Permselectivities of Aromatic Polyamide Membranes for Aqueous Alcohol Mixtures in Pervaporation

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Abstract: The separation of water/alcohol mixtures was carried out using a series of fluorine-containing aromatic polyamide membranes. Aromatic polyamides were prepared by direct polycondensation of fluorine-containing diamine (2,2-bis[4-(4-aminophenoxo)phenyl]hexafluoropropane, BAPPH) and various aromatic diacids. The separation factor toward water increased when the feed ethanol concentration was increased. The solubility of ethanol in aromatic polyamide membrane is higher than that of the water, but the diffusivity of water across the membrane is higher than that of alcohols. A separation factor of 83 and a permeation rate of 262 g/m²h with a 90 wt% feed ethanol concentration at 25 °C was obtained.

Keywords: Pervaporation, BAPPH, Aromatic polyamide, Solubility, Membrane.

Introduction

Recently, the separation of binary liquid mixtures by pervaporation has been receiving increasing attention. Because of its special characteristics, pervaporation separation has been widely considered as an alternative separation process for azeotropic mixtures, close-boiling point mixtures and isomers [1-4]. A hybrid distillation pervaporation process developed by Air Products & Chemicals has been shown to be significantly cost and energy saving [5]. Other experiments coupling pervaporation and a distillation process were reported by Chamberlain et al. on commercial membrane supplied by GFT in order to recover the different alcohols [6]. Among numerous applications of the pervaporation technique, the dehydration of ethanol is the earliest and best developed practical process. Pervaporation polymer membrane used for the dehydration of aqueous ethanol solutions should be highly water permselective. Proceeding from the viewpoint of mentioned above, many researchers have focused their attention on improving the membrane separation performance, including: ⁶⁰Co γ-ray irradiation or plasma grafting, polymer blending, chemical grafting, and preparing new polymers [7-12]. However, the efficiency of the pervaporation process depends mainly on the intrinsic properties of the polymers used to prepare the membrane. Thus, synthesizing new polymeric materials with good pervaporation performance is exceedingly important. In this article, a series of fluorine-containing aromatic polyamides was prepared. Aromatic polyamide is an appropriate material for pervaporation because of its attractive chemical, physical, and mechanical properties. Various aromatic diacids, such as isophthalic acid, 5-tert-butyl isophthalic acid and 2,6-naphthalic acid were introduced to the backbone of aromatic polyamide for studying the effect of the inhibition of polymer packing density on specific volume. Additionally, the effect of feed compositions, degree of swelling, feed solution temperature, and the molecular length of feed compound on the pervaporation performances were investigated.

Experimental

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1. Monomer synthesis

The monomer of 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, BAPPH, was prepared by following the procedures described in [13]. The final product was a brown-white crystal (mp. 162 ~ 163 °C) in 98% yield. Elemental analysis results of C_{27}H_{20}N_{2}O_{2}F_{6} agreed well with theoretical values. Caled: C, 62.55%; H, 3.89%; N, 5.40%. Found: C, 62.56%; H, 3.84%; N, 5.39%.

2. Polymerization

Three types of fluorine-containing polyamides were prepared by direct polymerization of BAPPH with various aromatic dicarboxylic acids using triphenyl phosphite and pyridine in N-methyl-2-pyrrolidinone (NMP). The synthesis procedure was carried out as described previously [14]. The IR spectrum exhibited absorption at 3314 cm^{-1} (N–H) and 1659 cm^{-1} (C=O). A typical example of polycondensation is shown in Scheme 1.

3. Measurement

Elemental analysis was performed using a Perkin-Elmer model 240 CHN analyzer. X-ray diffractograms were recorded with a D5000 diffractometer (Philips Model PW1710). Inherent viscosities were determined at 30 °C in a solution of DMSO with a concentration of 0.5 g/dL by using a Cannon-Fenske viscometer. The $M_n$ (number-average molecular weight) and the $M_w$ (weight-average molecular weight) were measured by size-exclusion chromatography (GPC) in THF at 30 °C.

4. Membrane preparation

The membrane was prepared from a casting solution containing 10 wt% of fluorine-containing aromatic polyamide in DMAc. The membrane was formed by casting the solution on a glass plate to a predetermined thickness. The glass plate was then heated at 70 °C for 40 min. It was found that the average thickness of the membranes was about 20 ~ 25 μm.

5. Pervaporation experiment

A traditional pervaporation process was used [15]. The effective membrane area was 10.2 cm² and the feed temperature studied was in the range of 25 ~ 55 °C. The permeation rate was determined by measuring the weight of the permeate. The compositions of the feed solutions, the permeates, and the solutions adsorbed in the membrane were measured by gas chromatography (GC China Chromatography 8700T). The separation factor water/alcohol $\alpha_{\text{water/alcohol}}$ was calculated from:

$$\alpha_{\text{water/alcohol}} = \frac{Y_{\text{water}}/Y_{\text{alcohol}}}{X_{\text{water}}/X_{\text{ethanol}}}$$

where $X_{\text{water}}$, $X_{\text{alcohol}}$ and $Y_{\text{water}}$, $Y_{\text{alcohol}}$ are the weight fraction of water and ethanol in the feed and permeate, respectively.

6. Sorption measurement

The membranes were immersed in ethanol-water mixtures for 24 h at room temperature. They were subsequently blotted between tissue paper to remove excess solvent and placed in the left tube of a twin tube set-up. The system was evacuated while the left tube was heated with hot water and the right tube was cooled in liquid nitrogen. The composition of the condensed liquid in the right tube was determined by GC.