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Pervaporation dehydration of binary and ternary mixtures of *n*-butyl acetate, *n*-butanol and water using PVA-CS blended membranes

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ABSTRACT

The blended membranes of polyvinyl alcohol (PVA) and chitosan (CS) (PVA-CS) were prepared for pervaporation dehydration of a binary system of *n*-butyl acetate/water and a ternary mixture of *n*-butyl acetate/*n*-butanol/water. Membranes were characterized by FTIR, DSC and XRD to investigate the intermolecular interactions, the blending compatibility and the effects of blending on crystallinity. Tensile strengths were measured to determine the influence of blending ratios on the membrane's mechanical properties. The membrane's degree of swelling in water dropped significantly with increasing CS fraction. The results agreed well with the calculation of the solubility parameter. Separation factor and permeation flux increased when the temperature was raised for both the binary and ternary pervaporation systems. An optimal separation factor of 27,000 with a total flux of 402 $g \cdot m^{-2} \cdot h^{-1}$ was obtained using the blend membrane containing 25 wt% CS at 40 °C for the binary system. For the ternary system, the maximum separation factor and total flux were obtained for blend membranes at 75 wt% and 50 wt% CS content, respectively.

1. Introduction

n-Butyl acetate is an important organic solvent and raw material that is used as a solvent associated with acrylic polymers, vinyl resins, cosmetic formulations and other applications [1,2]. Conventionally, *n*-butyl acetate is synthesized from the esterification of *n*-butanol with acetic acid. Reactive distillation has been widely used in the production of acetates to break the chemical equilibrium and achieve a larger percent conversion of reactants [3]. However, the organic product from the tower top decanter contains some water that must be removed by an extra refining column, an additional step that can increase the cost of both the equipment required and the energy consumed. In addition, the water produced in the esterification may lead to hydrolytic breakdown of the desired *n*-butyl acetate and impact the quality of the product.

Compared with traditional methods, pervaporation (PV) dehydration of *n*-butyl acetate is superior in terms of equipment and management costs, ease of operation and the ability to break through the limitations of vapor liquid equilibrium (VLE) [4]. In PV dehydration, great efforts have been made to develop membranes that have both high permeability and high selectivity [5,6].

Polymers with hydrophilic groups, such as polyvinyl alcohol (PVA), polyacrylic acid (PAA), polyacrylonitrile (PAN) and chitosan (CS), have been extensively investigated for use in the PV dehydration of the organic solvents [7–9]. In general, a trade-off must often be made between flux and selectivity, a problem that is particularly evident in pure polymer membranes and may restrict their industrial applications [10]. Therefore, significant efforts are being made to modify the polymer material through physical and chemical methods; e.g., crosslinking, grafting, filling and blending, to enhance its PV performance [11–13].

PVA has been widely investigated as a membrane material for use in the removal of water from organic-aqueous liquid mixtures; e.g., ethanol, isopropanol, *n*-butanol and ethyl acetate [14–16]. In addition to its good mechanical properties, PVA exhibits excellent hydrophilicity due to the number of hydroxyl groups on its chain segments [17]. Further, PVA has good chemical resistance and film-forming properties.

CS is a polysaccharide polymer product of chitin from crab and shrimp shells and is the second most abundant naturally occurring material [18]. However, CS has some disadvantages in the areas of mechanical properties, dimensional stability and thermoplasticity [19].

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Blending of materials is one of the more effective ways to beneficially modify one polymeric material to improve its desired properties by the addition of one or more other polymers through intermolecular interactions between polymers [20,21]. Specifically, PVA and CS blend membranes (PVA-CS) have been used in the fields of dehydration of organic solvents and the separation of organic-organic mixtures. Hyder and Chen [22] investigated the effects of PVA-CS blending ratios on pervaporation dehydration of ethylene glycol. The total flux and the separation factor reached maximum values (110 $g\cdot m^{-2}\cdot h^{-1}$ and 986, respectively) at 70–80 wt% CS in the membranes. Rao et al. [23] tested the PVA-CS blend membranes for pervaporation dehydration of isopropanol and tetrahydrofuran (THF) in close proximity to their azeotropic compositions which exhibited the highest selectivity of 17,991 (for isopropanol) and 4203 (for THF) when the blend polymer membranes contained 80 wt% CS. Nawawi et al. [24] used PVA-CS blend membranes to separate methanol from methyl t-butyl ether (MTBE) and found that blend membranes containing 20–40 wt% CS showed the highest permeation flux of 67 $g\cdot m^{-2}\cdot h^{-1}$ and the maximal separation factor of 81. Lu et al. [25] also found that the PVA-CS blend membranes exhibited high benzene permselectivity because benzene with π-bond electron clouds showed stronger interaction with the hydrophilic polymers than cyclohexane.

Previous work [26] by our research team has reported on the removal of water from the organic mixtures by pure PVA membrane in butyl acetate production via esterification. However, as far as we know, no reports are available to explore the pervaporation dehydration performance in *n*-butyl acetate solutions using PVA-CS blend membranes. Furthermore, the field lacks a persuasive explanation for why the optimal blend ratio of membranes is different for different PV systems. A more comprehensive understanding of the phenomena using PVA-CS membranes could have economic benefits for the production of *n*-butyl acetate production via esterification and subsequent separation of water from the product stream.

In this work, we report on the effects of PVA-CS membranes of different blending ratios on the dehydration of a binary mixture of *n*-butyl acetate/water and of a ternary system of *n*-butyl acetate/*n*-butanol/water in order to find an optimal blending ratio in each case. The membranes were prepared by the solution-casting method and their physiochemical properties were characterized by FTIR, XRD, DSC, tensile testing and swelling measurements. The solubility parameters of solvents and polymers were calculated by group contribution method. The optimum conditions for dehydration of *n*-butyl acetate/water and *n*-butyl acetate/*n*-butanol/water mixtures were experimentally determined.

2. Methods and experiments

2.1. Materials

Chitosan (MW ~ 1000,000, 94.5% deacetylation degree) was purchased from Aladdin Industrial Co., Ltd. (China). Polyvinyl alcohol (PVA1750) (MW ~ 78,000) with polymerization degree of 1700 ± 50 and alcoholysis degree of 50% was provided by Sinopharm Chemical Reagent Co., Ltd (China). The polyvinylidene fluoride (PVDF) microfiltration membrane with an average pore size of 0.22 μm was supplied by Beijing Beihualiming Membrane Separation Technology Co., Ltd (China). *n*-butyl acetate (analytical reagent (AR)), *n*-butanol (AR) and acetic acid (AR) were supplied by Guangdong Guanghua Sci-Tech Co., Ltd (China). Laboratory-generated deionized water was used in preparing all the aqueous solutions. All chemicals were used without further purification.

2.2. Membrane preparation

CS powder was dissolved in a 1 wt% aqueous acetic acid solution with stirring to obtain a 3 wt% homogeneous CS solution. A PVA solution (10 wt%) was prepared by dissolving the PVA powder in deionized water at 90 °C with stirring. The PVA and CS solutions were vacuum filtered to remove dust and other traces of insoluble impurities.

The mixed solutions were prepared by dripping the PVA solution into the CS solution and were vigorously stirred for 24 h to ensure blended homogeneity. The uniform solutions were maintained at room temperature for 24 h to remove bubbles that formed during stirring. The PVA-CS blend membrane was prepared as a composite membrane applying a thin layer of a homogenous blend on a PVDF membrane. The composite membrane was then placed in an oven at 40 °C for 24 h to remove the solvents and further dried in a vacuum oven at 80 °C for 24 h to remove any residues. Various weight ratios of PVA-CS blend membranes were obtained and stored in a desiccator. The thickness of resulting dried selective layer was approximately 20 μm as determined by SEM.

The density of the blend polymer was determined by the liquid pycnometer method (ISO 1183-1-2004) in which pure ethanol was used as the immersion liquid in the pycnometer with a density, ρ_L, at 30 °C of 0.78097 $g\cdot cm^{-3}$. The density ρ_m of the specimen at 30 °C, can be calculated using the following Eq. (1):

$$\rho_S = \frac{m_S \rho_L}{m_1 - m_2} \tag{1}$$

where m_S is the mass of the blend sample, m_1 is the mass of the ethanol-filled pycnometer, m_2 is the mass of the blend-filled pycnometer.

The physicochemical properties of the PVA-CS films with various blend ratios are shown in Table 1.

2.3. Membrane characterization

The chemical structure of PVA-CS blend films were analyzed by an FTIR spectrometer (Nicolet6700, Thermal Fisher, USA). The thicknesses of the tested films were less than 10 μm in order to insure that the spectra of the films obeyed the Beer-Lambert law [27]. The samples were scanned at the wavenumbers ranging from 4000 to 500 cm^{-1} with a scan speed of 32 cm^{-1} per second.

The thermal properties of the PVA-CS blend membranes were obtained on a differential scanning calorimeter (DSC) (C80CSEVO, SETARAM, France). The DSC thermograms were recorded from 50 °C to 400 °C with a heating rate of 10 °C min^{-1} in a nitrogen atmosphere.

The blend membrane samples' X-ray diffraction (XRD) patterns were obtained from an X-ray diffractometer (Smartlab, Rigaku, Japan) using Cu $K\alpha_1$ radiation (wavelength = 0.154 nm). The scan speed was 10° min^{-1} with a scan angle scope (2θ) ranging from 5 to 90°. The tube voltage and the electric current were set to 45 kV and 200 mA, respectively.

The mechanical properties of the membrane samples were tested with an electronic universal testing machine (3300, Instron, USA) at 25 °C. The test method involved stretching a test piece with an initial size of 200 mm × 10 mm × 0.05 mm at a rate of 0.5 $mm\cdot min^{-1}$until it broke. All the measurements were repeated five times and reported as the averaged value.

2.4. Prediction of solubility parameters of solvents and polymers

The solubility parameter (δ) is an important property of polymers that can predict the compatibility between the polymers and other compounds. The Hansen solubility parameters can be