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Effect of additives on the properties and performance of cellulose acetate derivative membranes in the separation of isopropanol/water mixtures

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ABSTRACT

In this work, various cellulose acetate (CA) membranes for pervaporation were prepared by the incorporation of different additives, i.e. polyethylene glycol-600 (PEG-600), propylene glycol (PG), and ethylene glycol (EG) to enhance the separation of isopropanol (IPA)/water mixtures. These membranes were characterized by FTIR, DSC, TGA, SEM and UTM. Each additive was responsible for its characteristic effect on the membrane morphology, mechanical strength, permeation flux and separation factor. The SEM micrograph showed that the additives were evenly dispersed in the membrane matrix with the formation of dense membranes. The UTM tests for the membrane reveled that both the Young's Modulus and tensile strength increased with the increase in additive contents. TGA studies for the CA/PEG blend membrane exhibited the highest thermal stability as compared to the CA/PG and CA/EG blends. For each of these synthesized membranes, the separation factor decreased while the permeation flux increased with the increase in additive contents, while the CA/PG membrane with 20 wt.% additive content showed highest permeation flux of 452.27 g/m^{2}h.

1. Introduction

In recent years, separation processes have gained considerable importance in the recovery processes, treatment of chemicals and purification of products. In these separation techniques, membranes play a vital role. For a desired performance and selectivity of separation, there is a requirement for the development of an appropriate synthetic membrane. For example in the textile industry the dyes are expensive chemicals which are recovered from the effluent by the use of ceramic membranes [1–3]. Similarly in the distillery where potable alcohol of 99.8% is desired, dense multi-layer membranes are used in molecular sieve modules. Membranes are making possible water supply purification and helping people survive from kidney diseases by removing undesired chemicals from the urine [4–6]. The chemical industry is also a growing field for the utilization of membranes, which however, often requires membrane materials with exceptional stability. Presently, a variety of membranes have been developed by unique ways conforming to their mode of application [7–9].

Pervaporation (PV) is a growing industrial process to separate closely boiling and azeotropic liquid mixtures. The best developed application is for the dehydration of organic solvents [10–14]. Dehydration of isopropanol (IPA) by PV has also gained attention in industry due to the competitive price of IPA and its utilization in various industries. For example, IPA dissolves a wide range of nonpolar compounds and its wide spread application as a coolant in beer manufacture, a coupling agent, a dehydrating agent, a polymerization modifier in the production of polyvinyl fluoride, a foam inhibitor, a de-icing agent, a preservative, a heat-exchange medium, and in windscreen wiper concentrates has prompted for its recycling. IPA is also used as a flavoring agent and in household and personal care products and pharmaceuticals [15–17].

Pervaporation membrane material commonly used for dehydration of IPA includes natural hydrophilic polymers, synthetic hydrophilic polymers and inorganic membranes [18–22]. The newly developed organic–inorganic hybrids and layer-by-layer assembled multi-layer membranes have also gained great importance [23–28].

Cellulose acetate (CA) is an easily available material and due to its hydrophilic nature can be used as a membrane for the permeation of hydrophilic compounds. The early CA membranes yielded low flux and were susceptible to biological attracts along with low thermal stability. However, recent studies have shown that these properties can be improved if appropriate additives are used by adjusting proper polymer to additive ratio [29, 30].

In this study, CA membranes incorporated with different additives were prepared which resulted in the development of dense membranes. These dense membranes were used for the PV separation of IPA/water mixtures. The synthesized membranes were characterized by Fourier transform-infrared spectroscopy, scanning electron microscope, differential scanning calorimetry, thermogravimetric analysis and universal testing machine. The effects of the additive contents on the PV performance were systematically investigated.

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2. Experimental

2.1. Materials

Cellulose acetate (CA) (BDH chemicals Ltd.) is a principle membrane developing material. Other chemical used are acetic Acid (Sigma-Aldrich Laboratories), propylene glycol (BDH chemicals Ltd), ethylene glycol (MERCK), polyethylene glycol-600 (MERCK) and isopropanol (IPA) (MERCK) and glycerin (MERCK). All these chemicals were used as received.

2.2. Membrane dope solution

20 g of CA was dissolved in 55 g of glacial acetic acid along with 21 g of distilled water. Varying amounts (4, 8, 12, 16 and 20 g) of glycol additives were added in CA solution to obtain different CA/glycol membranes. Optimal properties can be achieved by adjusting the weight percent of polymer to additive ratio [31–35]. The prepared solution was termed as membrane casting dope solution. The casting solution flask was dipped in an isolated water bath at a temperature of 80 °C for 8 h with continuous stirring until a clear light brown solution was obtained. Casting solution was allowed to cool down to room temperature (25 °C) and kept for 24 h in a sealed flask to remove micro bubbles formed in the solution.

2.3. Membrane casting

The membrane doped solution was spread slowly by hand casting knife on a glass plate. The plate containing membrane solution was dipped in a bath of distilled water at a temperature of 25–30 °C for 24 h to achieve slow precipitation for the formation of dense membrane. After membrane formation, the membrane was carefully removed from the glass plate by using a sharp blade. The newly developed membrane was washed in glycerol bath for post-cleaning to remove excess acetic acid and coagulated particles [36–39]. After post-cleaning the membrane was further washed in a bath of distilled water, dried up and stored in a clean atmosphere. The no (0 wt.%) additive content membrane was termed as plain CA membrane denoted by 'CA' in the figures. The thickness of the resulting membranes was measured to be in the range of 0.2–0.4 μm.

2.4. Characterization of membranes

2.4.1. Differential scanning calorimetry (DSC)/thermogravimetric analysis (TGA) studies

DSC/TGA measurement of prepared membranes was carried out using a TA instruments SDT Q600 simultaneous differential scanning calorimetery/thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. The glass transition temperature, Tg, was determined from the corresponding DSC curve.

2.4.2. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectra were obtained by a SHIMADZU, IR Prestige-21 instrument equipped with both horizontal attenuated total reflectance (HATR) accessories. The experiments were run with air as the background. For each spectrum 124 scans were accumulated with a resolution of 4 cm^{-1}.

2.4.3. Scanning electron microscopy (SEM)

Scanning electron micrographs of all the samples were performed on a Hitachi S-3400 scanning electron microscope (SEM) instrument.

2.4.4. Mechanical properties

The tensile strength of membranes was measured at room temperature using an Instron-type tensile testing machine (Testometric/M350-10CT ROCHOALL, England) with a crosshead speed of 1 mm/min. The width of the sample was approximately 25 mm and the length between the jaws was 45 mm. All the measurement was performed at 25 ± 2% RH (relative humidity).

2.5. Pervaporation experiment

Pervaporation experiments were carried out on a plate and frame membrane module. The process flow diagram is shown in Fig. 1. The feed was 75% IPA / 25% water by wt.%. The effective membrane area in contact with the feed was 154 cm^2.The vacuum was maintained at 0.7 bar using a vacuum pump. The feed temperature was set at 40 °C. The permeate was collected for 4 h in a continuous operation. The compositions of the feed and permeate were measured by gas chromatography (Varian CP-3800 gas chromatograph) equipped with a thermal conductivity detector (TCD) and a CP Wax 52 CB column. The separation performance of the membranes was evaluated in terms of Permeation Flux 'J' ($\text{g/m}^2\text{h}$) and separation factor 'α', determined by using the following two equations respectively [40–42].

$$J = \frac{Q}{A \times t} \tag{1}$$

$$\alpha = \frac{Ywater/Ypropanol}{Xwater/Xpropanol} \tag{2}$$

Where Q is the weight of permeate collected during a time interval of t, A is the effective membrane area, X_{water} and $X_{propanol}$ are the weight fractions of water and IPA in the feed respectively, and Y_{water} and $Y_{propanol}$ are the weight fractions of water and IPA in the permeate respectively.

3. Results and discussion

3.1. Membrane characterization

3.1.1. DSC studies

In a thermal analysis, the glass transition temperature (T_g) is indicative of the structure and packing of the polymer chain in the membrane. Fig. 2 shows identical T_g with endothermic peaks for CA/PEG, CA/EG and CA/PG blend membranes (4 wt.%) of 65.74 °C, 66.16 °C and 66.34 °C, respectively. The plain CA membrane (without any additive) exhibited a T_g of 87.38 °C. It was revealed that additives were responsible for lowering the T_g of cellulose acetate from 87.38 °C to 65.74 °C (CA/PEG), thus explains the plasticizing effect of PEG, which accordingly increased the mobility of the CA chains. In general all the additives contributed in lowering the Tg of CA matrix. Smaller molecules of additives embed themselves in between the CA chains, increasing the mean free volume fraction, and therefore, had a loose structure which is mainly liable for enhancing the permeation flux. The endothermic heat flow differences seen could be due to incorporation of different additives with CA as well as the different packing density in the membranes.

3.1.2. TGA studies

The thermal degradation expressed in terms of weight loss as a function of the temperature for the prepared membranes were shown in Fig. 3. The TGA studies were conducted on plain CA and CA blend membranes of 4 wt.% additive contents. From TGA plot of the plain CA membrane, it could be seen that decomposition took place in four unique steps. In the first step plain CA membrane shows decomposition between 20 and 100 °C with a weight loss of about 23% that may be due to the presence of highly volatile components. In the second step a gradual decomposition between 100 and 160 °C with a weight loss of about 13% may be due to the loss of water molecules present in the membrane. In the third step, there was the highest weight loss of about 51% from 160 to 350 °C probably due to main thermal decomposition