일반강연 2-7

Dehydration of Pyridine Aqueous Solution through Poly(acrylonitrile-co-4-styrene sulfonic acid) Membranes by Pervaporation

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Introduction

There has been many attempts to improve the membrane performance using pervaporation processes[1-3]. They are 1) blending polymer with the high flux and one with high selectivity, 2) an incorporation of functional groups interacting with permeants into a membrane through copolymerization or modification, 3) composite membrane or asymmetric membrane structure with a thin skin layer which acts as a selective layer. Among them, a polymeric membrane containing ion complex group receives an extensive attention recently because ionic complex is known to activate the water transport through ion-dipole interaction. It is especially advantageous in the separation of organic-water system.

We applied the ideas of the activation of water transport through ion-dipole. We have reported on the in-situ complex membrane to separate water from aqueous acetic acid and pyridine solution[4-5] based on the simple acid-base theory. Water transport was enhanced through in-situ complex between pyridine moiety in the membrane and the incoming acetic acid in the feed. In this case, catalytic transport mechanism was proposed. In the present study we used pyridine solution as a feed and the sulfonic acid group in the membrane.

Experimental

2.1.Materials

Acrylonitrile(AN, Katayama Chem., Japan) and 4-styrene sodium sulfonate(SS) were used as monomers. Potassium persulfate(Wako Pure Chem., Japan) and conc. HCl(Duksan Chem., Japan) were used as received. Reagent grade benzene (Duksan Chem., Japan), toluene(Junsei Chem., Japan) and dimethylformamide (DMF, Junsei Chem., Japan) were used without further purification. Ethanol and Pyridine were purchased from Junsei Chem.(Japan) and used without further treatment.

2.2. *Synthesis of PAN-SS*

200ml of distilled water, SS and AN were added into a four-necked round flask equipped with mechanical stirrer, thermometer and N_2 inlet tube. The reaction temperature was maintained at 70°C under an N_2 atmosphere. Then, 1.865×10^{-3} mol of potassium persulfate was added into the stirring solution. The copolymerization was continued for two hours to prepare PAN-SS that was precipitated by pouring the copolymer solution into excess 0.1N HCl aqueous solution. PAN-SS was filtered and washed with excess distilled water and toluene to remove residual monomers. For further purification, PAN-SS was dissolved in DMF and reprecipitated in distilled water. Then, PAN-SS was filtered and dried in a vacuum oven at 50°C and 100mmHg for three days. PAN-SS membrane was cast from DMF solution.

Results and discussion

Fig. 1 shows the effect of operating temperature on the dehydration of PAN-SS membrane measured at 56wt% aqueous pyridine solution. This membrane was very highly selective toward water measured from ambient to about 70°C. In each case, water flux(J_w) showed similar values with total flux(J) but pyridine flux(J_p) was extremely low, suggesting a high separation efficiency of this membrane. The basic explanation behind the good separation toward water using the current PAN-SS/pyridine solution lies in the same idea, that is, in-situ complexation. A membrane forming an in-situ complex between one component in the membrane and the incoming component from the feed interact with water molecules in the feed and build an ion-dipole interaction, which acts as a major role in the transport.

In general, α ranges between 33.9 and 355.7 and J between about 278.9 and 183.2 g/m^{2}hr.

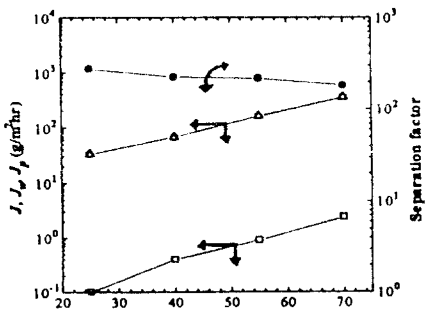

Fig. 1. Effect of operating temperature on separation factor(●), total flux(○), benzene flux(Δ)and cyclohexane flux(□). Pyridine concentration in feed was 56wt%.