THE INFLUENCE OF ION CROSSLINKING ON SEPARATION PERFORMANCE OF ASYMMETRIC SULFONATE POLYSULFONE MEMBRANES IN PERVAPORATION

Shih-Hsiung Chen[1,*], Rey-May Liou[1], Chi-Yu Shih[2], Cheng-Hsien Huang[1], Cheng-Lee Lai[1] Mu-Ya Hung[1], and Juin-Yih Lai[3]

1. Department of environmental engineering and Science, Chia-Nan University of pharmacy and science, Tainan, 717, Taiwan
2. Department of chemical and materials engineering, chengshiu university, Kaohsiung county, 833, Taiwan
3. Research & development center for membrane technology and department of chemical engineering, Chung Yuan University, Chung Li, 320, Taiwan

ABSTRACT

The ion crosslinking sulfonate polysulfones (Na-PSF, Mg-PSF, Al-PSF) were prepared by sulfonation technology and they were applied to prepare as asymmetric membranes for dehydrating of water/ethanol mixtures by pervaporation. The degree of ion crosslink showed a strongly influence on both of the membrane formation path ways in phase inverse process and the separation performance of pervaporation membranes with different cation crosslinking in casting solution. The cation crosslinking of polysufone enhanced the viscosity of casting solution and formed a denser skin layer during the wet phase inverse process. The swelling and hydrophilic properties measurements found that the water selective membranes can be formed by increased the ion crosslinking in polymer membrane and then the degree of swelling of modified membranes decreased with increasing the cation content in polymer matrix. The effect of water selectivity of ion crosslinking membranes on the water uptake of membranes were verified by the sorption test with 90% ethanol/water mixture at 25℃.

INTRODUCTION

The polyelectrolyte membranes were widely investigated and showed a good separation performance (1-3) for dehydration ethanol mixtures. That works also indicated that the separation performance of polyelectrolyte membranes were strongly dependent on the charge density of the membrane. Alginate is another candidate material to prepare polyelectrolyte membrane. The dense alginate membranes showed an outstanding performance for the dehydration of organic solution. Due to the limitation of membrane formation and ion crosslinking structure in alginate membranes, the high density ion crosslink significantly decreased the permeation flux of permeate in those membranes. Although the ion crosslinking well enhanced the permselectivity of membranes (4-9), the weak mechanical properties and stability of alginate membrane are still a problem for pervaporation application. Therefore, the asymmetric ion exchange sulfonate membranes were prepared by wet phase inverse method in this study. The pervaporation characteristics as well as the temperature dependence, feed composition, and degree of sodium substitution were discussed for the dehydration performance of modified membranes.

Experimental
Materials

Udel ® Polysulfone P-3500 was obtained from Amoco Performance Products, and Merck Chemical Co. supplied chlorosulfonic acid and ethanol.

Membrane preparation

The slufonated polysulfone was prepared from the direct sulfonation method by adding chlorosulfonic acid. The sulfonation of polysulfone was achieved by means of chorosulfonic acid. The sodium sulfonate polysulfone was prepared by pour the sulfonated polymer solution into 0.05N NaOH ethanol solution to obtain the sodium exchanged sulfonate polymer. After polymer was precipitated in ethanol solution over night, the sodium sulfonated polysulfone was washed by distilled water for at least three times until no pH change was observed in the water bath. The sodium sulfonated polysulfone were dry in vacuum oven over night at 60℃. The casting solutions of asymmetric membranes were prepared by dissolving 24wt% of sodium sufonate polymer in NMP. After the casting solution was well stirred for 24 h and then stopped stirring for removing the bubble air in the casting solution. The polymer solution was casted onto a glass plate to a predetermined thickness of 350 μm by using a Gardner Knife.

Pervaporation experiment

A traditional pervaporation process was used. In pervaporation, the feed solution of 90 wt% ethanol was in direct contact with the membrane and was kept at 25℃. The effective membrane area was 10.2 cm². The compositions of the feed solution permeate, and solution adsorbed in the membranes was measured by gas chromatography (GC, China Chromatography). The separation factor, $\alpha_{A/B}$, was calculated by the formula:

$$\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$$

where X_A, X_B and Y_A, Y_B are the weight fractions of A and B in the feed and permeate, respectively (A being the more permeative species).

Sorption measurements

The membranes were immersed in the ethanol-water mixture for 24 hours at 25℃. They were subsequently blotted between tissue papers to remove the excess solvent and placed in the left half of a twin tube set-up. The system was evacuated while the tube