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A comparative study of theoretical, electrochemical and ionic transport through PVC based $Cu_3(PO_4)_2$ and polystyrene supported $Ni_3(PO_4)_2$ composite ion exchange porous membranes

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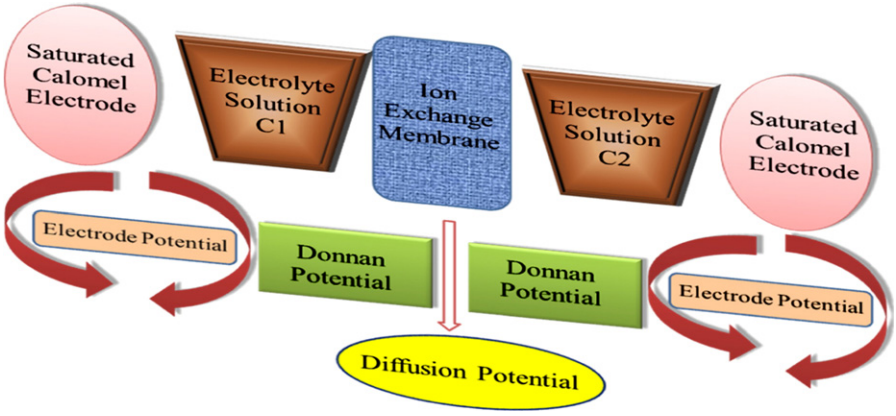
HIGHLIGHTS

- A comparative study of the ion exchange composite membrane
- The membrane was found to be quite stable.
- Good practical applications
- The electrochemical studies give up applicability of the membranes.

GRAPHICAL ABSTRACT



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ABSTRACT

The organic–inorganic composite ion exchange membranes, i.e. PVC based $Cu_3(PO4)_2$ and polystyrene supported $Ni_3(PO4)_2$ were chemically prepared by sol–gel method. The physico-chemical nature was determined by using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) characterization. Both the membranes were found to be crystalline in nature and no sign of visible cracks is there. The theoretical value of the potential was determined by Teorell–Meyer–Sievers method, electrochemical properties were measured by potentiometer. The observed potential for both the membranes was little different and positive, the potential offered by the electrolytes was in the order of KCl > NaCl > LiCl. The transport number, mobility ratio, distribution coefficient, charge effectiveness, and the fixed charge density of the ions were calculated by potential observation. The order of surface charge density of both the membranes was found to be LiCl < NaCl < KCl.

1. Introduction

Nowadays, ion-exchange membranes and its related process have received much attention in both theoretical and industrial applications. Ion exchange membrane-based processes are still lacking except for some

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Nomenclature

AR	Analytical reagent
C1, C2	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	ith ion concentration of external solution (mol/l)
$\overline{C}_i$	ith ion concentration in membrane phase (mol/l)
$\overline{D}$	Charge density in membrane (eq/l)
F	Faraday constant (C/mol)
100 MPa	Pressure (MPa)
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
$\overline{u}$	Mobility of cations in the membrane phase (m^2/v/s)
$\overline{v}$	Mobility of anions in the membrane phase (m^2/v/s)
V_k	Valency of cation
V_x	Valency of fixed-charge group
$\overline{U}$	$\overline{U} = (\overline{u}-\overline{v})/(\overline{u}+\overline{v})$
CP	Copper phosphate
PVC	Polyvinyl chloride
NP	Nickel phosphate

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

reviews on specific aspects, such as modifications of ion exchange membranes [1–3].

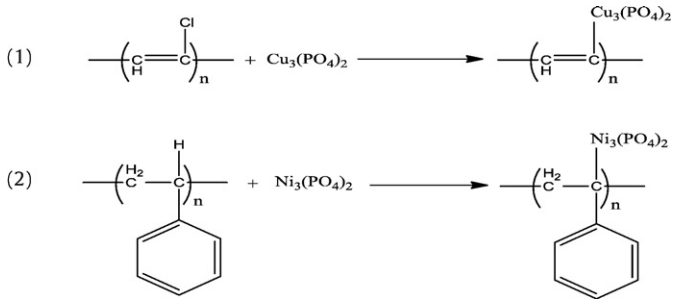
The inorganic and organic membranes have lower thermal and chemical resistance as well as a shorter lifetime and are expensive as compared to the inorganic–organic composite membranes [4–6].

The polymers are considered the main materials in preparation of composite membranes due to the advantages of its good membrane-forming ability, flexibility and low cost. Thus, organic–inorganic composite materials have attracted more and more interest. The composite membranes have the basic properties of organic and inorganic materials and put forward specific advantages for the preparation of synthetic membranes with good thermal and chemical resistance, outstanding separation performances, and adaptability to harsh environments [7–10].

The electrochemical studies look up the performance of the PVC based $Cu_3(PO4)_2$ and polystyrene supported $Ni_3(PO4)_2$ composite ion exchange membranes and hence have lot of industrial applications. The outstanding properties of these composite membranes as compare to those of the previously reported composite membranes offer important applications in chemical industry, biotechnology products and waste water treatment [11–13].

The surface charge density is the main parameter that controls the membrane phenomenon and this was calculated using the membrane potential values for different electrolytes by using Teorell, Meyer, and Sievers (TMS) method. Some other parameters including distribution coefficient, transport numbers, mobility ratio, charge effectiveness etc. were also calculated for PVC and polystyrene based composite membranes. The observed membrane potential studies are commonly used in the electrochemical study of these composite membranes [14–19].

The structural representation of composite membranes was shown as:



2. Experimental

2.1. Materials and chemicals used

Pure crystalline polystyrene (Otto Kemi, Mumbai, India) and polyvinyl chloride (Otto Kemi, India, AR grade) grounded and sieved through 200 meshes were used as a binder, 0.2 M tri-sodium phosphate solution (E. Merck, India with purity of 99.90%), 0.2 M copper chloride ($CuCl_2$) solution, 0.2 M nickel chloride ($NiCl_2$) solution from Otto Kemi, India and various electrolyte solutions (KCl, NaCl and LiCl) were procured from (E. Merck Limited, India); of different concentrations were also arranged. All the used reagents were of analytical grade and pure deionized water was used for the preparation of solutions of the above compounds.

2.2. Instruments

Scanning electron microscopy (SEM) was used for surface morphology and Fourier transform infrared spectroscopy (FTIR) was used to obtain an infrared spectrum of absorption, emission and photoconductivity. The X-ray diffraction (XRD) reveals the information about the chemical composition and crystallographic structure whereas thermo-gravimetric analysis and differential thermal analysis (TGA/DTA) measure the mass change or degradation characteristics of material as a function of temperature and time and lastly potentiometer was used for measuring the ionic potentials.

2.3. Synthesis of $Cu_3(PO_4)_2$ and $Ni_3(PO_4)_2$ materials

Copper phosphate and nickel phosphate (CP and NP) were prepared by sol–gel or co-precipitation method by mixing 0.2 M aqueous solution of tri-sodium phosphate with 0.2 M copper chloride and nickel chloride solution separately, resulting to a constant stirring of both the solutions for 1–2 h, and also the pH of the solution must be maintained. The resulting precipitate was well washed almost 4–5 times with deionized water to remove free electrolytes and dry the materials up to 3–5 h at 100 °C. The precipitate must be powdered with the help of pestle and mortar until the size of both materials should be less than 200 meshes. Pure crystalline polystyrene and PVC were also grounded and sieved through 200 meshes.

2.4. Preparation of PVC based CP and polystyrene based NP composite membranes

The synthesized precipitates that are CP and NP were mixed with PVC and polystyrene granules (less than 200 meshes) respectively with the help of pestle and mortar and mixing of the materials should be done very carefully and uniformly. After both the mixtures were