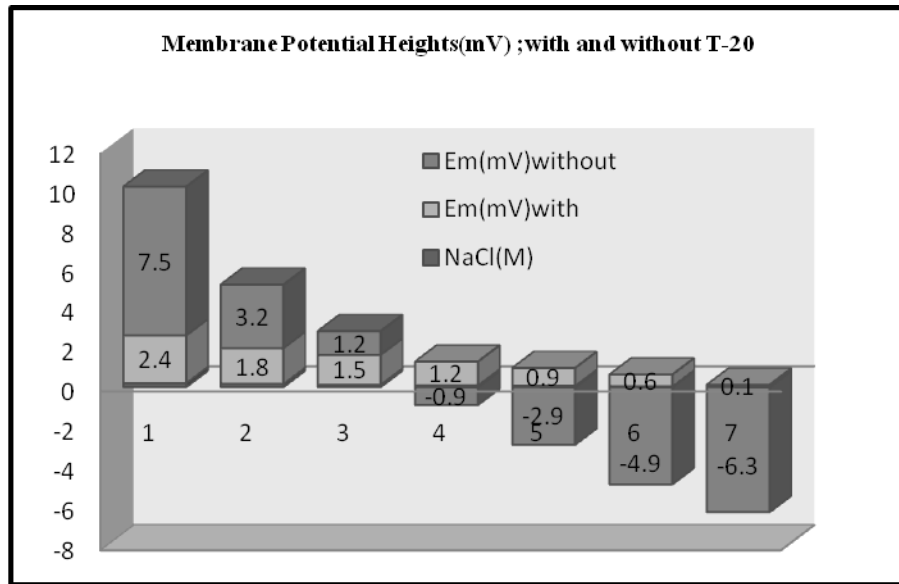
$$E_m = E_{Don} + E_d \qquad (3)$$

Fig.2

The generation of membrane potential is a consequence of the ability of a membrane to allow passage of ions through the membrane, which is quantified in terms of transport number. Permselectivity, P_s, for a cation-selective membrane is defined as [6, 11]:

$$P_s = \frac{\bar{t}_+ - t_+}{1 - t_+} \qquad (4)$$

$\bar{t}_+$ denotes transport number of the cation in the membrane phase and t_+ its transport number in solution. Transport numbers in the membrane phase were estimated using the relationship

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$$\bar{t}_+ = \frac{E_m}{2(E_{max})} + 0.5 \qquad (5)$$

E_m = Observed membrane potential, E_{max} = maximum membrane potential obtainable when the membrane exhibits ideal cation selectivity.

E_{max} values obtained using the relationship[4,6]

$$E_{max} = \frac{RT}{F} \ln \frac{C_1}{C_2} \qquad (6)$$

R,denotes gas constant, T= absolute temperature and F is Faraday number, C_1 and C_2 = concentration of electrolyte solutions used for observation.

Permselectivity is related to effective fixed charge density by the relation [6-11].

$$\varphi X = \frac{2 C_{mean} P_s}{\sqrt{1 - P_s^2}} \qquad (7)$$

The electrical character of a membrane is usually expressed in terms of fixed charge density. Due to presence of fixed charges ionic adsorption occurs onto the membrane interface which can be expressed by Gibbs equation [12]:

$$q = \frac{\Delta C.V}{m} \qquad (8)$$

where $\Delta C=(C_i - C_{eq})$ and m denotes the dry mass of the membrane; q is expressed in (mg/g).The amount of solute adsorbed onto membrane surface, q(mg/g), can be expressed as Freundlich adsorption isotherm[10]:

$$q \ (mg/g) = q*[NaCl(M)]^{\alpha} \ (\text{without surfactant}) \qquad (9)$$

and $\qquad$ q (mg/g) = q** [T-20 (mM)]$^{\acute{\epsilon}}$ (with surfactant) $\qquad$ (10)

Where q* >> q** and ά>>έ

The adsorption percentage A (%) depends on the external electrolyte concentration may be expressed as:

$\qquad$ A (%) (Without surfactant) =A*exp [α. NaCl(M)] (without surfactant) $\qquad$ (11)

and $\qquad$ A(%)(With surfactant) =   B*exp[β.T-20(mM)]   (with surfactant) $\qquad$ (12)

where A* < B* and α > β under such conditions. Maximum permselectivity values P_s (max) for both systems are given in the following figure:
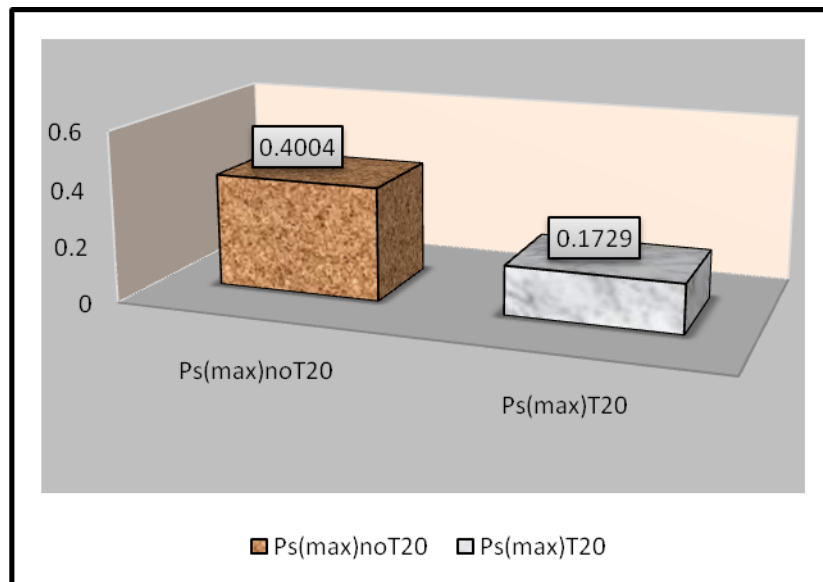
Fig.3

Membrane permselectivity also depends on external electrolyte as well as surfactant

concentrations, therefore relative changes in their values may be expressed as shown in Fig.4.
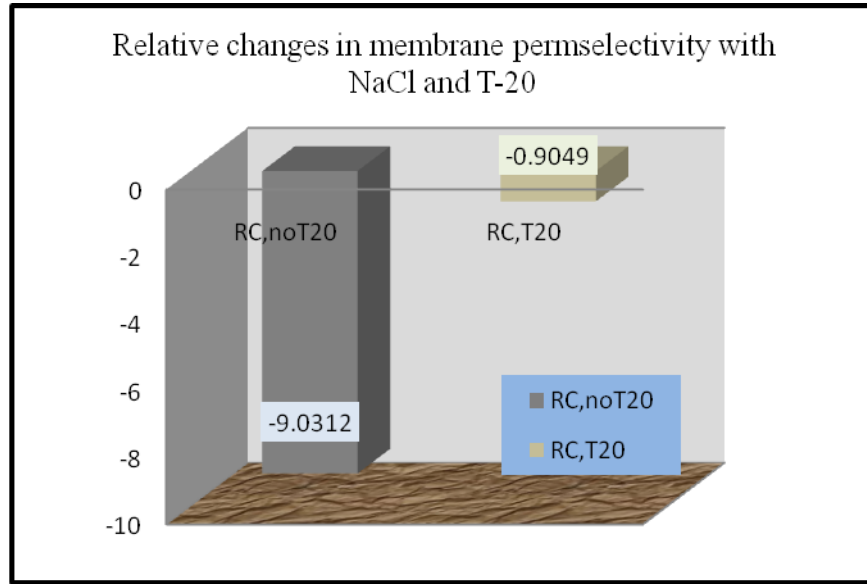
Fig.4

Membrane fixed charge density also depends on the electrolyte and surfactant concentrations. The minimum value of effective fixed charge density for both systems may be expressed in following bar diagram:
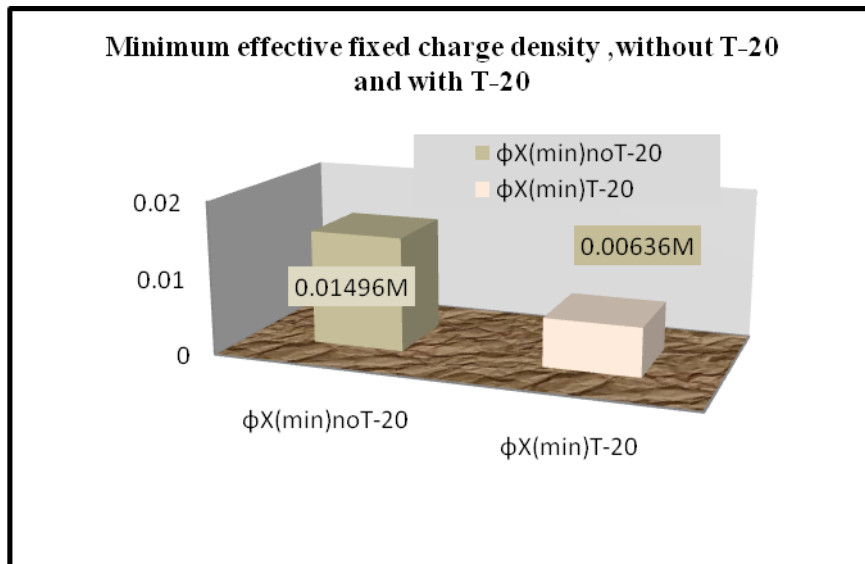

Fig.5

Membrane fixed charge density also depends on external electrolyte as well as surfactant concentrations, therefore relative changes in their values may be expressed as:
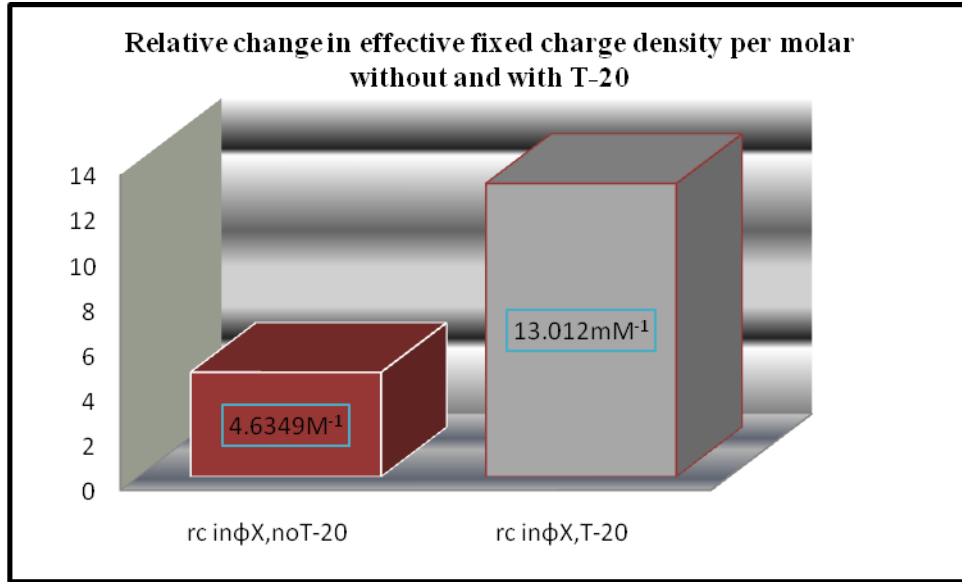

Fig.6

CONCLUSIONS

Surface of CA membrane can be modified by using aqueous solution of T-20.In the present systems, effective fixed charge density control coefficient, $C_{\bar{\phi X}}$ is greater for the system with T-20 than the system without T-20.In composite system, effective fixed charge density increases with the increase in NaCl concentration, the similar trend is also followed by the system without T-20 but the slope value is less than the system with T-20.Membrane water content also decreases with the increase of T-20 concentration, keeping NaCl concentration at=0.01M.The difference in both systems is the relative reduction in water content is less in the system with T-20 surfactant. In both systems anionic selectivity is retained, anion transport number increases with the increase of NaCl concentration. System without T-20 possesses relative change per molar is 1.8 and the system with T-20 holds value 0.25 per molar. Minimum percentage of adsorption is noticed 84% and 84.5% of solute in the system without and with T-20 wherein NaCl=0.01M is kept constant and T-20 concentration gradually varies.It can

conclusively be inferred that CA and T-20 can form reshaped membrane system of varying characteristics.

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FIGURE CAPTION

Fig.1. Variation of water content of membrane with time.

Fig.2. Membrane potential heights in mV; with and without surfactant, T-20.

Fig.3.Maximum permselectivity values, P_s(max) for systems; with and without,T-20.

Fig.4.Relative changes in permselectivity with change in NaCl and T-20 concentrations.

Fig.5.Minimum values of effective fixed charge density for systems; with and without, T-20.

Fig.6. Relative changes in effective fixed charge density per molar for systems; with and without, T-20.