Mixed matrix membranes of poly(vinyl alcohol) loaded with phosphomolybdic heteropolyacid for the pervaporation separation of water–isopropanol mixtures[☆]

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Abstract

Mixed matrix membranes of poly(vinyl alcohol) (PVA), loaded with phosphomolybdic heteropolyacid (HPA) and crosslinked with glutaraldehyde have been prepared by the solution casting technique. Pervaporation (PV) experiments have been performed at 30 °C to separate water–isopropanol feed mixtures containing 10–40 wt.% of water. The membranes were characterized by differential scanning calorimetry (DSC) and dynamic mechanical thermal analyzer (DMTA) to understand their thermal behavior and mechanical strength properties. At high content (i.e. 7 wt.% with respect to weight of PVA) of HPA, the mixed matrix membranes could extract water efficiently on the permeate side with a selectivity of 90,000 and a flux of 0.032 kg/m^2 h for 10 wt.% of water containing feed mixture (the lowest feed composition of water studied). Flux of the mixed matrix membranes decreased with increasing concentrations of HPA; however, a significant improvement in PV performance was observed for HPA-loaded membranes than the pristine PVA. DSC and DMTA analyses indicated a decrease in melting temperature and an increase in glass transition temperature, respectively.
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1. Introduction

Liquid separation using polymer membranes has been an active area of research over many decades in view of its importance in process engineering as a clean technology. Innumerable types of polymers and their modifications have been attempted to develop membranes for such applications, but the recent trend has shifted towards the preparation of mixed matrix membranes involving filler and a polymer matrix. Inorganic compounds, when combined at the molecular level, with organic polymers could offer better advantages such as lightweight, flexibility, good moldability, high strength, thermal and chemical stability compared to the neat dense membranes [1]. In this regard, a variety of fillers have been used to prepare the membranes that exhibit improved performances over those of the virgin polymer membranes [2–6].

Heteropolyacids (HPAs) are the widely used inorganic materials that contain ring transition metal oxygen anion clusters, which exhibit a wide range of well-defined molecular structures, surface charge densities, chemical and electronic properties [7] in addition to their inherent catalytic properties [8–10]. Among these, Keggin-type HPAs have been widely investigated as the catalytic materials [11]. The acid and redox catalytic properties of HPAs have been modified by replacing protons with metal cations and/or by changing the heteroatom or the framework polyatoms [12,13]. HPAs show an unmatched perspective in terms of synthesis, analysis, biological, medicinal and materials science applications [14–24]. Recently, Gong et al. [25] prepared the HPA-incorporated PVA hybrid membranes to study

their photochromic and thermal properties. A search of the literature indicated no previous studies on PVA membranes that are loaded with HPA particles to be used in pervaporation (PV) separation of water–isopropanol mixtures.

In PV separation, PVA membranes have been widely used, particularly for dehydrating alcohols. The commercial success of composite membranes of PVA with poly(acrylonitrile), popularly called as GFT membranes, have been commercialized by Germans. Many papers have dealt with different types of blends or grafts of PVA to enhance their separation characteristics [26–29]. However, the zeolite-filled PVA mixed matrix membranes are the recent trends in the PV separation of aqueous-organic mixtures [30]. Hitherto, no reports are available on the HPA-loaded PVA mixed matrix membranes for the PV separation of water–isopropanol feed mixtures. The present investigation is a continuation of our ongoing studies on the development of novel mixed matrix membranes wherein the HPA-loaded PVA mixed matrix membranes have been developed to achieve the optimum PV performance in terms of flux and selectivity over that of pristine PVA membrane. The results of this study exhibited better membrane performances than pristine PVA membrane in dehydrating isopropanol.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (MW: 125,000) with a degree of hydrolysis of 87%, isopropanol, glutaraldehyde (GA) and hydrochloric acid were all purchased from s.d. fine chemicals, Mumbai, India. Phosphomolybdic acid, $H_3[P(Mo_3O_{10})_4] \cdot 2H_2O$, was purchased from Thomas Baker Chemicals, Mumbai, India. All other chemicals were of analytical reagent grade samples used without further purification. Deionized water, having a conductivity of $20\,\mu S/cm$, was produced in the laboratory itself using the Permionics pilot plant (Vadodara, India).

2.2. Preparation of phosphomolybdic acid-incorporated PVA membranes

Phosphomolybdic acid-incorporated PVA mixed matrix membranes were prepared by the solution casting technique. PVA (4 g) was dissolved in 90 mL of deionized water at 60 °C and the solution was filtered through a glass fiber filter to remove insoluble impurities. A known amount of phosphomolybdic acid (1, 2, 3, 4, 5, 6 and 7 wt.%) dissolved in 10 mL of water was added to the prepared solution and was continuously stirred for 8 h at the ambient temperature. In situ crosslinking was done by adding 0.3 mL of glutaraldehyde and 0.3 mL of conc. hydrochloric acid to the above solution and further stirred for about 15 min. The resulting solution was cast on a clean glass plate in a dust free environment to prepare the membrane. Membranes were dried at ambient temperature and peeled off from the glass plate. Membrane thickness as measured by the micrometer screw gauge was around $50 \pm 1.0\,\mu m$. Seven different mixed matrix membranes were prepared by incorporating 1, 2, 3, 4, 5, 6 and 7 wt.% phosphomolybdic acid with respect to weight of PVA;

these are designated as: PVA/HPA-1, PVA/HPA-2, PVA/HPA-3, PVA/HPA-4, PVA/HPA-5, PVA/HPA-6 and PVA/HPA-7, respectively.

2.3. Characterization of membranes

2.3.1. Scanning electron microscopy (SEM)

Cross-sectional SEM micrograph of the mixed matrix membrane was obtained under a high resolution (magnification $300\times$, 5 kV) using JOEL MODEL JSM 840A, scanning electron microscope, equipped with Phoenix energy dispersive analysis of X-rays. Since the films were nonconductive, gold coating (15 nm thickness) was done. SEM micrographs were taken at Indian Institute of Chemical Technology (IICT), Hyderabad, India.

2.3.2. Differential scanning calorimetry (DSC)

DSC thermograms of the mixed matrix membranes were recorded on a Rheometric Scientific (Model DSC-SP, London, UK) equipment. Thermograms were recorded over the temperature range of 25–400 °C at the heating rate of 10 °C/min in a nitrogen atmosphere.

2.3.3. Dynamic mechanical thermal analysis (DMTA)

Tan δ curves of the uncrosslinked and crosslinked PVA and HPA-loaded mixed matrix membranes of PVA were recorded on a Rheometric Scientific DMTA IV instrument from 30 to 200 °C at the heating rate of 5 °C/min.

2.3.4. Degree of swelling

Swelling experiments were performed gravimetrically at 30 °C [31] on all the membranes taken in 10, 20, 30 and 40 wt.% water containing feed mixtures. Initial mass of the circularly cut (dia = 3 cm) PVA and HPA-incorporated PVA mixed matrix membranes were taken by placing them on a single-pan digital microbalance (model AE 240, Mettler, Switzerland) sensitive to ± 0.01 mg. Samples were then placed inside the specially designed airtight test bottles containing $30\,cm^3$ of the test solvent. Test bottles were transferred to a hot-air oven maintained at the constant desired temperature. Dry membranes were equilibrated by soaking in different compositions of the feed mixture in a sealed vessel at 30 °C for 48 h. The swollen membranes were weighed immediately after carefully blotting on a digital single pan microbalance. The % degree of swelling, DS was then calculated as:

$$\% \, DS = \left(\frac{W_\infty - W_0}{W_0} \right) \times 100 \qquad (1)$$

where W_∞ and W_0 are weights of the swollen and dry membranes, respectively.

2.3.5. Pervaporation experiments

Pervaporation experiments were performed in an apparatus designed indigenously [32,33], which consists of a stirred stainless steel cell tank in which feedstock is kept. Effective surface area of the membrane in the cell is $28.27\,cm^2$ with a diameter of 6.0 cm; volume capacity of the cell is about $250\,cm^3$. Temperature of the feedstock is kept constant using a thermostatic water