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Highly water selective silicotungstic acid ($H_4SiW_{12}O_{40}$) incorporated novel sodium alginate hybrid composite membranes for pervaporation dehydration of acetic acid[☆]

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Abstract

Silicotungstic acid incorporated sodium alginate (STA-NaAlg) hybrid composite membranes were prepared by incorporating 1, 2, 3 and 5 wt.% of silicotungstic acid (STA) into sodium alginate (NaAlg) and crosslinked with glutaraldehyde. Scanning electron microscopy and universal testing machine were used to investigate the morphology and the mechanical strength properties of the membranes. These membranes were tested for pervaporation (PV) dehydration of acetic acid at lower water concentrations of 10–25 wt.% in the feed. Addition of STA into NaAlg could result in a dramatic increase of water selectivity over that of plain NaAlg membrane dehydrating acetic acid for lowest STA containing NaAlg membrane. Thus, infinite selectivity was observed for STA-NaAlg membrane containing 1 wt.% of STA for all feed mixture compositions ranging from 10 to 25 wt.% water. With increasing STA content from 2, 3 and 5 wt.% in NaAlg membranes, selectivities ranged from 22,491 to 288, 12,848 to 192 and 6914 to 108, respectively for the studied composition range of the feed mixtures. PV performances of STA-NaAlg hybrid composite membranes were also tested at 40, 50, 60 and 70 °C typically in case of 10 wt.% water-containing feed mixture, which indicated a decrease in selectivity and increase in flux for all hybrid composite membranes. Arrhenius plots of flux data versus reciprocal of temperature exhibited linear trends. The hydrophilic STA is responsible to offer increased selectivity and flux to water as compared to plain NaAlg membrane for the feed mixtures studied. Of all the membranes tested, the 1 wt.% STA containing NaAlg membrane exhibited the best PV performance characteristics. Temperature did not influence much the selectivity data of STA-NaAlg membrane containing 1 wt.% of STA up to 50 °C, but flux increased with increasing temperature for all membranes. The results of this study are far superior to the previously reported data on acetic acid dehydration by the PV technique.
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Keywords: Pervaporation; Silicotungstic acid; Water–acetic acid mixture; Sodium alginate; Membrane; Activation energy

1. Introduction

Acetic acid (HAc) is one of the most basic organic intermediates used in chemical and other allied industries, which finds applications in synthesizing vinyl acetate, terephthalic acid, phthalic anhydride, acetic anhydride, cellulose esters, etc. Acetic acid is also used as a solvent in plastics industries in the production of resins as well as in pharmaceutical and biochemical industries. Currently used processes for acetic acid production include carbonylation of methanol, liquid-phase oxidation of hydrocarbons and oxidation of acetaldehyde [1–3]. It is however, difficult to separate acetic acid from industrial waste streams because acetic acid–water mixture does not form azeotrope, since the relative volatility of water and acetic acid is close to unity. Thus, their separation by conventional distillation becomes energy-intensive. Therefore, separation of acetic acid from water has been a challenging problem in chemical industries. In general, the more dilute the acetic acid solution is, the more attractive the solvent extraction becomes. In solvent extraction, acetic acid to water feed ratio is generally high, ranging from 2:1 to 5:1 [4]. Compared to other general types of solvent extraction and separation methods, from the energy-savings standpoint, pervaporation (PV) technique is a useful alternative method, since it is energy-intensive and environmentally clean.

In recent years, PV has been the widely accepted technique for the separation of aqueous–organic mixtures. It is also a

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promising technique for the fractionation of azeotropic mixtures, closely-boiling mixtures and mixtures consisting heat-sensitive compounds as well as low volatile aqueous solutions. In the past, hydrophilic and hydrophobic membranes have been used in PV dehydration of water–acetic acid mixtures [5–8]. Hydrophilic polymer membranes are preferred in PV dehydration studies of organics due to their strong affinity to water molecules. For PV dehydration of organic acids, new membranes with hydrophilic groups are preferred, which will absorb water molecules preferentially, leading to increased flux and selectivity. But, incorporation of hydrophilic groups in polymeric matrices will lead to polymer plasticization effect due to excessive membrane swelling. Swelling can be minimized by either crosslinking the polymer or by adding filler particles to improve the membrane performance.

In recent years, research efforts in membrane-based separations have been devoted to the separation of aqueous alcohol mixtures using NaAlg membranes [9–11], but acetic acid–water separation has received relatively a lesser attention. Many membranes used in water–acetic acid separation have met with a limited success to achieve the desired values of flux and selectivity. NaAlg and its modified forms are among the various types of membranes used in PV dehydration of acetic acid. Wang [12] used the modified NaAlg composite membrane for the PV dehydration of acetic acid. Toti and Aminabhavi [13] used different viscosity grade NaAlg and modified NaAlg membranes in PV separation of water–acetic acid mixtures.

Several reports have been published previously on the use of mixed matrix membranes by incorporating inorganic super acids (HPAs) into polymer matrix [14–16]. Such organic and inorganic hybrid compounds, when combined at the molecular level, have the proven advantages of both the organic materials of being light weight with a greater flexibility and good moldability, while inorganic components have high strength, thermal, and chemical stability [17]. HPAs have both acidic and redox catalytic properties [18], which show the characteristic adsorption behaviors, depending upon the properties of the adsorbates [19]. One of the distinctive features of HPAs is that they are highly soluble in polar solvents like water, alcohols and amines, but have generally poor solubility in non-polar solvents like benzene and olefins [20]. Taking advantages of their solubility properties, HPAs were blended with polymeric materials to form a membrane that has been used in catalytic applications [21,22].

In continuation of our ongoing efforts to develop novel types of membranes based on particulate filled NaAlg membrane with improved selectivity and flux [23–25], we now present some new experimental data on PV performance of STA filled-NaAlg membrane, for the first time used in acetic acid dehydration. The literature survey indicated that hitherto, no reports are available on the use of HPA-filled hybrid membranes of NaAlg for PV dehydration of water–acetic acid mixtures. The main objective of this study is to prepare of novel membrane of STA filled NaAlg hybrid composite membranes by incorporating different amounts of STA (1, 2, 3 and 5 wt.% based on the weight of NaAlg) into NaAlg matrix, and then crosslinking the membranes to achieve an effective dehydration of acetic acid. PV performance of the hybrid membranes of this study is much better than plain NaAlg membrane giving an improved flux and selectivity to water. Pervaporation performance of these membranes was studied at 30, 40, 50, 60 and 70 °C to evaluate the Arrhenius activation energy parameters using the PV results. Results are explained in terms of membrane–solvent interactions.

2. Experimental

2.1. Materials

Sodium alginate, glutaraldehyde (GA), acetic acid (HAc), acetone and conc. hydrochloric acid (HCl), all of analytical reagent grade chemicals, were purchased from s.d. fine Chemicals, Mumbai, India. Silicotungstic acid ($H_4SiW_{12}O_{40}$) was purchased from Loba Chemie, Mumbai, India. Deionized water, having a conductivity of 20 μS/cm, was produced in the laboratory itself from the Permeonics pilot plant (Vadodara, India) using the Nanofiltration membrane module.

2.2. Preparation of silicotungstic acid-filled NaAlg membranes

Silicotungstic acid-filled NaAlg membranes were prepared by solution casting. Required amounts of silicotungstic acid (1, 2, 3 and 5 wt.% based on the weight of NaAlg) were dissolved in 100 mL of water, to which 4 g of NaAlg was added and stirred thoroughly for 24 h at the ambient temperature. The resulting homogeneous solution was cast uniformly on a glass plate with the help of a casting knife and dried at ambient temperature. Membranes were immersed in a crosslinking bath containing 180 mL of water–acetone mixture (1:2, v/v) with 2 mL of glutaraldehyde and 2 mL of conc. HCl for about 10 h. The crosslinked membranes were washed with deionized water to remove the excess amount of GA and HCl. Membranes were dried at ambient temperature. The resulting 1, 2, 3 and 5 wt.% STA-loaded NaAlg membranes were designated, respectively as: STA-NaAlg-1, STA-NaAlg-2, STA-NaAlg-3 and STA-NaAlg-5. The crosslinked pristine NaAlg membrane was prepared in the same manner as described before in the absence of STA.

2.3. Mechanical properties

The equipment used for carrying out mechanical strength properties of the membranes was that of universal testing machine (UTM) (Model H25 KS Hounsfield, Surrey, United Kingdom). The test specimens were prepared in the form of dumbbell shapes as per the ASTM D-638 standards. Films of gauge length of 50 mm and width of 10 mm were stretched at a crosshead speed of 10 mm/min. Cross-sectional area of the sample of known width and thickness was calculated. Tensile strength was calculated using the equation:

$$\text{tensile strength} = \left[\frac{\text{maximum load}}{\text{cross-sectional area}}\right]\ (\text{N/mm}^2) \qquad (1)$$