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Electrochemical Characterization of Cellulose Acetate/Chitosan Membrane in Presence and Absence of Nonionic Surfactant in Monovalent Electrolytic Solution

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The influence of surfactant on cellulose acetate/chitosan membrane has been investigated. A basic approach to cellulose acetate/chitosan membrane is also mentioned. Nonionic surfactants are disrupted the normal permeability of the characteristic membrane. Electrochemical characterization such as conductance, flow, flux and permeability are measured in various concentrations of the electrolyte and surfactants. Membrane potential is determined by the combination of the properties of ions of the electrolyte, surfactant and membrane. The synthesized membrane was found to be cation selective with measured membrane potential found to be negative in all cases. The value of membrane potential was varying in different concentration of the electrolyte and surfactant. The Teorell Meyer and Sievers (TMS) theoretical method was employed for calculating the Transport number, perm selectivity and fixed charge density of the membrane by using the data of membrane potential across normal and surfactant modified membrane with electrolytic solution of NaCl. The variation of fixed density and perm selectivity also depends on the concentration of the electrolyte and surfactant (Tween 20 and Tween 60).

Keywords: Cellulose acetate/chitosan, Tween 20, Tween 60, Permeability, Transport number, Fixed charge density.

INTRODUCTION

The largest source of water pollution in India is due to the untreated sewage [1]. The shortage of water not only problem of proper technique, but it is a social and education problems. Membrane technology has been using for separation of the chemical substance; waste products from water for a long time [2,3]. The synthetic membrane can be used in purification and separation of the contaminant from sources [4,5]. Chitosan, a hetero-polysaccharide compound, is composed of β-(1-4)-2-deoxy-2-amino-D-glucopyranose unit and β-(1-4)-2-deoxy-2-acetamino-D-glucopyranose unit. Chitosan membrane has limited applications, because of amino group, which causes more hydrophilic character [6]. For improvement of stability of chisoan membrane, it is blend with cellulose acetate, a natural polysaccharide, which reduced the hydrophilic character and improve the stability of membrane [7].

Cellulose acetate/chitosan blend membrane has played important role for the separation processes such as ultrafiltration, microfiltration and nanofiltration [8]. When the fluid flows through selective membrane the transport of ions is passed toward membrane surface, some of the ions are accumulated on a thin layer adjacent to membrane surface, which is generated concentration gradient. Due to this, the concentration of solute is much higher near the membrane surface than that of the bulk solution. As a result the diffusive flux of the solute back to the feed solution. Therefore, the conductivity, flow, permeability and flux of the ion are decreased with the time interval [9].

In electrochemical separation, the cellulose acetate/chitosan membrane is used as the selective separator to allow passes the certain ions specially cations, while restrict the transport of other ions, often oppositely charged ions (anions).The efficiency of cation exchange and anion exchange depends on the ability of the membrane to exclude co-ions while simultaneously permit transport of counter ions across the membrane. If a membrane that allow to pass only counter ions while completely blocking the transport of co-ions is called perfectively permselectively membrane [10]. The nature of counter ions effects the properties of cellulose acetate/chitosan membrane, which is often effect the ions transport and fixed charge density group present on membrane surface. The nature of co-ions also affects the perm-selectivity of membrane.

The main advantages of membrane technology compared with other unit operations are related to this unique separation principal, *i.e.* the transport selectivity of the membrane, separation with the membrane do not require additives and can be performed isothermally at low temperature. The complex obtained from the electrostatic interaction between cellulose acetate/ chitosan and a non-ionic surfactant were characterized by the conductometric and surface active properties [11]. Such surfactant/ electrolyte complex was present very interesting surface active properties, event at very low surfactant concentration (much lower than CMC of pure surfactant). Amphiphilic system based on chitin and chitoasan derivatives may be obtained by two different processes; either by chemical modification of the macromolecular backbone or by the interaction between the hydrophilic chains and surfactant molecule [12].

Adsorption of Tween 20 and Tween 60 surfactant molecules on the membrane surface can modified their hydrophobicity, surface charge and other properties of membrane. Surfactant molecule improved the stability of membrane and also reduced the membrane fouling [13]. In general, adsorption of surfactant is governed by a various forces such as covalent bonding, electrostatic attraction and hydrogen bonding between the adsorbed surfactant and membrane surface [14].

In this work, cellulose acetate chitosan membrane and aqueous solution of Tween 20 and Tween 60 surfactants were interacted each other. The characteristic properties of the membrane were determined on the basis of water content, conductance measurement and membrane potential studies. The hydrophilicity and compactness of the membrane were determined by water content measurement. The conductance and membrane potential were determined by the combination of the properties of ions, cellulose acetate/chitosan membrane and surfactant. Flow, flux and permeability of the membrane were determined in presence and absence of surfactant. The transport number, perm selectivity and fixed charge density were calculated by membrane potential study.

EXPERIMENTAL

Cellulose acetate (BDH chemical Ltd., Poole, England), chitosan and acetone (Qualigens Fine Chemicals, India) were used for membrane formation. Sodium chloride (AR Grade, S.D. Fine Chemicals Ltd.), Tween 20 (S.D. Fine Chemicals Ltd.) and Tween 60 (Sigma) were used as received.

Preparation of cellulose acetate/chitosan membrane: For the formation of cellulose acetate/chitosan membrane, a desired quantity of cellulose acetate/chitosan was dispersed in acetone by constant stirring for 4-6 h on magnetic stirrer until thick slurry was obtained. It was spread on a clean, dried glass plate. The glass plate was kept in an electric oven at 60 °C for 0.5 h to remove the solvent. The plate was then immersed in distilled water to detach the membrane. Thereafter, the membrane was kept pressed between the fold of filter paper to avoid wrinkles.

Determination of water content: A piece of size 2.5 cm × 2.5 cm area of constant dried cellulose acetate/chitosan membrane was immersed in 50 mL of distilled water in absence and presence of Tween 20 and Tween 60 surfactants. After the completion of 24 h, the membrane piece was carefully taken out from water; the excess water from the membrane surface was removed with the help of filter papers and then weighed the membrane again.

Conductance measurement : A piece of membrane 1 cm diameter fixed in glass joint was equilibrated with 1 M of NaCl, Tween 20 and Tween 60. Then, it was equilibrated with experimental solution. Before starting the experiment, solution was renewed. Solution conductance was measured with the help of the conductivity meter. The experimental set up of conductivity measurement is shown elsewhere [15].

Conductance of solution through the membrane increases with time (Fig. 1). It also shows that Na^+ and Cl^- are transported through the membrane. In concentrate solution of NaCl conductance decreases with time steadily. While in dilute solution conductance decreases rapidly with time. This indicate that in dilute solution less ion available for permeation through the membrane.

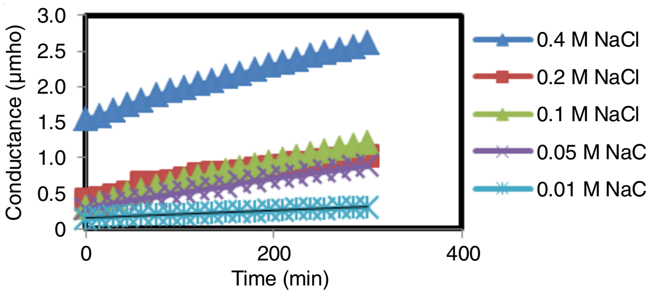

Fig. 1. Dependence of conductance of solution through membrane with time in various conc. of NaCl solution

The conductivity measurements were also performed for non-ionic surfactants (Tween 20 and Tween 60) electrolyte solutions. Fig. 2 show that change in conductivity with time is maximum, when the solution of surfactant is dilute, But on reaching CMC (CMC = 0.06 mM), the change in conductivity of NaCl with time is minimum. On attaining the value of CMC, the surfactant molecule undergoes aggregation, so ions are not easily transported and variation of conductivity is very low.

Fig. 3 shows that the change in conductivity with time is minimum near the CMC value of Tween 60 (CMC = 0.02 mM), when the surfactant solution is diluted, but at high concentration of the surfactant solution, the change in conductivity of NaCl with time is maximum.

Membrane potential measurements: The membrane potential was measured with the help of electrochemical setup, which is schematically shown in Fig. 4. The membrane was equilibrated with NaCl solution for 24 h to convert it to appropriate ionic form. The developed potential difference across the membrane was measured by digital multimeter (Systronic, 435). The membrane potential values of cellulose acetate/ chitosan in presence and absence of surfactant Tween 60 is shown in Table-1.

RESULTS AND DISCUSSION

Effect of surfactant on hydrophilicity of cellulose acetate chitosan membrane: Water content of the membrane was calculated at room temperature. The water uptake change is attributed

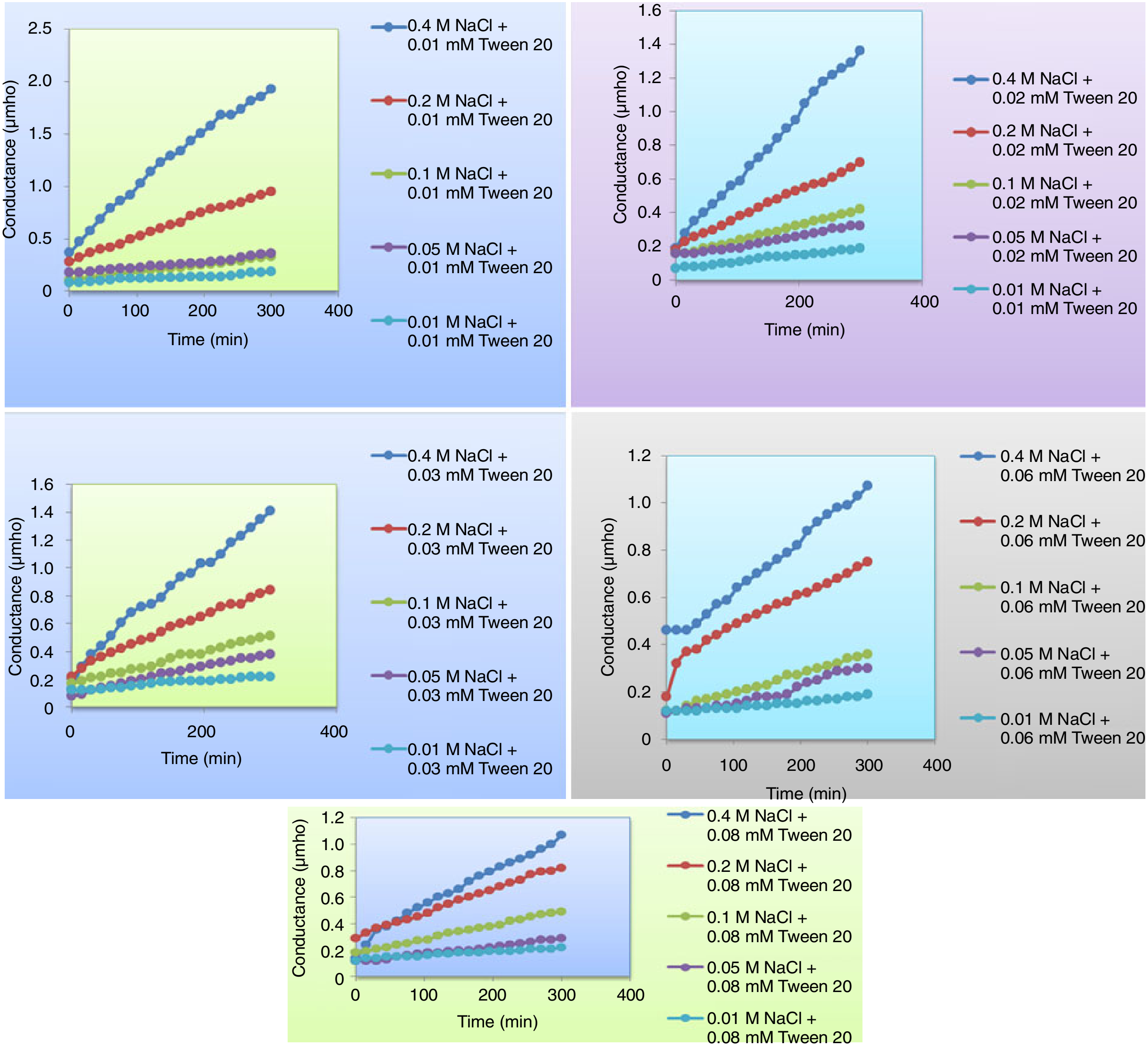

Fig. 2. Dependence of conductance of solution through membrane with time in various conc. of NaCl and Tween 20

TABLE-1
MEMBRANE POTENTIAL WITH DIFFERENT CONCENTRATION OF NaCl ELECTROLYTE IN PRESENCE AND ABSENCE OF SURFACTANT

C_{mean} (M)	C_1 (M)	C_2 (M)	Without Tween 20 and Tween 60 E_m (mV)	With Tween 20 E_m (mV)	With Tween 60 E_m (mV)
0.75	1.0	0.5	-2.752	-7.802	-5.425
0.60	0.8	0.4	- 2.442	-7.531	-5.338
0.45	0.6	0.3	- 2.242	-7.327	-5.756
0.30	0.4	0.2	-1.950	-9.234	-8.845
0.15	0.2	0.1	-2.111	-9.912	-7.359

to water molecule which produces polar bond with amide and hydroxyl group of cellulose acetate/chitosan [16]. In presence of the surfactant, the hydrophilicity of membrane increases. On adding the surfactant, the electrostatic repulsion is diminishing and an increase in the membrane-water area for absorption of water molecule is observed (Fig. 5).

Conductance variation with time of NaCl in presence and absence of surfactant: In presence of the surfactant, ions were easily transported through cellulose acetate/chitosan membrane. The surfactant reduced the surface tension which easily provides transportation of the ions. Fig. 6 shows that the maximum change in conductivity with time in case where

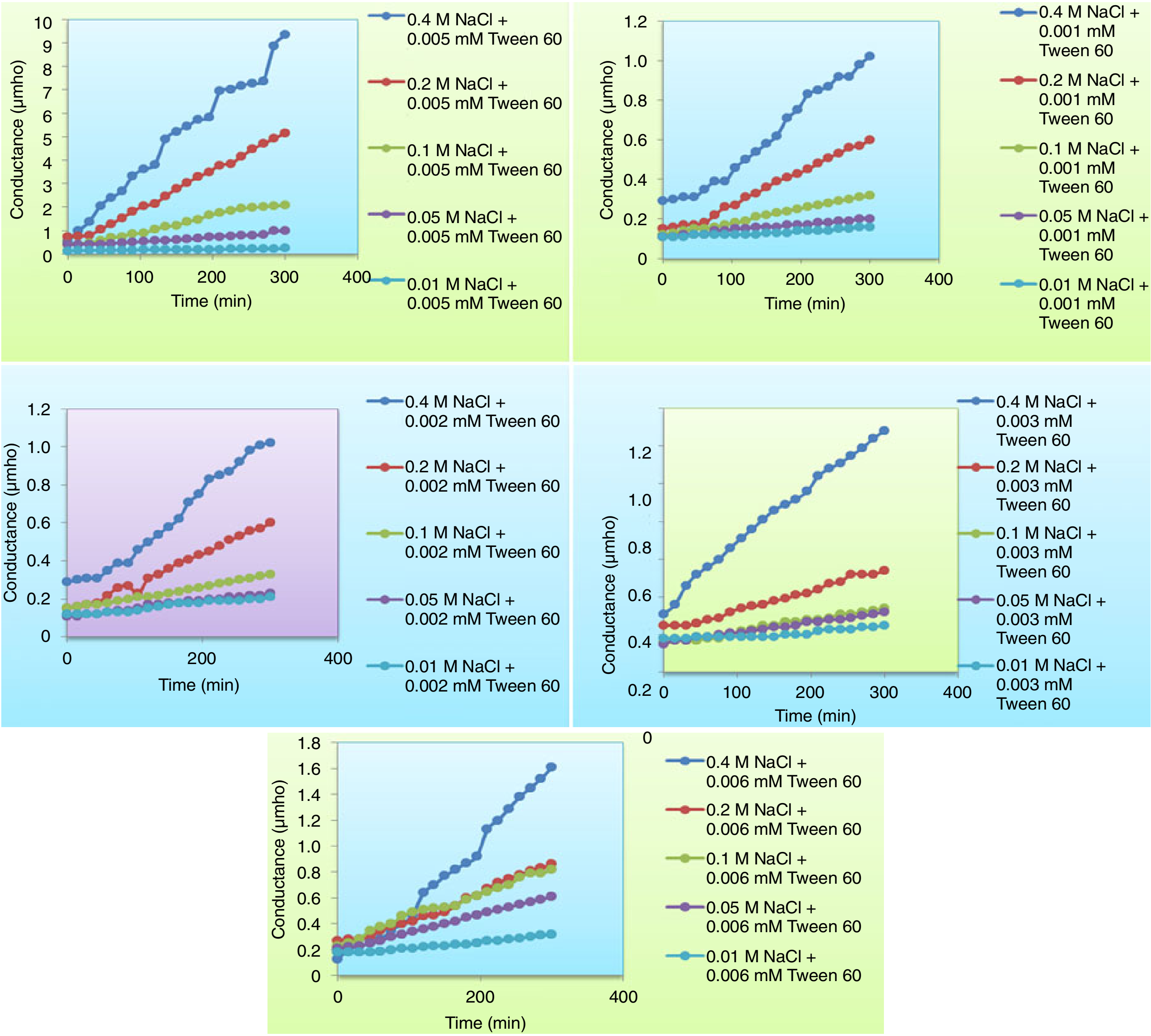

Fig. 3. Dependence of conductance of solution through membrane with time in various conc. of NaCl and Tween 60

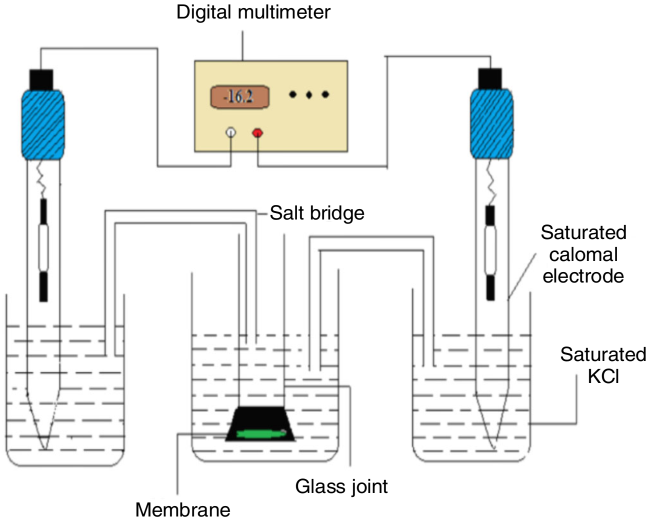

Fig. 4. Schematic diagram of electrochemical setup

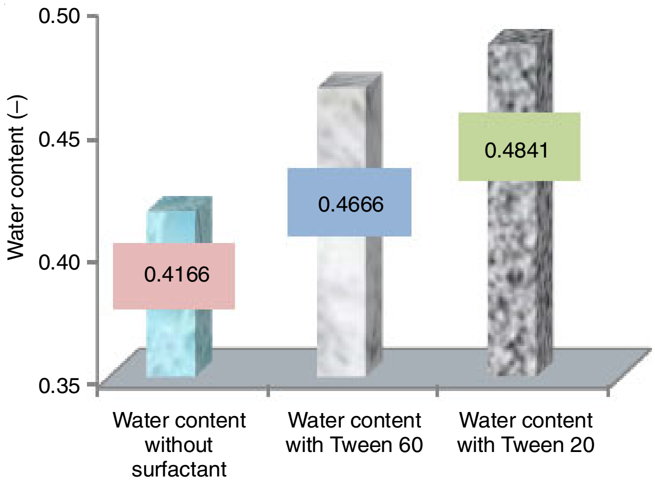

Fig. 5. Hydrophilicity of cellulose acetate chitosan/chitosan membrane in presence of Tween 20 and Tween 60

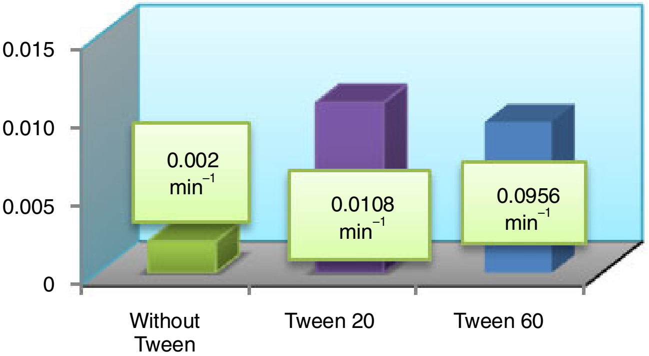

Fig. 6. Relative change per time in conductance in presence and absence of surfactant

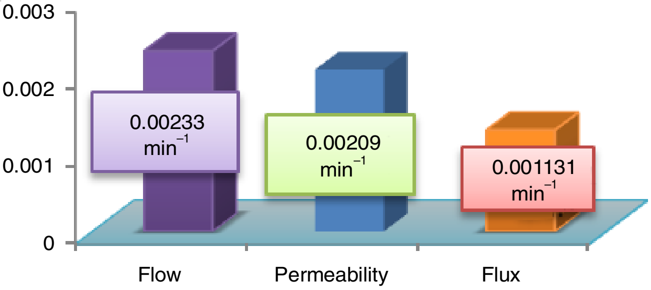

Fig. 8. Relative change per time of flow, permeability and flux through cellulose acetate chitosan membrane

Tween 20 (CMC 0.06) surfactant is used. Since electrostatic interaction diminishes in dilute surfactant solution and ions were easily transported through the membrane [17]. The change in conductivity was slight lower in case of Tween 60 (CMC 0.02), because the concentration of Tween 60 is near the CMC.

Change in conductivity with time of NaCl in different concentration of Tween 20 and Tween 60 surfactants: Fig. 7a-b show that change in conductivity with time was maximum when the diluted surfactant solution used. On reaching the value of CMC, the surfactant molecule undergoes aggregation, so ions are not easily transported and variation of conductivity is very low. This shows that at the point of CMC, there was no change in conductivity.

Dependence of flow, permeability and flux with time in different concentration of NaCl + 0.01 mM Tween 20 surfactant: In concentrate solution of NaCl and Tween 20 surfactant flow, permeability and flux decreases with time, whereas in dilute solution, flow, permeability and flux decreases rapidly with time. This indicates that in dilute solution, less ion available for permeation through the membrane. Relative change per time of flow, permeability and flux of the ion through membrane were 0.00233 min^{-1}, 0.00209 min^{-1} and 0.00113 min^{-1}, respectively (Fig. 8).

Determination of transport number, perm selectivity and fixed charge density: The transfer of the electrolyte from the concentrated solution to the dilute solution is taken place through the gradient concentration between the two solutions. The membrane potential becomes more negative with increasing concentration. According to the TMS theory [18-20], total membrane potential composed of two Donnan potential at the interface of two solutions/membranes and a diffusion potential develop from unequal activities of the ions at two membranes/interface.

$$E_m = E_{donn} + E'_{donn} + E_d \quad (1)$$

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 term of transport number [21]. The transport number in membrane phase was calculated using the following relation [22] for cation selective membrane:

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

where

$$E_{max} = \frac{RT}{F} \ln \frac{C_1}{C_2} \quad (3)$$

The variation of transport number of cation and anion with respect to concentration in presence and absence of surfactant are given in Table-2.

Perm selectivity is an important parameter for determining the performance of the membrane in a certain ion-exchange membrane in separation process. It describes the degree to which a membrane posse an ion of on charge and retains an ion of the opposite charge. The perm selectivity of cation and anion exchange membrane can be calculated by the following relation:

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

where $\bar{t}_+$ transport of the cation in the membrane is phase and t_+ is transport of the cation in solution.

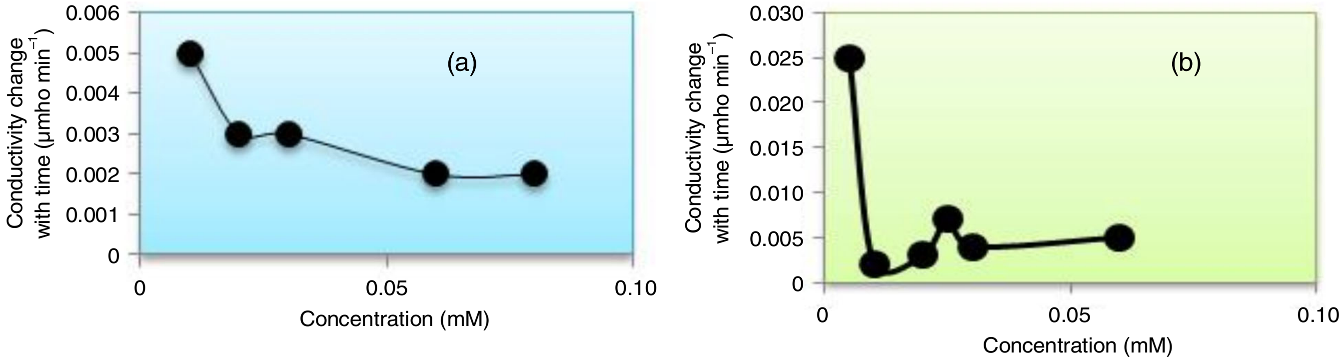

Fig. 7. Change in conductivity with time in different conc. of (a) Tween 20 and (b) Tween 60

TABLE-2
TRANSPORT NUMBER OF CATION AND ANION IN PRESENCE AND ABSENCE OF SURFACTANT

Concentration of NaCl (M)	Transport number of cation ($\bar{t}_+$)			Transport number of anion ($\bar{t}_-$)		
	Without surfactant	Tween 20	Tween 60	Without surfactant	Tween 20	Tween 60
0.75	0.5761	0.7160	0.6501	0.4239	0.2840	0.3499
0.60	0.5675	0.7084	0.6477	0.4325	0.2916	0.3523
0.45	0.5620	0.7027	0.6593	0.4380	0.2973	0.3407
0.30	0.5530	0.7556	0.7448	0.4470	0.2444	0.2552
0.15	0.5584	0.7744	0.7037	0.4416	0.2256	0.2963

TABLE-3
PERMSELECTIVITY AND FIXED CHARGE DENSITY VALUES IN PRESENCE AND ABSENCE OF SURFACTANTS

Concentration of NaCl (M)	Perm selectivity (P_s)			Fixed charge density (φX)		
	Without surfactant	Tween 20	Tween 60	Without surfactant	Tween 20	Tween 60
0.75	0.3206	0.5448	0.4392	0.5077	0.9742	0.7333
0.60	0.3035	0.5326	0.4326	0.3822	0.7551	0.5758
0.45	0.2901	0.5235	0.4478	0.2784	0.5529	0.4507
0.30	0.2696	0.8083	0.5830	0.1679	0.8304	0.4305
0.15	0.2901	0.6384	0.5126	0.0909	0.6105	0.1790

The effective fixed charged density is related to perm selectivity, which is calculated by following relation:

$$\varphi X = \frac{2C_{mean}P_s}{\sqrt{1-P_s^2}} \qquad (5)$$

The variation of perm selectivity and fixed charge density with respect to concentration in presence and absence of surfactant are given in Table-3.

Membrane permselectivity and fixed charge density depends on the external electrolyte as well as surfactant concentration, therefore relative change is shown in Fig. 9. The permselectivity of the membrane increased with increasing the concentration of electrolyte solution. The surfactant molecules (Tween 60) change the permselectivty of the membrane. The relative change in membrane permselectivity with concentration in presence and absence of surfactant were found to be -0.3461 M^{-1} and 0.2368 M^{-1}, respectively.

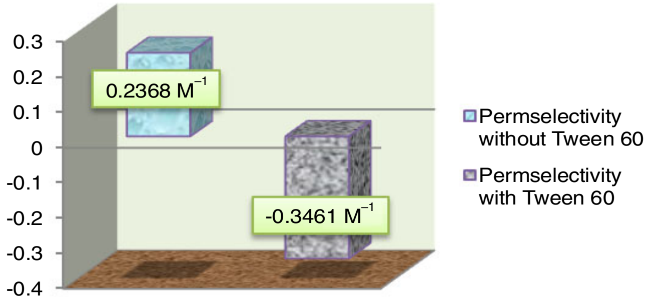

Fig. 9a. Relative change in membrane permselectivity with concentration of NaCl/Tween 60

The fixed charge density of the membrane is increased with increasing the concentration of electrolyte solutions. The change of fixed charge density is maximum when surfactant is used in NaCl solution. The relative change in fixed charge density with concentration in presence and absence of surfactant were found to be 8.6082 M^{-1} and -24.06 M^{-1}, respectively.

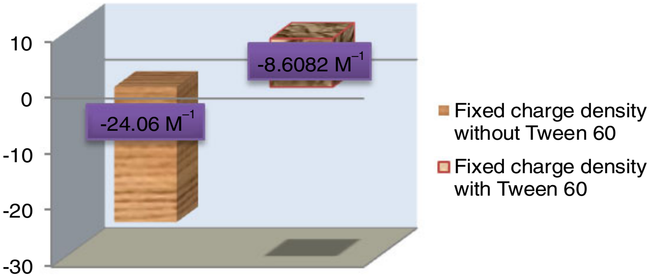

Fig. 9b. Relative change in fixed charged density of membrane with concentration of NaCl/Tween 60

Conclusion

In presence of the surfactant (Tween 20 and Tween 60) ion of NaCl easily transported through cellulose acetate/chitosan membrane. There is no change in conductivity at the point of CMC of surfactant. Maximum transportation occurs in dilute solution of surfactant. In presence of the surfactant membrane, potential is higher than normal solution of NaCl. The membrane potential is negative, which show that membrane is cation selective. Membrane permselectivity and fixed charged density are depended on concentration of electrolyte. In presence of the surfactant, the relative change of permselectivity and fixed charge density was very low, which is responsible for the improvement of the membrane stability.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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