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Electrochemical and transport properties of polystyrene - and polyvinyl chloride-based pyridine Th(IV) phosphate composite ion-exchange membranes: a comparative study[1]

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ABSTRACT

The polystyrene (PS)- and polyvinyl chloride (PVC)-based pyridine Th(IV) phosphate (PTP) composite membranes were fabricated successfully and characterized by scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy and thermogravimetric analysis. The ion-exchange membranes prepared by using 25% of organic polymers i.e. polystyrene and polyvinyl chloride and 75% of pyridine Th(IV) phosphate were possessed good water uptake, good mechanical, chemical and thermal stabilities, ion-exchange capacity and better permselectivity. The electrochemical properties such as transport number, mobility ratio, charge effectiveness and surface charge density of the composite membranes were also determined. The results of transport properties revealed that the developed composite ion-exchange membranes can be employed for the efficient desalination of saline water and electrodialysis process.

Keywords: Composite membranes; Pyridine Th(IV) phosphate; Electrochemical studies; Transport properties; Charge density

1. Introduction

Several physical, chemical and biological processes have been designed for the treatment of industrial effluents containing toxic heavy metal ions. These processes include adsorption, crystallization, membrane filtrations (nano, ultra and microfiltration) and bisorption. However, the practical use of these processes is still limited because of their high cost and low efficiency [1–4]. Moreover, the separation of heavy metal ions from aqueous solutions has been

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[1] Now-a-days, organic–inorganic composite membranes have attracted great attention for membrane preparation because of their unique opportunity to combine the remarkable features of organic materials with those of inorganic materials. For the preparation of this kind of materials, incorporation of inorganic network through co-precipitation method into a polymer matrix is commonly employed.The present composite membranes show a large number of applications in medicine, pharmacy, chemical industry, wastewater treatment including separation tasks in the beverage and textile industry and others. These applications are attributed to their high thermal resistance, chemical resistance, mechanical strength and high transport number.

conventionally carried out by chemical precipitation for its simplicity and effectiveness. Although the chemical precipitation is frequently used to treat wastewater containing high concentrations of heavy metal ions, it is ineffective when metal ion concentration is very low. In recent times, the ion-exchange membranes have been widely used for wastewater treatment because of their superior chemical, mechanical and thermal stabilities, long life, cost effectiveness and high level of bounded water [5–10]. Nowadays, organic–inorganic composite membranes have been increasingly used for removal of heavy metals from contaminated water. The composite membranes showed accountable importance for the removal of heavy metal ions due to the presence of polymer backbone in the ion-exchange material and also because of high efficiency and reasonable selectivity. The PS and PVC were selected as binders since they provide good cross-linked rigid framework with an adequate adhesion to the composite membranes.

The aim of the present work is to study and model the separation capability of composite membranes for toxic metal ions from wastewater by employing TMS method. The thermodynamics parameters such as membrane potential, transport numbers, mobility ratio and charge effectiveness etc. of the membrane-electrolyte system have been determined in order to understand the mechanism of ion transport through the membrane. The surface charge density ($\overline{D}$) is the most valuable parameter that controls the membrane phenomena. The TMS method has been utilized for charge density calculations [11–14].

$$\Delta\overline{\Psi}_{\mathrm{m}} = 59.2\left(\log\frac{C_2}{C_1}\frac{\sqrt{4C_1^2+\overline{D}^2}+\overline{D}}{\sqrt{4C_2^2+\overline{D}^2}+\overline{D}} + \overline{U}\log\frac{\sqrt{4C_2^2+\overline{D}^2}+\overline{D}\,\overline{U}}{\sqrt{4C_1^2+\overline{D}^2}+\overline{D}\,\overline{U}}\right) \tag{1}$$

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

where $\overline{u}$ and $\overline{v}$ are the ionic mobilities of cation and anion ($\mathrm{m^2\,v^{-1}\,s^{-1}}$), respectively, in the membrane phase, C_1 and C_2 are the concentrations of the membrane and $\overline{D}$ is the charge on the membrane expressed in equivalent per litre.

2. Experimental

2.1. Reagents and chemicals

Potassium chloride, sodium chloride, lithium chloride, thorium nitrate, pyridine, phosphoric acid, HCl, HNO_3, H_2SO_4, NaOH, $KMnO_4$, polystyrene (PS) and polyvinyl chloride (PVC) were obtained from E-Merck, India. Demineralized water was used in all experiments. All other reagents and chemicals used were of analytical reagent grade.

2.2. Instruments

Scanning electron microscopy (SEM), ZEISS EVO Series SEM EVO 50, Interspec 2020 Fourier transformed infrared (FTIR) spectrometer; Spectrolab (UK), thermogravimetric analyzer (TGA) (Shimdzu DTG-60H), an oven universal memmert type and digital potentiometer (Electronics India model 118) were used.

2.3. Preparation of the pyridine Th(IV) phosphate

Pyridine based Th(IV) phosphate (PTP) composite cation-exchanger was prepared as reported by Varshney et al. [15]. PTP was prepared by mixing one volume of 0.1 M thorium nitrate solution in two volumes of (1:1) mixture of 2 M H_3PO_4 and pyridine with constant stirring using magnetic stirrer at 90˚C. The resulting slurry obtained under these conditions was stirred for 5 h at the same temperature. The slurry was washed well with demineralized water to remove free electrolyte and then dried at 45˚C. The dried product was converted into H^+ form by treating with 1 M HNO_3 for 24 h with frequent shaking and blinking replacement of the supernatant liquid with 1 M HNO_3. Finally, the material was washed well with demineralized water to remove the excess of acid and dried at 40˚C. Finally, sieved to obtain particles of 60–70 mesh size and was used for further studies [15,16].

2.4. Preparation of composite membrane

The pyridine Th(IV) phosphate composite material, PVC and PS were ground into fine powder separately using mortar pestel and sieved through 200 mesh (granule size <0.07 mm). The PTP composite material was mixed with PS and PVC, respectively, with the help of mortar and pestle. Both the composite materials were then kept separately in a pellet casting die having a diameter of 2.45 cm and placed in an oven maintained at 200˚C for about 1 h to equilibrate the reaction mixture [17,18]. The die containing the mixture was then transferred to a pressure device and 100 MPa of pressure was applied during the fabrication of the membranes. The optimum ratio of binders (PS and PVC) with the PTP was maintained as 1:3 to obtain mechanically and chemically stable membranes. In case of increase or decrease in the binder and composite ion-exchange ratio, the obtained membranes do not show better results.

2.5. Physical and chemical properties of composite membranes

The physicochemical characterization parameters such as chemical stability, thickness, water uptake, porosity and ion-exchange capacity of PS- and PVC-based PTP composite membranes were studied as earlier reported method [19,20].

2.6. Scanning electron microscopy investigation of composite membranes

The membrane morphology was investigated by ZEISS EVO Series SEM 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. SEM image was taken to confirm the microstructure of fabricated membranes.

2.7. Fourier transformed infrared studies

The FTIR spectrum of PS- and PVC-based PTP composite membranes was done by Interspec 2020 FTIR 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.

2.8. X-ray diffraction study of the composite membranes

The X-ray diffraction (XRD) pattern of the composite ion-exchange membranes were recorded by X-ray diffractometer with Cu Kα radiation.

2.9. Thermogravimetric analysis of the composite membrane

The degradation process and thermal behaviour of the PS- and PVC-based PTP composite membranes were investigated using TGA under nitrogen atmosphere using a heating rate of $20^\circ\text{C min}^{-1}$ from 25 to 600°C.

2.10. Measurement of membrane potential

The membrane potential of PS- and PVC-based PTP composite membranes was measured by using digital potentiometer. The freshly prepared charged membranes were placed at the centre of the measuring cell, which had two glass containers, on either side of the membrane. The various salt solutions of K^+, Na^+ and Li^+ by using chloride salts were prepared in demineralized water. Both collared glass containers had 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.

3. Results and discussion

The PS- and PVC-based PTP composite membranes were immersed in water bath at 60°C for 2 h. Thereafter, the membranes were soaked in 0.5 mol/l solutions of HCl, NaOH and strong oxidant media ($KMnO_4$) for 180 h and their chemical stability were determined. The significant observations were obtained after 30, 60, 120 and 180 h in acidic, basic and strong oxidant demonstrating that the membranes were stable in such media. The synthesized membranes became fragile in 60 h and broken after 180 h showing low mechanical strength.

The good chemical stability and the specificity for cations are the special features of these composite membranes. The results of physicochemical characterization of PS- and PVC-based PTP composite membranes are summarized in Table 1. The water uptake of these composite membranes depends on the vapour pressure of the surroundings. In the prospect of transport studies, only the membrane water uptake at saturation is required as a function of solute concentration. Therefore, the low order of water content, swelling and porosity with less thickness of membranes suggests that interstices are insignificant and diffusion across the membrane would occur mainly through exchange sites [21,22].

The surface morphologies of the composite membranes have been studied by using SEM technique and the microscopic images are shown in Fig. 1(a) and (b). It is clear from the morphological characterization that the prepared membranes at 100 MPa pressure were smooth and uniformly mixed with the respective polymers with no sign of visible cracks. Therefore, these composite membranes were used for further studies [23].

The FTIR spectrum of PS- and PVC-based PTP composite membranes are shown in Fig. 2(a) and (b) which indicated the distinguishing peaks related to the presence of aromatic ring, PS, PVC, phosphate group and metal oxygen bonds. The PS-based PTP

Table 1
The physicochemical characterization of polystyrene and PVC based PTP composite membranes

Types of membrane	Thickness of the membrane (cm)	Water content as % weight of wet membrane	Porosity	Ion-exchange capacity	Swelling of % weight wet membrane
Polystyrene based PTP composite membrane	0.072	0.022	0.094	0.980	No swelling
PVC based PTP composite membrane	0.094	0.034	0.074	0.880	No swelling

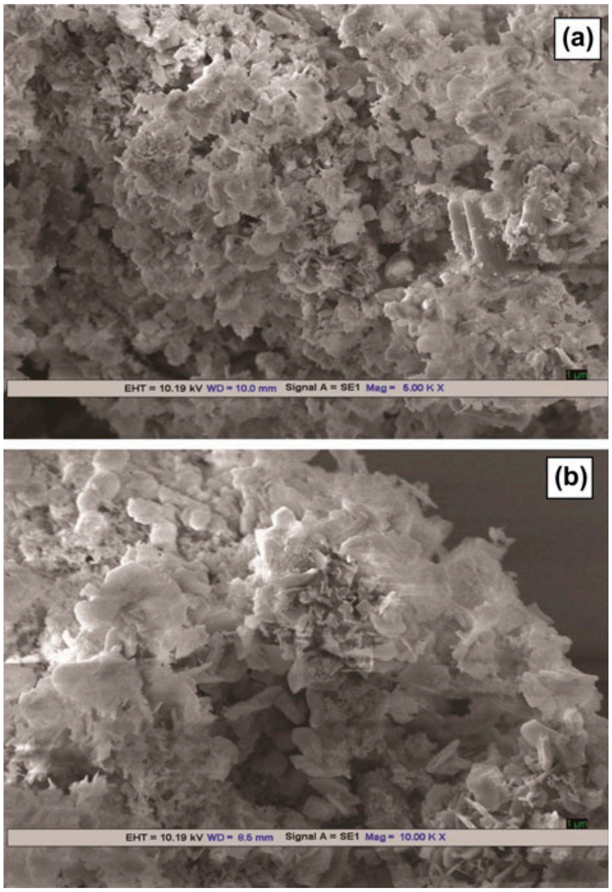

Fig. 1. SEM images of polystyrene based PTP composite membrane (a) and PVC based PTP composite membrane (b).

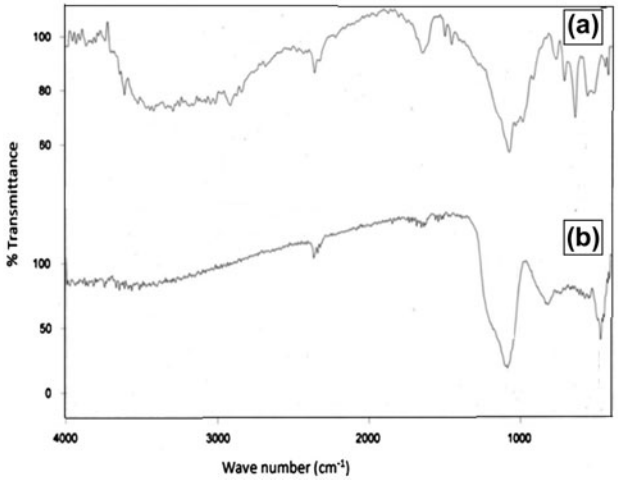

Fig. 2. FTIR spectrum of polystyrene based PTP composite membrane (a) and PVC based PTP composite membrane (b).

composite membrane in addition to the common peaks of aromatic pyridine ring shows aromatic peaks of PS (630, 698 and 750 cm^{-1}) which were absent in the FTIR spectrum of PVC-based PTP composite membrane. The PVC-based PTP composite membrane, on the other hand, exhibited peaks at 1,543 and 1,636 cm^{-1} confirming the presence of PVC. Additional peaks at 464 cm^{-1} confirm the presence of C–Cl bond of PVC in PVC-based PTP composite membrane. Both the composite membranes showed common peaks at 1,100 cm^{-1} corresponding to phosphate group present in PTP [24].

XRD analyses provide information about the structural characterization of composite membranes. For comparison, the XRD patterns for PS- and PVC-based PTP composite membranes are presented in Fig. 3(a) and (b). The sharp peaks of the PS-based pyridine thorium(IV) phosphate composite membrane (Fig. 3(a)) indicate that the composite membrane is crystalline in nature. It is a consequence of uniformly dispersed PTP in the polymer (PS) matrix. The XRD pattern of PVC-based PTP composite membrane (Fig. 3(b)) exhibited some sharp peaks in the spectrum and the membrane material is also found to be crystalline in nature. The sharp peak also indicates the confirmation of absolute homogeneity and compatibility among the components of the membrane.

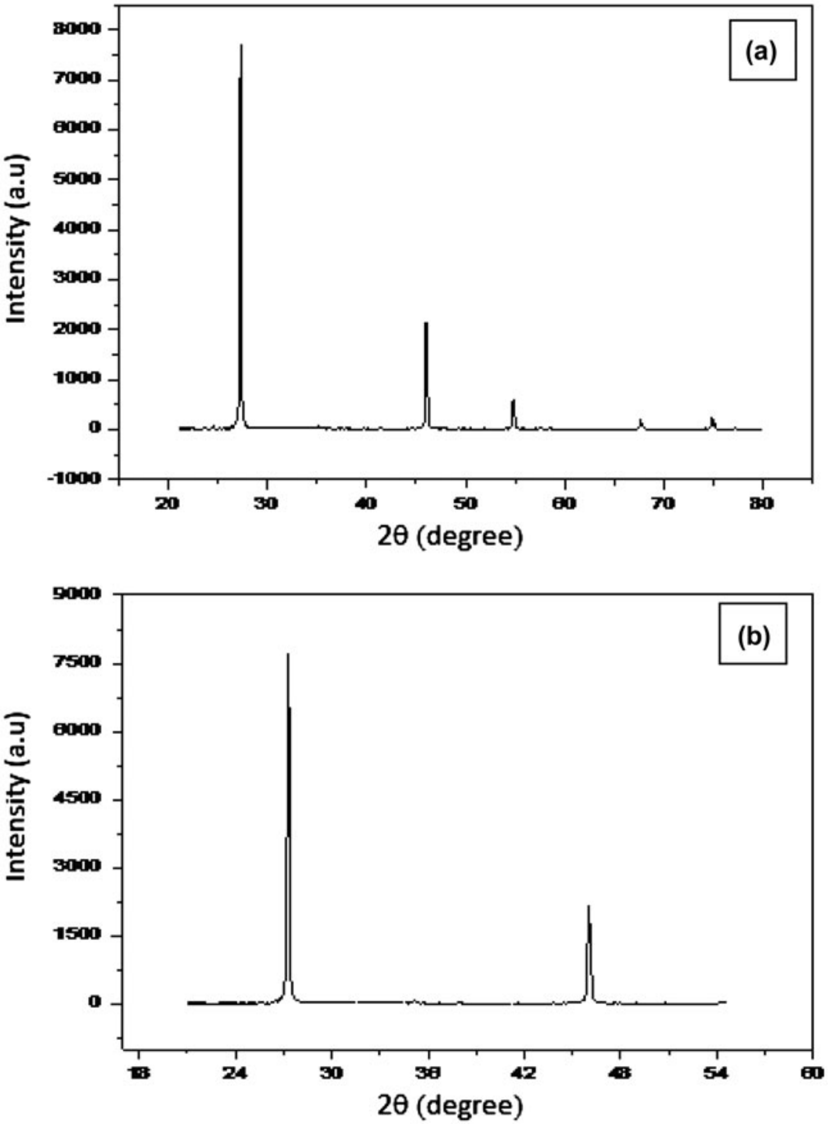

Fig. 3. XRD pattern of polystyrene based PTP composite membrane (a) and PVC based PTP composite membrane (b).

The thermal behaviour of PS- and PVC-based PTP composite membranes were analyzed by TGA under a nitrogen atmosphere as shown in Fig. 4(a) and (b). The PS- and PVC-based PTP composite membranes showed gradual weight loss of about 13.019% and 9.486% between 100 and 300°C, respectively, which may be attributed to the removal of external H_2O molecules present at the surface of the composite materials. The second weight loss 2.391 and 26.883% in the temperature range of 300–500°C of PS- and PVC-based PTP composite membranes, respectively, indicating the start of condensation due to the removal of the lattice water from the material and then organic counter parts were decomposed completely leading to the formation of oxides at 600°C onwards [25,26].

The inorganic–organic hybrid composite membranes have capacity to generate potential when two electrolyte solutions of different concentrations are separated by a membrane and driven by a different chemical potential acting across the membrane. The transfer of charged species is regulated by the electrical nature of the membrane and diffusion of electrolytes from higher to lower concentration takes place through the charged membrane. However, the mobile species penetrate into the membrane at different magnitude and various transport phenomena, including

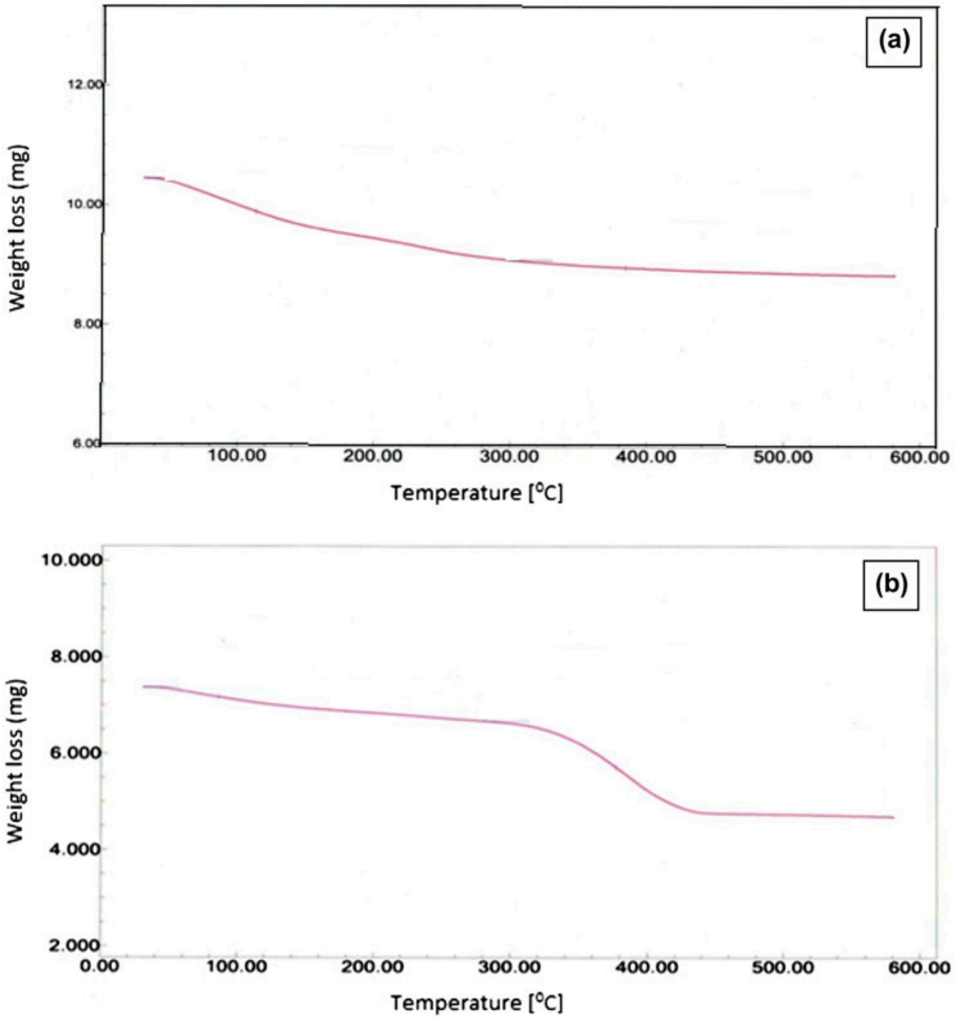

Fig. 4. TGA of polystyrene based PTP composite membrane (a) and PVC based PTP composite membrane (b).

the development of potential, are induced into the system [27–29].

The membrane potential data obtained with PS- and PVC-based PTP composite membranes using various monovalent electrolytes are plotted as a function of −log*C* as shown in Fig. 5(a) and (b). At higher concentration, the potential was found to be low, whereas on decreasing the concentration of electrolytes the potential increased. The membrane potential offered by these membranes of univalent electrolytes followed the order LiCl > NaCl > KCl. This shows that the membrane potential depends on the concentration of electrolytes and the membranes were found to be cation selective.

The membrane potential, according to TMS, applicable to an idealized system is represented in Eq. (1). The charge densities of composite membranes were estimated from the membrane potential measurement and could also be estimated from the transport number. To evaluate this parameter for the simple case of a 1:1 electrolyte and a 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 in Fig. 6(a) and (b). Thus, the coinciding curve for various electrolytes system gave the value of the charge density $\overline{D}$ within the membrane phase (Table 2). Thus, the 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 LiCl 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 $\Delta\Psi_{\mathrm{Don}}$, between the membrane surfaces and the external solutions, and the diffusion potential $\Delta\overline{\Psi}_{\mathrm{diff}}$ within the membrane [30,31].

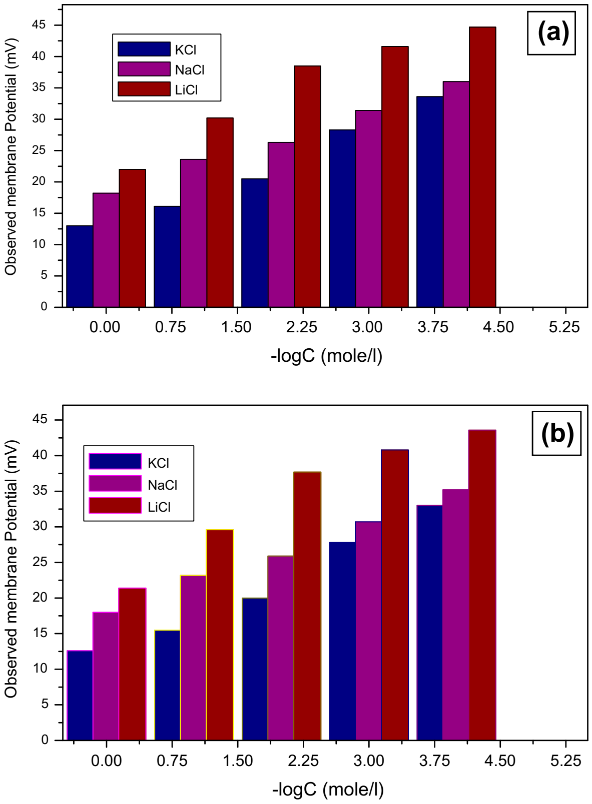

Fig. 5. Plots of observed membrane potentials against logarithm of concentration for polystyrene based PTP composite membrane (a) and PVC based PTP composite membrane (b) by using various electrolytes.

$$\Delta\overline{\Psi}_{\mathrm{m,e}} = \Delta\Psi_{\mathrm{Don}} + \Delta\overline{\Psi}_{\mathrm{diff}} \qquad (2)$$

where

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

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:

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

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 following equation.

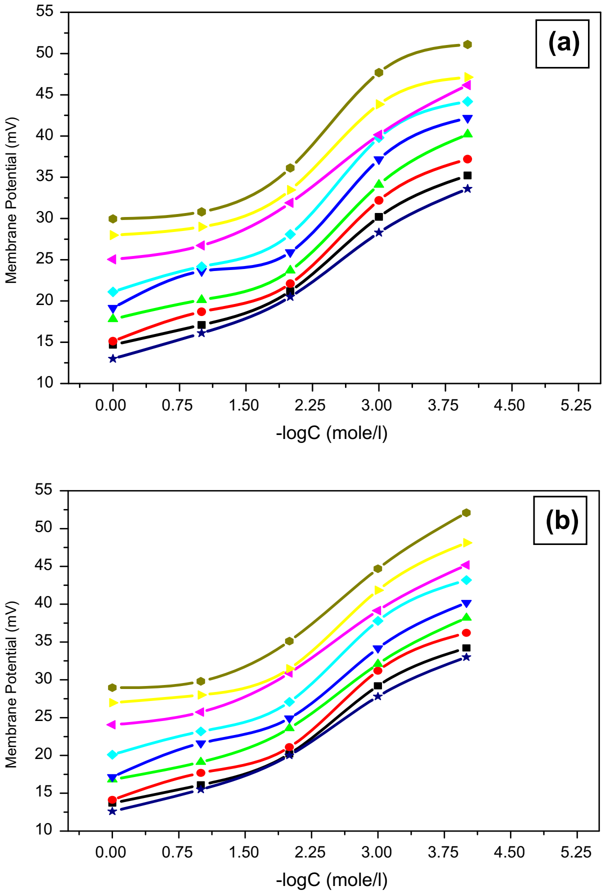

Fig. 6. Plots of theoretical and observed membrane potential (mV) vs. concentrations (mole/l) of KCl electrolyte for polystyrene based PTP composite membrane (a) and PVC based PTP composite membrane (b).

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

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

$$K_{\pm} = \frac{\overline{C}_{\mathrm{i}}}{C_{\mathrm{i}}}, \qquad \overline{C}_{\mathrm{i}} = C_{\mathrm{i}} - \overline{D} \qquad (6)$$

where $\overline{C}_{\mathrm{i}}$ is the i^{th} ion concentration in the membrane phase and C_{i} is the i^{th} ion concentration of the external solution. The 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

Table 2
The surface charge densities of polystyrene and PVC based PTP composite membranes

Types of membranes	Electrolytes	Charge density (eq/l)
Polystyrene based PTP composite membrane	KCl	0.056
	NaCl	0.034
	LiCl	0.017
PVC based PTP composite membrane	KCl	0.061
	NaCl	0.043
	LiCl	0.025

distribution coefficients, sharply increases and thereafter, a stable trend was observed.

The diffusion potential $\Delta\overline{\Psi}_{\text{diff}}$, is expressed as:

$$\Delta\overline{\Psi}_{\text{diff}} = -\frac{RT}{V_\text{k}F}\frac{\overline{\varpi}-1}{\overline{\varpi}+1} \times \ln\left(\frac{(\overline{\varpi}+1)\overline{C}_{2+} + (V_\text{x}/V_\text{k})\overline{D}}{(\overline{\varpi}+1)\overline{C}_{1+} + (V_\text{x}/V_\text{k})\overline{D}}\right) \tag{7}$$

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

$$\Delta\overline{\Psi}_{\text{m,e}} = -\frac{RT}{V_\text{k}F}\ln\left(\frac{\gamma_{2\pm}C_2\overline{C}_{1+}}{\gamma_{1\pm}C_1\overline{C}_{2+}}\right) - \frac{RT}{V_\text{k}F}\frac{\overline{\varpi}-1}{\overline{\varpi}+1} \times \ln\left(\frac{(\overline{\varpi}+1)\overline{C}_{2+} + (V_\text{x}/V_\text{k})\overline{D}}{(\overline{\varpi}+1)\overline{C}_{1+} + (V_\text{x}/V_\text{k})\overline{D}}\right) \tag{8}$$

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 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)

$$\Delta\overline{\Psi}_\text{m} = \frac{RT}{F}(t_+ - t_-)\ln\frac{C_2}{C_1} \qquad \frac{t_+}{t_-} = \frac{\overline{u}}{\overline{v}} \tag{9}$$

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 $\overline{\varpi} = \frac{\overline{u}}{\overline{v}}$ and $\overline{U}$ was calculated. The mobility $\overline{\varpi}$ of the electrolytes in the membrane phase was found to be high and the order is LiCl > NaCl > KCl as shown in Fig. 7(a) and (b). The high mobility is attributed to higher transport number of comparatively free cations of electrolyte which was also found to have the similar trend as the mobility in much diluted solution. The transport number of cation of the various electrolytes increases with the decreasing concentration of electrolytes and follows the increasing order KCl < NaCl < LiCl as shown in Fig. 8(a) and (b).

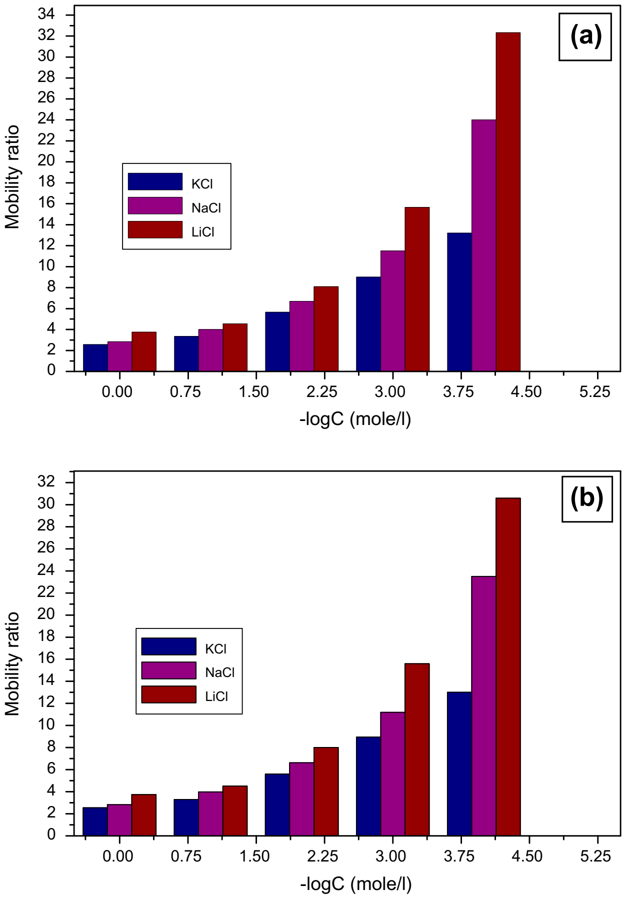

Fig. 7. The plot of mobility ratio vs. concentrations of various electrolytes of polystyrene based PTP composite membrane (a) and PVC based PTP composite membrane (b).

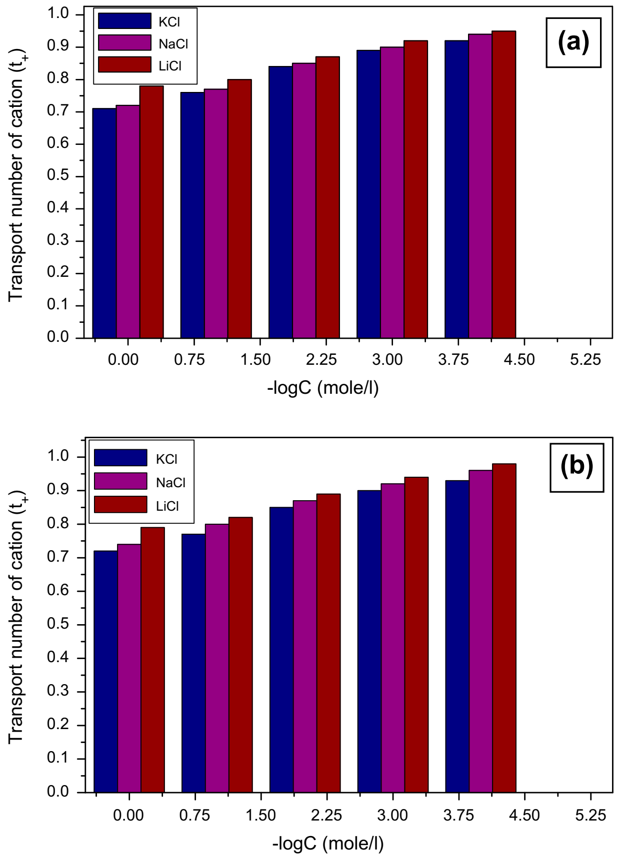

Fig. 8. The plot of transport number of cation vs. concentrations of various electrolytes of polystyrene based PTP composite membrane (a) and PVC based PTP composite membrane (b).

4. Conclusion

The polystyrene- and PVC-based PTP composite membranes were successfully fabricated by using die casting method. Finally, it may be concluded that the electrochemical studies and characterization details of the composite membranes shows good properties in terms of stability, thickness, water uptake, porosity, membrane potential and charge density. The decrease in electrolyte concentration tends to exhibit larger membrane potential and follows reverse order in charge densities. On the basis of comparative study between PS- and PVC-based PTP composite membranes, it is clear that the PS-based PTP composite membrane is superior than the PVC-based PTP composite membrane.

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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 (mole/l)
$\overline{C}_{2+}$	—	cation concentration in membrane phase 2 (mole/l)
C_i	—	i^{th} ion concentration of external solution (mole/l)
$\overline{C}_i$	—	i^{th} ion concentration in membrane phase (mole/l)
$\overline{D}$	—	charge density in membrane (eq/l)
F	—	faraday constant (C/mole)
q	—	charge effectiveness of the membrane
R	—	gas constant (J/K/mole)
t_+	—	transport number of cation
t_-	—	transport number of anion
$\overline{u}$	—	mobility of cations in the membrane phase ($m^2 v^{-1} s^{-1}$)
$\overline{v}$	—	mobility of anions in the membrane phase ($m^2 v^{-1} s^{-1}$)
V_k	—	valency of cation
V_x	—	valency of fixed-charge group
$\overline{U}$	—	$\overline{U} = (\overline{u} - \overline{v})/(\overline{u} + \overline{v})$

Greek symbols

$\gamma_\pm$	—	mean ionic activity coefficients
$\overline{\omega}$	—	mobility ratio
$\Delta\Psi_m$	—	observed membrane potential (mV)
$\Delta\overline{\Psi}_m$	—	theoretical membrane potential (mV)
$\Delta\Psi_{Don}$	—	donnan potential (mV)
$\Delta\Psi_{diff}$	—	diffusion potential (mV)

Abbreviations

IEC	—	ion-exchange capacity
PVC	—	polyvinyl chloride
PTP	—	pyridine Th(IV) phosphate
PS	—	polystyrene
SCE	—	saturated calomel electrode
SEM	—	scanning electron microscopy
TMS	—	teorell, Meyer and Sievers

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