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Electrochemical characterization and transport phenomena of polystyrene based barium– magnesium phosphate composite membrane

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KEYWORDS

XRD; FTIR; SEM; Membrane potential; Fixed charge density Abstract The polystyrene based barium-magnesium (BMP) composite membrane was prepared by sol-gel method. The physico-chemical characterization of the BMP composite membrane was established by XRD, FTIR and simultaneous SEM studies. The membrane was found to be crystalline in nature with uniform arrangement of particles indicating no sign of visible cracks. Membrane potential is a measurable and important parameter to characterize the charge property of the membrane. Membrane potentials have been measured across the polystyrene based barium-magnesium (BMP) composite membrane separating various 1:1 electrolytes at different concentrations and followed the order KCl < NaCl < LiCl. The membrane was found to be cation-selective. Membrane potentials have been used to calculate transport number, mobility ratio, distribution coefficient, charge effectiveness, and also the fixed charge density which is a central parameter governing the membrane phenomena by utilizing Teorell, Meyer, and Sievers method. The order of surface charge density for uni-univalent electrolytes solution was found to be LiCl < NaCl < KCl. © 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

1. Introduction

Membrane processes are currently being studied for numerous applications of practical importance. In such processes, ions

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interact with a membrane, with water, and with each other in a complex fashion (Vinod et al., 2003). Ion exchange charged membranes, which are now extensively utilized in industries, have attracted considerable attention due to their extraordinary properties and practical demands and thus a large number of researchers have concentrated on these investigations for many years (Davis et al., 1971; Saito et al., 1996; Linder and Kedem, 2001; Xu and Yang, 2001).

Now there are multiple approaches to create ion exchange charged membranes or materials. Among them, inorganic– organic hybrid charged membranes or materials have attracted particular attention due to their excellent properties, such as

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Nomenclature

C_1, C_2	concentrations of electrolyte solution on either
	side of the membrane (mol/L)
\overline{C}_{1+}	cation concentration in membrane phase 1 (mol/L)
\overline{C}_{2+}	cation concentration in membrane phase 2 (mol/L)
C_i	<i>i</i> th ion concentration of external solution (mol/L)
\overline{C}_i	<i>i</i> th ion concentration in membrane phase (mol/L)
\overline{D}	charge density in membrane (eq/L)
F	Faraday constant (C/mol)
q	charge effectiveness of the membrane
R	gas constant (J/K/mol)
SCE	saturated calomel electrode
SEM	scanning electron microscopy
TMS	Teorell, Meyer and Sievers
T+	transport number of cation
t-	transport number of anion
\bar{u}	mobility of cations in the membrane phase
	$(m^2/v/s)$

\overline{v}	mobility	of	anions	in	the	memb	rane	phas
	$(m^2/v/s)$							

 V_k valency of cation

valency of fixed-charge group

 $\frac{V_x}{U}$ $\overline{U} = (\overline{u} - \overline{v})/(\overline{u} + \overline{v})$

BMP barium-magnesium phosphate

Greek symbols

mean ionic activity coefficients γ_{\pm} mobility ratio $\bar{\omega}$ $\Delta \psi_m$ observed membrane potential (mV)

 $\Delta \overline{\Psi}_m$ theoretical membrane potential (mV)

 $\Delta \Psi_{\rm Don}$ donnan potential (mV)

 $\Delta \overline{\Psi}_{diff}$ diffusion potential (mV)

structural flexibility, thermal and mechanical stability (Mitzi, 2001).

The various membrane separation techniques such as microfiltration, nanofiltration, ultrafiltration, reverse osmosis, pervaporation, gas separation and liquid membranes, etc. have been studied and industrially used. The ion-exchange membrane is one of the most sophisticated separation membranes among these separation membranes. The important property of the cation-exchange membrane and anion-exchange membrane is to selectively permeate cations or anions through the membrane (Sata et al., 2002).

Inorganic-organic composite materials are increasingly important due to their extraordinary properties within a single molecular composite, which arise from the synergism between the properties of the components (Kickelbick, 2003). These materials have gained much interest owing to their remarkable change in properties, such as mechanical (Okada and Usuki, 1995), thermal (Gilman, 1999), electrical (Zanetti et al., 2000) and magnetic (Armes, 1995) compared to pure organic polymers or inorganic materials. In these materials, organic materials offer structural flexibility, convenient processing, tunable electronic properties and metallic behavior.

Ion-exchange membranes are used in electrodialysis as ionselective membranes and in power sources (such as fuel cells) as proton conducting separators. Basically, ion-exchange membranes are available for use in electrodialysis which is composed of cross-linked polymers having ion-exchange groups bound to the polymer backbone (Oren et al., 2004).

Polystyrene based membranes demonstrate a large number of applications, which make them attractive to filtration tasks in the beverage and textile industry, medicine, pharmacy, chemical industry, waste water treatment etc. These applications are attributed to their high thermal resistance, chemical resistance and the mechanical strength (Khan and Rafiuddin, 2011).

Polystyrene based membranes with improved selectivity, stability, and non-fouling properties will be important, in future chemical and waste treatment applications. They will be needed for mitigating the environmental burden of chemical production and for producing less expensive chemicals with lower energy consumption.

We have developed a new series of polystyrene based ion exchange membranes directly from engineering polymers and examined the influence of membrane preparation conditions on the membrane properties including water content, porosity ,swelling, thickness, chemical stability and transport number etc.

The surface charge density \overline{D} is the central parameter that controls the membrane phenomenon and was calculated using the membrane potentials values for different electrolytes by using Teorell, Meyer, and Sievers (TMS) method (Teorell, 1935a,b; Meyer et al., 1936; Chou and Tanioka, 1998). Some other parameters including distribution coefficient, transport numbers, mobility ratio and charge effectiveness etc. were also calculated for polystyrene-based barium phosphate composite membrane. Membrane potential studies are commonly used in the electrochemical characterization of composite membranes (Singh and Tiwari, 1987; Singh and Shahi, 1990).

2. Theoretical aspects of the composite membrane

2.1. Fixed charge density theory of Teorell-Meyer-Sievers

In the Teorell-Meyer-Sievers theory there is an equilibrium process at each solution membrane interface which has a formal analogy with the Donnan equilibrium. The assumptions made are (a) the cation and anion mobilities, fixed charge concentration are constant throughout the membrane phase and are independent of the salt concentration and (b) the transference of water may be neglected. The implications of these assumptions have been discussed (Singh and Shahi, 1990). Further assumption is that the activity coefficient of the salt is the same in the membrane and solution phase at each interface must also be made. The introduction of activities for concentrations can only be corrected by the Donnan potential using either the integration of Planck or Henderson equation.

According to TMS theory, the membrane potential (applicable to a highly idealized system) is given by the equation at 25 °C.

$$\Delta \overline{\Psi}_{m} = 59.2 \left(\log \frac{C_{2}}{C_{1}} \frac{\sqrt{4C_{1}^{2} + \overline{D}^{2}} + \overline{D}}{\sqrt{4C_{2}^{2} + \overline{D}^{2}} + \overline{D}} + \overline{U} \log \frac{\sqrt{4C_{2}^{2} + \overline{D}^{2}} + \overline{D}\overline{U}}{\sqrt{4C_{1}^{2} + \overline{D}^{2}} + \overline{D}\overline{U}} \right)$$
(1)

 $\overline{U} = (\bar{u} - \bar{v})/(\bar{u} + \bar{v})$

where \bar{u} and \bar{v} are the ionic mobility's of cation and anion $(m^2/v/s)$, respectively, in the membrane phase, C_1 and C_2 are the concentrations of the membrane and \bar{D} is the charge on the membrane expressed in equivalent per liter. The graphical method of TMS determines the fixed charge \bar{D} in eq/L and the cation-to-anion mobility ratio in the membrane phase.

3. Experimental

3.1. Preparation of membrane

BMP precipitate was prepared by mixing 0.2 M magnesium (II) chloride (99.98% purity, E. Merck, Mumbai, India) and 0.2 M barium (II) chloride with 0.2 M tri-sodium phosphate (99.90% purity, E. Merck, Mumbai, India) in 100 ml solution. The precipitate was washed well with deionized water (Water purification system, 'Integrate, whose RO conductivity 0–200 $\mu s/cm$ and UP resistivity 1–18.3 M $\Omega\text{-cm}$) to remove the free reactant and then dried and powdered. Membrane using suitable ratio of binder (1:3) was prepared Jabeen and Rafiuddin, 2007. The precipitate was ground into fine powder and was sieved through 200 mesh BSS standard (granule size <0.07 mm). Pure crystalline polystyrene (Otto Kemi, India, AR) was also ground and sieved through 200 mesh. The BMP along with appropriate amount of polystyrene powder was mixed thoroughly using mortar and pestle. The mixture was then kept into a cast die having a diameter of 2.45 cm and placed in an oven (Oven-Universal, Memmert Type) maintained at 200 °C for about an hour to equilibrate the reaction mixture (Beg et al., 1979, 1978). The die containing the mixture was then transferred to a pressure device (SL-89, UK), and pressure of 100 MPa was applied during the fabrication of the membrane.

Our effort has been to prepare the membrane of adequate chemical and mechanical stability. The membranes prepared by embedding 25% polystyrene were found to be mechanically most stable and give reproducible results. Those containing larger amounts (>25%) of polystyrene did not gave reproducible results, while the one containing smaller amount (<25%) was found to be unstable (Arfin and Rafiuddin, 2009a). The total amount of the mixture thus, utilized for the preparation of the membrane contained 0.125 gm polystyrene 200 mesh, 0.1875 gm barium phosphate and 0.1875 gm magnesium phosphate each of 200 mesh. These membranes were subjected to microscopic and electrochemical examinations for cracks and homogeneity of the surface and only those which had smooth surface and generated reproducible potentials were considered.

3.2. Measurement of membrane potential

Membrane potential was measured by using digital potentiometer (Electronics India model 118). The freshly prepared charged membrane was installed at the center of the measuring cell, which had two glass containers, on either side of the membrane. The various salt solutions (chlorides of K^+ , Na⁺, and Li⁺) were prepared from B.D.H. (A.R.) grade chemicals using deionized water. Both collared glass containers had a cavity for introducing the electrolyte solution and saturated calomel electrodes. The half-cell contained 25 ml of the electrolyte solution while the capacity of each of the half cells holding the membrane was about 35 ml. The electrochemical setup used for uni-ionic potential and membrane potential measurements may be depicted as:

SCE Solution	Membrane	Solution	SCE
C_1	Diffusion potential	C ₂	
Donnan potential		Donnan potential	

3.3. Characterization of membrane

The pre-requisite criterion for understanding the performance of an ion-exchange membrane is its complete physico-chemical characterization, which involves the determination of all such parameters that affects its electrochemical properties. These parameters include membrane water content, porosity, thickness and swelling etc. These were determined in accordance with the method described by Khan et al. (2007) and Arfin and Rafiuddin (2009).

3.3.1. Water content (% total wet weight)

The conditional membrane was first soaked in water, blotted quickly with Whatmann filter paper to remove surface moisture and immediately weighed. These were further dried to a constant weight in a vacuum over P_2O_5 (dehydrating agent) for 24 h. The water content (total wet weight) was calculated as:

% Total(weight_{wet}) =
$$\frac{W_{\rm w} - W_{\rm d}}{W_{\rm w}} \times 100$$

Where W_w is the weight of the soaked or wet membrane and W_d the weight of the dry membrane.

3.3.2. Porosity

Porosity was determined as the volume of water incorporation in the cavities per unit membrane volume from the water content data:

$$Porosity = \frac{W_{\rm w} - W_{\rm d}}{AL\rho_{\rm w}}$$

Where W_d is the weight of the dry membrane, W_w is the weight of the soaked or wet membrane, A is the area of the membrane, L is the thickness of the membrane and ρ_w is the density of water.

3.3.3. Thickness

The thickness of the membrane was measured by taking the average thickness of the membrane using screw gauze.

3.3.4. Swelling

Swelling was measured in accordance with the procedure described by Arfin and Rafiuddin (2009). It was calculated as the difference between the average thickness of the membrane equilibrated with 1 M NaCl for 24 h and the dry membrane.

3.3.5. Chemical stability

Chemical stability was evaluated on the basis of ASTM D543-m95 method. Membrane was exposed to several media commonly used. Membrane was evaluated after 24, 48 and 168 h, analyzing alteration in color, texture, brightness, decomposition, splits, holes, bubbles, curving and stickiness (ASTM D543-95, 1998).

3.4. SEM investigation of membrane morphology

Scanning electron microscopic image was taken to confirm the microstructure of fabricated porous membrane. The membrane morphology was investigated by ZEISS EVO series scanning electron microscope EVO 50 at an accelerating voltage of 20 kV. Sample was mounted on a copper stub and sputter coated with gold to minimize the charging.

3.5. X-ray diffraction studies of the composite membrane

X-ray diffraction pattern of the polystyrene based BMP composite membrane was recorded by Miniflex-II X-ray diffractometer (Rigaku Corporation) with Cu K α radiation.

3.6. FT-IR Spectra of membrane

The IR spectrum of polystyrene based BMP composite membrane was done by Interspec 2020 FT-IR spectrometer, spectrolab (UK). The sample compartment was 200 mm wide, 290 mm deep and 255 mm high. The entrance and exit beam to the sample compartment was sealed with a coated KBr window and there was a hinged cover to seal it from the environment.

4. Results and discussion

Inorganic composite membranes have the ability to generate potential when two electrolyte solutions of unequal concentration are separated by a membrane and driven by different chemical potential acting across the membrane (Eisenman, 1961; Barragan et al., 1995). The migration of charged species is regulated by the electrical behavior of the membrane and diffusion of electrolytes from higher to lower concentration takes place through the charged membrane. Infact, the mobile species penetrate into the membrane at different magnitudes and various transport phenomena, including the development of potential across it, are induced into the system (Lakshminarayanaiah, 1969).

Membrane was tested for chemical resistance in acidic, alkaline and strongly oxidant media. In acidic ($1 \text{ M H}_2\text{SO}_4$) 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 the same amount of water, where density ionisable groups are same throughout the membrane (Koter et al., 1999).

The results of thickness, swelling, porosity and water content capacity of polystyrene based BMP composite membrane are summarized in Table 1. The water content of a membrane depends on the vapor pressure of the surroundings. In case of most of the transport measurements, only the membrane water content at saturation is needed, and that too mostly as a function of solute concentration. Thus, low order of water content, swelling and porosity with less thickness of membrane suggests that interstices are negligible and diffusion across the membrane would occur mainly through exchange sites (Arfin and Rafiuddin, 2009b).

The characterization of polystyrene based BMP composite membrane morphology has been studied by a number of investigators using scanning electron microscopy (Liu et al., 2006; Silva et al., 2005). The surface morphologies of the membranes show uniform arrangement of particles while cross-sectional SEM image shows no visible cracks. The composite pore structure, micro/macro porosity, homogeneity, thickness, cracks and surface texture/morphology have been studied (Titilove et al., 2008; Resina, 2007). The SEM, surface and cross-sectional images of the polystyrene based BMP composite membrane prepared at 100 MPa applied pressure, respectively are shown in Fig. 1(a) and (b). SEM images have provided ideas regarding the preparation of well ordered crack free membranes. Membrane had random non-preferential orientation with no visible cracks and appeared to be composed of dense and loose aggregation of small particles.

The FTIR spectral technique has been used as a valuable tool to explain the binding sites of polystyrene based BMP composite membrane. The spectra of the composite material containing barium-magnesium metals and polystyrene back bone were performed as KBr pellets. The FTIR data (Fig. 2) exhibit the presence of various important band characteristics of the functional group present in the membrane. The aromatic bands due to benzene ring are present in the region 584–699 cm⁻¹. The C–H stretching mode of the same is shown at 2361 and 2441 cm⁻¹. The peaks at 1557 and 1749 cm⁻¹ are due to the C=C of the aromatic ring (Nakamoto, 1986).

The comparison of the polystyrene based BMP composite membrane with that of the free polystyrene or metal phosphates shows a negative shift confirming that polystyrene has been bound to the barium–magnesium metals. The C–H stretching frequency of the polystyrene species is observed at weak peak at 3371 cm^{-1} in the spectra. Other normal IR bands were also observed at their appropriate position in the spectra (Nakamoto, 1986).

X-ray powder diffraction (XRD) is one of the most powerful techniques for qualitative and quantitative analysis of crystalline compounds. The X-ray diffraction spectrum of the polystyrene based BMP composite membrane is shown in

Table 1 Characterization	parameter of polystyrene ba	sed BMP composite membrane.		
Applied pressure (MPa)	Thickness of the membrane (cm)	Water content as % weight of wet membrane	Porosity	Swelling of % weight wet membrane
100	0.075	0.029	0.0027	No swelling



Figure 1 SEM image of polystyrene based BMP composite membrane at 100 MPa. (a) Surface SEM image. (b) Cross-sectional view.



Figure 2 FTIR Spectra of polystyrene based BMP composite membrane.

Fig. 3. The X-ray diffraction pattern of this material recorded in the powdered sample exhibited strong intensities in the spectrum (2θ range) which indicates the crystalline nature of the polystyrene based BMP composite phosphate membrane.

The values of observed membrane potentials, measured across polystyrene based BMP composite membrane in contact with various uni-univalent electrolyte (KCl, NaCl and LiCl) solutions at different concentrations at 25 ± 1 °C are



Figure 3 X-ray diffraction pattern of composite polystyrene based BMP composite membrane.

given in Table 2. These values were found to be concentration dependent. At low concentration, the potential was found to be high, whereas on increasing concentration of electrolytes the potential decreased. The membrane potential offered by various 1:1 electrolytes followed the order LiCl > NaCl > KCl. The values for the membrane potential are of the order of positive mV and increase with a decrease in external electrolytes' concentration. This shows that the membrane is cation selective.

Inorganic precipitate membranes were found to have the ability to generate potentials when interposed between electrolyte solutions of different concentrations due to the presence of net charge on the membranes (Shahi et al., 2003; Chai and Moon, 2001). These charges play a crucial role in the transport of electrolytes (Schaep and Vandecasteele, 2001). The membrane potential data obtained with polystyrene based BMP composite membrane using various 1:1 electrolytes are plotted as a function of $-\log C_2$ (Fig. 4).

The fixed charge concept of TMS model (Teorell, 1935a; Chou and Tanioka, 1998) for the charged membrane is an appropriate starting point for the investigations of the actual mechanisms of ionic or molecular processes which occur in membrane phase. The membrane potential according to TMS applicable to an idealized system is represented in Eq. (1).

The charge densities of inorganic membranes were estimated from the membrane potential measurement and can also be estimated from the transport number. To evaluate this parameter for the simple case of a 1:1 electrolyte and a

Table 2 Observed membrane potential in mV across the
polystyrene based BMP composite membrane in contact with
various 1:1 electrolytes at 100 MPa pressure and different
concentrations at 25 ± 1 °C.

Applied pressure	100 (MPa)		
Membrane potent	ial (mV)		
C ₂ (mol/L)	KCl	NaCl	LiCl
1	0.5	1.6	2.8
0.1	3.7	5.5	7.6
0.01	15.4	17.7	20.3
0.001	22.6	25.2	28.1
0.0001	30.5	32.8	35.6



Figure 4 Plots of observed membrane potentials against logarithm of concentration for polystyrene based BMP composite membrane using various 1:1 electrolytes at 100 MPa pressure.

membrane carrying various charge density $\overline{D} \leq 1$. The theoretical potential and observed potential were plotted as a function of $-\log C_2$ as shown by solid and broken lines, respectively in Fig. 5. Thus, the coinciding curve for various electrolytes system gave the value of the charge density \overline{D} within the membrane phase as shown in Table 3. The surface charge density \overline{D} of polystyrene based BMP composite membrane is found to depend on the applied pressure to which the membrane was subjected to its initial stage of preparation. Thus order of charge density for electrolytes used were found to be KCl > NaCl > LiCl. The charge density in the case of KCl is higher than in NaCl case due to the size factor (the smaller size, the larger ionic atmosphere).

The TMS Eq. (1) can also be expressed by the sum of Donnan potential $\Delta \psi_{\text{Don}}$, between the membrane surfaces and the external solutions, and the diffusion potential $\Delta \overline{\Psi}_{\text{diff}}$ within the membrane (Matsumoto et al., 1998; Chou and Tanioka, 1999).

$$\Delta \overline{\Psi}_{m,e} = \Delta \Psi_{\text{Don}} + \Delta \overline{\Psi}_{\text{diff}} \tag{2}$$

Where

$$\Delta \Psi_{\text{Don}} = -\frac{RT}{V_k F} \ln \left(\frac{\gamma_{2\pm} C_2 \overline{C}_{1+}}{\gamma_{1\pm} C_1 \overline{C}_{2+}} \right)$$
(3)



Figure 5 Plots of membrane potential (theoretical and observed) (mV) versus $-\log C_2 \pmod{L}$ at different concentrations of KCl electrolyte solution for polystyrene based BMP composite membrane prepared at pressure of 100 MPa.

Table 3 Derived values of membrane charge density $(\overline{D} \times 10^{-3} \text{ eq/L})$ of polystyrene based BMP composite membrane for various electrolyte system using TMS equation.

Applied pressure (MPa)	$\mathrm{KCl}\overline{D} \times 10^{-3}$	$NaCl\overline{D} \times 10^{-3}$	$\text{LiCl}\overline{D} \times 10^{-3}$
100	6.61	5.74	5.19

The *R*, *T* and *F* have their usual significance; $\gamma_{1\pm}$ and $\gamma_{2\pm}$ are the mean ionic activity coefficients; \overline{C}_{1+} and \overline{C}_{2+} are the cation concentration in the membrane phase first and second, respectively. The cation concentration is given by the equation

$$\overline{C}_{+} = \sqrt{\left(\frac{V_{x}\overline{D}}{2V_{k}}\right)^{2} + \left(\frac{\gamma_{\pm}C}{q}\right)^{2}} - \frac{V_{x}\overline{D}}{2V_{k}}$$
(4)

where V_k and V_x refer to 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

$$q = \sqrt{\frac{\gamma_{\pm}}{K_{\pm}}} \tag{5}$$

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

$$K_{\pm} = \frac{\overline{C}_i}{C_i} \quad \overline{C}_i = C_i - \overline{D} \tag{6}$$

Where \overline{C}_i the *i*th ion concentration in the membrane is phase and C_i is the *i*th ion concentration of the external solution. The transport of electrolyte solutions in pressure-driven membrane has shown that the transport properties of membrane are also controlled by ion distribution coefficients. It appeared that utilizing the Eq. (6) for evaluating the distribution coefficients were found to be low at lower concentration and as the concentration of electrolytes increases the value of distribution coefficients, sharply increases and thereafter, a stable trend was observed and is presented in the Table 4.

Table 4 The values of t_+ , \overline{U} , $\overline{\omega}$ and K_{\pm} , q, \overline{C}_+ evaluated using Eqs. (9), (6), (5), and (4) respectively, from observed membrane potentials for various electrolytes at different concentrations for polystyrene based BMP composite membrane prepared at 100 MPa pressure.

KCl (Electrolyte)						
$C_2(mol/L)$	t_+	\overline{U}	$\bar{\omega}$	K_{\pm}	q	\overline{C}_+
1.000	0.51	0.02	1.04	0.9933	1.0033	0.99102
0.1000	0.54	0.08	1.17	0.9339	1.0347	0.09111
0.0100	0.64	0.28	1.77	0.3390	1.7175	0.00244
0.0010	0.70	0.40	2.33	5.61	0.4222	0.00047
0.0001	0.76	0.52	3.16	65.1	0.1239	0.000056
NaCl						
1.000	0.52	0.04	1.08	0.9942	1.0029	0.99142
0.1000	0.55	0.10	1.22	0.9426	1.0299	0.09156
0.0100	0.65	0.30	1.85	0.4260	1.5321	0.00296
0.0010	0.72	0.44	2.57	4.74	0.4593	0.00040
0.0001	0.78	0.56	3.54	56.4	0.1331	0.000049
LiCl						
1.000	0.53	0.06	1.12	0.9948	1.0026	0.99172
0.1000	0.57	0.14	1.32	0.9481	1.0270	0.09183
0.0100	0.68	0.36	2.12	0.4810	1.4418	0.00327
0.0010	0.74	0.48	2.84	4.19	0.4885	0.00035
0.0001	0.81	0.62	4.26	50.9	0.1401	0.000044

The diffusion potential $\Delta \overline{\Psi}_{diff}$, is expressed in the form.

$$\Delta \overline{\Psi}_{\text{diff}} = -\frac{RT}{V_k F} \frac{\bar{\omega} - 1}{\bar{\omega} + 1} \times \ln \left(\frac{(\bar{\omega} + 1)\overline{C}_{2+} + (V_x/V_k)\overline{D}}{(\bar{\omega} + 1)\overline{C}_{1+} + (V_x/V_k)\overline{D}} \right)$$
(7)

where $\bar{\omega} = \frac{\bar{u}}{\bar{v}}$ is the mobility ratio of the cation to the anion in the membrane phase. The total membrane potential $\Delta \overline{\Psi}_{m,e}$, was thus obtained by simple addition of Eqs. (3) and (7).

$$\Delta \bar{\Psi}_{m,e} = -\frac{RT}{V_k F} \ln \left(\frac{\gamma_{2\pm} C_2 \overline{C}_{1+}}{\gamma_{1\pm} C_1 \overline{C}_{2+}} \right) - \frac{RT}{V_k F} \frac{\bar{\omega} - 1}{\bar{\omega} + 1} \\ \times \ln \left(\frac{(\bar{\omega} + 1) \overline{C}_{2+} + (V_x / V_k) \overline{D}}{(\bar{\omega} + 1) \overline{C}_{1+} + (V_x / V_k) \overline{D}} \right)$$
(8)

In order to test the applicability of these theoretical equations for the system under investigation, the Donnan potential and



Figure 6 The plot of mobility ratio of polystyrene based BMP composite membrane for 1:1 electrolytes (KCl, NaCl and LiCl) versus concentrations.

diffusion potential were separately calculated from the membrane parameters obtained from membrane potential measurements using a typical membrane prepared at a pressure of 100 MPa.The transport properties of the membrane in various electrolyte solutions are important parameters to further investigate the membrane phenomena as shown in Eq. (9)

$$\Delta \bar{\Psi}_m = \frac{RT}{F} (t_+ - t_-) \ln \frac{C_2}{C_1} \quad \frac{t_+}{t_-} = \frac{\bar{u}}{\bar{v}}$$
(9)

Eq. (9) was first used to get the values of transport numbers t_+ and t_- from experimental membrane potential data and consequently, the mobility ratio $\bar{\omega} = \frac{\bar{u}}{\bar{v}}$ and \bar{U} were calculated. The mobility $\bar{\omega}$ of the electrolyte in the membrane phase were found to be high and the order is LiCl > NaCl > KCl and shown in Fig. 6. The high mobility is attributed to the higher



Figure 7 The plot of transport number of cation of polystyrene based BMP composite membrane for 1:1 electrolytes (KCl, NaCl and LiCl) versus concentrations.

transport number of comparatively free cations of electrolyte which was also found to have the similar trend as the mobility in least concentrated solution.

The transport number of cation of the various electrolytes (KCl, NaCl and LiCl) increases with decreasing the concentration of electrolytes and follows the increasing order KCl \leq NaCl \leq LiCl shown in Fig. 7.

Donnan and diffusion potential at various electrolyte concentrations can be calculated from the parameters $\gamma_{1\pm}$, $\gamma_{2\pm}$, \overline{C}_1 +, \overline{C}_2 +, $\overline{\omega}$, V_x , V_k and the experimentally derived values of charge density \overline{D} by using Eqs. (3) and (7). The values of the parameters K_{\pm} , q and \overline{C}_+ derived for the system are also shown in Table 4. The values of γ_{\pm} were the usual charted values for electrolyte (KCl, NaCl and LiCl).

5. Conclusion

The polystyrene based BMP composite membrane was prepared by sol-gel process and it was found quite stable and did not show any dispersion in water and in other electrolyte solutions. The polystyrene was selected as binder because its cross-linked rigid framework provides an adequate adhesion to the BMP composite, and accounts for the mechanical stability to the membrane.

The fixed-charge density is the central parameter governing transport phenomena in membranes, and depends upon the feed composition and applied pressure due to the preferential adsorption of ions and accounted for altering the charge density and, in turn, performance of membrane. The order of surface charge density for uni-univalent electrolytes solution was found to be LiCl < NaCl < KCl.

The membrane potential of polystyrene based BMP composite membrane for different 1:1 electrolytes was found to follow an increasing order KCl < NaCl < LiCl. The result indicates that the behavior of the investigated membrane is cation selective and this composite membrane can be used for commercial application.

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