Electrochemical Characterization of TiO_2 Membrane with varying concentrations of aqueous $MgCl_2$ solutions

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Abstract: *Kynar supported titanium dioxide membrane has been prepared and characterized on the basis of membrane potential and membrane conductance measurements. Alteration in the ion selective character of the membrane on immobilization of cetyl pyridinium chloride (CPC) has been investigated with the object of exploring possibility of obtaining titanium dioxide membrane endowed with enhanced permselectivity. Structural and functional intactness of the immobilized structure has also been examined.*

Key words: Ion selectivity, Membrane potential, Membrane conductance, Titanium dioxide.

Introduction:

Electrochemical examination of ion exchange membrane reveals that the ion selectivity of these membranes are endowed with ,under ambient conditions ,needs substantial improvement [1,2].Titanium dioxide membrane, for instance, exhibits composition and pH dependent ion selectivity to a moderate degree when magnesium chloride solutions are used[3].In the present investigation we have explored possibility of obtaining improvement in the ion selective character of titanium dioxide membrane upon immobilization of cetyl pyridinium chloride ,an anionic surfactant. For this purpose membrane potential and membrane conductance measurements with and without the surfactant have been carried out. Considerable improvement in ion selectivity is observed with increase in surfactant concentration up to a certain concentration beyond which increased surfactant concentration does not result in any detectible change in selectivity. Ion selectivity of membranes declines with increase in concentration [4-6].

Experimental :

For titanium dioxide membrane formation 1g of the titanium dioxide (CDH,India) was dispersed in 20% Kynar (polyvinylidene flouride) (Pennwalt Corporation PHILA USA) solution in N,N-dimethyl acetamide (CDH,India) containing 2 g of the binder and cast into a membrane in the usual manner [5,7]. CPC (Kempnasol) was dissolved in water to prepare solutions of known composition .Its critical micelle concentration (CMC) was determined on the basis of surface tension measurements and found to be 9.12×10^{-4}M (Fig.1).
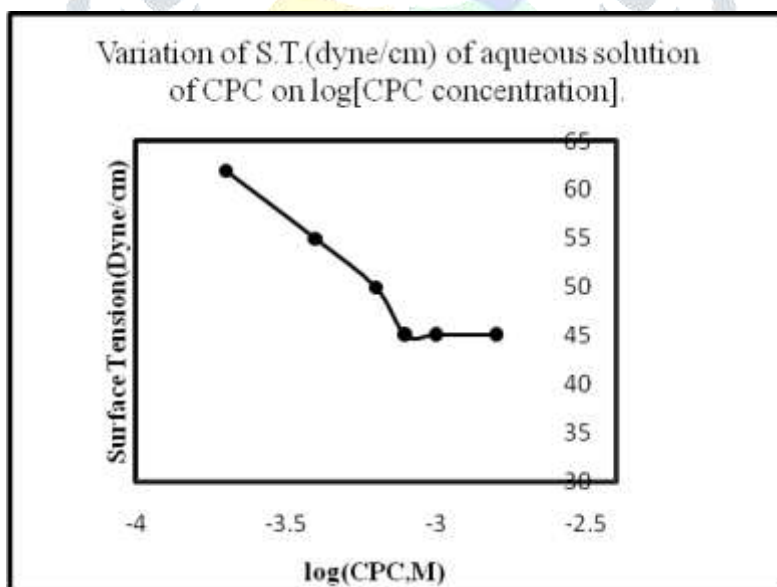

Fig.1

For surface tension measurements Fisher Tensiomat (Model-21) has been used. The measurements were done in such a way that the vertically hung ring was dipped into the liquid to measure the surface tension. The surface tension measurements were made at 25°C.Surfactant layer thickness, **l_surface** varies with CPC concentration as well as effective fixed charge density differently.Thicness of surfactant layer, **l_surface,** varies with CPC concavely and ΦX,convexly.

The experimental set-up described elsewhere [7, 8] was used for membrane potential and membrane conductance measurements. The membrane (cross sectional area = 0.156 mm^2 and thickness= 0.232 millimetre) under investigation was fixed in an all glass cell and kept overnight in with the experimental solutions. The solutions were renewed and membrane potential recorded with the help of a digital multimeter (HIL,2665) using saturated calomel electrodes (SES).The solutions were repeatedly renewed till reproducible values were obtained. For membrane conductance measurements, the current-voltage behaviour was examined. Potentials applied across the membrane were measured using SCE electrodes. For current measurements, silver-silver chloride electrodes were used. Digital multimeters (HIL 2161)

were used for recording applied potentials and ensuing currents. Conductance values were derived from the slopes of the current vs. potential plots. A representative plot is shown in Fig.2.
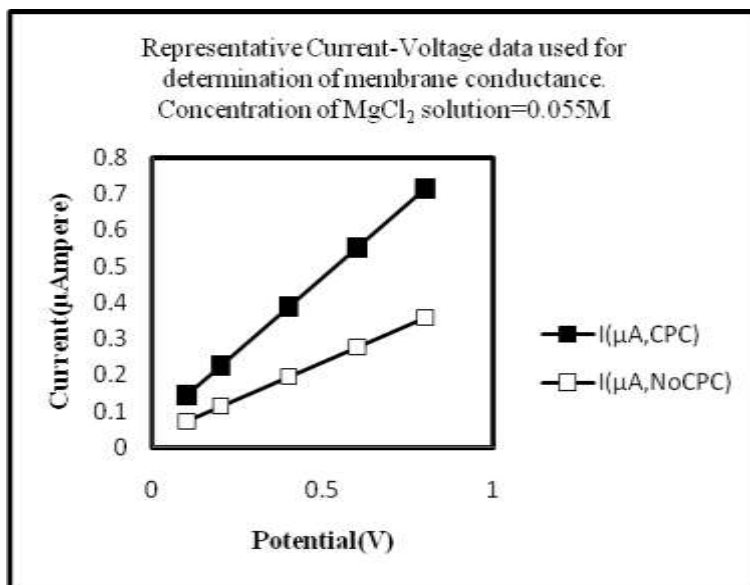

Fig.2

All measurements were carried out in an air thermostat maintained at $35\pm0.25^{O}C$.

Results and Discussion:

Normalized membrane potentials obtained using Kynar supported titanium dioxide membrane are compared with normalized liquid junction potentials under similar experimental conditions are shown in **Table 1**

Table 1
Normalized liquid junction and membrane potentials with and without CPC.
$$\Delta C = 0.1M$$

Concentration of $MgCl_2$ solution (M)	Normalised transport number,(t_+^N),(bulk phase)	Normalized membrane potential $E_m^N(-)$;(without CPC)	Normalized membrane potential $E_m^N(-)$;(withCPC)	Maximum value of membrane potential, E_m(without CPC)(mV)	Maximum value of membrane potential, E_m(with CPC)(mV)
0.1	0.9885	0.4902	0.4916		
0.2	0.9772	0.2403	0.2417		
0.3	0.9659	0.1178	0.1188	18.1	32.9
0.4	0.9548	0.0577	0.0584		

when magnesium chloride solutions having different concentrations are used. Liquid junction potentials E_L were calculated using the relationship [9].

$$E_L =(\frac{3t_-}{2} - \frac{1}{2})\frac{RT}{F}\ln\frac{a2}{a1} \qquad (1)$$

t_- denotes transport number of anion in the solution phase. a_1 and a_2 represent mean activities of the electrolyte solutions. In present case $a_2/a_1=C_2/C_1$are concentrations of electrolyte solutions bathing the membrane. The membrane obviously exhibits concentration dependent anion selectivity; and this was earlier [3] attributed to preferential Mg^{+2} ion adsorption. Ionic adsorption is known to alter and even reverse the nature of ion selectivity in some cases [10, 11]. Increase in concentration results in lowering of Ion selectivity because of reduced co-ion (Mg^{+2}) exclusion. Maximum and minimum values of membrane potential, E_m(without and with CPC)(mV) are also included in the same table. It is noted that in the presence of CPC, maximum membrane potential is observed. Charge separation tendency of the membrane is enhanced due to presence of surfactant CPC.

Cetyl pyridinium chloride when present along with the electrolyte in the solution is expected to alter the membrane character as a result of accumulation of the surfactant molecules in the interfacial region. The conductance data included in **Fig.3** which shows to increase in conductance of the composite system with concentration of the surfactant due to its increased accumulation.
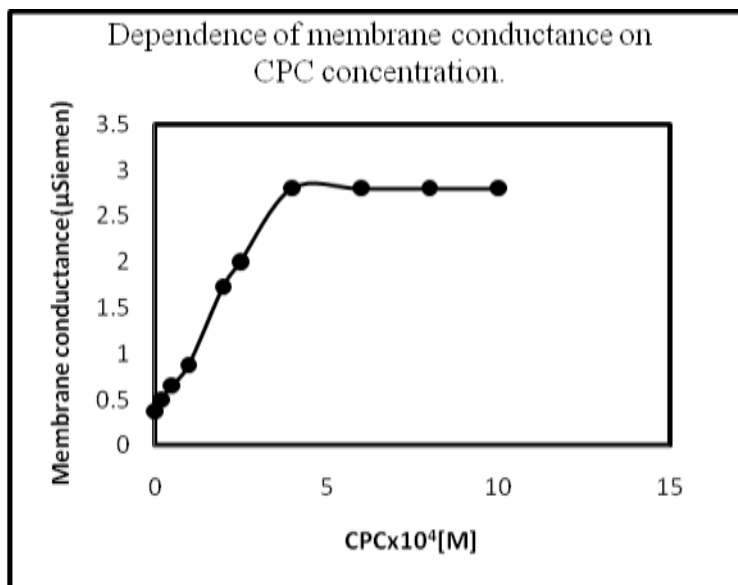
Fig.3

The conductance values were derived on the basis of current-voltage behaviour of the membrane system.

Relative changes in important electrochemical membrane parameters estimated from membrane potential data show significant variation with surfactant concentration till its concentration approaches 0.4mM. Progressive accumulation of the surfactant molecules clearly confer enhanced ion selectivity onto the membrane because of increased membrane positivity. Transport number values estimated using the relationship [12, 13].

$$E_m = \left(\frac{3\bar{t}_-}{2} - \frac{1}{2}\right) \frac{RT}{F} \ln \frac{a_1}{a_2} \tag{2}$$

And permselectivity, P_s, and the fixed charge density $\varphi\bar{X}$ values obtained from the relationships [14].

$$P_s = \frac{\bar{t}_- - t_-}{1 - t_-} \tag{3}$$

and

$$\varphi\bar{X} = \frac{2C_s \cdot P_s}{\sqrt{1 - P_s^2}} \tag{4}$$

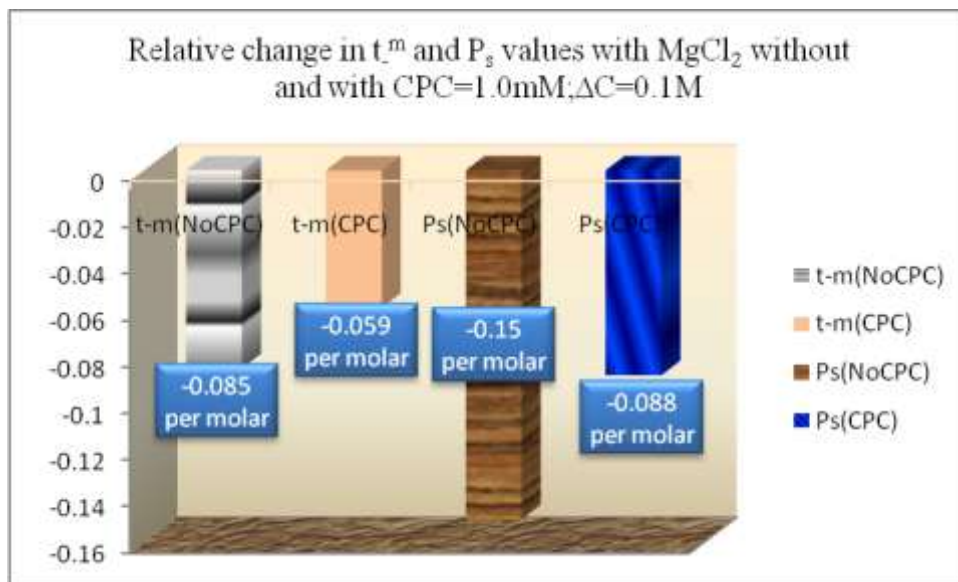Relative changes in P_s and $\varphi\bar{X}$ with $MgCl_2$ concentration are shown in **Fig.4**.

Fig.4

t_-^m denotes transport number of the anion in the membrane phase, C_s is the mean concentration. A significant enhancement in transport number of the anion, permselectivity and fixed charge density is observed in the presence of the surfactant. The relative changes in these electrochemical parameters are shown in Fig.5:
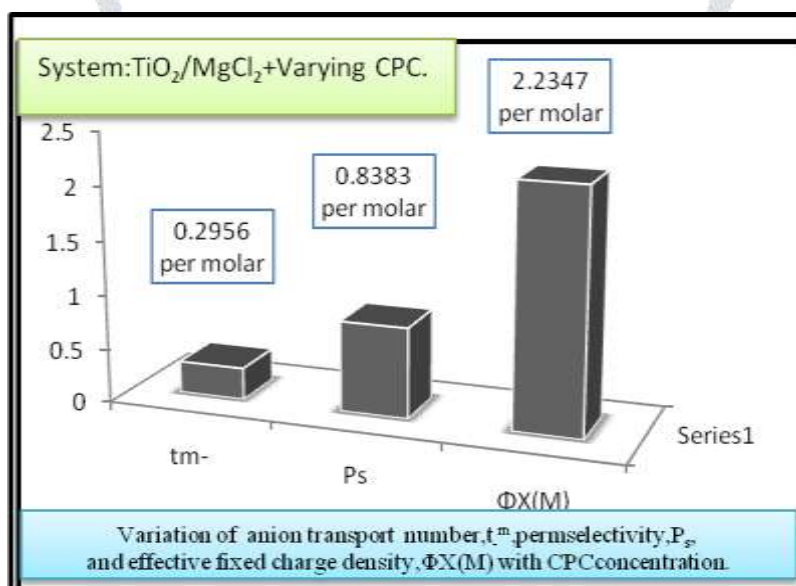

Fig.5

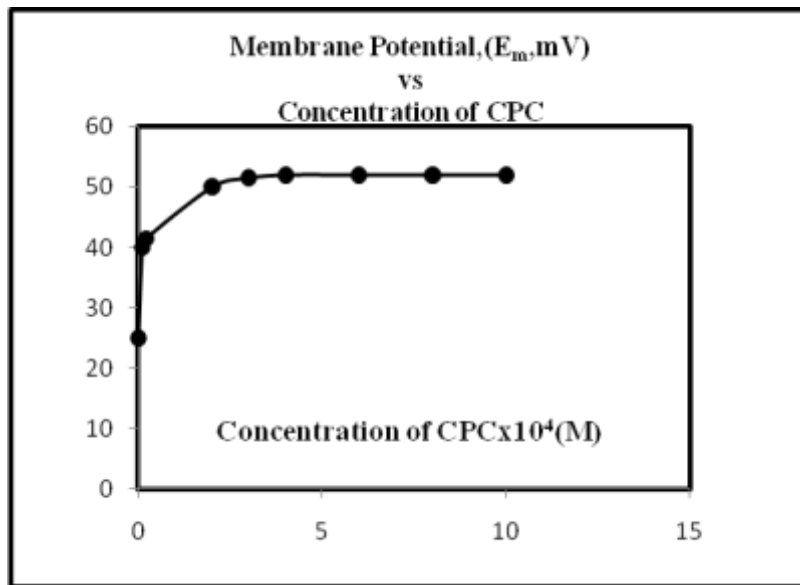Variation of membrane potential with concentration of $MgCl_2$ with and without CPC is depicted in Fig.6 (a) and 6(b).
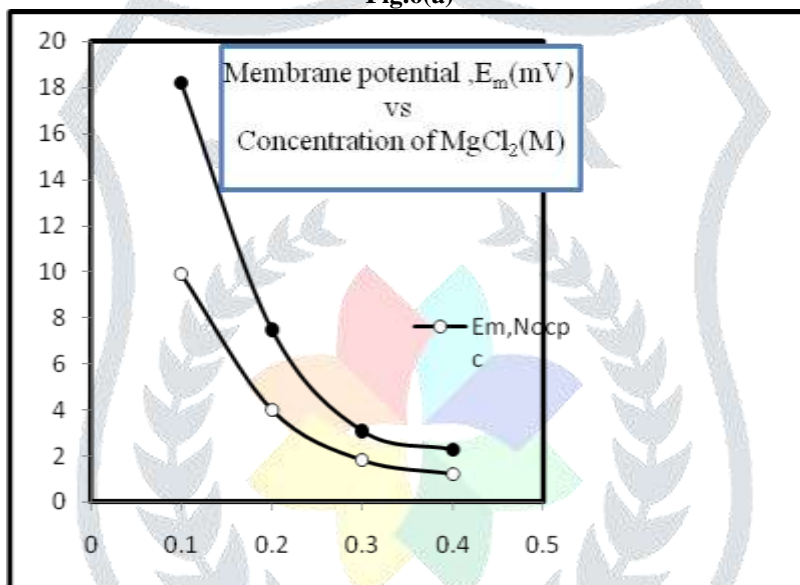
Fig.6(a)

Fig.6 (b)

CPC concentration was fixed at 4×10^{-4} M, the concentration beyond which no alteration in membrane anion selectivity is observed. In all these measurements difference of concentration was kept equal to 0.1. Transport number values estimated using eqn.(2) and (3) show that the transport number of the counter ion decreases when $MgCl_2$ concentration is increased. On the other hand in the presence of the surfactant, the transport number is substantially higher and practically does not change when concentration is increased beyond 4×10^{-4} M.

Examination of the results presented above clearly shows that the ion selective character of the titanium dioxide membrane increases in a substantial measure and almost ideal ion selectivity at a certain concentration beyond which further attachment of CPC molecules onto the membrane matrix does not take place.

Presence of ionic surfactant alters membrane conductance and surface tension and both vary with concentration. These data can be expressed linearly as:

$$\gamma = A\text{-}B \text{ [CPC (mM)]} \qquad (5)$$

γ denotes surface tension of the surfactant solution; A and B are intercept and slope respectively whose value is 69.9 dyne/cm and 32.5dyne/cm/mM respectively. This linear relationship is valid up to CMC of CPC. The membrane conductance, G_m, increases with the increase of CPC concentration. Its dependence may be expressed as:

$$G_m \, (\mu S) = D + E \text{ [CPC (mM)]} \qquad (6)$$

Where D and E are system constants as intercept and slope respectively. Their respective values are $0.33\mu S$ and $7.01\mu S/mM$. The above dependence is valid till 0.4mM beyond this concentration, membrane conductance becomes invariant. A correlation between interfacial excess and fixed charge density estimated on the basis of surface tension.(and membrane potential measurements respectively, can be correlated. It is obvious that progressive increase in fixed charge density arises on account of enhanced immobilization of surfactant when its concentration is increased till the membrane surface is saturated with the immobilized surfactant molecule. In the present study it is found that Γ and φX convexly dependent on each other.

CPC is a cationic surfactant and titanium dioxide matrix is anion selective in nature because it bears a positive charge. Attachment of CPC molecules to the supporting titanium dioxide matrix results in increase in the positive charge which increases with increase in surfactant concentration and is responsible for the observed enhancement in ion selectivity. It may be noted that presence of CPC does not result in any change in pH of the magnesium chloride solutions. Accordingly change in selectivity in the presence of the surfactant cannot attribute to alterations in pH. Presence of ionic surfactant alters membrane conductance and surface tension and both vary with concentration. These data have been used to estimate interfacial excess, Γ, using adsorption isotherm as

$$\Gamma = -\frac{C}{R.T} \cdot \frac{d\gamma}{dC} \tag{7}$$

γ denotes surface tension of aqueous solution of CPC,Fig.1. The interfacial excess, values obtained using the above relationship is shown in Fig.7.
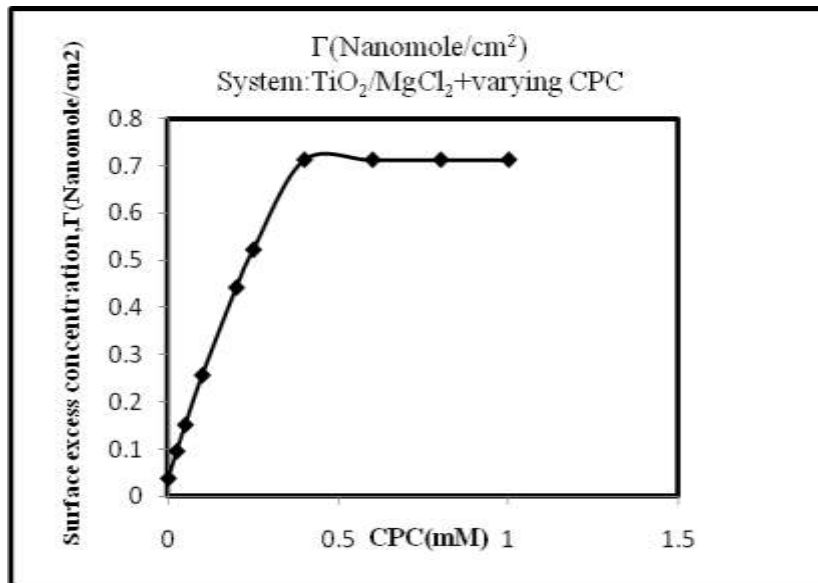

Fig.7

Interfacial saturation is seen to occur when surfactant concentration approaches 4.0×10^{-4} M. It is obvious that progressive increase in fixed charge density arises on account of enhanced immobilization of surfactant when its concentration is increased till the membrane surface is saturated with the immobilized surfactant molecule.

With ion exchange membranes, ion selectivity is known to diminish with increase in concentration of the electrolyte solution because of lowered co-ion exclusion [15-17].When CPC is used no significant alteration in co-ion exclusion with concentration occurs in the range of electrolyte concentration used in the experiment. As a result of this ion selectivity of the membrane does not change with concentration of the electrolyte solution. Significant effect of electrolyte and surfactant on the membrane can clearly be shown in **Figs.8 (a)** and **8(b)**.
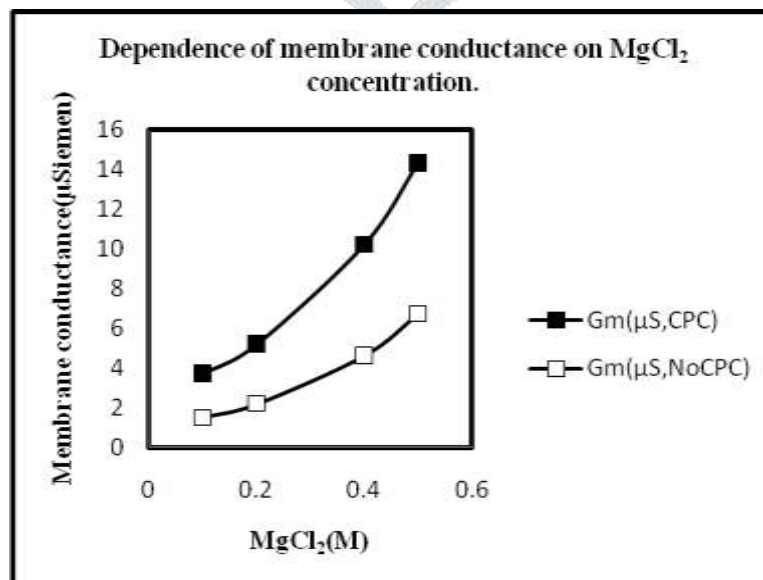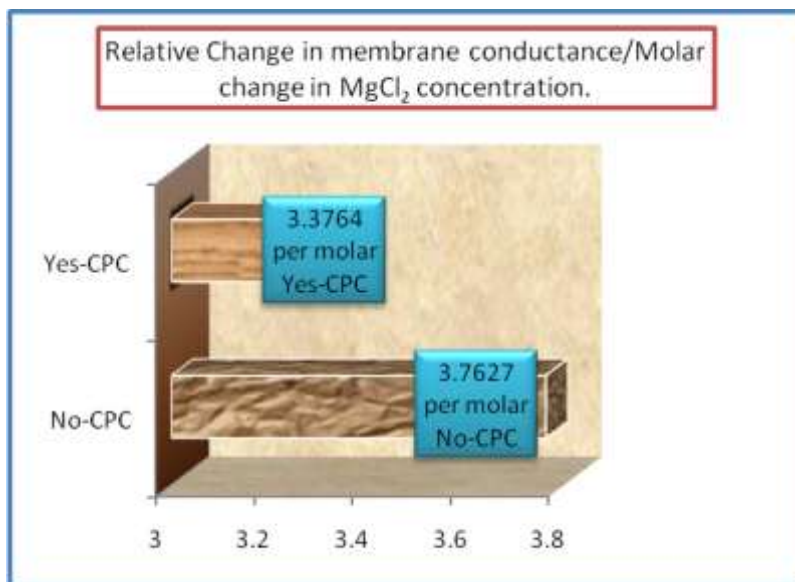

Fig.8(a)

Fig.8(b)

In Fig.8 (a) it is clear that membrane conductance in both cases increases with $MgCl_2$ aqueous concentration and relative change in conductance per molar change in electrolyte concentration is significant in case of No-CPC condition. Electrical nature of the membrane is governed by effective fixed charge density of the membrane. This effective fixed charge density is more influenced by $MgCl_2$ solution without CPC can be shown in Fig.9.
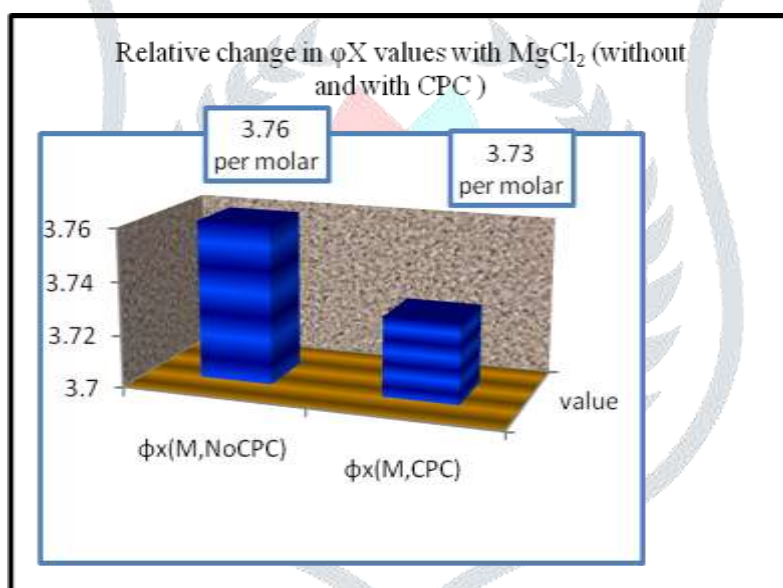

Fig.9

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