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Water–methanol separation characteristics of annealed SA/PVA complex membranes

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ABSTRACT

Polymeric membranes based on sodium alginate (SA)/polyvinyl alcohol (PVA) were prepared with the SA/PVA blending ratio of 80/20, 90/10 and 95/05 wt% and complexed with divalent calcium ions. The prepared membranes were modulated by post-heat treatment to achieve good vapor permeation (VP) separation characteristics of water–methanol mixture. Membranes performances for water–methanol separation were investigated in terms of their flux and permselectivity. The effect of various parameters like operating temperature, annealing time and PVA contents on membranes performances was also investigated. To study the effect of operating temperature on flux and permselectivity, vapor permeation experiments were performed in the range of 40–70 °C. As a whole, the maximum selectivity was observed at minimum flux conditions and vice versa. The only water component was penetrated through SA/PVA (90/10) annealed complex membrane for the operating temperature of 40–60 °C. A comparable performance was shown by the SA/PVA (80/20) annealed complex membrane at 40 °C. The structural characteristics, morphology and stability of complex membranes were investigated using FTIR, XRD, SEM, TGA and DTG analysis. The results confirmed that annealing process affects the structure morphology and leads to free volume shrinkage between polymer chains. So, it is concluded that the Ca-complex SA/PVA annealed membranes exhibited the molecular sieving mechanism for separation of water–methanol mixtures because of decrease in free volume and strong intermolecular interactions between the membranes components.

1. Introduction

Purity of chemicals has always remained a big challenge in chemical industry as it brackets the value of products. Several separation processes like distillation, extraction, and evaporation have been employed but each of them is associated with its own limitations. Membrane technology got much attention in last few decades and is found to be a good substitute of conventional energy-intensive separation processes. The beauty of this process lies in its low-energy demand, simplicity of design, low-cost and eco-friendly nature. Recently, it has successfully been used in-water treatment, food, pharmaceutical and chemical industries.

Pervaporation (PV) is one of the emerging membranes based process and is an attractive alternate of other's separation processes. It involves the selective absorption and/or diffusion of a component of mixture through a dense membrane under the driving force of pressure difference. Hence, in contrast to thermal processes, separation is based on the relative permeation rate of components [1]. Generally, PV separation occurs in three successive steps, absorption of feed components by the surface layer of membrane, diffusion of the component through the membrane, and its desorption at the permeates side [2,3]. Its relatively low operating temperature, low pressure, independence on vapor–liquid equilibria and feasibility for heat sensitive mixtures make it suitable for dehydration of organic solvents [4], removal of organic traces from wastewater [5] and organic–organic separations [6].

Industrialization of PV membranes was started with the development of hydrophilic membranes for dehydration of organic solvents. Ethanol dehydration by PV was the first ever commercialized membrane based process installed at France [7]. The most common industrial application is the dehydration of low molecular weight alcohols [16]. Ethanol–water PV separation system is the extensively studied process, and a lot of work has already been published [7,10–13,27–34]. But we rarely found a literature on the PV separation of water–methanol mixture.

Polymers with glass transition temperatures above room temperatures are usually used for dehydration of alcohols.

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Polyvinyl alcohol (PVA) is a good example of this type of material and has been extensively studied as a hydrophilic membrane component [8]. Sometimes PVA membranes are modified by cross linking, complexing or grafting to improve its chemical stability and separation performances. Many other materials like chitosan, polyetherimide (PEI), acrylic acid (AA), polyacrylonitrile (PAN), carrageenan, sodium alginate and zeolites has also been studied for this type of membranes [14–20].

Won and Feng examined the performance of alkaline treated chitosan membrane for dehydration of dimethyl ether (DME) and methanol but better results were achieved for water–DME separation [15]. As simple polyvinyl alcohol (PVA) based hydrophilic membranes are unsuitable for high-water content feed, hydrophilic zeolite and some nano-silica doped composite membranes have also been studied for water–methanol separation [14–17]. D. Shah et al. studied the performance of NaA-zeolite membranes for dehydration of alcohols, but less permselectivity is reported for methanol as compared to propanol and ethanol dehydration [14]. A notable improvement in water–methanol separation factor was observed by doping silica nano-particles in acrylic acid, acrylonitrile and polyvinyl alcohol based composite membrane [9]. Keeping in mind the structure of zeolites, Kim and Lee investigated the effect of annealing on sodium alginate-carrageenan based polyelectrolyte membranes for water–methanol separation [17]. Unlike above, some hydrophobic flat-thin composite polydimethylsiloxane (PDMS) membranes have been explored for low methanol contents (0.3–3%) [19]. As the similar physiochemical properties of water and methanol makes their separation difficult so, still it remains a big challenge for the membrane scientists to develop a PV membrane for water–methanol separation.

Vapor permeation (VP) is a special type of pervaporation in which no phase change occurs across the membrane hence, both feed and permeate remains in vapor phase. As within the permeation cell, there is a gap between the liquid level and membrane so, unlike pervaporation the coupling phenomenon can be avoided [20]. In this study, we have prepared some novel annealed Ca-complex membranes and employed them for water–methanol VP separation. Sodium alginate (SA) and polyvinyl alcohol (PVA) were chosen as the polymeric materials because of their good hydrophilic characteristics [12,23,24,34]. After casting, they were cross linked by divalent calcium ions, and their structure morphology was controlled by post-heat treatment. VP separation performances of prepared membranes were investigated in terms of flux and selectivity for water–methanol mixture. Effect of operating temperature, annealing time, and membrane composition was also examined. Moreover, various analytical techniques like SEM, FTIR, XRD, TGA and DSC were utilized to characterize them and the characterization data were found to be compatible with that of experimental one.

2. Experiments

2.1. Materials

Sodium alginate (SA) supplied by SHOWA Chemical Inc. was used to prepare the membranes. Polyvinyl alcohol (PVA) (hydrolyzed 99+%, average M_w 85,000–124,000) and anhydrous calcium chloride was purchased from Aldrich Chemical Company. Methanol was supplied by Burdick and Jackson and a methanol–deionized water solution with a predetermined composition of 80/20 wt% was employed as the feed mixture for vapor permeation (VP) experiment. All the desired solutions were prepared in ultra-pure de-ionized water. As all the chemicals were of analytical grade so, they were used without further purification.

2.2. Membranes preparation

All the membranes were prepared by "Solution-Evaporation" method. The homogeneous solutions of sodium alginate (SA) and polyvinyl alcohol (PVA) were prepared by dissolving 2 wt% of each polymers in deionized water. The prepared solutions were mixed with SA/PVA weight ratios of 95/05, 90/10 and 80/20% and stirred well at room temperature for 24 h. After removing the air bubbles; the solutions were cast on clean petri dishes and dried at room temperature from 3 to 4 day in a dust-free environment. The dried films were removed from petri dishes and immersed into 5 wt% aqueous solution of anhydrous $CaCl_2$ for 16 h to make their calcium complex. Then membranes were thoroughly washed with distilled water to remove the residues of calcium ions. As the withstanding capacity of membrane strongly depends upon the cross linking agent used, that is why prepared membranes were unstable in water, while completely stable in 5 wt% aqueous solution of $CaCl_2$. Moreover, the mechanical stability of the Ca-complex SA/PVA (90/10) membrane was measured in terms of ultimate tensile measurement (UTM) and found to have a good tensile strength of 65 MPa with the elongation at break of 10.12%. This decent balance of tensile strength and elongation at break of membrane is acceptable for the required application of vapor permeation. The thickness of the membranes was 52 ± 3 μm as measured by the digital micrometer screw gage. At the end, heat treatment was done in an oven at 110 °C each for a total of 12 h in two steps (4 and 8 h) to control the morphology of membranes.

2.3. Vapor permeation experiment

Vapor permeation experiments were performed using the experimental setup shown in Fig. 1. The stainless steel made permeation cell hold two parts. In the lower cylindrical part, liquid feed was circulating between feed tank and the cell with a constant flow rate. So, the feed and retentate lines were connected to the lower part of the cell, while the upper porous stainless steel part was connected to the permeate collection line. Membrane and a filter paper (as support) having the effective area of 15.5 cm^2 was placed in the cell and sealed with a rubber O-ring. The feed tank was wrapped with heating tape to keep it at the constant experimental temperatures. Feed pump was used to circulate the feed and retentate with a controlled flow rate. On the permeate side, a vacuum was applied to maintain the driving force of pressure difference across the membrane. After achieving the steady state within 4 h, permeate was collected in a pre-weighed Pyrex glass tube by dipping it in liquid nitrogen. The condensed permeate was allowed to heat at room temperature and then weighed to calculate the permeation rate or flux passed through the membrane using Eq. (1)

$$F = \frac{w}{at} \tag{1}$$

where 'F' is the flux or sometimes called the permeation rate of membrane having a unit of kg/m^2 h, 'w' is the weight of permeate in kg, 'a' is the effective area of membrane and 't' is the collection time of flux. To calculate the selectivity of membrane, permeate composition was analyzed by Gas Chromatograph (Shimadzu, model GC 14B) fitted with Porapak-Q packed column and TCD detector. Then the selectivity or separation factor (α) of membrane for water–methanol mixture separation was calculated by following equation:

$$\alpha_{\text{water/methanol}} = (Y_{\text{water}}/Y_{\text{methanol}})/(X_{\text{water}}/X_{\text{methanol}}) \tag{2}$$