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Effect of Cationic Surfactant (Cetyl Pyridinium Chloride) on the Solute Adsorption onto Cellulose acetate phthalate Surface in Brine Solution

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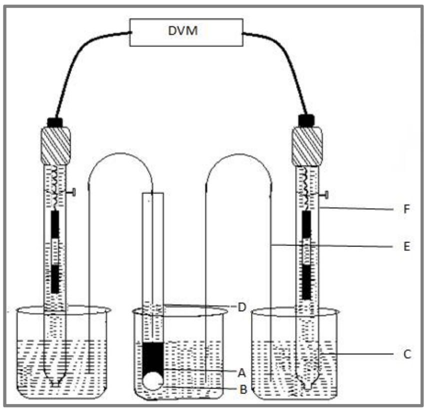
ABSTRACT

The effect of interaction of cationic surfactant (CPC=cetyl pyridinium chloride) on cellulose acetate phthalate (CAP) membrane has been investigated. The conductivity of membrane system with and without surfactant is studied. Structural properties of surfactant based membrane were characterized in terms of water-content, conductivity, membrane potential by investigating permeation and separation performance of Membrane-aqueous electrolyte system. Solute adsorption on the membrane interface in the presence of CPC is responded by the system and adsorption estimation has been carried out.

Graphical Abstract



Schematic presentation of membrane system for membrane potential data acquisition

Keywords: Cetyl pyridinium chloride, Cellulose acetate phthalate, Surfactant, Membrane potential.

INTRODUCTION

CAP has a superior characteristics compare to cellulose acetate due to the presence of numerous acidic and carbonyl functional groups on its structure and it was interacted with CPC solution to improve its properties [1]. It is well known that in membrane separation process, the separation performance of membrane solely related to the structural properties (such as pore size) of their upper layer of the membrane.

An extensive literature survey revealed that there is no published document discussed about the effect of CAP on structural properties and performance of CPC/CAP membrane [1-2]. Cellulose acetate phthalate bears fixed negative charges. They generally used in the treatment of ionic aqueous solution. It was thought that the structural effect of the cationic surfactant may play an important role in the interaction. In the present study, the physico-chemical parameters were obtained by conductivity, water content, membrane potential measurements for the interaction of CAP with CPC. The effect of bulkiness of hydrophobic group of cationic surfactants on the process of adsorption has been focused.

The structure of the adsorbed surfactant layer at the solid-solution interface and the way in which it modifies the surface properties depends upon the nature of the surfactant and its interaction with the surface (whether due to electrostatic attraction, hydrogen or covalent bonding, or hydrophobic forces) [2]. Adsorption of surfactant onto hydrophilic surface aggregates, which are related to the associated solution aggregate structure. The cooperative nature of the adsorption is reinforced for ionic surfactants adsorbed onto hydrophilic surfaces of opposite charge by electrostatic attraction [3]. The adsorption is in the form of a monolayer and is similar to that observed at the air-solution interface. Cationic surfactants onto a hydroxylated surface resulted in a thin layer consistent with the surfactant molecules lying flat on the surface of cellulose acetate phthalate [3]. It is assumed that there is only partial exchange between the H_2O that initially hydrated the cellulose film and the subsequent exposure to H_2O.Intermixing between the outer cellulose layer and the surfactant monolayer occurs, whereas for the hydrophilic cellulose surface, there is little penetration of the CPC aggregates into the diffuse cellulose acetate phthalate layer [4].

Mechanism of surfactant adsorption: The adsorption of surfactants on solid surfaces can modify their hydrophobicity, surface charge and other properties that govern interfacial processes. Adsorption is governed by a number of forces such as covalent bonding, electro-static attraction, hydrogen bonding or non polar interaction between the adsorbed species. The adsorption of membrane /solution interface is affected by the chemical structure of surfactant, the nature and charged surface of membrane[5].In the present system, based on the chemical structure of CPC have several possible active sites for the adsorption processes [6]. Surfactant exerts attraction towards the surface by adsorption of the cation part on the CAP surface through hydrophilic part that means pyridinium ring (the polar or ionic group) attacks the surface, hydrophobic part $C_{16}H_{33}$ extends to solution face to form a hydrophobic barrier to increase conductance. Chloride ions are initially adsorbed on CAP surface and then surfactant cation is adsorbed on the layer of acetate ion by coulombic attraction forming ion pair on CAP Surface [5, 12]. Aromatic compounds are found to involve the pi-cloud in hydrogen bonding with CAP- OR(acidic) and carbonyl functional group during adsorption [3]. A polar part of the surfactant also contributes to the adsorption process. On modification of the CAP by treatment with NaCl with cationic surfactant, the initially rate of adsorption of CPC increased proportionally with the amount of charge.

MATERIALS AND METHODS

Chemicals and membrane materials: Cellulose acetate phthalate (LR Grade, CDH P Ltd.)-were used for membrane formation. Sodium Chloride (AR Grade , S. D. Fine Chemicals ,India) and Tetra Hydro Furan (AR Grade, SDFCL, India) were used as received and CPC(AR Grade, CDH. P. Ltd).

Membrane preparation: Cellulose acetate phthalate (CAP) membrane has been prepared via solvent vaporization method. A simple method was used for the formation of the (CAP) membrane. To ensure uniformity of composition, a casting solution, was prepared by dissolving 4g CAP and 4g of polyvinyl chloride in 36mLof tetra hydro furan by constant stirring for 1-2 days on magnetic stirrer. It was spread on a clean dried glass plate with the help of a scale. The glass plate was kept in an electric oven at 60 degree centigrade for about half an hour to remove the solvent. The plate was then immersed in distilled water to detach the membrane. The membrane was kept pressed between a folded filter paper to avoid wrinkles. Its dimensional characterization was done by using suitable technique in dry and wet state. The prepared membrane was cut in three piece of equal size.

It is dried in incubator at 60 degree centigrade regularly to get constant dry weight. Thickness of these membranes is measured with the help of screw gauge having least count $1x10^{-3}$cm. The water content of the membrane was measured in water and different concentrations of NaCl solution for 24 h at room temperature.

Membrane water content in distilled water: The membrane was conditioned by immersing it for 24h in water at 25°C after which it was removed from the water, blotted with a filter paper to remove any excess water, weighed its weight was recorded as wet weight. The membrane was then dried for 24h in desiccators and weighed; its weight was recorded as dry weight. The water content was calculated as:

$$Q_w = (\text{wet weight- dry weight})/\text{dry weight}$$

Membrane water content with different concentration of aqueous NaCl solution: Cellulose acetate phthalate membrane of size 2x2 cm^2 was dipped in aqueous solution of NaCl of different concentration for 24 h and Water content and other related parameters were determined.

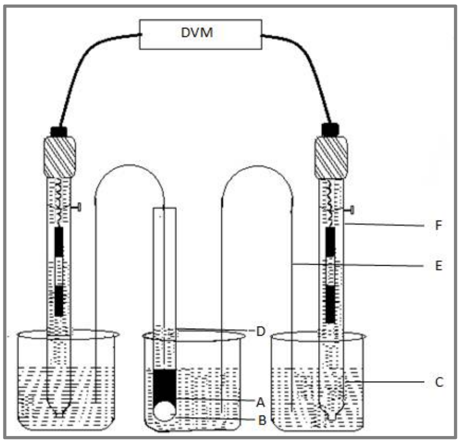
Membrane water content in aqueous NaCl solution along with surfactant: Cellulose acetate phthalate membrane of size 2x2 cm^2 was dipped in different concentration of aqueous solution of NaCl mixed with surfactant (CPC). The same process was followed as done previously for the estimation of membrane water content.

Conductance measurement through membrane: A piece of membrane 1 cm^2 is fixed in glass cell, equilibrated with 1 M of sodium chloride solution, to convert it to appropriate ionic form. Then it was equilibrated with experimental solution. Before starting the experiment, the solution was renewed. Solution conductance was measured with the help of the conductivity meter. Dependence of conductance of solution through membrane with time in various concentrations of NaCl and NaCl with cetyl pyridinium chloride under various concentration gradients was observed and shown in respective figures 4 and 5 and table 3 [11].

Measurement of membrane potential: The potential time measuring cell was made of glass as shown in figure 1. A piece of the membrane under investigation was fixed in glass-cell. The membrane was equilibrated with 1M sodium chloride to convert it to the ionic form. Desired solutions of known concentration of electrolyte were kept on two side of the membrane. The potential across the membrane was measured with the help of a digital multimeter (Systronic, 435) using calomel electrodes. The solutions were connected to saturated calomel electrode through salt bridge fixed close to membrane surface. The solutions were renewed after allowing equilibration and potential measurements were carried out repeatedly until a constant potential difference across the membrane could be measured [7-8].

The electrochemical set up used for membrane potential measurements may be represented as-

$$\text{SCE} \,\|\, \begin{matrix}\text{Solution}\\ \text{(C1)}\end{matrix} \,|\, \text{Membrane} \,|\, \begin{matrix}\text{Solution}\\ \text{(C2)}\end{matrix} \,\|\, \text{SCE}$$



DVM=Digital Voltmeter; A=Cellulose Acetate Phthalate Membrane Fixed with Glass Joint;
B=Electrolyte solution(Reciever);C=Saturated Potassium Chloride Solutions;
D=Electrolyte Solution(Source); E=Salt bridges; F=Saturated Calomel Electrodes.

Figure 1. Schematic presentation of membrane system for membrane potential data acquisition.

RESULTS AND DISCUSSION

Water content study: The water uptake of the membrane was calculated at room temperature as shown in table1 and 2.There is observed changed in water uptake measurement during the 24h. These water uptake changes are responsible for water molecules inside the membrane that produce polar bonds with the acetyl or phthalyl groups of the CAP membrane. The dependence of membrane water content on aqueous NaCl without surfactant and with surfactant is shown in figure 2 and 3.

Table 1. Water content, fraction of void volume (p) and volume ratio values of NaCl system

NaCl(M)	Water content, (Q_w)(-)	Fraction of void volume, (p)(-)	Volume ratio, (V_r)(-)
0.01	0.1975	0.7920	0.927
0.02	0.1946	0.7609	1.121
0.03	0.1920	0.7375	1.150
0.04	0.1888	0.7440	0.949
0.06	0.1832	0.7260	1.104
0.08	0.1778	0.6797	1.214
0.10	0.1725	0.6647	1.299

Table 2. Water content, fraction of void volume (p) and volume ratio values of NaCl + CPC system

NaCl (M)	Water content, (Q_w)(-)	Fraction of void volume, (p)(-)	Volume ratio, (V_r)(-)
0.01	0.1938	0.1623	1.1937
0.02	0.2796	0.2185	1.2796
0.03	0.2913	0.2256	1.2913
0.04	0.3012	0.2315	1.3012
0.06	0.3342	0.2588	1.3342
0.08	0.3491	0.5150	1.3492
0.10	0.4721	0.3207	1.4721

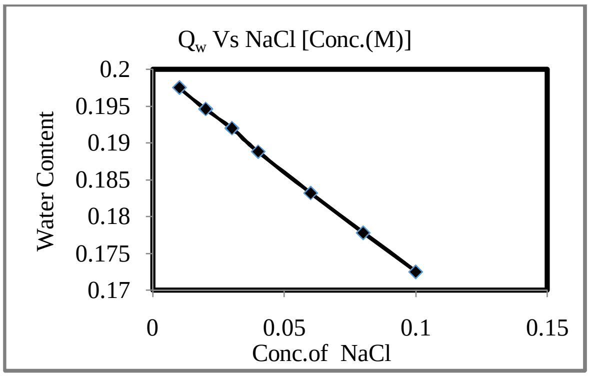


Figure 2. Dependence of water content on concentration of aqueous solution of NaCl.

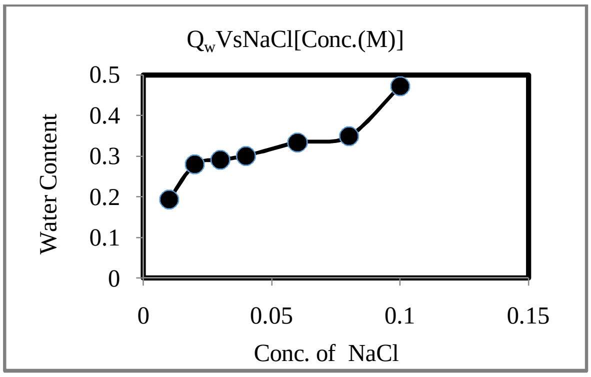


Figure 3. Dependence of water content on concentration of aqueous solution of NaCl with cationic surfactant.

Conductance time-study: Conductance is typically measured in aqueous solutions of electrolytes. Electrolytes are substances containing ions that mean solution of ionic salts or of compounds that ionize in solution. The ions formed in solution are responsible for carrying the electric current. Interfacial properties of membrane such as their surface charge, the presence of surface functional groups and surface hydrophilicity/hydrophobicity are known to influence the efficiency of the membrane transporting ion from bulk to receiving phase by affecting their interaction with solution environment. For the conductance-time study, membrane separates source and receiving phase. Source phase contains known electrolyte concentration and receiving phase has distilled water of known volume is connected with conductivity cell. As the time passes, conductivity of receiving phase increases which transmit information concerning the membrane permeability, flux, flow. The graph of conductance vs concentration is shown in figure 4 and 5. The conductance data furnish the information concerning the variation of concentration difference between the sources and receiving phase with concentration (Table-3).

.**Table 3.** Conductance behavior of NaCl Concentration with respect to CAP with or without CPC

Concentration of NaCl (M)	Cellulose acetate-phthalate Conductance (μmho)*	Cellulose acetate phthalate with cationic surfactant(CPC) Conductance(μmho)**
0.01	0.254	0.611
0.02	0.191	0.679
0.03	0.253	0.837
0.04	0.161	0.827
0.06	0.267	1.010
0.08	0.369	1.126
0.10	0.426	1.206

*Energy required for conductance enhancement = 4.8129 KJ/mole; ** Energy required for conductance enhancement = 4.6960 KJ/mole; Relative change in conductance per molar = 7.8677M^{-1} (*); 7.4737M^{-1}(**)

Membrane potential study: When a membrane is separating two solutions of the same electrolyte but of different concentrations, C_1 and C_2, the transfer of the electrolyte from the concentration solution to the dilute solution takes place due to the concentration gradient between those two solutions. If one ion move faster than another ion (of the opposite charge),separation of charge takes place, which sets up slow down the faster ion and accelerates the slower ion. The membrane maintains the electro-neutrality of the system. An electrical potential (membrane potential) develops, regulating the flow of ions through the membrane. The membrane potential data obtained with CAP-CPC in various1:1 electrolyte solutions. The change in membrane potential with concentration may be due to the changes produced in the effective double layer with dilution. The electrical nature of membranes is an important characteristic since it can strongly affect the transport of electrolytes or charged species. The effective charge affects the transport of ions or charge species across a membrane and its effect is usually characterized by determining the ion transport number, and for single electrolytes $t_+^m + t_-^m = 1$.The ion transport no. can be determined by measuring the membrane potential difference at both sides of a sample separating two solutions of the same electrolyte but a different concentrations. The description of a membrane, its charged state is one of the most important properties to explain the functioning of a membrane. The membrane charge defined from the membrane potential is opposite in sign to that the predicted by the chemistry of the membrane material, it is reported that the membrane charge density depends on both the pore size and bulk concentration. When the characteristic properties of the membrane charge are not explained by the chemistry of the membrane material, it would indicate that the character of the material in the membrane phase is different from that in aqueous solution. Possible reason for this are that, within the membrane, water is confined in an extremely narrow space of the membrane pore and the water is therefore restricted in a bound state, the ionization group of the membrane can be dissociated as it would be in an aqueous solution. However, some ions are absorbed by the pore wall which affects the charge of the membrane [10]. Cationic surfactant is enhanced by increasing the negative charge density on the membrane surface. The adsorption of cationic surfactant is due to ion-pair interaction between the CAP-CPC (acetate ion of the membrane and the polar ions). The effect of NaCl concentration on the adsorption of CPC is studied.

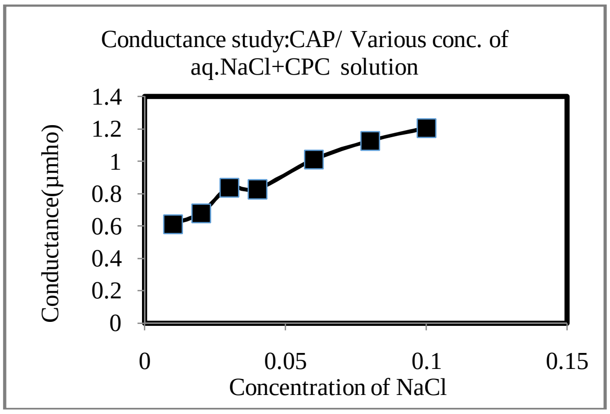


Figure 4. Dependence of conductance on concentration of aqueous solution of NaCl with cationic surfactant.

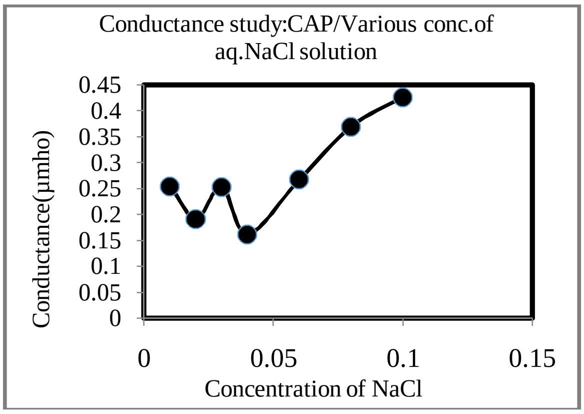


Figure 5. Dependence of conductance on concentration of aqueous solution of NaCl.

According to TMS theory, the potential across a membrane separation two cell having different concentrations of aqueous solutions is the sum of the two Donan potential and one diffusion potential between the membrane surface and inside the membrane. For the description of membrane potential across cellulose acetate phthalate membrane the Teorell-Meyers-Siever theory [8-9] is used, according to which the membrane potential is given by the equation:

$$(\Delta\Phi)_{I=0} = \frac{RT}{F}(t_-^m - t_+^m)\ln\frac{c_1}{c_2} \qquad \ldots (1)$$

Where t_+^m and t_-^m denote transport numbers of ions in the membrane phase, R is gas constant, F is Faraday number and T is the temperature in degrees Kelvin [13]. The membrane potential data for cellulose acetate phthalate membrane shows that the membrane potential decreases with increase in concentration.

The maximum value of membrane potential [14] is given by the equation

$$[(\Delta\Phi)_{I=0}]_{max} = \frac{RT}{F}\ln\frac{C_1}{C_2} \qquad \ldots (2)$$

Values of $[(\Delta\Phi)_{I=0}]_{max}$ calculated using Eq.(2) show that the maximum value of membrane potential decreases with increase in concentration of NaCl solution. This obviously arises on account of progressive enhancement of the negative charge borne by the membrane.

The values of apparent transport numbers calculated using the equation

$$t_-^m = \frac{[\Delta\varphi_{I=0}]}{2[(\Delta\varphi)_{I=0}]\max} + 0.5 \qquad \ldots(3)$$

show that the transport number decreases with increase in concentration . The decrease in transport numbers with increase in concentration. The dependence of the apparent transport number on concentration is similar to the dependence of membrane potential on concentration. Both these characteristics are measured of the ability of membrane to allow the passage of ions through it. The electrical character of a membrane is usually expressed in terms of fixed charge density. Effective fixed charge density of a membrane can be expressed in terms of permselectivity defined as

$$P_s = \frac{(t_-^m - t_-)}{(1 - t_-)} \qquad \ldots(4)$$

Where t_- denotes the transport number of the anion in solution, t^m - denotes the transport number of the anion in membrane phase.

Permselectivity is related to effective fixed charge density,$\Phi\bar{X}$, by Eq (5)

$$\Phi\bar{X} = 2\frac{C_e P_s}{\sqrt{(1 - P_s^2)}} \qquad \ldots(5)$$

Permselectivity and fixed charge density values derived using Eqs (4) and (5) respectively are included in table 4 and 5.

Table 4. Transport number, Permselectivities and fixed charge densities at different NaCl concentration ($\Phi\bar{X}$ mM)

C_1(M)	C_2 (M)	C_{mean}(M)	E_m(mV)	t^m_+	t^m_-	P_s	$\Phi\bar{X}$ (mM)
0.016	0.004	0.01	-6.80	0.5941	0.4059	0.3326	0.0070
0.032	0.008	0.02	-6.38	0.5883	0.4117	0.3248	0.0136
0.048	0.012	0.03	-6.00	0.5830	0.4170	0.3165	0.0200
0.064	0.016	0.04	-5.63	0.5779	0.4221	0.3088	0.0259
0.096	0.024	0.06	-5.00	0.5692	0.4308	0.2960	0.0371
0.128	0.032	0.08	-4.40	0.5609	0.4391	0.2841	0.0473
0.160	0.040	0.10	-3.86	0.5534	0.4466	0.2733	0.0567

Table 5. Transport number, Permselectivities and Fixed charge densities at different NaCl concentration ($\Phi\bar{X}$ in mM) with cationic surfactant (CPC)

C_1(M)	C_2 (M)	C_{mean}(M)	E_m(mV)	t^m_+	t^m_-	P_s	$\Phi\bar{X}$ (mM)
0.016	0.004	0.01	-6.72	0.5930	0.4070	0.3308	0.0069
0.032	0.008	0.02	-7.42	0.6027	0.3973	0.3484	0.0148
0.048	0.012	0.03	-8.19	0.6133	0.3867	0.3661	0.0235
0.064	0.016	0.04	-9.04	0.6251	0.3749	0.3861	0.0333
0.096	0.024	0.06	-11.01	0.6524	0.3476	0.4320	0.0574
0.128	0.032	0.08	-13.41	0.6856	0.3144	0.4874	0.0892
0.160	0.040	0.10	-16.34	0.7261	0.2739	0.5543	0.1331

Adsorption study: Amount of adsorption of ions onto membrane interface (mmole gram^{-1}) may be expressed as:

$$q = \frac{\Delta C.V}{m} \qquad \ldots(6)$$

Where V is the volume of solution taken for adsorption study, m denotes dry mass of the membrane and ΔC is proportional to external mean concentration of NaCl. The dependence of adsorption is shown in figure 6 and 7.

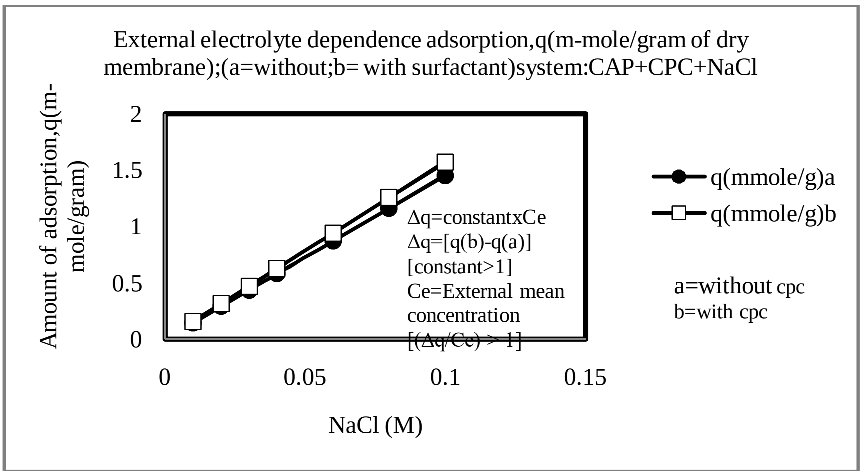


Figure 6. Dependence of adsorption on external electrolyte NaCl solution.

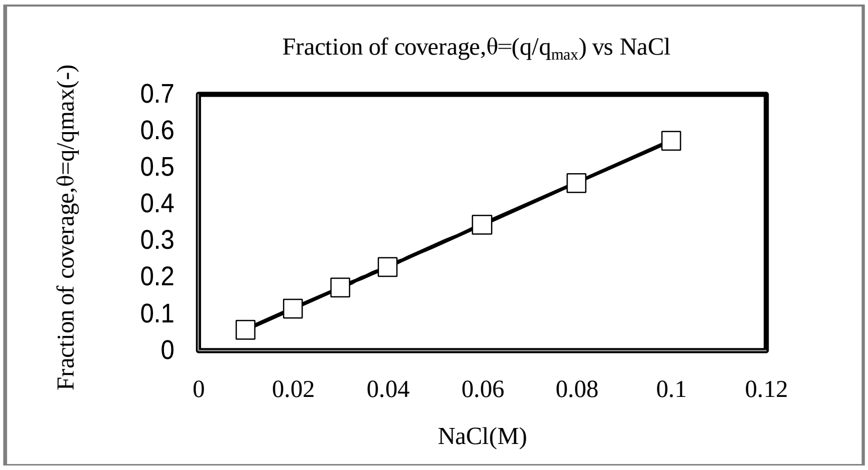


Figure 7. Dependence of fraction of coverage, θ, on external electrolyte NaCl solution in presence of surfactant.

APPLICATION

Application of this work is to modify the separation performance of the cellulose acetate phthalate membrane by using cetyl pyridinium chloride surfactant. The mixed membrane system showed 49.33% maximum rejection of the aqueous brine solution. It is the important achievement of the mixed membrane system. It retains water in the membrane phase resulting longevity of the membrane system

CONCLUSION

It is clear from the table 4 and 5 that effective fixed charge densities change with concentration. Fixed charge groups influenced the membrane permselectivity. Permselectivity increases with mean concentration. When CAP membrane is interacted with aqueous NaCl solution, Na^+ ion transport no. decreases with increase concentration of aqueous NaCl solution. In presence of CPC, Na^+ ion transport no. is increases with increase of aqueous NaCl solution. Permselectivity of Na^+ ion decreases with the increase in the concentration of aqueous NaCl solution. Permselectivity and fixed charge density increase with the increase in the concentration of aqueous NaCl. In CAP/NaCl, non conducting phase increase with NaCl concentration.CAP/NaCl+CPC System, non-conducting phase decreases with increase of NaCl concentration. Solute adsorption on the membrane interface is proportional to the external electrolyte concentration. In presence of surfactant, extent of adsorption is enhanced. Energy associated for the adsorption is 3.747 kJ mole^{-1}.

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