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TECHNICAL NOTE

Separation of Water/Ethanol Vapor Mixtures through Chitosan and Crosslinked Chitosan Membranes

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ABSTRACT

The separation of water/ethanol vapor mixtures through chitosan membranes and crosslinked chitosan membranes was studied by means of the vapor permeation technique. The permeation performance was discussed in terms of separation factor and permeation flux. Crosslinking the chitosan membrane by glutaraldehyde enhanced the selectivity. The highest separation factor obtained was 6000 for a crosslinked chitosan membrane with a degree of deacetylation of 100%.

INTRODUCTION

Polysaccharide membranes, such as cellulose and chitosan, have high selectivity for the separation of water/alcohol mixtures (1–4). The membranes prepared from these hydrophilic polymers are permselective to water. Chitosan is obtained by deacetylation of chitin, which is the second most abundant natural polymer after cellulose. As shown in Fig. 1, the chemical structures of chitin and chitosan are similar to cellulose. Varieties of chitin and chitosan applications have been developed recently (e.g., adsorbent, fiber, film). Since chitosan can be dissolved in such dilute acids as formic acid and acetic acid, membranes are easily prepared from chitosan. Chitosan membranes have high water permselectivity and solvent stability. The selectivity and permeability of chitosan membranes

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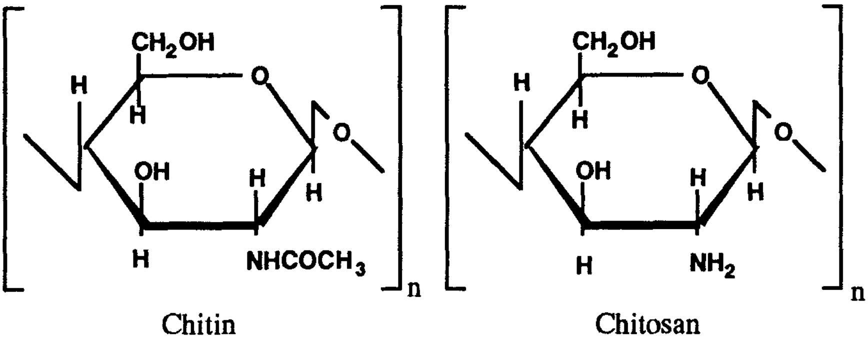

FIG. 1 Chemical structure of chitin and chitosan.

may be influenced by their physical and chemical properties such as crystallinity, degree of deacetylation, and crosslinking. Uragami reported that crosslinking the chitosan membrane enhanced selectivity (3).

Water/alcohol mixtures have been separated by both pervaporation and vapor permeation (evapomeation) (4). Pervaporation is a separation process accompanied by vaporization through membranes from a liquid mixture. Vapor permeation is a separation process of a vapor mixture without direct contact with the liquid feed mixture. The vapor permeation technique is used in this work to avoid swelling the membranes because that might influence the permeation and separation performance.

The objective of this paper is to study the performance of membranes for vapor permeation of water/ethanol mixtures. Chitosan membranes and chitosan membranes crosslinked by glutaraldehyde were prepared. The effects of chemical modification on the selectivity and permeability were evaluated.

EXPERIMENTS

Chitosans with a nominal degree of deacetylation of 70 and 100% were obtained from Katokichi Co. Ltd., Japan. Membranes were prepared by the following procedure developed by Mochizuki et al. (1). Chitosan (0.5 wt%) was dissolved in a 1 wt% acetic acid aqueous solution. The chitosan solution was degassed, filtered, and then cast onto a Petri glass. The casted membrane was dried at 323 K for 8 hours. The membrane was immersed in a 3 wt% sodium hydroxide solution to convert chitosan acetate to chitosan. Finally, the membrane was washed with distilled water and dried at room temperature. A membrane with a thickness of 14 μm was obtained.

The chitosan membrane was further modified to prepare a crosslinked chitosan membrane. A chitosan membrane was crosslinked by glutaraldehyde by immersing it in a glutaraldehyde aqueous solution for 5 minutes. The degree of crosslinking of the membrane was controlled by the glutaraldehyde concentration (10^{-7}–10^{-3} weight fraction).

A schematic of the experimental apparatus for vapor permeation is shown in Fig. 2. The test cell is similar to those developed by Kataoka et al. (5). A feed solution consisting of a water/ethanol mixture in the cell was circulated through a reservoir 0.2×10^{-3} m^3 in volume. A small fan connected to a magnetic stirrer bar was used to agitate the vapor phase to avoid polarization at the membrane surface. The permeated vapor was collected in traps cooled by liquid nitrogen. The experiments were carried out at 323 K at a downstream pressure of 10 kPa. The effective membrane area was 7.1×10^{-4} m^2. The compositions of the feed and the permeate solution were determined by a gas chromatograph (Yanaco G2800, 1 m-long column packed with Porapak Q) equipped with an FID detector.

The separation factor α and the permeation flux Q were calculated by

$$\alpha = x(1 - y)/[y(1 - x)] \tag{1}$$

$$Q\ [\mathrm{kg/m^2 \cdot s \cdot Pa}] = \frac{\text{weight of permeate [kg]}}{(\text{membrane area [m}^2])(\text{permeation time [s]})(\text{pressure difference [Pa]})} \tag{2}$$

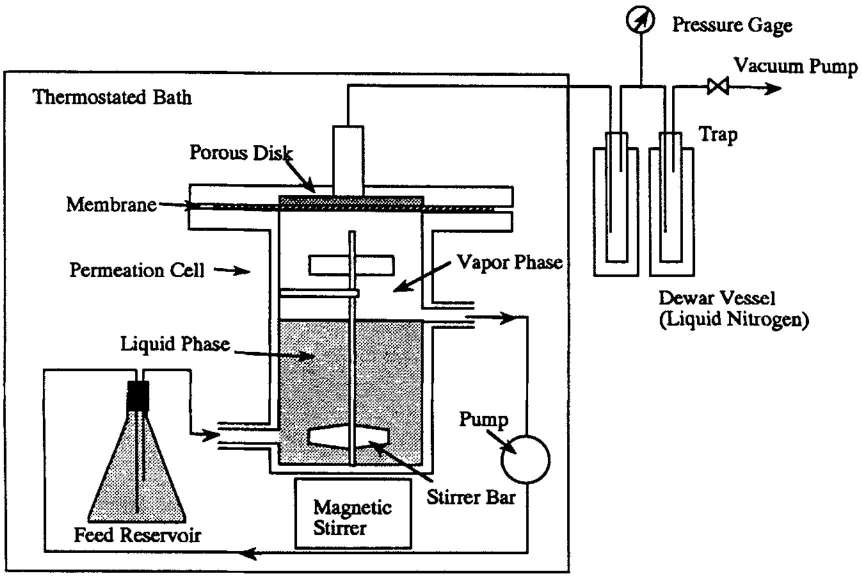

FIG. 2 Experimental apparatus for vapor permeation.

where x and y denote the mole fractions of ethanol in the feed and in the permeate solution, respectively.

RESULTS AND DISCUSSION

Effect of Degree of Deacetylation

The permselectivities are shown in Fig. 3 for two membranes of 70 and 100% degrees of deacetylation at various feed compositions. The separation factor and permeation flux are plotted against ethanol concentration in the feed mixture. Water permeated selectively through the chitosan membrane. The separation factor increased as the ethanol concentration increased in the feed mixture. A separation factor of 10–1000 orders of magnitude was obtained. The permeability decreased at higher ethanol concentrations in the feed mixture, mainly because of less swelling of the membrane. Separation may result from easier permeation of the smaller water molecule as compared to ethanol.

The permeation flux for a membrane with a 70% degree of deacetylation is larger than that of a membrane with a 100% degree of deacetylation. On the other hand, the degree of deacetylation was less influential on the separation factor. The separation factor is higher for a membrane with a 70% degree of deacetylation at lower ethanol concentrations in the feed mixture but this is reversed at higher ethanol compositions. Mochizuki et al. (1) observed that both separation factor and permeation flux are not affected by a degree of deacetylation in the 72–98% range for the feed of a 50/50 ethanol/water mixture because separation occurs only in the amorphous region. The separation factor obtained in this work was independent of the degree of deacetylation as reported by Mochizuki et al. (1).

Effect of Crosslinking

The effect of crosslinking by glutaraldehyde is shown in Fig. 4 as a function of glutaraldehyde concentration, C_{ga}, used in the modification process of the membrane. The permselectivity was measured for the feed of a 50/50 ethanol/water mixture. The permeation flux for water was not affected by crosslinking whereas the permeation flux for ethanol decreased as the glutaraldehyde concentration increased. Consequently, a higher separation factor was observed for the membrane with a higher degree of crosslinking. The degree of crosslinking could not be higher than those used in this work because further crosslinking made the membrane fragile.

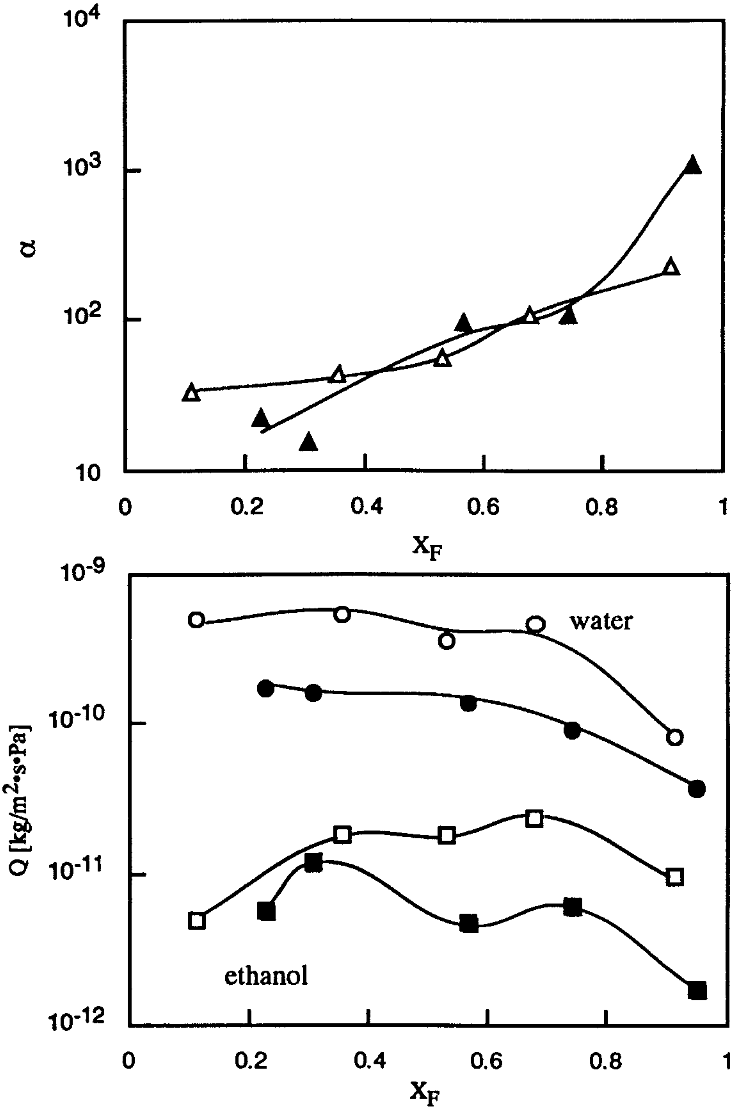

FIG. 3 Effect of degree of deacetylation on the separation factor and permeation flux. Degree of Deacetylation = 70% (○), 100% (●).

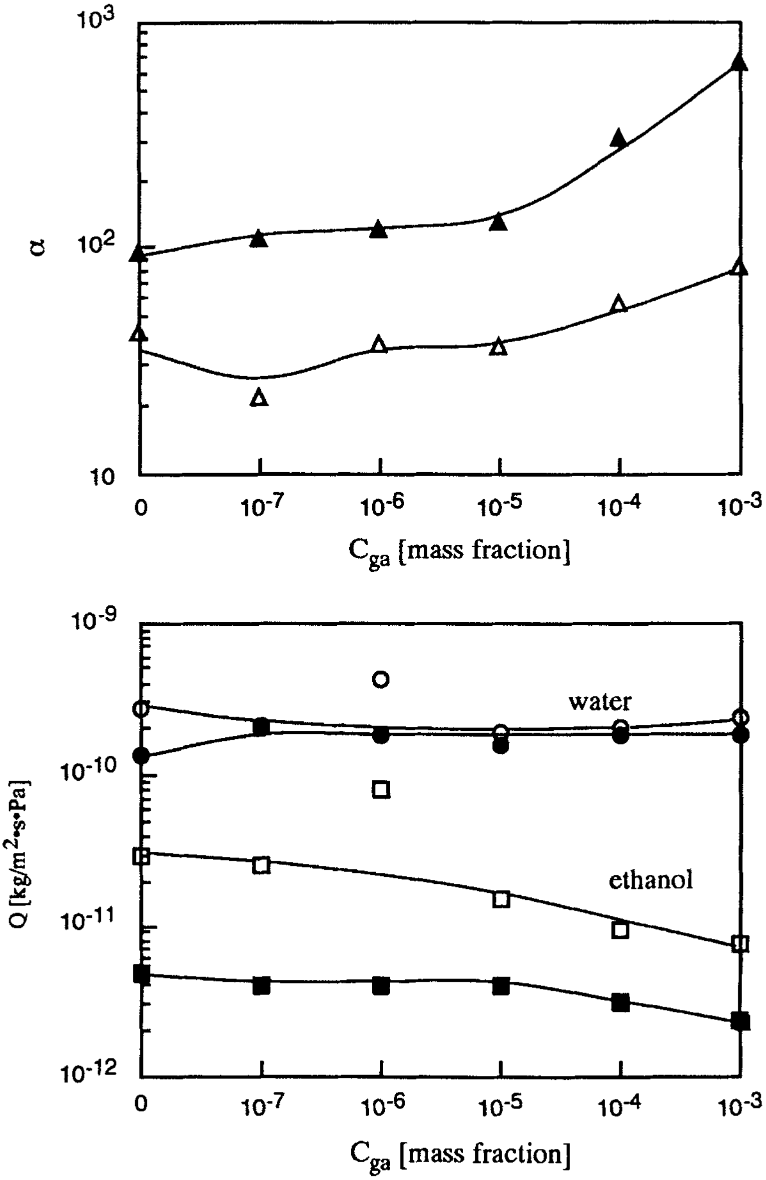

FIG. 4 Effect of glutaraldehyde concentration for crosslinking on the separation factor and permeation flux. Degree of Deacetylation = 70% (○), 100% (●). x_F = 0.5.

The membrane with a 100% degree of deacetylation had higher selectivity for any degree of crosslinking. The difference resulted from the lower permeability of ethanol for the membrane of the higher degree of deacetylation since the permeability of water was almost identical for both membranes. Uragami and Takigawa (3) observed that both the separation factor and the permeation flux increased by crosslinking with glutaraldehyde. Their results were explained by the higher hydrophilicity formed during the crosslinking process.

The permselectivities for various feed mixtures are shown in Fig. 5 for the membrane crosslinked with glutaraldehyde with a degree of deacetylation of 100%. The separation factor reached about 6000 for the feed mixture with 90% ethanol.

Mochizuki et al. (2) observed that chitosan membranes neutralized by polybasic acids such as H_2SO_4 had a higher separation factor than monobasic acids such as HCl. Neutralization by a polybasic acid may produce crosslinking of chitosan molecules. They explained that the enhanced selectivity is due to structural changes of the chitosan molecule, resulting in contraction of the "holes" produced by the thermal motion of chitosan molecules through which the permeant molecule diffuses. Thus, the permeation of larger molecule becomes more restricted by neutralization. As compared with the results of membranes neutralized by a polybasic acid, the permeation of larger molecule is considerably restricted by structural modifications due the crosslinking. The higher the degree of deacetylation of the chitosan membrane is, the higher the degree of crosslinking that could be attained. Therefore, the membrane with a degree of deacetylation of 100% had higher selectivity.

The crosslinking by glutaraldehyde may restrict the permeation of ethanol, which is larger molecule than water, because the mobility of a chitosan molecule in the membrane is restricted by the crosslinking. However, the separation behavior observed in this work cannot be easily understood by only physical restriction. When the membrane became denser by crosslinking, the separation factor must have increased whereas the permeation flux must have decreased. In our study, modification of the membrane increased the separation factor without decreasing the permeation flux. Changes in chemical properties, such as hydrophilicity, together with structural restrictions may have affected the separation behavior.

CONCLUSION

The vapor permeation of a water/ethanol mixture through a chitosan membrane was studied. The effects of the degree of deacetylation of chito-

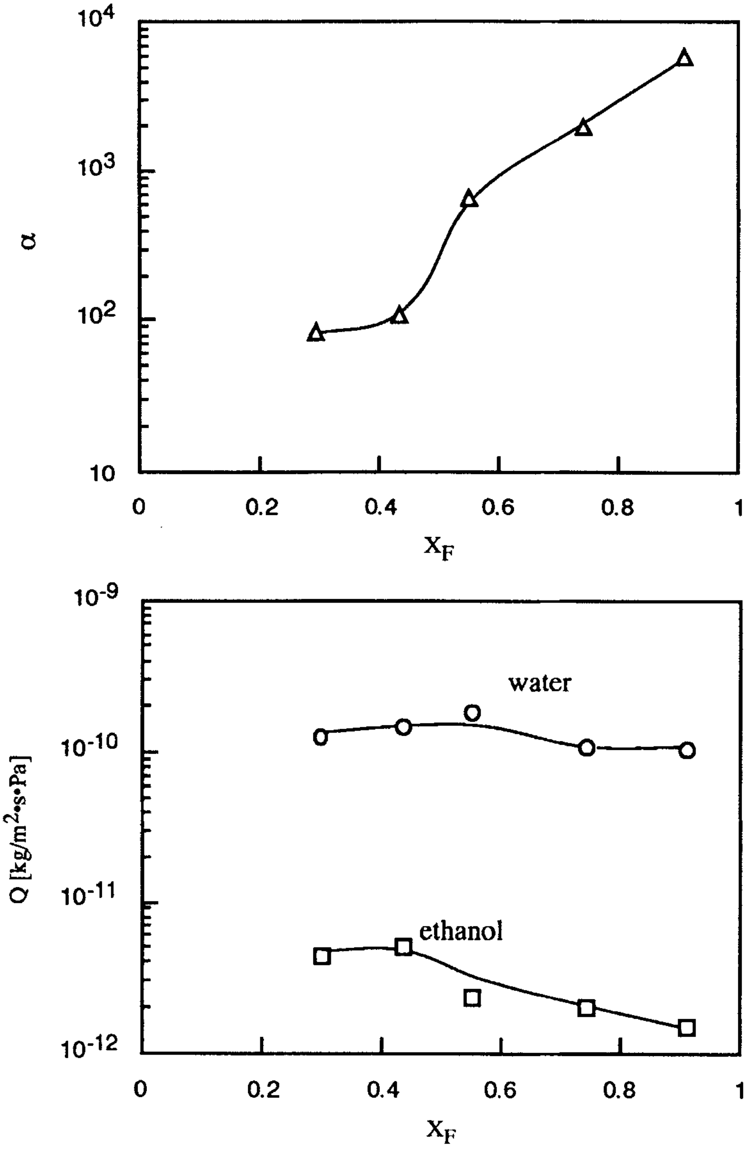

FIG. 5 Separation factor and permeation flux for crosslinked chitosan membrane. Degree of Deacetylation = 100%, C_{ga} = 10^{-3}.

san and crosslinking of the membrane on permselectivity were measured. Crosslinking by glutaraldehyde enhanced the selectivity. The highest selectivity was observed for the membrane with a degree of deacetylation of 100% crosslinked by glutaraldehyde. The increase in selectivity is mainly due to a decrease of ethanol permeation as compared to water permeation.

REFERENCES

1. A. Mochizuki, Y. Sato, H. Ogawara, and S. Yamashita, *J. Appl. Polym. Sci.*, *37*, 3375–3384 (1989).
2. A. Mochizuki, S. Amiya, Y. Sato, H. Ogawara, and S. Yamashita, *Ibid.*, *37*, 3385–3398 (1989).
3. T. Uragami and K. Takigawa, *Polymer*, *31*, 668–672 (1990).
4. T. Uragami and H. Shinomiya, *J. Membr., Sci.*, *74*, 183–191 (1992).
5. T. Kataoka, T. Tsuru, S. Nakao, and S. Kimura, *J. Chem. Eng. Jpn.*, *24*, 334–339 (1991).

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