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Dehydration of isopropanol by PVA–APTEOS/TEOS nanocomposite membranes

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ABSTRACT

In the present work, dehydration of isopropanol was investigated by novel organic–inorganic nanocomposite membranes which were prepared through sol–gel reaction of polyvinyl alcohol (PVA) with γ-aminopropyl-triethoxysilane (APTEOS) and tetraethoxysilane (TEOS). The PVA chains were crosslinked by mixing silane coupling agents. This reaction between polymer chains and silanols agents could control degree of swelling of the nanocomposite membranes in aqueous isopropanol (IPA) solutions. The membranes were characterized by SEM and ATIR. Effects of APTEOS content in the membranes, feed concentration and temperature on pervaporation (PV) performance were investigated. It was found out that separation factor and permeation flux increase with increasing APTEOS content in the membranes. Arrhenius-type relationship was used for describing the temperature dependence of permeation flux. It was also found out that separation factor decreases with increasing temperature.

Keywords: Nanocomposite membranes; Polyvinyl alcohol; Silica nanoparticles; Isopropanol; Pervaporation

1. Introduction

Membrane technology is a novel and promising separation method which has been widely used in industrial processes due to its easy and effective operation and high-energy savings (Zhang et al., 2007a,b; Feng and Huang, 1997; Vane, 2005). Pervaporation (PV) is one of the membrane processes which has been most actively researched for its applications in separation and purification of liquid mixtures, particularly for dehydration of organic compounds or separation of azeotropic or close-boiling point mixtures (Zhang et al., 2007a,b).

Aqueous isopropanol (IPA) is widely used as a cleaning agent in modern chemical, semiconductor, pharmaceutical and electronic industries, where recycling of wasted IPA is essential from an environmental and economical point of view. It forms an azeotrope with water in a mixture of 87.8% IPA, and this causes difficulties in its recovery by conventional distillation (Devi et al., 2005; Liu et al., 2005; Lee et al., 1999). Azeotropic distillation is an energy-consuming process and the use of third component such as entrainer like benzene which has been traditionally used for purification of IPA, can cause unwanted impurities in the final products as well as the side streams. Moreover, with liquid feed streams, the total area coverage on the feed side is quite close to saturation, so that sorptive transport takes place through the membranes (Bhat et al., 2006). Therefore, PV can be considered as a better alternative for simple distillation (Naidu et al., 2005). PV separation of water–IPA mixtures has received widespread attention and considerable literature on successful dehydration of IPA by PV is available (Sairam et al., 2006a,b; Adoor et al., 2006a,b).

Nowadays, some modifications have been attempted to enhance performance of the membranes in such applications and recent trend has shifted towards preparation of mixed matrix membranes involving fillers and polymer matrixes. Combination of inorganics with organic polymers at nano levels can offer advantages such as lightweight, flexibility, good moldability, high strength and thermal and chemical stability (Teli et al., 2007; Nakane et al., 1999; Cong et al., 2007). In this regard, a variety of fillers have been used to prepare the membranes that exhibit improved performances over those of virgin polymeric membranes (Teli et al., 2007; Nakane et al., 1999; Cong et al., 2007). Some studies have revealed that introducing inorganics extracted from Si-containing precursors into organic polymers can form

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homogeneous nanocomposite membranes with enhanced physicochemical stability and separation performance (Guo et al., 2006, 2007; Kariduraganavar et al., 2004). However, there are some researches performed on other fillers in the polymer matrix in the nanocomposite membranes.

Polyvinyl alcohol (PVA) is a glassy, semi-crystalline polymer, and is used in many areas of science and technology, including membrane separation and it is one of the most important materials for dehydration of organic mixtures owing to its good chemical stability, film-forming ability and high hydrophilicity (Lue et al., 2008; Chen et al., 2008). Unfortunately, the hydrophilic nature of PVA in aqueous organic systems leads to instability of its chemical and mechanical properties, limiting its applications (Lue et al., 2008) and this results in increasing both solubility and diffusivity of organic components and this consequently lowers its water permselectivity.

To improve membrane stability and permeation properties, some modifications have been attempted, such as crosslinking, filling, blending and surface modification (Chen et al., 2008; Alghezawi et al., 2005). In this study, PVA–APTEOS/TEOS (PAT) nanocomposite membranes were prepared by sol–gel process and by co-incorporating APTEOS and TEOS into PVA aqueous solutions. The relationship between structure of PAT nanocomposite membranes and their PV performance for dehydration of water/IPA aqueous mixtures were discussed. The chemical and physical structures were studied by Fourier transform infrared (FT-IR) and scanning electron microscopy (SEM). The degree of swelling and sorption selectivity of prepared nanocomposite membranes were investigated. Effects of operating conditions on PV performance were studied and effect of APTEOS content was also investigated.

2. Methods and materials

2.1. Materials

PVA with 98% hydrolization degree and molecular weight of 145,000 was purchased from Merck. Also TEOS, APTEOS and hydrochloric acid (HCl) (1N) were supplied by Merck and were used without any purification. IPA (99%) was purchased from Rankem, India. Deionized water was used to make the feed solutions and as solvent.

2.2. Membrane preparation

PVA solution was prepared by complete dissolving of the polymer powder (5.0 g) in 100 mL of deionized water (18.0 MW), at a temperature of 90 °C under magnetic stirring. The PVA solution (5.0 wt.%) was cooled down to room temperature with stirring (25 °C). The pH value was adjusted to 2.0 with HCl (1N). Then, according to the polymer composition, TEOS and APTEOS were added to the solution gently with a fixed mass ratio of 1:1 (APTEOS + TEOS to PVA). If pH value of the solution increased, it would be necessary to add more acid as catalyst to the solution to readjust it to 2 in all the solution preparation process. The pH is of crucial importance on coupling silanes to polymers. Then the solution should be stirred for 12 h to complete hydrolization reaction until no phase separation occurred and the hydrolyzed silane with –OH group could be dispersed through the water molecules. Hydrolization reactions of TEOS and APTEOS are presented as follows:

$$Si(OC_2H_5)_4 + xH_2O \xrightarrow{HCl/H_2O} Si(OH)_x(OC_2H_5)_{4-x} + xROH$$

$$H_2NCH_2CH_2Si(OC_2H_5)_3 + xH_2O \xrightarrow{HCl/H_2O} H_2NCH_2CH_2Si(OH)_x(OC_2H_5)_{3-x} + xROH$$

After stirring for 12 h the solution would be cast on a Plexi glass plate by a casting knife and dried for 48 h at 25–30 °C. Then the membranes would be pealed off and more dried at higher temperature in an oven at 80 °C for 2 h and 150 °C for 8 h. To investigate the effect of APTEOS/(APTEOS + TEOS) or (A) ratio on the physical structure and PV performance of the nanocomposite membranes, it was varied as 0, 0.25, 0.33, 0.50, 0.75 and the resulting membranes were designated as PAT00, PAT25, PAT33, PAT50 and PAT75, respectively. Thickness of the prepared membranes was 35 ± 5 μm, as measured by a digital micrometer.

2.3. Membrane characterization

2.3.1. Fourier transform infrared (FT-IR) spectroscopic analysis

Fourier transform infrared (FT-IR) spectra were obtained by an instrument [8400S SHIMADZU, Japan] equipped with attenuated total reflectance accessories (ATR).

2.3.2. Scanning electron microscopic (SEM) studies

Scanning electron micrograph of the PAT membranes was performed by an instrument [Philips XL-30, Holland] scanning electron microscope (SEM).

2.4. Swelling measurements

The nanocomposite membranes were dried completely at 80 °C for 8 h and weighed. Then, these membranes were immersed in a water–IPA mixture with various water concentrations in a sealed vessel at 30 °C for 24–48 h to allow them to reach an equilibrium swelling. The swollen membranes were weighed as quickly as possible after wiped with filter paper. Each run was performed at least three times, until the weight of the membranes was kept constant, and the results were averaged. The degree of swelling (DS) of the membrane was calculated by the following equation where W_s and W_d are the mass of the swollen and dry membranes, respectively.

$$DS = \frac{W_s - W_d}{W_d} \times 100$$

2.5. Sorption experiments

Sorption experiments were performed gravimetrically on all the membranes in 10, 20 and 30 wt.% water-containing feed mixtures at 30 °C. Initial weights of the PAT20, PAT33, PAT50 and PAT 75 nanocomposite membranes were taken on a single-pan digital microbalance. Samples were placed inside the specially designed airtight test bottles containing 20 cm^3 of the test solvent. Test bottles were transferred to the oven maintained at a constant desired temperature. Dry membranes were equilibrated by soaking in different compositions of feed mixtures in a sealed vessel at 30 °C for 48 h. Sorbed membranes were weighed after careful blotting by pressing between soft tissue papers immediately. The %sorption was