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Application of interfacially polymerized polyamide composite membranes to isopropanol dehydration: Effect of membrane pre-treatment and temperature

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ABSTRACT

Commercial thin-film composite reverse osmosis (RO) membranes (SWC5, ESPA2 and CPA5) were dried under different membrane pre-treatments and evaluated for isopropanol dehydration at increased temperatures in pervaporation and vapor permeation systems.

Water permeance was enhanced in the membranes pre-treated with ethanol–hexane and freeze drying, compared with those membranes dried by room temperature and in an oven. In particular, ethanol–hexane dried samples showed an enhanced water permeance by a factor of 1.7–3.5, depending on the structural characteristics of each membrane.

The membranes exhibited stability for up to 25 operation hours in the vapor permeation system. Moreover, the operation temperature was an important factor in determining water and isopropanol permeances. With an increase in temperature, the highly permeable regions, which showed low selectivity, were plugged more rapidly. As a result, the maximum water/isopropanol separation factor was reached at 150 °C, α(water/IPA)=284, with a considerably high flux of 5.93 kg/(m^2 h) for a CPA5 high-rejection RO membrane.

The induced changes in the polymer morphology and separation performance data were compared to single gas permeation. The results are discussed in terms of membrane swelling, which softens the polymer and decreases the diffusion resistance to molecules in pervaporation by comparison with vapor permeation.

1. Introduction

Nowadays, polymeric membranes are utilized for pervaporation (PV) and vapor permeation (VP) systems because of their reasonable separation performance and easy fabrication at low cost. It is generally accepted that both systems work according to a solution–diffusion mechanism, where separation performance is defined by the affinity between the polymeric membrane and the separated species. However, due to an extraordinary and interconnected free volume, the performance of some polymeric materials, such as PIM (polymeric intrinsic microporous), respond to pore-flow transport and separation can be explained by molecular sieving. In particular, for organic solvent dehydration, the ideal polymeric membrane may be a rigid-chain polymer that acts as a molecular sieve (diffusion-selectivity) and contains active groups that are capable of some interactions with water, i.e., ion-dipole or hydrogen bonding, (solubility-selectivity) [1].

Among the currently used materials, aromatic polyamide (PA) membranes are promising candidates. The application of PALS denoted a sub-nano free volume pores in PA membranes [2], and, therefore, the transport may be described by size exclusion (molecular sieving), solubility differences (solution–diffusion), and Knudsen diffusivity in the local spaces (free volume pores) of the membrane. These membranes present excellent resistance to organic solvents, as well as high selectivity across a wide range of concentrations [3–8]. However, they also present a low permeation flux due to a limited free volume and a low degree of water solubility [9,10].

In this sense, a feasible membrane morphology improvement to enhance the permeation flux of PA membranes without sacrificing the separation factor is the so-called thin-film composite (TFC) PA membrane, which consists of a thin PA top and a porous support layer (often polysulfone and non-woven polyester). Today, most commercial TFC membranes are formed *in-situ* by interfacial polymerization, which involves the fast reaction of an aromatic polyamine, such as m-phenylenediamine (MPD), with aromatic polyacyl halides (for example, trimesoyl chloride (TMC)). [11]. This method is well known to be adequate for the preparation

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of composites with an ultrathin PA active layer for RO. However, only a few researchers have recently reported on the dehydration of alcohol mixtures in PV and/or VP [12–14], by comparison with the use for RO or nanofiltration [15–23]. Besides, membrane pre-treatment of these membranes prior to their use is a very sensitive process due to the extremely thin PA top layer. This procedure usually includes two general steps: (1) cleaning of the membrane surface by a solvent; and, (2) drying of the residual solvent from within the membrane structure. Both processes affect water–polymer and polymer–polymer interactions. When drying the residual solvent from interfacial polymerized RO membranes, shrinkage may occur due to the water-swollen hydrogel that fills the membrane spaces. This layer is hydrated and offers little resistance to water flow, but when the membrane is dried, the disruption of water–polymer interactions turns the gel to a rigid glass, which may lower permeance by reducing water–polymer interactions and/or collapsing the membrane voids [24,25].

In PV, however, because the aqueous alcohol mixture is directly in contact with the PA, a swelling of RO TFC membrane is expected. In general, this softens the polymer and decreases the diffusion resistance to molecules in the feed, which results in lower separation factors. For instance, Zuo et al. [12] recently post-treated TFC PA hollow-fiber membranes with methanol for isopropanol (IPA) dehydration. As a result, total flux increased from 1282 g/(m^2 h) to 1920 g/(m^2 h), while the separation factor dropped from 624 to 349 by comparison with the original membrane state.

As a result, the separation performance of TFC RO membranes may be explained by the balance between two effects: the drying of the water-swollen hydrogel that fills the membrane spaces and the membrane swelling effect, and both depend on the operation temperature. Hence, it must be evaluated on a case-by-case basis.

In our previous study [3], gas permeation tests revealed that the PA separating layer of the RO TFC membranes was not perfectly homogeneous, but rather consisted of a dense matrix and highly permeable regions in a bi-modal structure, in which gases permeated via activated and Knudsen diffusion, respectively, and determined the membrane separation performance in samples dried under three different pre-treatments. These procedures caused shrinkage and swelling processes, removal of residual monomers or additives, and morphological changes that effectively varied membrane properties. Moreover, the operation temperature importantly influenced gas permeance and a maximum He/N$_2$ gas selectivity with a high permeance was achieved at a temperature of 150 °C.

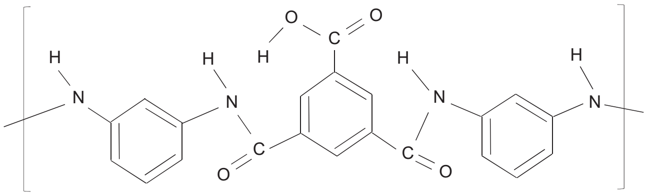

Fig. 1. Chemical structure of the PA layer in a TFC membrane.

The present work had three objectives: (1) to test the separation performance of TFC RO membranes for IPA dehydration in PV and VP systems; (2) to determine if either drying pre-treatment or an increase in operation temperature can result in performance enhancements; and, (3) to fundamentally elucidate the transport of molecules through the dense and highly permeable regions of the inhomogeneous TFC PA layer. The results are discussed in terms of permeance and separation factors achieved, and are compared with the data previously obtained for single-gas permeation through the same TFC membranes.

2. Experimental

2.1. Materials

Three commercial RO membranes kindly provided by Niito Denko (Japan) were applied for IPA dehydration: SWC5 (Seawater), ESPA2 (energy saving RO membrane) and CPA5 (high-rejection RO membrane). They consist of a thin-film-composite membrane comprising top skin aromatic PA layer, a middle microporous polysulfone and a bottom polyethylene terephthalate (PET) layer. The chemical structure of the PA layer and the potential hydrogen-bonding sites are shown in Fig. 1.

All high-purity chemicals of analytical grade applied in this study were provided by Sigma Aldrich (Japan).

2.2. Membrane pre-treatment methods

Commercial PA membranes were tested immediately after the following common pre-treatments, as described in our previous work [3]. The basic steps in these procedures are as follow:

- *Room temperature-oven* (*RTO*): Membranes were washed several times in a pure-water bath, then dried at room temperature for 24 h, and finally placed in an oven at 120 °C for 30 min.
- *Ethanol–hexane* (*EH*): Membranes were washed several times in a pure-water bath, then immersed in ethanol for 5 min and afterwards soaked in a hexane bath for 1 min. Finally, the solvent was evaporated at room temperature for 15 min.
- *Freeze drying* (*FD*): Membranes were washed several times in a pure-water bath, then immersed in 50, 75, 90, 95, and 100 wt% t-butanol aqueous solutions for 15 min. Then, membrane coupons were placed in pure t-butanol in freeze-dried equipment under vacuum (gradually decreasing from 533 to 0.4 Pa) for 2 h.

2.3. PV and VP experiments

Membrane samples (2.21 cm^2) were tested using an apparatus equipped with a flat membrane module set inside a forced-air-flow oven and a vacuum pump as schematically represented in Fig. 2.

Experiments were performed using a 90 wt% IPA aqueous solution. The permeate side was kept under vacuum to reduce

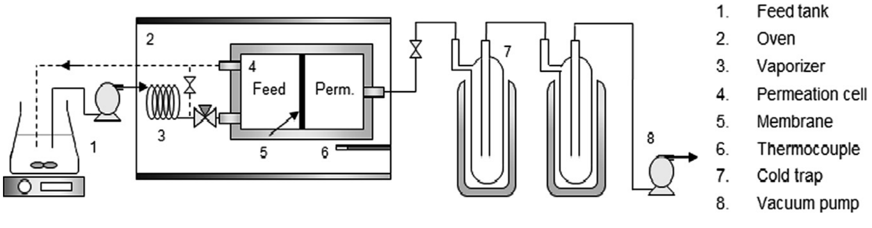

Fig. 2. Schematic drawing of the experimental setup.