

Dehydration Performance of Alcohol from Biomass Fermentation by Various Chitosan Membranes

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Abstract

In this study, quaternized chitosan (q-Chito) derivative membranes of three types, which are q-Chito membranes cross-linked with diethylene glycol diglycidil ether (DEDEGE), q-Chito membranes cross-linked with polyethylene oxydiglycolic acid (PEO acid), and q-Chito membranes cross-linked with tetraethoxysilane (TEOS), were prepared, and the characteristics of permeation and separation for an EtOH/H₂O azeotrope during pervaporation or evapomeation were investigated.

In the q-Chito/DEDEGE membranes, the permeation rate decreased and the water permselectivity increased, with increasing DEDEGE content. In the q-Chito/PEO acid membranes, a q-Chito/PEO acid membrane prepared from an equimolar ratio of carboxylate groups in the PEO acid versus quaternized ammonium groups in the q-Chito showed a maximum water permselectivity without lowering permeation rate. In the q-Chito/TEOS membranes, a q-Chito/TEOS membrane with 20 mol% TEOS content showed extremely high water permselectivity and relatively high permeation rate. The above results are discussed from the viewpoint of chemical and physical structure of the membrane.

Introduction

Ethanol (EtOH) concentration produced by biomass fermentation is about 10 wt%. This aqueous ethanol solution is generally concentrated by distillation. However, its azeotrope (96.5 wt%) cannot be concentrated further by distillation. Pervaporation and evapomeation in membrane separation techniques are very effective for the separation of azeotropes, and can yield high energy savings and great efficiency. To steer a success to such a system, improvement of the membranes for removal of water in an EtOH/H₂O azeotrope is strongly required.

Chitin and chitosan have been receiving much attention in many different areas (Skjak-Break *et al.*, 1989; and Uragami *et al.*, 2001). Chitosan can be used as a separation material for coagulants (Hashimoto, 1986), adsorbents (Sakaguchi *et al.*, 1982; Choi, 1990; and Kurita *et al.*, 1979) and membranes (Uragami, 1998). Hydrophilic chitosan membranes showed high water permselectivity (Uragami *et al.*, 1989; Uragami, 1990; Uragami *et al.*, 1993; Mochizuki *et al.*, 1989; Feng *et al.*, 1996;

Wang *et al.*, 1996; and Ghazali *et al.*, 1997) for aqueous alcohol solutions during pervaporation and evapomeation (Uragami *et al.*, 1989; Uragami *et al.*, 1990; and Uragami *et al.*, 1993). Chemical modifications such as cross-linking (Uragami *et al.*, 1993; and Uragami *et al.*, 1994) and *N*-alkylation. (Uragami *et al.*, 1997) enhanced the water permselectivity for aqueous alcohol solutions.

In this study, in order to obtain highly water permselective membranes for an EtOH/H₂O azeotrope for pervaporation and evapomeation, quaternized chitosan (q-Chito) was selected as a membrane material. Q-Chito derivative membranes of three types, which are q-Chito membranes cross-linked with diethylene glycol diglycidil ether, q-Chito membranes cross-linked with polyethylene oxydiglycolic acid, and q-Chito membranes cross-linked with tetraethoxysilane, were prepared, and permeation and separation characteristics for an EtOH/H₂O azeotrope of these cross-linked q-Chito membranes during pervaporation or evapomeation were investigated.

Experimental

Materials

Chitosan, which has 100% deacetylation and an average molecular weight of 3×10^5 – 4×10^5 , was supplied by Koyo Chemical Co. Ltd. Japan. Diethylene glycol diglycidyl ether (DEGDGE), produced by Nagase Sangyo Co. Ltd., polyethylene oxydiglycolic acid (PEO acid), which has a molecular weight of 4000, was from Kawaken Chemical Co. Ltd., and tetraethoxysilane (TEOS), purchased from Shinetsu Chemical Co. Ltd., were used as a cross-linker of the membranes. All other reagents and solvents used in this study were supplied by commercial sources.

Preparation of Membrane

Q-Chito/DEGDGE membranes were made by pouring an aqueous solution of 1 wt% q-Chito at 18% quaternization containing appropriate desired amount of DEGDGE onto a rimed glass plate treated with silicone oil, and allowing water to evaporate at 60°C for 6 h in an oven. Q-Chito/PEO acid membranes were prepared by coating mixtures with a desired amount of aqueous 2wt% q-Chito at 21% quaternization plus the desired amount of an aqueous solution of sodium PEO acid onto the porous poly (ether sulfone) (PES) support membrane and allowing water to evaporate at 60°C for 2 h in an oven and then drying under reduced pressure. Q-Chito/TEOS membranes were prepared by the sol-gel reaction of q-Chito with TEOS as follows: q-Chito was dissolved in DMSO by stirring for 12 h at 80°C and TEOS was added to the q-Chito solution at room temperature, and then this mixed solution was stirred for 30 h. An aqueous HCl solution as a catalyst was homogeneously mixed with the above mixed solution containing q-Chito at 18% quaternization and TEOS. The q-Chito/TEOS hybrid membranes were prepared by pouring the casting solution onto Teflon plates, and then allowing the solvent to evaporate completely at 80°C for 40 h.

Permeation measurements

Pervaporation (Miyata *et al.*, 1995; Miyata *et al.*, 1996; Miyata *et al.*, 1996; Miyata *et al.*, 1997; Uragami *et al.*, 1999; Miyata *et al.*, 1999; Miyata *et al.*, 2000; Uragami *et al.*, 1999; Uragami *et al.*, 2001; and Miyata *et al.*, 2001) and evapomeation (Uragami *et al.*, 1989; and Uragami *et al.*, 1989) experiments were carried out using the apparatus described in previous studies (Uragami

et al., 1997; Uragami *et al.*, 1986; Miyata *et al.*, 1995; Miyata *et al.*, 1996; Miyata *et al.*, 1996; Miyata *et al.*, 1997; Uragami *et al.*, 1999; Miyata *et al.*, 1999; Miyata *et al.*, 2000; and Uragami *et al.*, 1999) under the following conditions: permeation temperature, 40°C; pressure on the permeated side, 1×10^{-2} Torr. The effective membrane area was 13.8 cm². An aqueous solution of 96.5 wt% ethanol was used as a feed solution. The permeate was collected in a U-tube at liquid nitrogen temperature. The permeation rate (kg/(m² h)) for an EtOH/H₂O azeotrope during pervaporation and evapomeation was determined from the weight (kg) of permeate collected in a cold trap, the permeation time (h), and the effective membrane area (m²).

The separation factor, $\alpha_{\text{sepH}_2\text{O}/\text{EtOH}}$, during pervaporation and evapomeation was calculated from Eq. (1),

$$\alpha_{\text{sepH}_2\text{O}/\text{EtOH}} = (P_{\text{H}_2\text{O}}/P_{\text{EtOH}})/(F_{\text{H}_2\text{O}}/F_{\text{EtOH}}) \quad (1)$$

where $F_{\text{H}_2\text{O}}$ and F_{EtOH} , $P_{\text{H}_2\text{O}}$ and P_{EtOH} are the weight fractions of water and ethanol in feed solution and the permeate, respectively.

Membrane Density

The densities of the q-Chito/DEGDGE, q-Chito/PEO acid, and q-Chito/TEOS membranes were measured by the flotation method (Nakamae *et al.*, 1991) using a mixture of benzene and carbon tetrachloride at 40°C.

Degree of Swelling

The q-Chito/DEGDGE, q-Chito/PEO acid, and q-Chito/TEOS membranes were completely dried under reduced pressure at 40°C and weighed. These dried membranes were exposed to a vapor of EtOH/H₂O azeotrope (96.5 wt% ethanol) in a sealed vessel at 40°C until an equilibrium was reached. The membranes were removed from the vessel, wiped quickly with filter paper, and weighed. The degree of swelling of the membrane (DS) was determined from Eq. (2):

$$DS = W_s/W_d \quad (2)$$

where W_d and W_s are the weights of the dried membrane and the swollen membrane in the feed vapor, respectively.

Measurement of Contact Angle

The contact angles for methylene iodide on the surface of the q-Chito/DEDGE, q-Chito/PEO acid membranes, and for chloroform on the surface of the q-Chito/TEOS membranes were measured by a contact angle meter (Erma Model G-1) at 25°C. The contact angle, θ , was calculated from Eq. (3): (Miyata *et al.*, 2001)

$$\theta = \cos^{-1}\{(\cos \theta_a + \cos \theta_r)/2\} \quad (3)$$

where θ_a and θ_r are the advancing contact angle and the receding contact angle, respectively.

Results and Discussion

Permeation and Separation Characteristics of q-Chito/DEDGE Membranes

The effects of the DEDGE content on the permeation rate and the separation factor for water permselectivity of the q-Chito/DEDGE membranes for an EtOH/H₂O azeotrope during evaporation are shown in Figure 1. As can be seen from Figure 1, with increasing DEDGE content the permeation rate decreased, but the separation factor for water permselectivity increased remarkably.

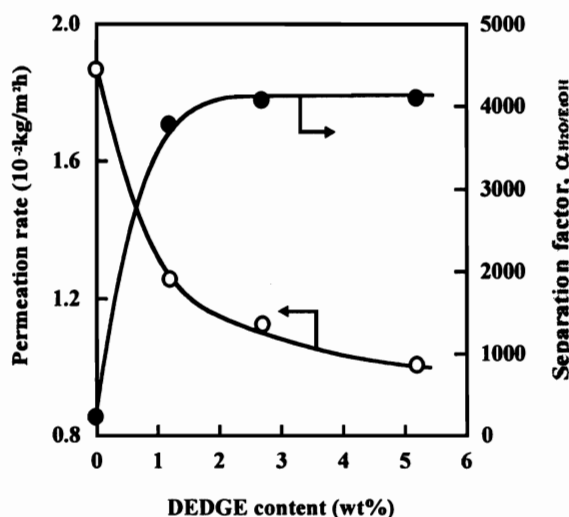


Figure 1. Effects of the DEDGE content on the permeation rate (○) and the separation factor for water permselectivity (●) for an EtOH/H₂O azeotrope through the q-Chito/DEDGE membranes during evaporation. Q-Chito:18% quaternization.

The effect of the DEDGE content on the contact angle for methylene iodide on the surface of the q-Chito/DEDGE membranes is shown in Figure 2. The contact angles of the q-Chito membranes support an increase in the separation factor for water permselectivity with an increase in the degree of hydrophilicity of the q-Chito membrane. As can be seen in Figure 2, as the chitosan is quaternized, the contact angles for methylene iodide of the q-Chito membranes increased slightly, but did not change significantly with the DEDGE content. This result suggests that the cross-linking of the q-Chito membrane with DEDGE cannot improve the hydrophilicity on the surface of the q-Chito membrane. Consequently, the increase in the separation factor for water permselectivity in Figure 1 was not due to the hydrophilicity of the q-Chito/DEDGE membrane, but depended on the difference in the diffusivity of the permeating molecules in the q-Chito/DEDGE membrane.

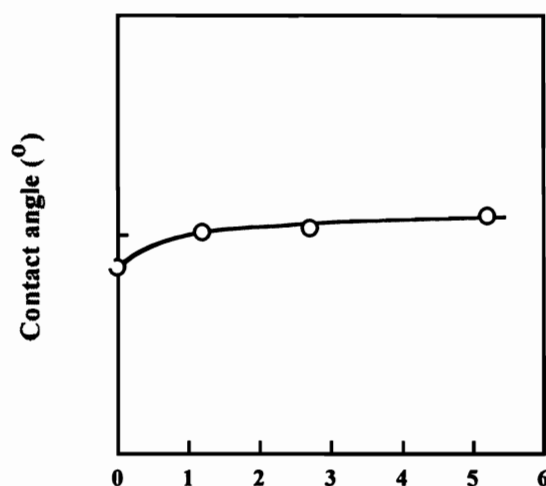


Figure 2. Effect of the DEDGE content on the contact angle for methylene iodide on the surface of the q-Chito/DEDGE membranes.

In Figure 3, the degree of swelling and the density of the q-Chito/DEDGE membrane for the feed vapor (96.5 wt% ethanol) are shown. The degree of swelling of the q-Chito/DEDGE membrane decreased slightly, but the density of the q-Chito/DEDGE membrane increased slightly, upon increasing the DEDGE content. From the above results, it is suggested that the decrease in the permeation rate in Figure 1 was due to a decrease in the diffusivity of the permeating

molecules, based on an increase in the density of the membrane with DEDGE content. The increase in the separation factor can be attributed to an increase in the diffusion selectivity of the water molecule.

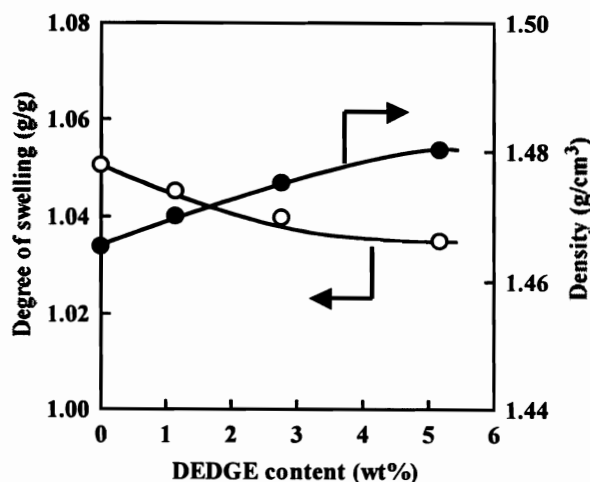


Figure 3. Degree of swelling (○) and the density (●) of the q-Chito/DEDGE membranes as a function of the DEDGE content.

The effects of the permeation temperature on the permeation rate and the separation factor for an EtOH/H₂O azeotrope through the q-Chito/DEDGE membranes are shown in Figure 4. The permeation rate increased with an increase in the permeation temperature, and the separation factors for water permselectivity were remarkably high. The permeation rates in the q-Chito/DEDGE membranes were of approximately the same order as that in the q-Chito membrane, but the separation factors in the former were greater by two orders of magnitude as compared to the latter. Cross-linking the q-Chito membrane chains with DEDGE controls the kinetic motion of the membrane matrix. Thus, both a strong interaction between the water molecule and the ammonium group of the q-Chito/DEDGE membrane at high temperatures and the control of the diffusivity of the ethanol molecules resulted in high separation factors for water permselectivity. Therefore, it is presumed that the water permselectivity of the q-Chito/DEDGE membrane was dependent on both high sorption and diffusion selectivities at a relatively high permeation temperature.

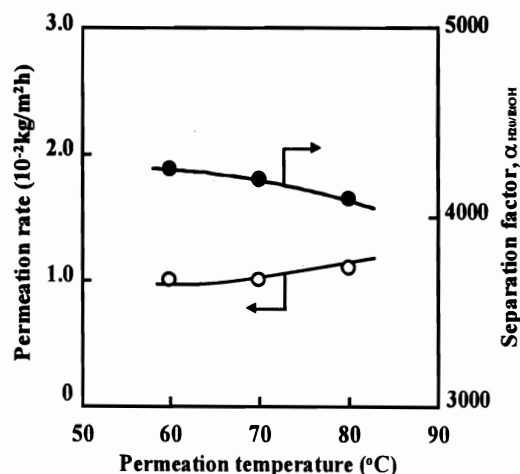


Figure 4. Permeation rate (○) and the separation factor for water permselectivity (●) of an EtOH/H₂O azeotrope through a q-Chito/DEDGE membrane as a function of the permeation temperature

Permeation and Separation Characteristics of q-Chito/PEO acid Membranes

Figure 5 shows the permeation rate and the separation factor for water permselectivity of an EtOH/H₂O azeotrope through the q-Chito/PEO acid membranes during evaporation, as a function of the molar ratio of the carboxylate groups in PEO acid and the quaternized ammonium groups in q-Chito. The separation factors for water permselectivity were increased by cross-linking the q-Chito with PEO acid, and by cross-linking the q-Chito with PEO acid, and reached a maximum at an equimolar ratio between the carboxylate and ammonium groups. The permeation rates were also affected by the molar ratios of the carboxylate and ammonium groups.

In order to further investigate the permeation and separation characteristics of an EtOH/H₂O azeotrope through the q-Chito/PEO acid membranes from a chemical and physical perspective, we measured the contact angle at the surface of the membrane, the density of the membrane, and the degree of swelling of the membrane.

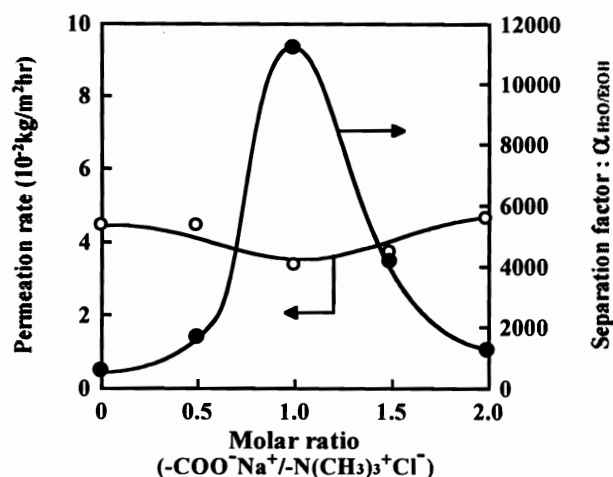


Figure 5. Permeation rate (\circ) and the separation factor for water permselectivity (\bullet) of an EtOH/H₂O an EtOH/H₂O azeotrope through the q-Chito/PEO acid membranes as a function of the molar ratio of the carboxylate groups in PEO acid and the quaternized ammonium groups in q-Chito. PEO acid: molecular weight of 4000

In Figure 6, the effect of the molar ratio of the carboxylate groups and the quaternized ammonium groups on the contact angle for methylene iodide at the surface of the q-Chito/PEO acid membranes is shown. When the q-Chito was cross-linked with PEO acid, the contact angle increased with increasing PEO acid content in the q-Chito/PEO acid membranes. This result suggests that the membrane surface gradually became hydrophilic with the introduction of a hydrophilic cross-linker, PEO acid, and that the hydrophilicity of the membrane increased with an increase in the PEO acid content.

In Figure 7, the effect of the molar ratio of the carboxylate groups and the quaternized ammonium groups on the membrane density is shown. The membrane density decreased with increasing PEO acid content. This decrease in the membrane density can be explained as follows. When the PEO acid molecule used as the cross-linker was introduced between the chitosan molecule chains, the spaces between their chains become expanded, and consequently, the membrane structure becomes looser.

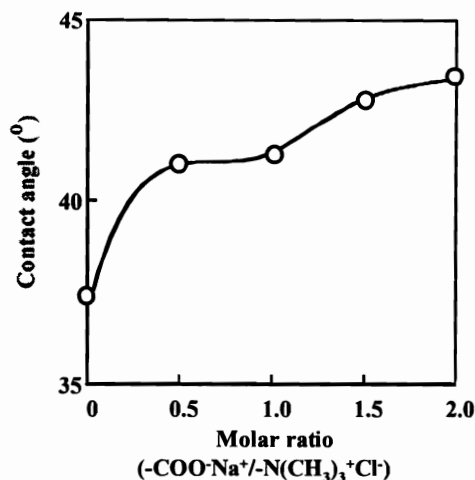


Figure 6. Effect of the molar ratio of the carboxylate groups and the quaternized ammonium groups on the contact angle for methylene iodide on the surface of the q-Chito/PEO acid membranes

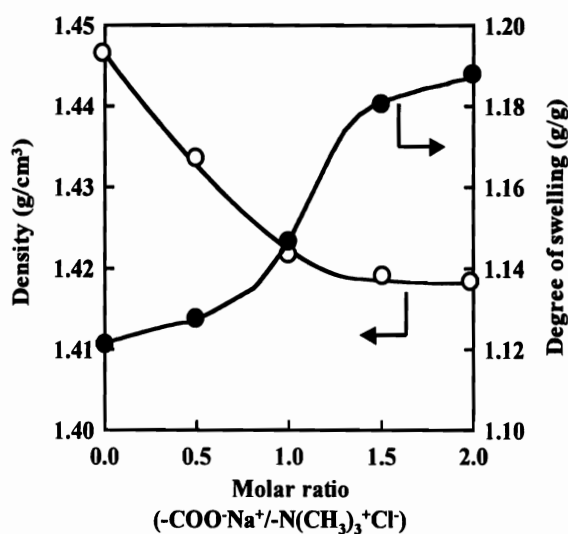


Figure 7. Membrane density and degree of swelling of the q-Chito/PEO acid membranes as a function of the molar ratio of the carboxylate groups and the quaternized ammonium groups

Figure 7 also includes the degree of swelling of the q-Chito/PEO acid membrane as a function of the molar ratio of the carboxylate groups and the quaternized ammonium groups. The degree of swelling of the membrane increased with an increase in the molar ratio of the carboxylate and ammonium groups. This increase in the degree of

swelling of the membrane can be attributed to the fact that water was preferentially absorbed into the *q*-Chito/PEO acid membrane due to the increased hydrophilicity of the membrane. This contention is also supported by the results for the contact angle and membrane density measurements.

Based on the above results, the fact that the separation factors for water permselectivity in Figure 5 were maximized at an equimolar ratio of the carboxylate and quaternized ammonium groups can be explained as follows. At a molar ratio less than an equimolar ratio between the carboxylate and quaternized ammonium groups, as can be seen from the contact angle measurements, the hydrophilicity of the *q*-Chito/PEO acid membranes increased with increasing PEO acid content. Consequently, the water permselectivity of the membrane also increased. On the other hand, *q*-Chito/PEO acid membranes with an increased equimolar ratio of carboxylate to quaternized ammonium groups became more hydrophilic. However, the membrane density decreased remarkably. Accordingly, the separation performance also decreased due to the more open structure of the *q*-Chito/PEO acid membrane. These results suggest that the permeation and separation characteristics for an EtOH/H₂O azeotrope through the *q*-Chito/PEO acid membranes were significantly influenced by physical and chemical properties of the membrane. Therefore, *q*-Chito/PEO acid membranes with an equimolar ratio of carboxylate and ammonium groups had an optimal structure, and demonstrated the best separation for an EtOH/H₂O azeotrope.

Permeation and Separation Characteristics of *q*-Chito/TEOS Membranes

In Figure 8, the normalized permeation rate and the ethanol concentration in the permeate of an EtOH/H₂O azeotrope through the *q*-Chito/TEOS membranes during pervaporation are shown as a function of the TEOS content in the *q*-Chito/TEOS membranes. The ethanol concentrations in the permeates of all *q*-Chito/TEOS membranes were very low compared to that in the feed solution. These results suggest that the *q*-Chito/TEOS membranes show high water permselectivity. At up to 45 mol% TEOS content in the *q*-Chito/TEOS membranes high water permselectivity was maintained, but it decreased when the TEOS content increased. Especially, in the *q*-Chito/TEOS membrane with at 20 mol% TEOS content, the ethanol could not be detected in the permeate by a gas chromatography. Namely, this result suggests

that ethanol in the feed could be approximately perfectly rejected by this *q*-Chito/TEOS membrane. The normalized permeation rate gradually decreased at up to 45 mol% TEOS content, but increased at over 45 mol%. These results can be due to both the formation of a cross-linked structure and the difference in the cross-linking state.

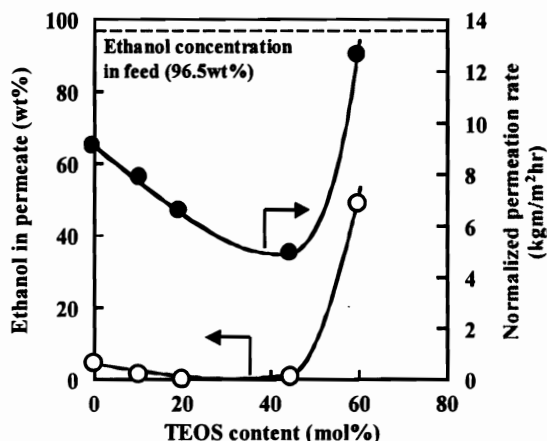


Figure 8. Effects of the TEOS content on the normalized permeation rate (●) and the ethanol concentration in the permeate (○) for an EtOH/H₂O azeotrope through the *q*-Chito/TEOS membranes during pervaporation

In Figure 9, the ethanol concentration absorbed into *q*-Chito/TEOS membranes immersed in an EtOH/H₂O azeotrope and the contact angle for chloroform are shown as a function of the TEOS content in the *q*-Chito/TEOS membrane. The ethanol concentration absorbed into the *q*-Chito/TEOS membranes decreased at up to 45 mol% TEOS content and increased over this TEOS content. The contact angle for chloroform increased with an increase of the TEOS content. This increase in the contact angle for chloroform, which is a hydrophobic solvent suggests that the membrane surface of the *q*-Chito/TEOS membranes became more hydrophilic with increasing TEOS content. The decrease in the ethanol concentration in the *q*-Chito/TEOS membranes with up to 45 mol% of TEOS content is attributed to an improvement in the hydrophilicity of the *q*-Chito/TEOS membrane surface. This suggests that the solubility of water into the *q*-Chito/TEOS membrane is improved by introducing TEOS into the *q*-Chito molecule.

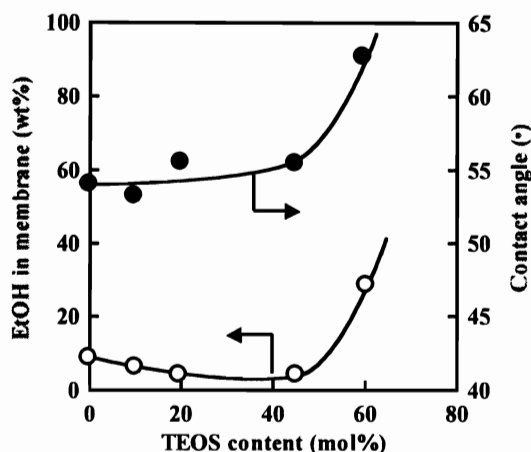


Figure 9. Effects of the TEOS content on the ethanol concentration in the q-Chito/TEOS membranes for an EtOH/H₂O azeotrope and the contact angle for chloroform on the surface of the q-Chito/TEOS membranes

Figure 10 shows the effects of the TEOS content on the membrane density and the degree of swelling of the q-Chito/TEOS membrane. The density of q-Chito/TEOS membrane increased with increasing TEOS content. The degree of swelling of the hybrid membrane decreased with up to 45 mol% TEOS content, but increased at over 45 mol% of TEOS content. This increase in the degree of swelling of the q-Chito/TEOS membrane with the excess TEOS may be due to a lowering of the cross-linking density of the q-Chito/TEOS membrane based on the formation of large cohesive tetrasilanol silane domains.

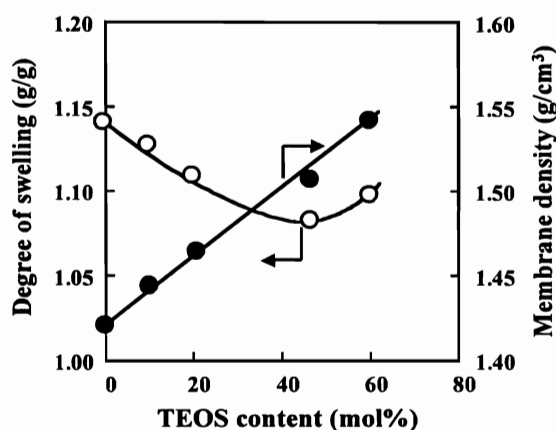


Figure 10. Effects of the TEOS content on the membrane density (○) and the degree of swelling (●) of the q-Chito/TEOS membranes.

On the basis of the above results, we found that both the decrease in the water permselectivity and the increase in the normalized permeation rate at high TEOS content in Figure 8 are related to the increase in the swelling of q-Chito/TEOS membranes due to the decrease in cross-linking density.

Conclusions

Cross-linked q-Chito membranes of three kinds such as q-Chito/DEDGE, q-Chito/PEO acid, and q-Chito/TEOS membranes were prepared for the dehydration of an EtOH/H₂O azeotrope. The permeation and separation characteristics of an EtOH/H₂O azeotrope through these cross-linked q-Chito membranes during pervaporation and evaporation were investigated. The characteristics of permeation and separation of the q-Chito/DEDGE membranes in which with increasing DEDGE content, the permeation rate decreased and the water permselectivity increased, were general results. Those of the q-Chito/PEO acid membranes were very peculiar, i.e., the water permselectivity showed a maximum in a q-Chito/PEO acid membrane prepared from an equimolar ratio of carboxylate groups in the PEO acid versus quaternized ammonium groups in the q-Chito. Those of the q-Chito/TEOS membranes were significantly influenced by the TEOS content. A q-Chito/TEOS membrane with a suitable TEOS content approximate perfectly rejected ethanol in an EtOH/H₂O azeotrope. In this study, we demonstrated that membranes with high water permselectivity can be designed by cross-linking q-Chito with various hydrophilic cross-linkers such as DEDGE, PEO acid, and TEOS, and q-Chito offers potential for the dehydration of an EtOH/H₂O azeotrope.

Acknowledgements

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