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Membrane Applications of Polyaniline based Nano-composite Ion-exchanger and its Electrochemical Properties for Desalination

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Abstract

A novel polyaniline based composite ion-exchange membrane of Sn(IV) silicophosphate (TSP) was synthesized by inorganic TSP nanoparticles and the organic polymer matrix by sol-gel method. Physical and electrochemical properties of the composite membrane were investigated in order to evaluate their key parameters as electromembrane candidates in their application in electrodialysis water purification. The results revealed that incorporation of TSP enhanced the properties of the ion-exchange membranes with influence of their thermal and mechanical properties. Membranes were found to have the optimal properties, with good water uptake, ion-exchange capacity (IEC = 1.40 meqg^{-1}), transport properties and excellent permselectivity. Membrane potential measurements have been carried out in different electrolytes such as KCl (aq), NaCl (aq) and LiCl (aq) at different concentrations to figure out the correlation between effective fixed charge density and transport properties of the membrane. The study reveals that the inorganic-organic nanocomposite membrane shows higher cation-selectivity towards K$^+$ ion. The effective fixed charge densities were found to follow the order K$^+$ > Na$^+$> Li$^+$. This newly-developed membrane can be considered as excellent candidates suitable for water desalination by Electrodialysis.

Keywords: Synthesis; Characterization; Nanocomposite; Thermal and chemical stability; Transport properties

Introduction

The ion-exchange composite membranes find applications in various processes such as electro-dialysis, desalination, diffusion, electro-deionization, membrane electrolysis, electrochemical synthesis, fuel cells, and storage batteries also. Therefore, they are useful in pollution control, energy saving, power generation, resource recovery, etc. [1]. Polyaniline (PANI) is a technologically important material due to its unique electrical, electrochemical, and optical properties which enable its use in energy storage systems [2-5], electrochromic devices [6], electronics [7], electrochemical actuators [8], sensors [9,10] and separation science [11,12]. In the latter case, PANI was used as free-standing membranes, supported films, and surface layers for applications ranging from gas separation and pervaporation to electrodialysis [13]. PANI separation properties can be tailored by the nature of the dopant as well as by the doping level of the polymer [13] PANI, separation is possible based on the size of the molecules, molecules larger than 4.5 Å being prevented from permeating. The major breakthrough in the preparation of thin film composite (TFC) membrane via interfacial polymerization technique has resulted in tremendous achievements in producing a membrane with a right combination of flux and salt rejection, and generating huge interest in industrial sectors. Over the past decade, there have been intensive and continuous efforts in the development of TFC membrane, both from the industry and academia with the interests to further improve the membrane productivity and selectivity as well as its tolerance against metal ions, solvent, fouling etc. The transport properties when the composite is used as a membrane have also been explored by measuring its electric potential when it is in contact with different electrolyte solutions of KCl, NaCl and LiCl. The effective fixed charge density has been calculated by means of different approaches as proposed by various research groups [14-18]. The experimental values of potential have also been used to calculate the mobility ratio, transport numbers of counter-ions and permselectivity of the polystyrene blended hybrid membrane. On basis of a brief introduction of the development history of composite membranes, this paper reviews the recent research progress of the composite membrane science and technology, particularly in the fields of water-related separation processes. Reviewing the research progress is imperative and necessary in order to provide an insight for the future development and perhaps open a door to extend the applications to other more challenging areas.

Experimental

Preparation of hybrid membranes

The composite mixture was powdered and sieved through 200 mesh (Granule size < 0.07 mm). To improve the stability of the membrane, polystyrene have been used as a binder as its cross-linked rigid framework provides adequate adhesion to the molecules of composite which accounts for the higher mechanical stability to the membrane over other binders like poly(vinyl chloride), cellulose acetate, etc. Pure crystalline polystyrene was also ground to fine powder and sieved through 200 mesh. The powdered composite were then mixed with granulated polystyrene with the help of a pestle and mortar to crush and get ion-exchange membranes [19] having a varying percentage (by mass) of polystyrene (15-35%). The membranes having 25% polystyrene were only selected for electrochemical studies because it showed excellent results.

Apparatus

As reported in previous paper [18] additionally digital potential was used to measure the membrane potential.

Measurement of potential

The freshly prepared inorganic-organic nanocomposite membrane was cemented in a Pyrex glass tube cell having two compartments in which a saturated calomel electrode was placed for measuring the membrane potential; the schematic diagram of the constructed electrochemical cell of the above type is shown in Figure 1. The monovalent electrolytes of concentrations c1 and c2 in both the compartments of the cell, where the ratio $\gamma(=c_2/c_1)$ is fixed at 10, were vigorously stirred by a magnetic stirrer to minimize the effects of boundary layers on the membrane potential (mV ± 0.5). The experiment was conducted at room temperature and atmospheric pressure.
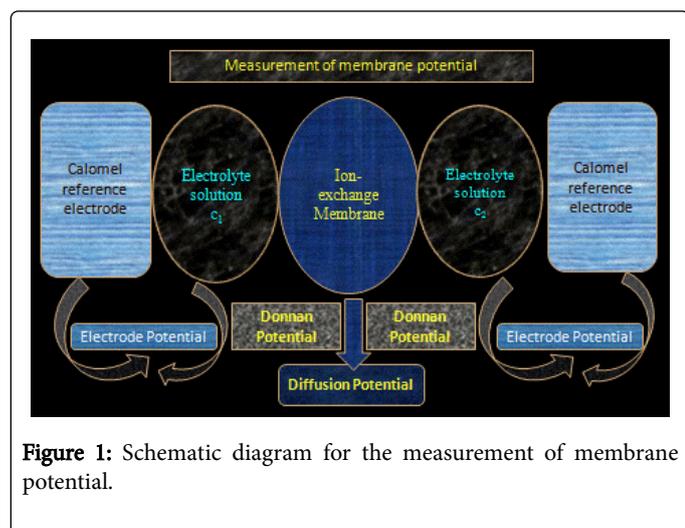
Figure 1: Schematic diagram for the measurement of membrane potential.

Results and Discussion

Physicochemical properties

As reported in previous paper that the ion uptake capacity of the synthesized material increased with increasing the mixing volume ratio of ionogenic groups Sn(IV)silicophosphate ionogenic groups are the groups to which counter ions are attached [18]. To establish the relationship between the ion exchange capacity and size of metal ions, some alkali and alkaline earth metal ions were selected.

Metal ions	Ionic radii (A°)	Hydrated ionic radii(A°)	IEC/g of exchanger exchanger(meq g^{-1})
Li$^+$	0.68	3.4	0.75
Na$^+$	0.97	2.76	1.32
K$^+$	1.33	2.32	1.44
Mg^{2+}	0.78	7	0.82
Ca^{2+}	1.43	5.9	0.92
Sr^{2+}	1.27	6.3	1.98
Ba^{2+}	1.43	5.9	2.33

Table 1: Ion-exchange capacity of various exchanging ions on Polyaniline Sn (IV) silicophosphate cation-exchanger

The results are shown in Table 1 in terms of ion exchange capacity indicate that the ion uptake of monovalent and divalent ions is sequentially increased with shrinking the hydrated ionic radii, ensuring enhanced adsorption [20,21].
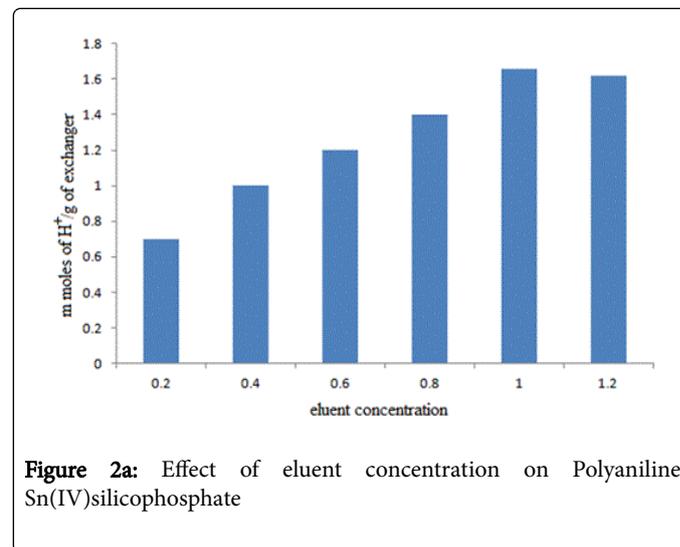
Figure 2a: Effect of eluent concentration on Polyaniline Sn(IV)silicophosphate

To determine the most favourable concentration and minimum volume of eluent (NaNO$_3$) needed for the complete elution of counter ion (H$^+$ ions) from the composite material. The effect of effluent concentration and elution behavior are shown in Figure 2a. It was found that the only 120 mL solution of NaNO$_3$ (1.0 M) was required for the complete removal of H$^+$ ions from the column containing 1.0 g exchanger depicting good efficiency of the column. The pH titration curves of composite material and their mixture indicates one inflection point which signifies its monofunctional behavior (Figures 2b and 2c).
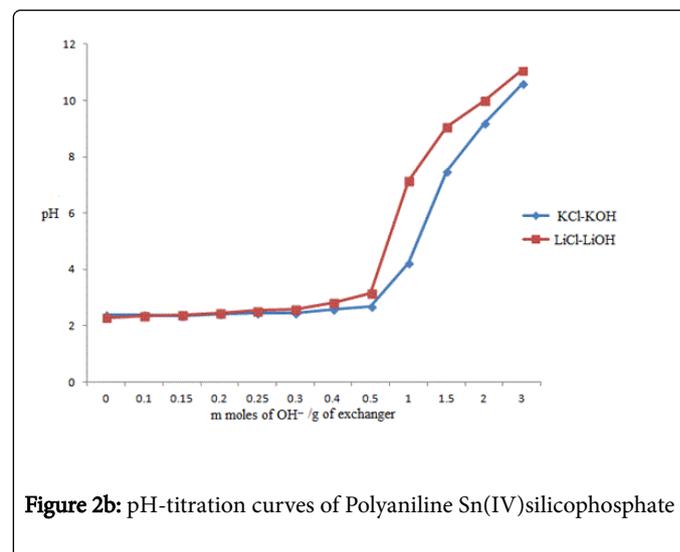
Figure 2b: pH-titration curves of Polyaniline Sn(IV)silicophosphate
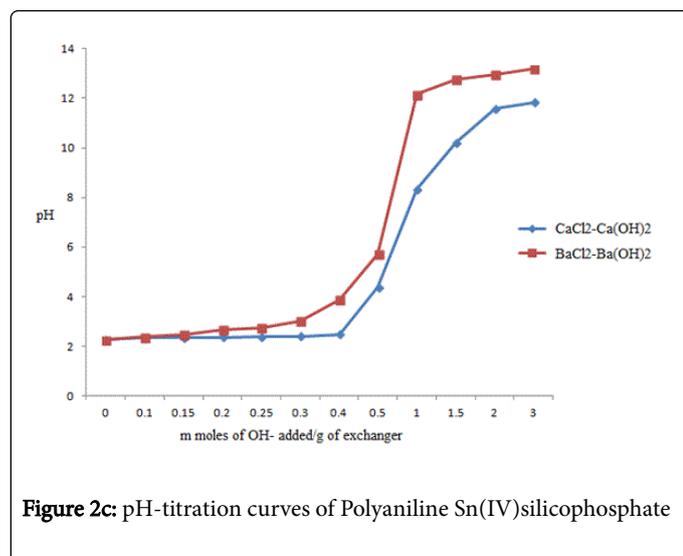
Figure 2c: pH-titration curves of Polyaniline Sn(IV)silicophosphate

The strong cation exchange ability of the exchanger is apparent (pH values below 3.0) in the absence of OH^- ions. The pH of the solutions of metal chlorides is increased sharply with the addition of the base and above pH 10, the exchanger begins to hydrolyze. It is also inferred from pH titrations curves (Figure 2b) with decreasing hydrated ionic radii, the ion uptake capacity simultaneously increases (uptake of K^+ ion is greater than that of Li^+ ion and which is again repeated in Figure 2c, Ca^{2+} ion uptake is greater than that of Ba^{2+} ion) which confirm the results of the ion exchange capacity of alkali metal ions (Table 1).

FTIR and TGA studies

As reported in the paper "Synthesis, Characterization, and Biological Applications of Nano composites for the Removal of Heavy Metals and Dyes" by Khan et al. [18].

Morphological characterizations

X-ray and SEM image confirm the semi-crystalline morphology. TEM analysis shows aggregation of nanoparticles (in the range of 30-50 nm) of polyaniline Sn(IV)silicophosphate cation exchange material [18].

In order to examine the sorption studies of polyaniline Sn(IV)silicophosphate columns, were performed in DMW and DMSO systems. The distribution coefficients values (K_d values) indicate that the material was found to be selective for heavy metal pollutants Pb(II), Hg(II) and Co(II). Some quantitative binary separations of metal ions were achieved on columns packed with this composite material. The separations are quite sharp and recovery was quantitative and reproducible [18].

For the electrochemical and transport properties of the composite membrane, membrane potential values have been measured. When electrolyte solutions (KCl, NaCl and LiCl) of different concentrations ranging between 1 and 0.007 mol/dm3 are separated by a membrane, an electrical potential difference develops across the membrane due to the diffusion of oppositely charged ions through it with different mobilities. This charge imparts some important electrochemical properties to the membrane, the most important being the differences in the permeabilities of co-ions, counter ions and neutral molecules. The quantity of charge required to generate the potential is small,

especially when dilute solutions are used. The magnitude of the membrane potential is dependent on many factors such as applied pressure at the membrane preparation stage, concentration of electrolyte solutions used, the counter-ion to co-ion mobility ratio, the exchange characteristics of the membrane material for various cations. It was observed that the hybrid membrane prepared at higher applied pressure exhibited higher membrane potential for a fixed c2/c1. The membrane potential, ψ_m data obtained with the composite membrane using different electrolytes are plotted as against electrolyte concentration, C, where C = (c1+c2)/2 (Figure 3). The values of membrane potentials observed across membrane in contact with various monovalent electrolytes show the potential order to be K+ > Na+> Li+.
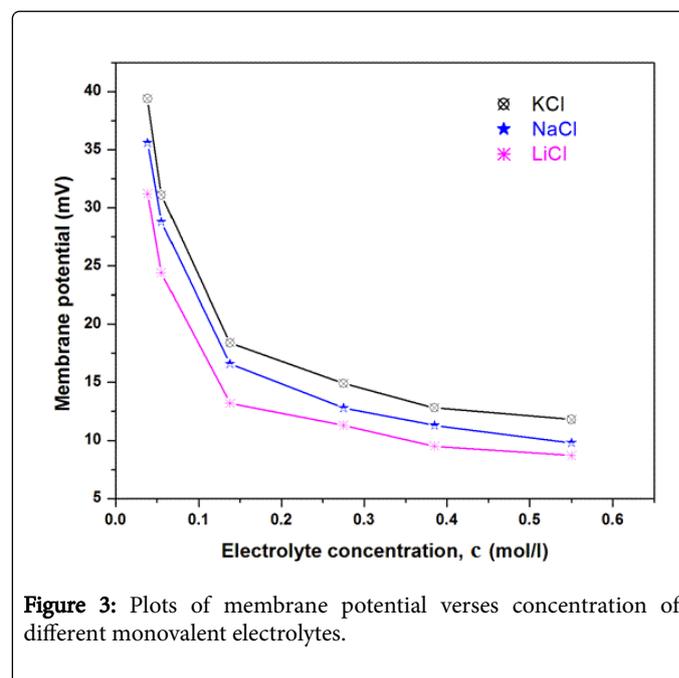
Figure 3: Plots of membrane potential verses concentration of different monovalent electrolytes.

It was observed, during the experiment, that the membrane potential increased with time up to a maximum value and then decreased gradually. Such variation was also reported by other workers [22]. The time taken for the attainment of maximum potential is found to be concentration dependent, more time being required for concentrated solution, and it differs with different electrolytes. Membrane potential has been regarded as a measure of membrane selectivity for a long time. The measurement of ion activity by means of a membrane electrode is most successful in the concentration range over which the membrane behaves as ideally permselective and obeys the Nernst equation. An ideally permselective membrane is one in which the permeability for co-ions is negligible as compared to that for counter-ions.

The deviation from Nernstian behaviour is due to the co-ion transference [23] and the dependence of the exchange of cations between the solution and the membrane phase and on the electrolyte concentration. The values in Figure 3 show that the potential values increase with decrease in concentration of all the tested electrolyte solutions and are of the order of positive mV indicating that the membrane is negatively charged i.e. cation selective. The selectivity increases with decrease in the concentration because of the structural changes occurring in the electrical double layer at the membrane-

solution interface. The increase in selectivity with dilution is also supported by the increasing values of the counter-ion transport numbers, t_+ (Table 2).

Electrolyte	c^2 (mol/dm³)	t_+	$\overline{\omega}$
KCl	1	0.59	1.42
	0.7	0.61	1.55
	0.5	0.63	1.67
	0.25	0.66	1.95
	0.1	0.78	3.59
	0.07	0.83	4.74
NaCl	1	0.58	1.40
	0.7	0.60	1.47
	0.5	0.61	1.55
	0.25	0.65	1.87
	0.1	0.74	2.90
	0.07	0.79	3.84
LiCl	1	0.57	1.35
	0.7	0.58	1.38
	0.5	0.60	1.47
	0.25	0.61	1.55
	0.1	0.71	2.48
	0.07	0.76	3.18

Table 2: The values of transport number t_+ and mobility ratio $\overline{\omega}$ of the nanocomposite membrane calculated from the measured membrane potential values for different electrolytes at different concentrations with c2/c1 = 10 at an applied pressure 146 MPa at 25 ± 1°C.

When an ionic gradient is maintained by using two solutions of different concentrations of same electrolyte on both sides of the membrane, the mobile species infiltrate the membrane at different magnitudes inducing various transport phenomena into the system, including the development of potential across it. The influence is greater in case of counter-ions than in the co-ions. The ratio of the molar mobilities of the cation and anion 'u_+/u_-' is defined as the mobility ratio ($\overline{\omega}$) of the membrane. The values of the mobility ratio calculated for the composite membrane are also incorporated in Table 2. The values of $\overline{\omega}$ in the membrane phase were found to be increasing with decrease in concentration for all the monovalent electrolytes used (KCl, NaCl and LiCl). The high mobility is attributed to higher transport number of comparatively free cations as compared to the anion of electrolytes.When a negatively charged membrane is imposed between two solutions of a monovalent electrolyte of unequal concentrations c1 and c2 (c2>c1), the observed membrane potential, ψ_m is related to electrolyte concentration by the following equation [14,15]:

$$-\psi_m = \frac{RT}{F}\left(\frac{\gamma}{\gamma-1}\right)\left(\frac{\varphi X}{2}\right)\frac{1}{c_1} \qquad (1)$$

Here, φX is the effective fixed charge density of the negatively charged membrane. Equation (1) indicates that the plot of ψ_m against 1/c1 will be linear (Figure 4a) with a slope equal to $\frac{RT}{F}\left(\frac{\gamma}{\gamma-1}\right)\left(\frac{\varphi X}{2}\right)$ from which the values of φX for different electrolytes have been evaluated (Table 2).
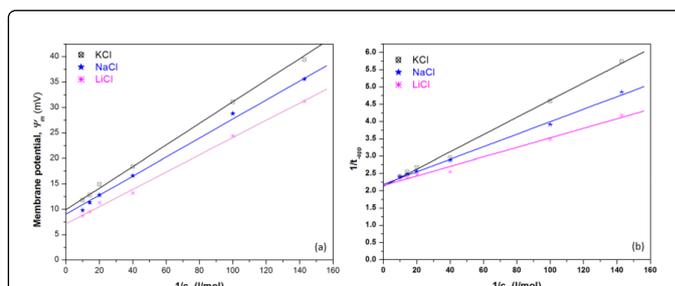
Figure 4: Plots of (A) potential values, ψ_m and (B) $\frac{1}{t_{-app}}$ against $\frac{1}{c_1}$ of polystyrene based composite membrane for different monovalent electrolytes.

Another widely accepted approach to calculate the fixed charge density was derived in literature [16] who suggested that when two solutions of an electrolyte of different concentrations c1 and c2 separated a membrane, the inverse of the apparent transport number of the anion, t_{-app} in a high salt concentration range could be expressed by the following equation:

$$\frac{1}{t_{-app}} = \frac{1}{1-\alpha} + \frac{\alpha(\gamma-1)}{(1-\alpha)\gamma\ln\gamma}\left(\frac{\theta\overline{X}_c}{c_1}\right) \qquad (2)$$

Here, α is the ratio of molar mobility of cation to the sum of molar mobilities of cation and anion, $\theta\overline{X}_c$ is the effective fixed charge density of the membranes under investigation and c1 (in mol/dm3) the concentration of the monovalent electrolyte in the lower concentration side of the cell. The apparent transport number of the anion t_{-app} is defined by the Nernst equation:

$$\psi_m = (RT/F)(1-2t_{-app})\ln\frac{c_2}{c_1} \qquad (3)$$

Equation (2) indicates that the values of α and $\theta\overline{X}_c$ can be evaluated by using the values of intercept $\left(\frac{1}{1-\alpha}\right)$ and slope $\left(\frac{\alpha(\gamma-1)}{(1-\alpha)\gamma\ln\gamma}\theta\overline{X}_c\right)$ from the linear plot of $1/t_{-app}$ against $1/c_1$ (Figure 4b). The calculated values of the fixed charge densities $\theta\overline{X}_c$ of the polystyrene blended calcium tungstate composite membrane are also given in Table 3. The fixed charge density of the hybrid membrane under different electrolytic environments is found to be in the order KCl > NaCl > LiCl.

Electrolyte	KCl	NaCl	LiCl
φX	0.0144	0.0126	0.0108
$\theta\overline{X}_c$	0.0543	0.0388	0.0288

Table 3: Values of the effective fixed charge densities, calculated from different approaches, of the nanocomposite membrane in contact with different electrolytes.

The data in Table 3 show that the fixed charge density is highest for KCl and lowest in case of LiCl for the same electrolytic concentration, indicating that the composite membrane shows higher cation selectivity towards K+ ions. The same result has also been explained in terms of counter-ion transport numbers.

Conclusions

The newly developed composite material shows selective behavior towards K+ ions and some of heavy metal ions. It can successfully be used for the quantitative separation of metal ions from synthetic mixture and real samples. The transport properties of the composite membrane have been studied and found that the membrane potential and the fixed charge density values are in the order KCl > NaCl > LiCl and the membrane is found to show higher selectivity towards K+ ions. This newly-synthesized membrane can be considered as excellent candidates suitable for water desalination by Electrodialysis.

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