



PREPARATION, CHARACTERIZATION AND ELECTROCHEMICAL PROPERTIES OF CATION SELECTIVE MEMBRANES

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Keywords: Polystyrene-based strontium phosphate membrane; membrane potential; charge density

Polystyrene based strontium phosphate membranes (SPM) prepared by applying different pressures. The membrane potential was measured with uni-univalent electrolytes (KCl, NaCl, and LiCl) solutions using saturated calomel electrode (SCEs). The effective fixed charge density of these membranes was determined by TMS method and it showed dependence of membrane potential on the porosity, charge on the membrane matrix, charge and size of permeating ions. The membranes were characterized by X-ray diffraction, scanning electron microscopy, and IR spectroscopy. The order of surface charge density for electrolytes is found to be KCl > NaCl > LiCl. Other important parameters such as transport number, distribution coefficient, charge effectiveness and related parameters were calculated. The membrane was found to be mechanically stable, and can be operated over a wide pH range. Moreover, the experimental results were found to be quite satisfactorily with theoretical values.

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Introduction

Membrane can be employed in several applications, including drinking water treatment, waste water treatment and reclamation, and industrial water treatment, to produce high water quality. The membrane has also been applied to water softening due to rejection efficiency for monovalent and multivalent ions in hard water. It was found that an increase of NaCl concentration or a presence of divalent cations increased membrane fouling.¹ The behavior of membrane systems has extensively been investigated by studying the transport properties of artificial membrane used by some of the recent analytical and electronic, techniques have added impetus to such investigations.^{2,3} The inorganic precipitated membranes have acquired particular significance in the last two decades. These membranes have several advantages over organic ion-exchangers e.g. their ability to withstand ionizing radiations and very high temperatures without undergoing degradation and their remarkably high selectivity for heavy toxic metals.^{4,5}

Variety of transport phenomena arise across a membrane when subjected to different driving forces.^{6,7} Some of these phenomena such as ion migration, electro osmosis, self diffusion, salt migration and membrane potential etc. occurring across the ionic membrane have been described by spiegler⁸ applying the principles of non-equilibrium of thermodynamics.

A precipitated membrane is a system consisting of a thin inorganic precipitate such that when in contact with salt solutions containing some of the precipitated generating ions, two oppositely charged layer at each membrane solutions

interface are formed. These layers are due to the absorbed ions on the precipitated membrane which can easily be joined or removed from membrane. The electrical properties of these membranes can dramatically change due to the absorption, deposition or diffusion of ions into these structures.

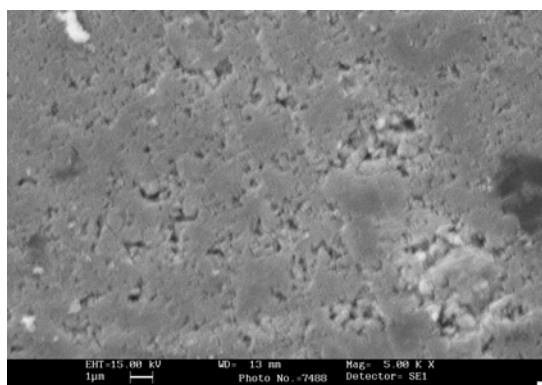
In this paper, we describe the preparation of strontium phosphate membranes using an appropriate concentration of polystyrene (25%) as a binder were found to be quite stable by applying different pressures.⁹ An attempt has been made to examine the validity of the recently developed method used for one determination of charge densities are based on the equations for membrane potential using different electrolyte concentration by Torell, Meyer, and Siever (TMS).^{10,11} The evaluation of charge density of membrane which is an important parameter controlling the membrane phenomenon have been used to calculate the membrane potential at different electrolyte concentration using the extended TMS theory to test the applicability of these recently developed equation for membrane potential for system under investigation.

TMS developed a theory of membranes with charges fixed within the lattice. This theory has been described in detail by Lakshminarayanaiah and has been applied by Siddiqi et al for the determination of thermodynamic fixed charge density of precipitated membranes.

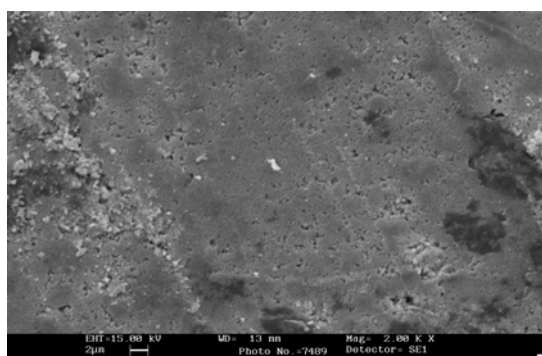
Experimental

Preparation of membrane

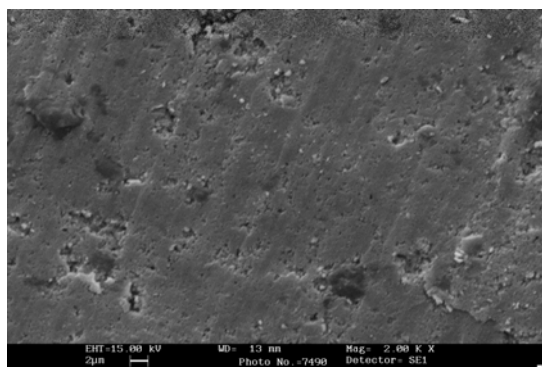
Strontium phosphate membranes were prepared by method suggested by Beg and coworkers.^{12,13} The main reagents used for the synthesis are 0.2 mol trisodium phosphate solution (E. Merch. India with purity of 99.90%)



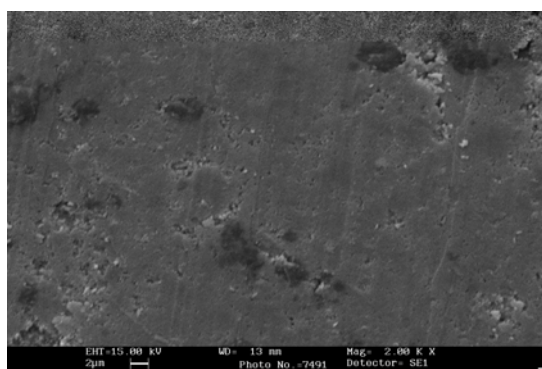
a)



b)



c)



d)

Figure 1. SEM images of polystyrene-based SPMs (a), (b), (c) and (d) prepared at different applied pressures (50, 70, 90 and 110 MPa), respectively.

The FTIR spectra were performed to a certain composition and the possible addition sites of the strontium phosphate membrane and pure polystyrene. The spectra contained weak to strong intensity peaks assigned to various functional groups in the material synthesized (**Fig 2**). The peaks in the range 696 to 874 cm^{-1} show the presence of aromatic ring in the polystyrene based strontium phosphate membrane¹⁹. The peaks 2852 and 2927 cm^{-1} support the C-H bond frequency due to stirring moiety in the material. The characterization peaks of phosphate groups are present in the spectra exhibiting the presence of phosphate group attached to the metal in the composite. The IR result, generally showing the negative shift in the spectra for most of the functions in the synthesized material is shown in **Fig 2**.

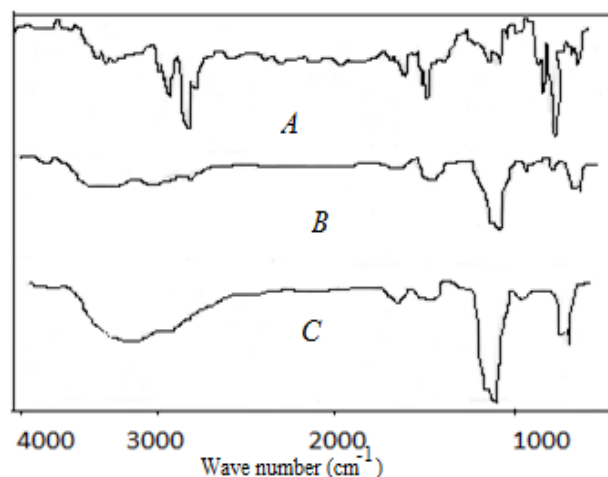


Figure 2. IR spectra of polystyrene (A), composite (B), strontium phosphate (C).

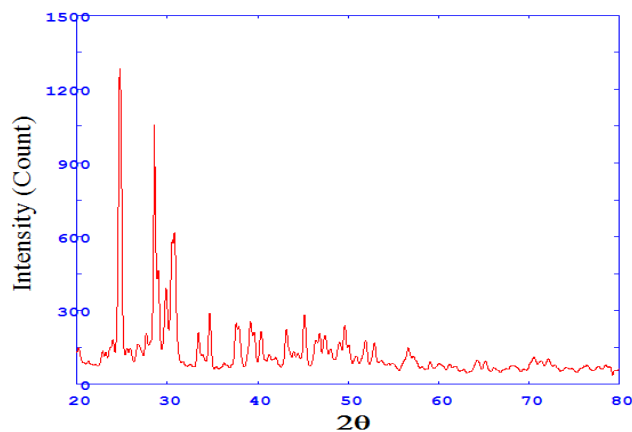


Figure 3. XRD pattern of polystyrene based strontium phosphate composite material.

The polymeric nature of the composite has also been supported from the other studies (Vide Supra). And the X-ray diffraction pattern of strontium phosphate cation exchange material recorded in powdered sample exhibited some sharp peaks in the spectrum in **Fig 3**. It is clear from the figure that the nature of composite cation exchange material is semi-crystalline.

The characterization parameters of the polystyrene-supported strontium phosphate membrane are given in Table 1.

Table 1. Characterization parameters of SPMs at different pressure

P, MPa	Membrane thickness, (cm)	H ₂ O content (wt. %, wet membrane)	Porosity, (unit less)	Swelling (wt.%, wet membrane)
50	0.090	0.0476	0.0201	no swelling
70	0.080	0.0361	0.0150	no swelling
90	0.070	0.0240	0.0115	no swelling
110	0.060	0.0123	0.0067	no swelling

This membrane shows a negligibly small swelling when immersed in sodium chloride solution. Porosity is determined by relationship:

$$\varepsilon = \frac{W^w - W^d}{AL\rho}$$

where W^d is the weight of the dry membrane and W^w is the weight of the wet membrane, ρ the density of water and L and A the thickness and area of the membrane respectively ($\text{g}/(\text{cm}^3 \cdot \text{g}/\text{cm}^3)$). Like the swelling, the membrane has low porosity. The electrical potential increases with increasing pressure. The thickness of the membrane was measured by taking the average thickness of the membrane by using screw gauze and the swelling is measured as the difference between the average thickness of the membrane equilibrated with 1 M NaCl for 24 h and the dry membrane. Membrane was tested for chemical resistance in strongly oxidant, acidic and alkaline media. In acidic (1 M HCl) and in alkaline media (1 M NaOH) few significant modifications were observed after 24, 48 and 168 h, demonstrating that the membrane was quite effective in such media. However, in strong oxidant media the synthesized membrane became fragile in 48 h and broken after 168 h, losing mechanical strength. In general membranes having the same chemical composition were found to absorb same amount of water, where density of the ionisable groups are same throughout the membrane.²⁰

When two-electrolyte solutions of different concentrations are separated by a membrane, the mobile species penetrate the membrane and various transport phenomena like diffusion potential, electro osmosis, are induced in the system. This field maintains on macroscopic scale electro neutrality by increasing the speed of slow moving ion and decreasing that of the faster ion. The magnitude and sign of the potential depend on the characteristics of the membrane and the permeating species. If the membrane carries no fixed charges or sites the electric potential across the membrane would be the same as the liquid junction potential. On the other hand, if the membrane carries some charges the magnitude of the potential is usually determined by the concentration of the electrolyte solution surrounding the membrane and its sign by the nature of the fixed charge.

The charges fixed in the lattice are determined by the theory developed by Teorell, Meyer and Sievers.²¹ In the TMS method there is an equilibrium process at each solution membrane interface which has a formal analogy with the Donnan equilibrium. With this, there is an internal salt diffusion potential, which was first represented by the

Henderson equation and later by the more nearly correct Planck expression.

According to TMS theory, the membrane potential in $8\Psi_m$, mV (applicable to a highly idealized system) is given by the equation (1) at 25 °C.

$$\Delta\Psi_m = 59.2 \left(\log \frac{C_2 \sqrt{4C_1^2 + D^2} + D}{C_1 \sqrt{4C_2^2 + D^2} + D} + U \log \frac{\sqrt{4C_2^2 + D^2} + UD}{\sqrt{4C_1^2 + D^2} + UD} \right) \quad (1)$$

where

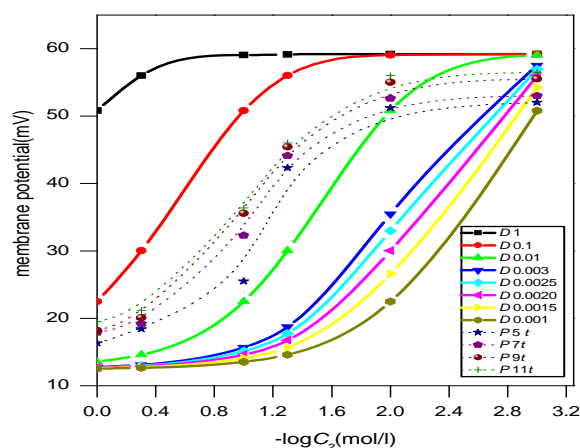
$$U = (u-v)/(u+v)$$

u and v are the mobilities of the cation and anion ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$), respectively, in the membrane phase.

C_1 and C_2 are concentrations of the electrolyte solution on either side of the membrane and

D is the charge on the membrane expressed in equivalent per liter.

To evaluate this parameter for the simple case of a 1:1 electrolyte and a membrane carrying a net negative charge of $D = 1$ as well as $D \leq 1$, theoretical concentration potentials across the membrane were calculated as a function of $-\log C_2$, the ratio C_2/C_1 being kept at a constant value of 10 for different mobility ratios u/v and plotted as in graph by smooth curves in Fig. 4. The experimental $8\Psi_m$ values for strontium phosphate with KCl electrolyte were



plotted in the same graph as function of $-\log C_2$.

Figure 4. Plots of membrane potential vs $-\log C_2$ for SPMs prepared at different pressures 50-110 MPa. Smooth curves are the theoretical concentration potentials for $D = 1$ at different mobility ratio. Broken lines are the experimental values $\Delta\Psi_m$ for different concentration of KCl solution.

For various electrolyte solutions the observed membrane potential of SPM at 25 ± 1 °C are given in Table 2.

The magnitude of the membrane potential depends on several factors, like the ratio of counter ion to co-ion mobility, concentration of salt solution and the exchange characteristics of the membrane material for various cations.

Table 2. $8\Psi^m \pm 0.5$ mV across the strontium phosphate membranes in contact with 1:1 electrolyte solutions at different concentrations.

Concentration $C_2, \text{mol L}^{-1}$	Applied pressure(MPa)											
	50			70			90			110		
	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl
1.0	16.3	19.0	20.0	17.9	20.0	20.5	18.2	21.0	22.2	19.5	22.9	23.8
0.50	18.4	25.9	26.6	19.2	25.6	27.0	20.1	36.5	37.4	21.2	37.2	39.1
0.10	25.5	26.4	28.0	32.3	35.2	36.6	35.6	37.0	38.0	36.4	38.8	39.9
0.05	42.3	45.3	46.2	49.1	48.5	49.0	51.5	52.6	53.3	52.0	53.0	53.5
0.01	51.2	52.0	52.5	52.6	53.2	54.0	55.0	55.5	56.0	57.0	56.5	57.0
0.001	52.0	52.5	53.0	53.0	54.5	54.8	55.5	56.0	56.3	58.5	57.0	57.5

The values of membrane potential (Table 2) reveal the following order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. The higher membrane potential observed with Li^+ is due to the fact that Li^+ is not thermodynamically favoured in the membrane phase.

The coinciding curve for all membrane gave the values for the charge density D within the membrane phase. The values of the D obtained in this for various membrane electrolyte systems are given in **table 3**. The surface charge density D of strontium phosphate membrane is found to depend on applied pressure. The increase in the values of D with higher applied pressure may be due to increase of charge per unit volume of the membrane and the order for electrolytes used is $\text{KCl} > \text{NaCl} > \text{LiCl}$.

Table 3. Calculated values of membrane charge density ($D \pm 0.1 \times 10^{-3}$ eqv. L^{-1}) for various SPMs electrolyte systems using TMS equation.

Applied pressure, MPa	Electrolyte, $D \times 10^{-3}$		
	KCl	NaCl	LiCl
50	1.20	1.10	0.90
70	1.40	1.20	1.00
90	2.50	2.00	1.80
110	3.60	2.40	2.10

The values for the membrane potential are of the order of positive mV and decrease with an increase of external electrolytes concentration. This shows membrane is negatively charge (cation selective)^{22,23} and selectivity of the cation increases with dilution. The selectivity character of ion exchange membrane with (1:1), (1:2), (1:3) has been reported.^{24,25}

This TMS method gave satisfactory result for fixed charge density evaluation. This technique has been used to estimate the capacity of thin polymer membranes of polyvinyl chloride and poly vinyl acetate. It has also been used to determine the charge of Keratin, to evaluate the fixed charge on thin parlodian and parchment supported membranes. In addition to the Eqn. (1), Teorell, Meyer and Sievers further extended their theory and derived another equation for membrane potential considering the total potential, as the Donnan potential $8\Psi_{\text{donnan}}$, between the membrane surfaces and the external solutions, and the diffusion potential $8\Psi_{\text{diff}}$, within the membrane.^{26,27}

$$8\Psi_{\text{m,e}} = 8\Psi_{\text{don}} + 8\Psi_{\text{diff}} \quad (2)$$

where

$$8\Psi_{\text{don}} = -\frac{RT}{V_k T} \ln \left(\frac{\gamma_{\pm}'' C_2 C_{1+}}{\gamma_{\pm}' C_1 C_{2+}} \right) \quad (3)$$

R , F and T have their usual significance, γ_{\pm}' and γ_{\pm}'' are the mean ionic activity coefficient C_{1+} and C_{2+} are the cation concentration on the two sides of the charged

$$C_+ = \sqrt{\left(\frac{V_x D}{2V_k} \right)^2 + \left(\frac{\gamma_{\pm} C}{q} \right)^2} - \frac{V_x D}{2V_k} \quad (4)$$

where V_k and V_x refer the valency of cation and fixed charge group on the membrane matrix, q is the charge effectiveness of the membrane and is defined by the equation (5).

$$q = \sqrt{\frac{\gamma_{\pm}}{K_{\pm}}} \quad (5)$$

where K_{\pm} is the distribution coefficient expressed as

$$K_{\pm} = \frac{\bar{C}_i}{C_i}; \quad \bar{C}_i = C_i - D \quad (6)$$

where C_i is the i^{th} ion concentration in the membrane phase and C_i is the i^{th} ion concentration of the external solution. The diffusion potential, $8\Psi_{\text{diff}}$ was expressed in the form

$$8\Psi_{\text{diff}} = -\frac{RT\varpi - 1}{V_k F \varpi + 1} \times \ln \left(\frac{(\varpi + 1)C_{2+} + (V_x/V_k)D}{(\varpi + 1)C_{1+} + (V_x/V_k)D} \right) \quad (7)$$

Here $\varpi = u/v$ is the mobility ratio of the cation to anion in the membrane phase. The total membrane $8\Psi_{\text{m,e}}$ potential was, thus, obtained by simple addition of Eqns. (3) and (7).

$$8\Psi_{m,e} = -\frac{RT\varpi - 1}{V_k F \varpi + 1} \times \ln \left(\frac{(\varpi + 1)C_{2+} + (V_x/V_K)D}{(\varpi + 1)C_{1+} + (V_x/V_k)D} \right) \quad (8)$$

$$\Delta\psi^m = \frac{RT}{F} (t_+ + t_-) \ln \frac{C_2}{C_1} \quad (9)$$

$$\frac{t_+}{t_-} = \frac{u}{v} \quad (10)$$

In order to test the applicability of these theoretical equations for the system under investigation, the Donnan potential and diffusion potential were separately calculated from membrane potential measurement using a typical membrane prepared at 70 MPa pressure. Eqs.(9) and (10) were first used to get the values of transport numbers t_+ and t_- from experimental membrane potential data and consequently, the mobility ratio $\varpi = u/v$ within the membrane phase. The values of mobility ratio (\square) of the electrolytes in the membrane phase were found to be high at lower concentration of all electrolytes (KCl, NaCl, LiCl). Further increase in concentration of electrolytes led to a sharp drop in the values of \square as given in **Fig 5**.

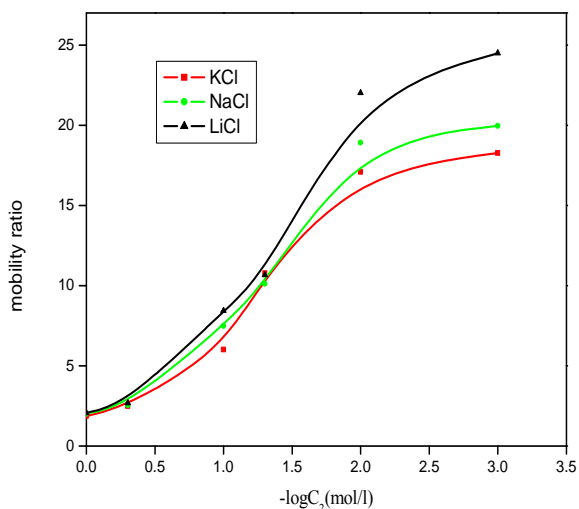


Figure 5. Plots of mobility ratio against $-\log C_2$ for SPM using 1:1 electrolytes.

The higher mobility is attributed to higher transport number of comparatively free cations of electrolytes and also be similar trend as the mobility in least concentrated solution. The values of t_+ calculated from observed membrane potential are given in **Table 4**.

Here, t_+ is not a true transport number since water permeation has not been taken into account, however, in dilute solutions the values of t_+ approach closer to the true values. **Fig. 6** shows that the transport number decreases with increase in concentration of the salt solution.

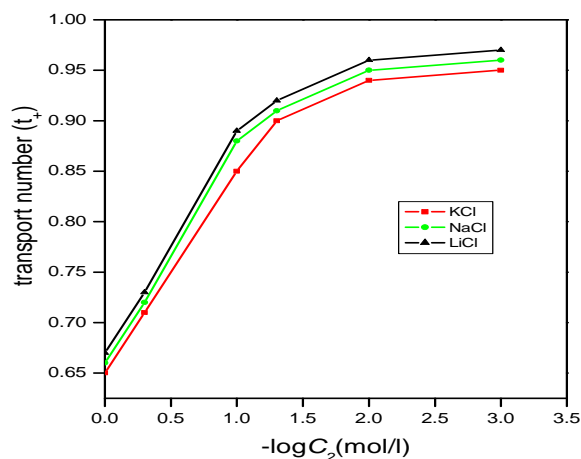


Fig. 6. Plots of t_+ (transport number) of various electrolytes

As the concentration of the electrolytes increased, the values of distribution coefficient decreased, thereafter, a stable trend was observed as shown in **Fig. 7**. The large deviation in the value at lower concentration of electrolytes was attributed to the high mobility of comparatively free charges of the strong electrolyte.

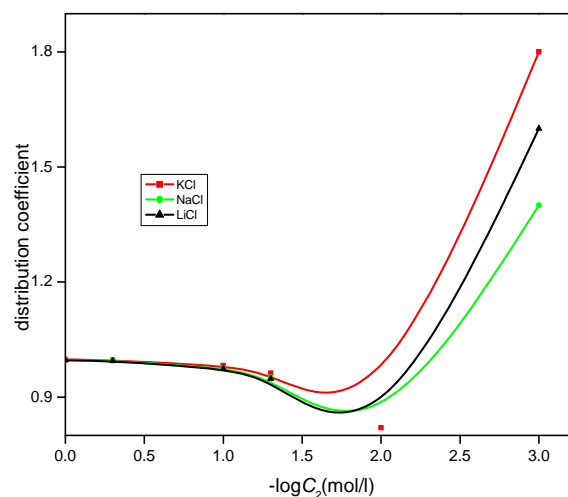


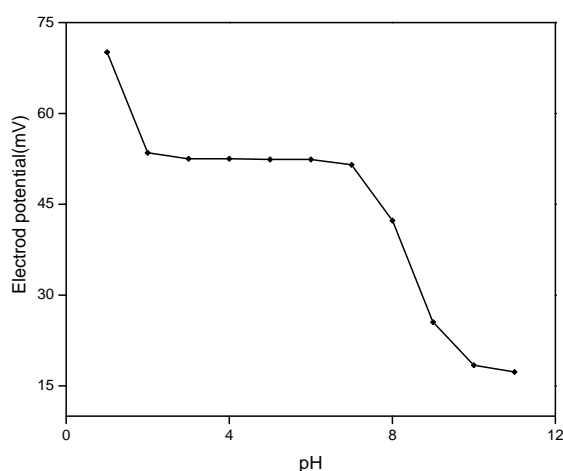
Figure 7. Plots of the distribution coefficient against $-\log C_2$ for SPM using various 1:1 electrolytes.

Donnan potential at various electrolyte concentration were then calculated from the parameters, C_{2+} , ϖ , q'' and K_{\pm} by using Eqs. 3-7 and values of the parameters derived for the systems have been given in **Table 5**. The values of γ_+ were the usual values for electrolytes. For comparison, the experimentally obtained values of membrane potentials for the system have also been drawn in the same figure. It may be noted that the experimental data follow the theoretical curve quite well. Whereas some deviations may be due to various non-ideal effects, such as swelling and osmotic effects, membrane inhomogeneity and hydrophobic/hydrophilic effects which were prominent and simultaneously present in the membrane.²⁷ These effects are often simultaneously present in charged membranes.

Table 4. The calculated values of the parameters (t_+ , K_{\pm} , q'' , C_{2+} , and $\bar{\omega}$) of SPM prepared at a pressure of 70 MPa with different concentration of electrolytes using Eqs. (4)- (6), (9) and (10).

KCl(electrolyte) C_2	t_+	K_{\pm}	q''	C_{2+}	$\bar{\omega}$
1.00	0.65	0.99	1.00	0.9937	1.760
0.50	0.66	0.996	1.001	0.4937	2.220
0.10	0.77	0.98	1.009	0.0938	4.00
0.05	0.89	0.962	1.018	0.0439	6.020
0.01	0.94	0.820	1.104	0.0051	13.89
0.001	0.95	0.80	1.118	0.0007	15.56
NaCl(electrolyte) C_2	t_+	K_{\pm}	q''	C_{2+}	$\bar{\omega}$
1.00	0.66	0.997	1.001	0.9916	1.94
0.50	0.70	0.995	1.002	0.4916	2.53
0.10	0.79	0.976	1.012	0.0918	4.20
0.05	0.91	0.952	1.024	0.0421	7.55
0.01	0.95	0.76	1.147	0.0041	15.56
0.001	0.96	1.40	1.245	0.0009	16.81
LiCl(electrolyte) C_2	t_+	K_{\pm}	q''	C_{2+}	$\bar{\omega}$
1.00	0.67	0.996	1.002	0.990	2.02
0.50	0.73	0.994	1.003	0.490	2.63
0.10	0.89	0.974	1.013	0.091	4.70
0.05	0.92	0.948	1.027	0.415	8.14
0.01	0.96	0.740	1.162	0.004	16.81
0.001	0.97	1.600	1.390	0.0001	18.26

The pH response profile for the membrane was tested by use of (1×10^{-2} mol L $^{-1}$) electrolytes solution over the pH range 2.0 – 11.0. The pH was adjusted by introducing small drops of hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M) into the solutions. The influence of the pH response on the composite membrane electrode is shown in Fig 8.

**Figure 8.** The effect of pH of the KCl solutions (1×10^{-2} mol L $^{-1}$) on the potential response of membrane.

As seen in figure, the potential remained constant from pH 2.0 to 7.0, beyond which some drifts in the potentials were observed. The observed drift at higher pH values could be due to the formation of some Hydroxyl complexes of cations (K^+ , Cl^+ , Li^+) the solution. At the lower pH values, the potentials increased, indicating that the membrane responded to protonium ions, as a result of the some extent

protonation of phosphorus atoms of the phosphate. In the other hand, at lower pH values H_3O^+ ions start to contribute to the charge transport process by the membrane, thereby causing interference.

Conclusions

With uni-univalent electrolyte (KCl, NaCl, and LiCl) solution membrane potential were measured for inorganic membranes using saturated calomel electrodes. The membrane potential offered by electrolytes is in the order $LiCl > NaCl > KCl$ and the obtained data indicates that the behavior investigated membrane is cation selective and the order of selectivity of cation transporting through the membrane has been found as $K^+ > Na^+ > Li^+$. The effective fixed charge densities and transport number of strontium phosphate membrane were evaluated by a TMS method. Charge density values obtained, by the frequently used TMS procedure, has been used to test the recently extended TMS equation by computing membrane potentials at different concentrations. Membranes prepared at high pressure (110 MPa) carry higher charge density and have narrow surface openings and low porosity. And the strontium phosphate membranes work well in the pH range 2.0–7.0. The theoretical predictions for membrane potential are borne out quite satisfactorily by our experimental results for all membranes.

Nomenclature

C_1, C_2 Concentration of electrolyte solution either side of the membrane (mol L $^{-1}$)

C_{1+}^-	Cation concentration in membrane phase 1 (mol L ⁻¹)
C_{2+}	Cation concentration in membrane phase 2 (mol L ⁻¹)
C_i	i^{th} ion concentration of external solution (mol L ⁻¹)
D	Charge density in membrane (eq L ⁻¹)
F	Faraday constant (C mol ⁻¹)
K_{\pm}	Distribution coefficient of ions
$K_{2\pm}$	Distribution coefficient of ions (electrolyte solution C_2)
P	Pressure (5-11 MPa)
q_1	Charge effectiveness of membrane phase 1
q_2	Charge effectiveness of membrane phase 2
R	Gas constant (J K ⁻¹ mol ⁻¹)
SCE	Saturated calomel electrode
SEM	Scanning electron microscopy
TMS	Teorell, Meyer and Sievers
XRD	Powder X-Ray diffraction
FTIR	Fourier Transform Infrared Studies
t_+	Transport number of cation
t_-	Transport number of anion
u	Mobility of cations in the membrane phase (m ² V ⁻¹ s ⁻¹)
U	($u-v/(u+v)$)
V	Mobility of anions in the membrane phase
V_k	Valency of cation
V_x	Valency of fixed charge group
$\gamma_{\pm}^{\prime}, \gamma_{\pm}^{\prime\prime}$	Mean ionic activity coefficient for electrolytes solution C_1 and C_2
ϖ	Mobility ratio (TMS extension theory)
$\Delta \Psi_m$	Membrane potential (mV)
$8 \Psi_{m,e}$	Membrane potential (mV) (TMS extension theory)
$8 \Psi_{\text{don}}$	Donnan potential (mV)
$8 \Psi_{\text{diff}}$	Diffusion potential (mV)

Acknowledgement

The authors are thankful to the Chairman, Department of Chemistry for providing research facilities, All India Institute of Medical Sciences (AIIMS), New Delhi for providing SEM micrograph, Zakir Hussain College of Engineering and Technology AMU for X-Ray Analysis and financial assistance provided by the University Grant Commission (UGC). India is also acknowledged.

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Received: 19.06.2013.

Accepted: 25.10.2013.