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Effect of sulfonation on characterizations and morphology of asymmetric Polycarbonate Membranes by wet phase inversion method

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ABSTRACT

This paper presents an original approach to study the dependence of the sulfonation conditions of polycarbonate membranes on the separation performance and their influence on the membrane morphology. The degrees of sulfonation of polycarbonate membranes can be prepared by various dosages of sulfonic acid in the sulfonation process. The degree of sulfonation and polymer concentration in casting solution showed the significant effect on the membrane formation in wet phase inverse process. It was found that the permselectivity of sulfonate asymmetric polycarbonate membranes showed a strongly enhancement by increasing the degree of sulfonation. Both of the permeation rate and permselectivity increased with increasing the degree of sulfonation of polycarbonate membranes. It was found that the separation performances of the sulfonation membranes were dominated by the enhancement of hydrophilic property of modified membranes.

INTRODUCTION

Separation by pervaporation is included dehydration water from water/organic mixture and organic-organic separation. The dehydration membrane attracted much more attentions for their industrial applications. Mostly water-permselective pervaporation membranes focus on separation based on solubility selectivity rather than mobility selectivity. Generally, high water-permselective membranes[1-5] can be achieved by increasing either the sorption ratio of water to ethanol or the diffusion ratio of water to ethanol. Introduction hydrophilic moiety into the polymer chain to enhance the water selectivity is the one of the effective methods to achieve this attempt. However, much more hydrophilic moiety in membrane usually accompanied with excessive swelling and loss its selectivity [6-7].

Direct sulfonation was a powerful method, which can be used to simultaneously render these polymers proton conductive as well as hydrophilic in nature. Sulfonation reaction was a popular modification technique for improving the hydrophilicity of polymer [12-15]. For the purpose of improving separation performance of PC membrane, this study prepared sulfonated polycarbonate membranes for dehydration of water/ethanol mixture. The sulfonic groups were induced onto PC backbone by using direct sulfonation method[8] improving the hydrophilic properties of polymer. The relationship between the degree of sulfonation and hydrophilic properties of sulfonated membrane were discussed by measuring the permeation and swelling properties. The analyzed of sorption components in sulfonated membranes were also made for clarifying the selective permeate during pervaporation process.

Experimental

Materials

Polycarbonate (Uplion S-2000)(M_W =28000) was supplied by Mitsubishi Gas Chemical Co. Chloroform and Merck Chemical Co. supplied chlorosulfonic acid and ethanol.

Membrane preparation

The slufonated polycarbonate was prepared from the direct sulfonation method by adding chlorosulfonic acid. The casting solutions of polycarbonate membranes were prepared by dissolving 24wt% sufonated polymer in chloroform. 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 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 cm^2. 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 XA , 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 was heated with hot water for 30 minutes and the right tube was cooled in liquid nitrogen. The composition of the condensed liquid with the right tube was determined by G.C. The separation factor of sorption was calculated by:

$$\alpha_{sorp}=(Yw/Ye)/(Xw/Xe)$$