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Dehydration of acetic acid by pervaporation using SPEK-C/PVA blend membranes

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ABSTRACT

Sulfonated cardo polyetherketone (SPEK-C) and poly(vinyl alcohol) (PVA) blend membranes were prepared by solution casting method and used in pervaporation (PV) dehydration of acetic acid. The membranes were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and contact angle meter. The results show that thermal crosslinking occurred to the membrane under high temperature annealing. The effective *d*-spacing (inter-segmental spacing) decreased with PVA content decreasing. The hydrophilicity of the blend membrane increased with SPEK-C content increasing. Swelling and sorption experiments show that the swelling degree of the blend membrane increased, however both the sorption and diffusion selectivities decreased with increasing PVA content. The diffusion selectivity is higher than the sorption selectivity. This suggests that PV dehydration of acetic acid is dominated by the diffusion process. The pervaporation separation index (PSI) of the membrane increases with increasing PVA content and arrives at a maximum when the SPEK-C/PVA ratio is 3/2, then decreases with further addition of PVA. The membrane has an encouraging separation performance with a flux of 492 g m^{-2} h^{-1} and separation factor of 59.3 at 50 °C at the feed water content 10 wt%.

1. Introduction

Pervaporation is one of the rapidly developing and promising technologies for the dehydration of organic liquids in various industrial processes. It is especially cost effective in separating azeotropic and close boiling liquid mixtures [1–4], as well as being safe to handle the heat-sensitive and hazardous compounds [5]. Acetic acid is known to rank among the top 20 organic intermediates in chemical industries [6,7] and is mainly used for the production of vinyl plastics, hot-melt adhesives, textile finishes, latex paints and acetic anhydride [8]. Water/acetic acid mixtures are often encountered in the preparation of several intermediates like vinyl acetate, phthalic anhydride, acetic anhydride, etc. [6,9]. Furthermore, the synthesis of acetic acid itself results in the production of water as a by-product. Water must be removed to obtain pure acetic acid. However, due to the close boiling points of water and acetic acid [10], a large number of trays and a high reflux ratio are necessary to obtain glacial acetic acid by distillation. From an energy-saving standpoint, PV can be a promising alternative to distillation for water/acetic acid separation.

PVA is one of most important polymer membrane materials used for the dehydration of organic mixtures owing to its good chemical stability, film-forming ability and high hydrophilicity [11,12]. However, the swelling of PVA membrane in an aqueous solution, especially in water/acetic acid mixture, often results in a rapid decrease in water permselectivity [13]. To improve the membrane stability and permeation properties, some modified methods have been attempted, such as crosslinking, filling, blending and surface modification [14–17]. For example, Huang and Yeom [18] studied the dehydration of acetic acid through PVA membranes crosslinked with amic acid. The membranes show high flux, however, the selectivity is not so encouraging. Hilmioglu et al. [7] studied PVA membranes modified with glutaraldehyde and formaldehyde. The glutaraldehyde crosslinked PVA membrane shows higher selectivity and lower flux than those of formaldehyde crosslinked PVA membrane. Alghezawi et al. [11] investigated acrylonitrile (AN) grafted PVA membranes for acetic acid dehydration. The results show high flux and low selectivity (separation factors 2.3–14 and permeation fluxes 0.18–1.17 kg m^{-2} h^{-1}). Meanwhile, PVA-g-AN membranes were found to have lower permeation rate and higher separation factors than those of plain PVA membranes under the same operation condition.

Cardo polyetherketone (PEK-C) is a thermally stable polymer with high mechanical properties and solvent resistance especially showing excellent mechanical stability in aqueous environment.

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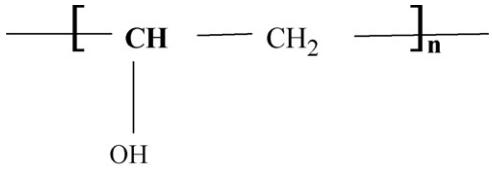


Scheme 1. Molecular structure of PVA.

PEK-C was studied in the preparation of ultrafiltration (UF) and gas separation membranes [19,20]. However, there are few literatures regarding PEK-C-based membrane in pervaporation. In our previous study, SPEK-C membranes were prepared and used for PV dehydration of acetic acid [21]. The results show that the PV performance is related to the sulfonation degree. The SPEK-C membranes display high selectivity; however, the flux is not so encouraging.

Preparation of novel membranes with high selectivity together with high permeability is still a challenge to many researchers. Blended polymer membranes are widely studied for pervaporation [22–25] because of possessing the intrinsic chemical, physical, mechanical, and morphological properties of each component. By blending SPEK-C with PVA in this work, we intend to combine the advantage of high selectivity of SPEK-C and high flux of PVA membranes. The effect of blending ratio and annealing temperature as well as operation condition on PV separation of water/acetic acid was investigated.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (as shown in Scheme 1), polymerization degree of 1750 ± 50, was supplied by Sinophatm Chemical Reagent Co. Ltd. Cardo polyetherketone (PEK-C), polymerization degree of 101, was purchased from Xuzhou Engineering Plastic Factory (Jiangsu, China). Dimethyl sulfoxide (DMSO), concentrated sulfuric acid and glacial acetic acid, of analytical grade and used without further purification, were purchased from Shanghai Chemical Reagent Store (Shanghai, China).

2.2. Membrane preparation

SPEK-C (as shown in Scheme 2) prepared according to the method described in the previous study [21] was dissolved in DMSO to form 5% (w/v) polymer solutions at ambient condition, and then it was filtered to remove the insoluble materials. PVA was dissolved in DMSO to form 5% (w/v) at 90 °C. SPEK-C and PVA blends were then prepared by mixing the individual solutions in different mass ratio (1/0, 4/1, 3/2/, 2/3, 1/4 and 0/1). The membranes thus prepared are designated as SPEK-C, SPEK-C-80, SPEK-C-60, SPEK-C-40, SPEK-C-20 and PVA, respectively. The mixture was then stirred vigorously for 2 h to form a homogeneous solution. The bubble-free blend solution was cast to the desired thickness on a clean glass plate, and then dried in an oven at 70 ± 1 °C with relative humidity 65 ± 2% for about 10 h. The obtained membranes were peeled off gently, and were further annealed under vacuum at 100 or 150 °C for 10 h. The thickness of the membranes, measured by scanning electron microscopy (SEM), is about 26–29 μm.

2.3. Membrane characterization

2.3.1. XRD patterns of the membranes

Crystal structure of membranes was characterized by X-ray powder diffraction (XRD Panalytical X'pert Philip, Holland) using Cu Kα radiation. The diffraction was operated at 40 kV and 30 mA, and the angle of diffraction was varied from 5° to 50° to identify the change in the crystal structure and intermolecular distances between the inter-segmental chains of the SPEK-C /PVA blend membranes, using a step size of 0.0167° and a counting time of 10 s per step. The *d*-space can be calculated by substituting the scattering angles (2θ) of the peak into the Bragg's equation

$$n\lambda = 2d\sin\theta \quad (1)$$

where 2θ is the X-ray diffraction angle, λ wavelength = 1.54 Å, *d* effective *d*-spacing and $n = 1, 2, 3 \ldots$

2.3.2. Fourier transform infrared (FTIR) spectroscopic studies

FTIR spectra of the prepared plain SPEK-C, PVA and SPEK-C/PVA blend membranes were scanned in the range from 4000 to 400 cm^{-1} with an accumulation of 16 scans on a Nicolet-740.

2.3.3. Scanning electron microscope (SEM) study

The surface morphology and thickness of the membranes were measured by using SEM (XL30, Oxford Instruments) operating at EHT = 20 kV.

2.3.4. Contact angle measurement

Static contact angles between membranes and water were measured by the pendant drop method using contact angle meter (SL200B, SOLON TECH, Shanghai, China) at 26 ± 1 °C with 65 ± 2% relative humidity. All the reported values are the average of ten measurements taken at different location of the same membrane surface. The errors are less than 5%.

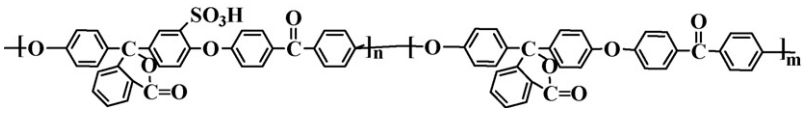
2.4. Swelling measurements and sorption experiments

The prepared membranes were weighed and immersed in water/acetic acid mixtures at a temperature of 50 °C for 48 h to reach equilibrium swelling. The sample was taken out at appropriate intervals, wiped with tissue paper carefully to remove the surface solvent, and weighed as quickly as possible, then dipped again into the liquids. The experiments continued until the weight of the sample keeping approximate constant. All experiments were repeated at least for three times and the results were averaged. The errors are less than 3.5%. The degree of swelling (DS) is calculated by

$$\mathrm{DS}\ (\%) = \frac{M_W - M_D}{M_D} \times 100\% \quad (2)$$

where M_D and M_W denote the mass of the dried and swollen membranes, respectively.

For sorption in a binary solution, the prepared membranes were immersed in water/acetic acid mixtures at a temperature of 50 °C for 48 h to reach sorption equilibrium. Then, the absorbed liquid was collected in a liquid nitrogen trap by desorbing the equilibrated sample in the purge-and-trap apparatus (shown in Scheme 3), and



Scheme 2. Molecular structure of SPEK-C ($n = 1, 2, 3 \ldots$, $m = 0, 1, 2, 3 \ldots$).