Toward improved hydrophilicity of polymers of intrinsic microporosity for pervaporation dehydration of ethylene glycol

Mengmeng Chen, Xinmei Wu, Faizal Soyekwo, Qiugen Zhang *, Ruixue Lv, Aimei Zhu, Qinglin Liu

Department of Chemical and Biochemical Engineering, Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

ABSTRACT

Polymers of intrinsic microporosity (PIMs) are attractive materials and have drawn increasing attention in separation membranes. Here carboxy groups are introduced to improve hydrophilicity of the PIMs membranes for pervaporation dehydration of ethylene glycol (EG). The resulting carboxylated PIM–1 (cPIM–1) membranes have adjustable carboxylation degree of up to 0.94. Carboxylation produces many small diffusion channels and greatly improves the membrane hydrophilicity that increases linearly with the carboxylation degree. The membranes show excellent pervaporation performances that depend on the membrane hydrophilicity. The fluxes and permeance greatly increase and likewise the separation factor and water selectivity linearly increase with the hydrophilicity. Compared with other membranes, the cPIM–1 membranes show the high flux. Typically, the cPIM–1 membrane with the carboxylation degree of 0.94 has a total permeation flux of 13.68 kg μm m^{-2} h^{-1} and separation factor of 75.92 in the dehydration of the 80 wt% EG mixture at 30 °C. The cPIM–1 presents a wide application in the pervaporation dehydration of organics.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Pervaporation is an energy-efficient separation technology and has been widely used in separation of liquid mixtures, especially for azeotropes and close boiling point liquid mixtures [1–3]. Conventionally, the applications of pervaporation can be classified into three major categories thus; dehydration of aqueous organic mixtures, removal of trace volatile organic compounds from aqueous solution and separation of organic-organic solvent mixtures [4–6]. Of those, organic dehydration was the first to be established in industry and remains the main application of pervaporation [7]. Presently, most of the polymer membranes used in dehydration of aqueous organic mixtures are hydrophilic membranes, such as poly(vinyl alcohol) and chitosan [8,9]. However, the strong interaction between water molecules and the highly hydrophilic polymers results in the high swelling degree of the membranes. In addition the permeation flux of common polymer membrane are considerably low due to the compact microstructure [10]. Therefore, membranes with anti-swelling, high permeation flux and selectivity are highly desired in the pervaporation dehydration of organics.

Ethylene glycol (EG) is an intermediate in the production of polymers like polyethylene glycol and polyester [11,12]. Currently, EG is mainly produced from the hydrolysis of ethylene oxide and direct synthesis from syngas [13,14]. Water-EG and methanol-EG mixtures are inevitably generated in the production process, thus it's imperative to remove water and methanol from EG solutions in order to obtain pure EG product. Conventional distillation for the removal of EG has proved to be very expensive as high-pressure steam is required for a reboiler due to the high boiling point of EG (198 °C) [11]. Meanwhile, pervaporation dehydration of alcohols as the successful process in the chemical industry represents an alternative and has great potential in the production of highly-pure EG [15]. Whereas, some polymer membranes with good pervaporation performances have been successfully prepared to separate water-EG mixtures, their permeation fluxes are still low for typical industrial production. For example, the surface cross-linked chitosan membranes exhibits a moderate separation factor of 141 and a low flux of 0.560 kg μm m^{-2} h^{-1} in the pervaporation of water (10 wt%)-EG mixtures at 30 °C [16]. Hence, the development of polymer membranes with high permeation flux in the removal of water from the EG solution requires further exploration.

Polymers of intrinsic microporosity (PIMs), synthesized from contorted monomers and of great rigidity, have drawn much attention in various fields, such as gas separation, hydrogen storage and

---

* Corresponding author.
   E-mail address: qgzhang@xmu.edu.cn (Q. Zhang).

homogeneous catalysis [17–19]. As a typical example of PIMs, PIM–1 shows great potential in many membrane separation processes due to its high specific surface, excellent chemical stability and easy processability [20–22]. Several reports that have investigated the pervaporation performance of PIM–1 membrane in the removal of volatile organic compounds from aqueous solutions, exhibits high fluxes due to its porosity and high hydrophobicity [23–26]. In our previous work, the PIM–1 membrane was prepared and used to separate water- and methanol-EG mixtures by pervaporation [27]. The PIM–1 membranes displays high flux in the separation of both water- and methanol-EG mixtures due to its microporosity. However, the water selectivity is low due to the hydrophobicity of PIM–1 membrane, which results in the weak interaction between water molecules and the membrane. Therefore, it was the objective of this study to examine the possibility of improving the hydrophilicity of PIM–1 membrane so as to strengthen the interaction between water molecules and PIM–1 membrane.

In the present work, the hydrophilicity of PIM–1 membrane was improved by converting the nitrile group into the carboxyl group. The resulting carboxylated PIM–1 (cPIM–1) membranes were used for the pervaporation separation of water-EG mixtures, and characterized in details by instruments, such as Fourier transform infrared spectroscopy (FT-IR), elemental analysis, X-ray diffraction (XRD), scanning electron microscope (SEM), and water contact angle. The membrane hydrophilicity was controlled by adjusting the PIM–1's carboxylation degree. Furthermore, the effects of the membrane hydrophilicity on the solubility and diffusion processes was carefully studied during the pervaporation of water-EG mixtures.

2. Experimental

2.1. Materials

5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (TTSBI) and 2,3,5,6-tetrafluoroterephthalonitrile (DCTB) were purchased from *Sigma–Aldrich*, and were purified by re-crystallization and vacuum sublimation respectively. Potassium carbonate was

obtained from *Shanghai Chemical Reagent Store* (Shanghai, China) and dried for 24 h under vacuum at 120 °C. EG, ethanol, sodium hydroxide, and other chemicals of analytical grade were also obtained from *Shanghai Chemical Reagent Store* (Shanghai, China) and used without further purification.

2.2. Preparation of cPIM–1 membranes

As described in our previous work, PIM–1 was synthesized by a condensation polymerization with potassium carbonate as catalyst, in which the reaction take place between the groups "—OH" and "—F" in the monomers TTSBI and DCTB respectively [27]. The as-synthesized PIM–1 powder with Mw 65 kDa was dissolved in chloroform to form a bright yellow solution containing 2 wt% PIM–1. The solution was then filtered using a 0.45 μm cut-off syringe filter and cast onto a Teflon holder. The solvent was allowed to evaporate at 30 °C for 3 days, resulting in the formation of the PIM–1 membrane that was further dried under vacuum at 100 °C for 24 h.

The carboxylated PIM–1 (cPIM–1) was prepared by base hydrolysis of the nitrile group of PIM–1, as shown in Scheme 1 [28–31]. The as-prepared PIM–1 membrane was boiled in a 20 wt% sodium hydroxide solution (water:ethanol = 1:1) at 120 °C for 1–5 h. After which, it was washed with deionized water, followed by boiling in water with the addition of hydrochloric acid (pH 4–5) at 120 °C for 1 h. Finally, the cPIM–1 membranes with different carboxylation degree were obtained after drying under vacuum at 120 °C for 12 h.

2.3. Membrane characterizations

The membrane structure was characterized by FT–IR (Nicolet Avatar 330, *Thermo Electron Corporation*, USA), which records in the range of 1000–4000 cm^{-1} with an accumulation of 32 scans. The element composition of the membranes was analyzed by elemental analyzer (Vario EL III, *Elementar Analysen Syetem GmbH*, Germany). The morphologies were observed by SEM (S-4800, *Hitachi*, Japan), and the physical structure was analyzed by XRD (X'pert PRO, *Panalytical*, Holland). The thermostability of the
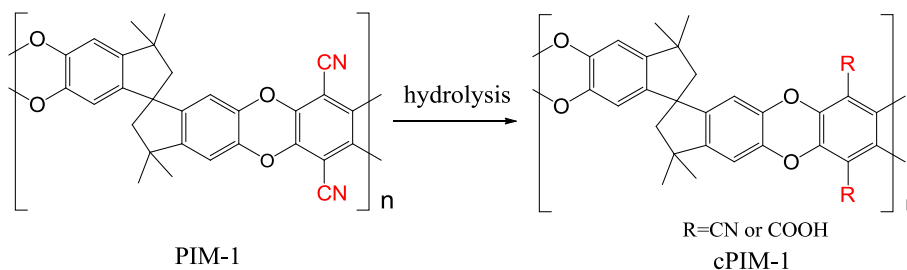
Scheme 1. Hydrolysis reaction from PIM–1 to cPIM–1.