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Pervaporation Properties for an Azeotrope of Ethanol/Water through Organic-Inorganic Hybrid Membranes from Quaternized Chitosan with Tetraethoxysilane

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In the field of membrane separation technique, the membrane structures must be designed to develop membranes with high permselectivity and permeability. In this study, high water-permselective organic-inorganic hybrid membranes were prepared as pervaporation membranes for separating EtOH/H_2O azeotrope. We selected quaternized chitosan (*q*-Chito) as an organic component and tetraethoxysilane (TEOS) as an inorganic component for preparing the organic-inorganic hybrid membranes. In the separation of EtOH/H_2O azeotrope by pervaporation, the effects of TEOS content on water-permselectivity of the *q*-Chito/TEOS hybrid membranes were investigated. The hybrid membranes with a TEOS content of less than 45mol% showed the higher water-permselectivity than the *q*-Chito membrane. This is due to that the swelling of the membranes was depressed by formation of cross-linking structure. However, introduction of excess TEOS led to larger swelling of the hybrid membranes. This is why the water-permselectivity of the hybrid membranes with a TEOS content of more than 45mol% was lower than that of the *q*-Chito membrane in pervaporation.
Key words: pervaporation, water-permselectivity, organic-inorganic hybrid, membrane, quaternized chitosan

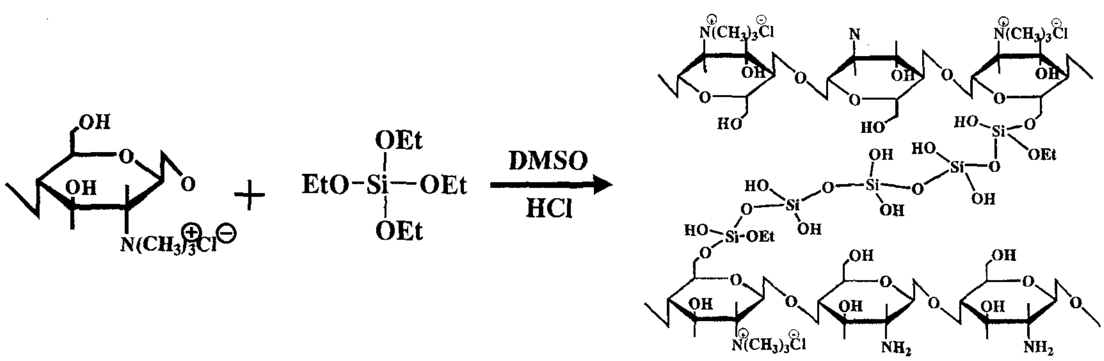
1. INTRODUCTION

Membrane separation techniques attract much attention in many fields, since they have high efficiency with energy savings. Pervaporation is one of the membrane separation techniques for multicomponent solutions[1-5]. Especially, pervaporation is a promising technique for separation of azeotropes, such as 96.5wt% ethanol aqueous solution and 88wt% acetone aqueous solution, due to an energy conservative system [5-9].

Many materials have been investigated as pervaporation membranes for separation of EtOH/H_2O azeotrope to develop the dehydration systems with high performance[6-9]. Chitosan, which is an amino polysaccharide, has potential applications as a promising material for developing hydrophilic membranes because it has many reactive amino and hydroxyl groups. We have reported that chemical modifications of chitosan, such as cross-linking and *N*-alkylation, can enhance the water-permselectivity of the membranes for an EtOH/H_2O azeotrope[9-11]. In particular, quaternized chitosan (*q*-Chito) membranes prepared by *N*-alkylation of chitosan showed the high water-permselectivity in the separation of EtOH/H_2O by pervaporation. However, swelling of the *q*-Chito membranes in the feed solution prevented their water-permselectivity from being strongly enhanced by the quaternization. Therefore, controlling physical structures of the *q*-Chito membranes is required to improve their water-permselectivity in pervaporation.

Organic-inorganic hybrid materials are expected from many fields as the next generation materials since they have both functions of organic compounds and stability of inorganic compounds. Previously, we prepared organic-inorganic hybrid membranes by sol-gel reactions of various polymers and tetraethoxysilane (TEOS) to improve the permselectivity of polymer membranes[12].

In this study, *q*-Chito/TEOS hybrid membranes were



Scheme 1. Sol-gel reaction of *q*-Chito with TEOS.

prepared as pervaporation membranes for the separation of the EtOH/H_2O azeotrope. The separation characteristics of their membranes for EtOH/H_2O azeotrope in pervaporation were discussed from the viewpoint of their physical and chemical structures.

2. EXPERIMENTAL SECTION

2.1 Preparation of *q*-Chito/TEOS Hybrid Membranes by Sol-Gel Methods.

The organic-inorganic hybrid membranes were prepared by sol-gel reaction of *q*-Chito with TEOS (scheme 1) as follows: *q*-Chito was dissolved in DMSO by stirring for 12 hour at 80 °C. TEOS was added to the *q*-Chito solution following stirring for 30 hours at room temperature. An aqueous HCl solution as catalyst was homogeneously mixed with the solution containing *q*-Chito and TEOS. The resultant solution was cast on a Teflon plate, and then dried for 40 hours at 80 °C. The resultant membranes were transparent and defect-free. The hybrid membranes with various TEOS contents had strength enough to be used for separation of EtOH/H_2O in pervaporation.

2.2 Permeation Measurements.

Pervaporation experiments were carried out for the separation of the EtOH/H_2O azeotrope using apparatus shown in Figure 1 under the following conditions: Permeation temperature, 40 °C; Pressure on the permeated side, 1×10^{-2} Torr. The effective membrane area was 13.8 cm^2. An aqueous solution of 96.5wt% ethanol was used as a feed solution. The ethanol concentrations of the feed solution and permeate were determined by gas chromatography (Shimadzu, GC-9A) equipped with a thermal conductivity detector.

The normalized permeation rate was determined to evaluate permeability of the membranes, since the thickness of the hybrid membranes ranged from 70μm to 100μm. The normalized permeation rate was obtained from weight of the permeate collected into a U-tube, effective membrane area, membrane thickness and permeation time.

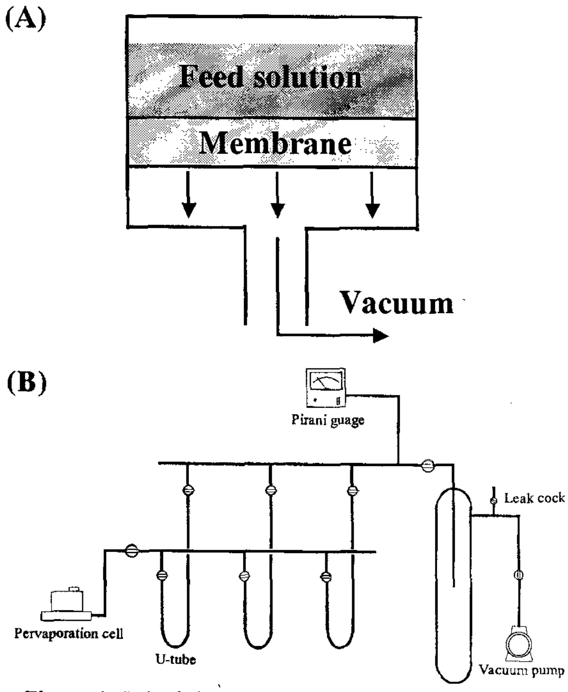


Figure 1. Principle of pervaporation (A) and models of pervaporation system (B). Leak cock controls the pressure, permeate is trapped in U-tube by cooling with liquid N_2

2.3 Determination of Degree of Swelling and Ethanol Concentration in Membranes.

The *q*-Chito/TEOS hybrid membranes were immersed in the EtOH/H_2O azeotrope in sealed vessel at 40 °C. When swelling of the membranes reached equilibrium, the membranes were take out of the vessel and wiped quickly with a filter, and weighed. The degree of swelling of the membranes was determined from eq.(1),

$$\text{Degree of swelling} = W_s / W_d \quad (1)$$

where W_s is the weigh of the membrane swollen in the feed solution and W_d is the weight of dried membrane.

The solution sorbed in the swollen membranes was desorbed by vacuum and collected in a cold trap. The ethanol concentration of the solution sorbed in the swollen membranes was determined with gas chromatography.

3. RESULTS AND DISCUSSION

3.1 Pervaporation Characteristics of *q*-Chito/TEOS Hybrid Membranes.

Previously, we reported the effects of quaternization of *q*-Chito membranes on their water-permselectivity in the separation of EtOH/H_2O azeotrope[9]. The water-permselectivity of the *q*-Chito membranes was higher than that of chitosan membrane. Furthermore, both the water-permselectivity and permeability were enhanced by an increase in degree of quaternization. The high water-permselectivity of the *q*-Chito membranes is due to the very high hydrophilicity of the membranes. However, the increase in permeability by quaternization was strongly dependent upon the swelling of the membrane in the EtOH/H_2O azeotrope. Generally, the

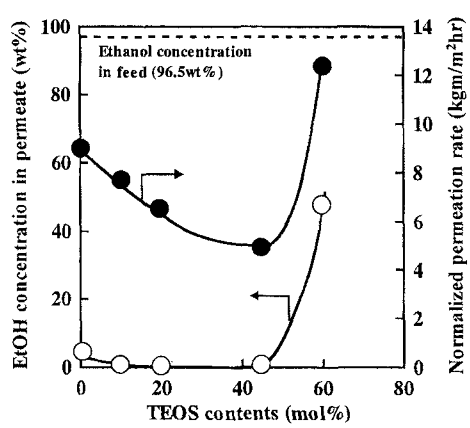


Figure 2. Effects of the TEOS content on the ethanol concentration in the permeate (○) and normalized permeation rate (●) for an aqueous solution of 96.5wt% ethanol through q-Chito/TEOS hybrid membranes by PV.

swelling of a membrane results in a decrease in its water-permselectivity. Therefore, the swelling of membranes must be depressed to enhance the water-permselectivity of the *q*-Chito membranes. In this study, our strategy is to depress the swelling of the *q*-Chtito membranes by introducing TEOS as an inorganic component.

Figure 2 shows the effects of TEOS contents on the ethanol concentration in the permeate and normalized permeation rate of EtOH/H_2O azeotrope through the *q*-Chito/TEOS hybrid membranes. Ethanol concentration in the permeate through the hybrid membranes was much lower than that of feed solution. This means that the *q*-Chito/TEOS hybrid membranes have high water-permselectivity in the separation of EtOH/H_2O azeotrope. The ethanol concentration in the permeate through the hybrid membranes decreased with an increase in TEOS contents of less than 45mol%. However, the introduction of excess TEOS made the water-permselectivity of the hybrid membranes very low. In addition, the normalized permeation rate through the hybrid membranes decreased when their water-permselectivity was improved by introducing TEOS.

3.2 Structures in *q*-Chito/TEOS Hybrid Membranes.

Generally, permeation mechanism of liquid organic mixtures in pervaporation is based on the solution-diffusion theory[4]. The ethanol concentration sorbed into membrane and degree of swelling of membrane are strongly correlated with the solution and diffusion process during pervaporation. The degree of swelling of membranes and ethanol concentration in the solution sorbed into membranes were investigated to clarify the permeation mechanism of the *q*-Chito/TESO hybrid membranes.

Figure 3 shows the effects of TEOS content on the ethanol concentration of the solution sorbed into the membranes and degree of swelling of membranes immersed in a EtOH/H_2O azeotrope. The ethanol concentration in the *q*-Chito/TEOS hybrid membranes decreased with an increase in TEOS content of less than 45mol%. This indicates that the addition of TEOS into the *q*-Chito membranes can enhance the preferential sorption of water into the membranes. On the other hand, the degree of swelling of the *q*-Chito/TEOS hybrid membranes decreased with an increase in TEOS contents of less than 45mol%. This is due to the formation of cross-linking structure in the *q*-Chito/TEOS hybrid membranes. At a TEOS content over 60mol%, however, the degree of swelling of the hybrid membranes increased.

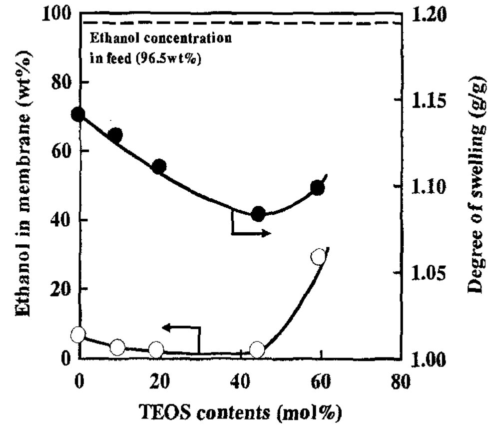


Figure 3. Effects of the TEOS content on the ethanol concentration in the *q*-Chito/TEOS hybrid membrane (○) and the degree of swelling of the membranes immersed in an aqueous ethanol solution(●).

To characterize the cross-linking structures of the *q*-Chito/TEOS hybrid membranes, their glass-transition temperatures (T_gs) were measured by differential scanning calorimetry (DSC). T_gs of the *q*-Chito/TEOS hybrid membranes increased linearly with an increase in TEOS content. The increase in T_gs suggests that formation of cross-linking structure in the hybrid membranes inhibits the mobility of *q*-Chito polymer chains.

In addition, to clarify the effect of TEOS content on the degree of swelling of the *q*-Chito/TEOS hybrid membranes, their physical structures were observed by transmission electron microscope (TEM). It is apparent from the TEM images of the *q*-Chito/TEOS hybrid membranes that the introduction of excess TEOS resulted in aggregation of TEOS in the hybrid membranes. This suggests that the self-reaction between TEOS may be more predominant than that of TEOS with *q*-Chito in the hybrid membranes with excess TEOS. Therefore, the swelling of membranes was promoted by addition of excess TEOS due to the heterogeneous structures. As the result, the water-permselectivity of the hybrid membrane with a TEOS content of 60mol% became low and its

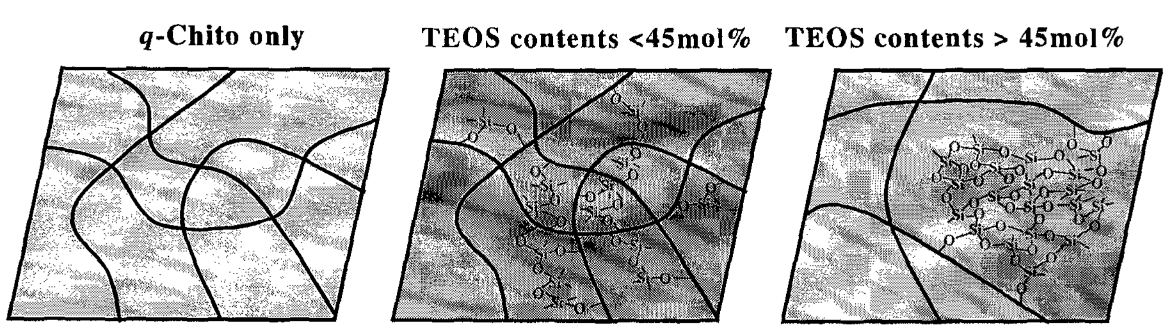


Figure.4 Tentative model of structures of the *q*-Chito/TEOS hybrid membranes with various TEOS contents.

permeability increased because of their swelling in the feed solution.

3.3 Permeation Mechanism of EtOH/H_2O through *q*-Chito/TEOS Hybrid Membranes.

In general, permeation and separation of organic liquid mixtures through membranes by pervaporation can be discussed on the basis of the solution-diffusion theory. Therefore, the permeation and separation characteristics of the *q*-Chito/TEOS hybrid membranes can be explained as follow: The decrease in the ethanol concentration of solution sorbed into membranes with a TEOS content of less than 45mol% reveals that the relative solubility of water is enhanced in the solution process. Contrary, the increase in ethanol concentration in the hybrid membranes with a TEOS content of 60mol% indicates that the relative solubility of water is reduced.

On the other hands, as the swelling of the hybrid membranes is depressed by formation of cross-linking structure with TEOS in the membrane, the diffusivity of both water and ethanol is reduced. Then, the diffusion of ethanol is inhibited more strongly than water because of its bigger molecular size. As the results, the water-permselectivity of the hybrid membranes also increases in the diffusion process. In addition, Figure 3 demonstrates that the ethanol concentration in the hybrid membranes is similar to that in permeates shown in Figure 2. Therefore, the sorption process may govern the water-permselectivity of the hybrid membranes more preferentially than the diffusion process. Consequently, the *q*-Chito/TEOS hybrid membranes exhibit high water-permselectivity in the separation of EtOH/H_2O by pervaporation due to high hydrophilicity and efficient cross-linking structures.

4. CONCLUSION

The *q*-Chito/TEOS organic-inorganic hybrid membranes with various TEOS contents were prepared by sol-gel reaction. The permeation and separation for EtOH/H_2O azeotrope through the hybrid membranes in pervaporation were studied. The hybrid membranes with a TEOS content of less than 45mol% showed high water-permselectivity for EtOH/H_2O azeotrope. This is because the swelling of the hybrid membranes was depressed by formation of cross-linking structure with TEOS. However, as the introduction of excess TEOS caused the swelling of the hybrid membranes, the water-permselectivity of the hybrid membrane with a TEOS content of 60mol% became low. The TEM images of the *q*-Chito/TEOS hybrid membranes demonstrated that TEOS was heterogeneously aggregated in the hybrid membrane with a TEOS content of 60mol%. This means that the self-reaction among TEOSs was more predominant than that of TEOS with *q*-Chito in the hybrid membranes with excess TEOS. Therefore, the swelling of membranes was caused by addition of excess TEOS due to the heterogeneous structures. In this study, we revealed that high water-permselective membranes can be designed by hybridization of *q*-Chito as an organic component and TEOS as an inorganic component using sol-gel reaction

5. REFERENCE

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