Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Lee, Young Moo , Park, Ho Bum , Nam, Sang Yong , Won, Jang Mook and Kim, Hoagy(1998) 'Effect of Deacetylation Degree in Chitosan Composite Membranes on Pervaporation Performance', Separation Science and Technology, 33: 9, 1255 — 1269

To link to this Article: DOI: 10.1080/01496399808544982

URL: http://dx.doi.org/10.1080/01496399808544982

SEPARATION SCIENCE AND TECHNOLOGY, 33(9), pp. 1255–1269, 1998

Effect of Deacetylation Degree in Chitosan Composite Membranes on Pervaporation Performance

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ABSTRACT

The effect of the degree of deacetylation in chitosan composite membranes on their pervaporation performance for ethanol dehydration was investigated. The degree of deacetylation of chitosans was measured by using an infrared spectroscopic method and elemental analysis. The chitosan composite membranes were prepared by coating a chitosan solution onto a microporous polyethersulfone membrane with 3–7 nm pore sizes. Then the surface of the top layer (chitosan) of well-dried membranes was crosslinked with sulfuric acid, and pervaporation experiments for binary mixtures (water–ethanol) were carried out at various conditions. In the case of a chitosan membrane with a high degree of deacetylation, the flux increases while the separation factor decreases compared with membranes with a low degree of deacetylation.

Key Words. Pervaporation; Deacetylation of chitosan; Water/ethanol separation; Composite membrane

INTRODUCTION

Currently, many studies on membrane materials for the pervaporation process are being actively carried out. Chitosan, which has good hydrophilicity,

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is especially preferred as a pervaporation membrane materials for dehydration of water/ethylene glycol (1) and water/ethanol (2–5). Chitosan, a derivative of chitin and the second most plentiful natural polymer, has a structure similar to cellulose and is manufactured commercially on a large scale from the outer shells of crustaceans. Because of the widespread availability of purified chitosans, coupled with its ability to be used in a variety of forms including powder, solution, gel, film, fiber, and membrane (6), it is used in many commercial applications.

When chitosan is used as the top layer in composite membranes, it is very effective for the separation of organic mixtures because it is readily prepared in a thin film form and has good mechanical properties and hydrophilicity. Recently, a blend membrane of chitosan and carboxylmethyl cellulose (7) and a membrane of a chitosan layer and a polyacrylonitrile layer (8) having good performance for pervaporation have been reported. Since chitosan can be classified as an anionic permselective membrane, it should show very good selectivity after being crosslinked with appropriate crosslinking agents such as glyoxal, terephthaldehyde, and glutaraldehyde (9).

The earliest studies in separation technology using pervaporation employed dense membranes. However, asymmetric membranes and composite membranes have been vigorously developed in order to increase the permeation rate and to fortify the mechanical properties in reverse osmosis, gas separation, and so on. Most composite membranes have a structure composed of a permselective coating material as a top layer and an ultrafiltration membrane cast onto nonwoven polyester as a supporting layer (10). If coating materials swell excessively, mechanical properties and thermal stability become weak, so mixtures cannot be easily separated. Consequently, composite membranes having a high permeation performance with a very thin top layer need to be developed.

Significant factors to consider in the manufacture of a selective top layer are a membrane material that possesses both high permeability and selectivity and the ability to be deposited as an ultrathin skin layer on a supporting layer surface. The current commercialized GFT pervaporation membrane for dehydration is a composite type (11). Recently, the pervaporation performances of a chitosan membrane modified with aldehydes (12) and of a chitosan-modified sulfonated poly(ethersulfone) as a support (13) have been investigated. In order to fabricate membranes with high flux and high selectivity for use in pervaporation processes, the chemical structures and features of chitosan can be modified.

Chitosan can be characterized in terms of such intrinsic properties as molecular weight, viscosity, degree of deacetylation, stability, etc. For the subsequent deacetylation of chitin to prepare chitosan, a strong aqueous alkali like sodium hydroxide (40–50%) at an elevated temperature (>100°C) is employed. The degree of deacetylation as well as the viscosity of the product varies widely, depending on the conditions of the reaction. Commercial chitosan still contains between 5 and 30% acetyl groups, depending on the origin of the chitin employed and the processing conditions. The chain formation of chitosan reflects the helical structure of the parent polymer chitin to some extent and is also influenced by its origin.

Chitosan readily dissolves in an acid medium, such as aqueous acetic acid, to a solution of very high viscosity. The viscosity depends on the origin of the chitin as well as on the deacetylation procedure. The degree of deacetylation has a pronounced influence on chitosan solubility. The product dissolves in water of approximately neutral pH only in the presence of a large amount of about 50% acetyl groups, due to the amorphous character and therefore highly accessible structure of the solid product, while after deacetylation to a residual acetyl content of 10%, an acid medium, preferentially acetic acid, is required for dissolution of the sample which has, like the original chitin, a crystalline structure.

In the present study the separation of ethanol/water mixtures by pervaporation through different deacetylated chitosan membranes was attempted.

EXPERIMENTAL

Materials

Chitosan flakes (76% degree of deacetylation) were supplied by Shin Nippon Kagaku Co., Japan. Polyethersulfone ultrafiltration membrane (molecular weight cutoff = 20,000 dalton) was obtained from Fluid Systems Co., USA. Acetic acid was of reagent grade and was supplied by Junsei Chem. Co. Ltd., Japan. Sodium hydroxide (99%, Duksan Pharmaceutical Co. Ltd.), sulfuric acid (97%, Duksan Pharmaceutical Co. Ltd), and ethanol (99.9%, Carlo-Erba Reagent) were used without further purification. Water was deionized by the Milli-Q system (Millipore) and distilled before use.

Deacetylation of Chitosan

Chitosan with 76% DA was treated for 4, 6, and 8 hours in a 40% NaOH solution in a reactor at 100°C under nitrogen atmosphere. The chitosan product obtained by alkali treatment was washed in water to neutrality every 2 hours. Deacetylation was about 92% or more after the first treatment. After the first deacetylated chitosan was washed in water, it was treated again in the alkaline solution for further deacetylation. The alkali treatment and washing processes were repeated three times to obtain chitosan products with a deacetylation degree of over 99%.

Measurements of Degree of Deacetylation

After deacetylated chitosans were completely dried in a vaccum oven, the degree of deacetylation of all samples was measured by an infrared spectrometer (FT-IR, Nicolet Magna IR 550) and an element analyzer (Carlo-Erba, EA 1110).

Membrane Preparation

In our investigations the microporous substrate used as a support was a flat sheet ultrafiltration membrane (3–7 nm pore sizes) made from polyethersulfone. All the membranes were made by coating 1 wt% chitosan solution onto a microporous support held flat on a glass plate. A glass rod with tape wound around it was used to spread and coat the substrate evenly. The coated membranes were dried completely at 40°C for 24 hours in a convection oven. During the drying process the coating thickness decreased because of the loss of solvent present in the chitosan casting solution. The thickness of the top layer of the membrane was measured by using a scanning electron microscopy (SEM, Jeol Model 35CF) as shown in Fig. 1 and was about 3.5 μm. All the fabricated membranes were ionically crosslinked with sulfuric acid of an appropriate concentration in a crosslinking bath for 60 minutes at room temperature. In all cases, the membranes were taken out of the crosslinking bath after the crosslinking reaction and washed several times with pure ethanol. The crosslinking was confirmed by FT-IR spectra analysis.

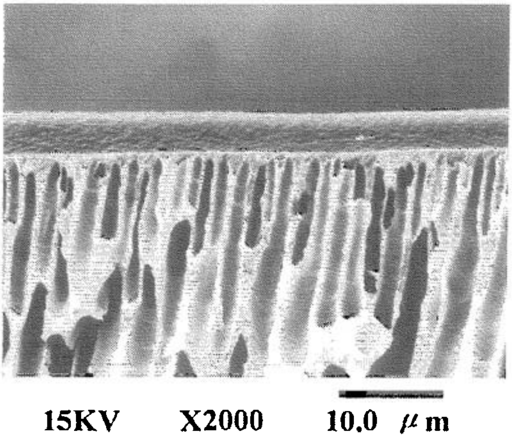

FIG. 1 Scanning electron microscopy (SEM) of chitosan/polyethersulfone composite membrane.

Pervaporation

The feed mixture was continuously supplied to the pervaporation cell. The effective membrane area in contact with the liquid phase in the permeation cell was about 25.98 cm^2. The downstream pressure was less than 3 torr and the upstream pressure was kept at atmospheric pressure because hydrodynamic pressure has little effect on pervaporation performance. The range of operating temperature was 50–80°C, and the feed concentration was kept constant at 95 wt% ethanol. The permeates were condensed in a cold trap immersed in liquid nitrogen or in a cooling bath. Analysis for the permeate was measured by using a GC-14B gas chromatography (Shimadzu Co.) equipped with a thermal conductivity detector. The characteristics of membrane performance were directly obtained from pervaporation experiment in terms of permeate flux, permeate, and feed concentration. The separation factor was calculated by using the following relationship:

$$\alpha = \frac{Y_1/Y_2}{X_1/X_2} \tag{1}$$

where X_i is the weight fraction of the feed and Y_i is the weight fraction of the permeate. Subscripts 1 and 2 denote water and ethanol, respectively.

RESULTS AND DISCUSSION

Characterization

The acetyl content was determined by an infrared spectroscopic method (14). Infrared spectra were recorded using a KBr disk and are shown in Fig. 2. The method involves the use of the amide I band at 1650 cm^{-1} as a measure of the *N*-acetyl group content, and the hydroxyl band at 3450 cm^{-1} is used as an internal standard peak. The percentage of the amide groups acetylated is given by

$$\%\ N\text{-acetylation} = (A_{1650}/A_{3450})/1.33 \times 100 \tag{2}$$

where A is the infrared absorbance. The deacetylation values were calculated to be 91, 96, and 99%, respectively, for samples treated in alkaline solution for 4, 6, and 8 hours.

The deacetylation was measured again by using an infrared spectrometric method. The formulas used for calculating the deacetylation values are the following:

$$\text{Chitosan: } (C_8H_{13}NO_5)_{1-X} + (C_6H_{11}NO_4)_X \tag{3}$$

$$\text{Carbon: } 12/M \times [8(1 - X) + 6X] = \%\ \text{Element} \tag{4}$$

$$\text{Nitrogen: } 14/M = \%\ \text{Element} \tag{5}$$

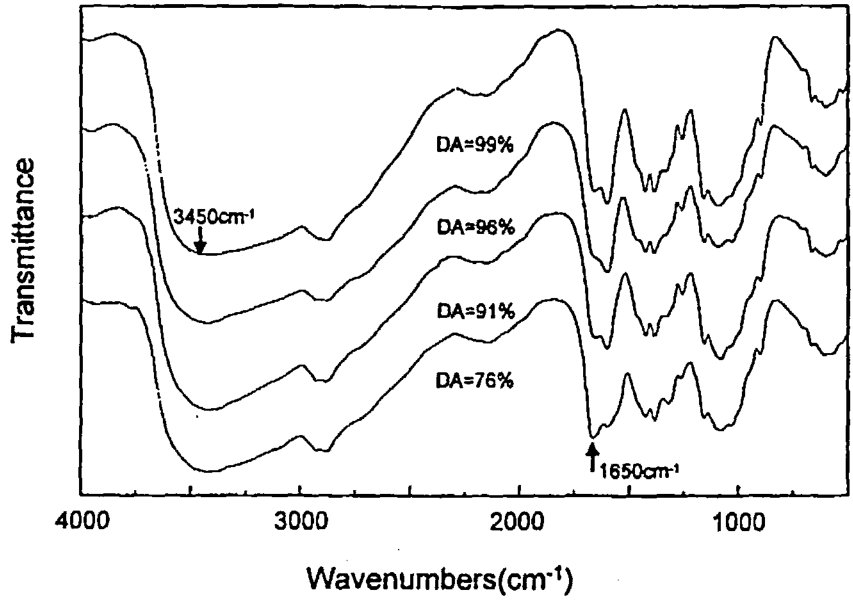

FIG. 2 Infrared spectra of different deaceylated chitosans.

In the above, X is the degree of deacetylation as shown in Fig. 3 and M is the total mass of the structural unit components. The results, given in Table 1, were calculated by using elemental analysis. From these results the deacetylation values obtained by an infrared spectroscopic method using the ratio A_{1650}/A_{3450} were 91, 96, and 99% respectively, in good agreement with that of elemental analysis.

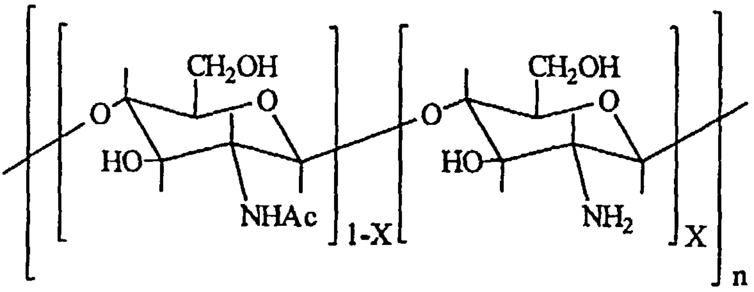

FIG. 3 Scheme of chitosan with different degrees of deacetylation (X).

TABLE 1
Elemental Analysis of Deacetylated Chitosans

Elements	C	H	N	DA (%)
% Mass (4 hours)	41.2	7.3	7.8	91.7
% Mass (6 hours)	39.1	6.9	7.6	96.1
% Mass (8 hours)	40.8	7.1	8.0	99.4

After the preparation of all the membranes, the FT-IR spectra of the surface of chitosan composite membrane before and after crosslinking are shown in Fig. 4. Mochizuki (15) reported the permselectivity of chitosan membranes neutralized by HCl, $CoSO_4$, and H_2SO_4, and suggested that ionic crosslinking was stronger than that by the coordination bond in chitosan. Characteristic peaks of chitosan are located at 1650 and 1550 cm^{-1}, representing amide I and II, respectively (16). With increasing crosslinking time, amide I and II peaks shift to lower wavenumbers because of crosslinking of chitosan chains. Amino groups in chitosan and sulfate

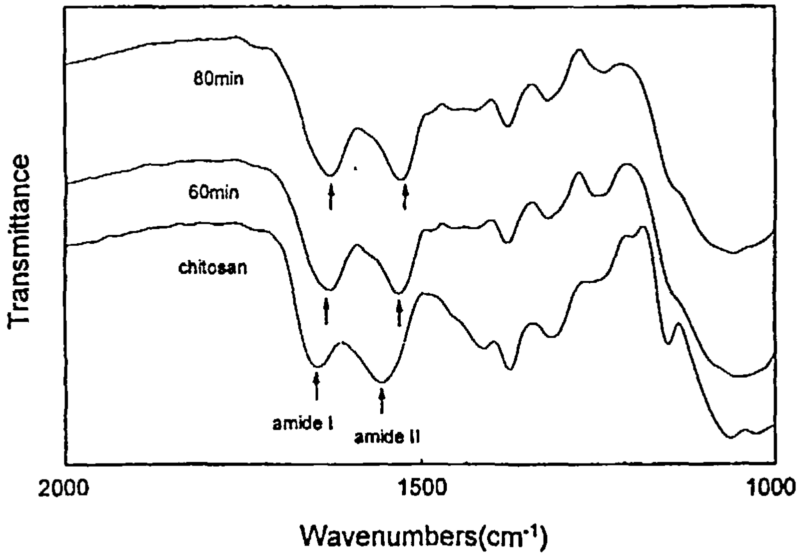

FIG. 4 FT-IR spectra of chitosan (76% degree of deacetylation) before and after ionic crosslinking.

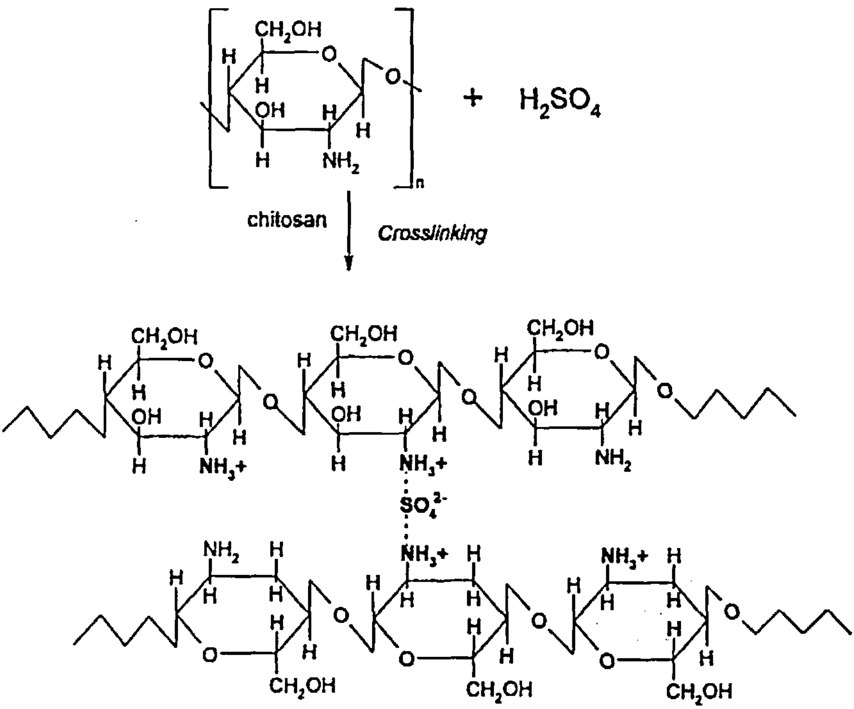

FIG. 5 Ideal crosslinking scheme of chitosan with sulfuric acid.

ions have a Coulombic interaction. Therefore, they crosslink the chitosan main chains ionically as shown in Fig. 5. In the case of ionically crosslinking chitosan, the amide I and II peaks also shift toward lower wavenumbers due to interactions between amide groups and the strong complex of amino groups in chitosan with sulfate ions. Therefore, it is confirmed that the chitosan surface is crosslinked with sulfuric acid.

Swelling Behavior of Deacetylated Chitosans

The swelling data of deacetylated chitosans in water/ethanol solutions are shown as a function of the mass fraction of water in Fig. 6. These data can be measured from changes in weight before and after equilibrium swelling for uniformly crosslinked chitosan membranes which undergo weight changes during the swelling processes. The swelling ratio was determined according to

$$\text{Swelling ratio (g/g)} = \frac{(W_s - W_d)}{W_d} \tag{6}$$

where W_s and W_d represent the weight of swollen and dry samples, respectively. The degree of swelling of all chitosan samples increases with water content. Also, with an increase of deacetylation, the degree of swelling of chitosan increases slightly. Usually the swelling of polymer in the permeants has a large influence on the effective surface per unit membrane area available for mass transport. In composite membranes, the coating material is fixed onto a rigid support layer, which prevents extension of the surface area. Swelling of coating material can lead to more uptake of preferential permeant though an increase in the top layer thickness. Consequently, an increase of swelling due to deacetylation can enlarge

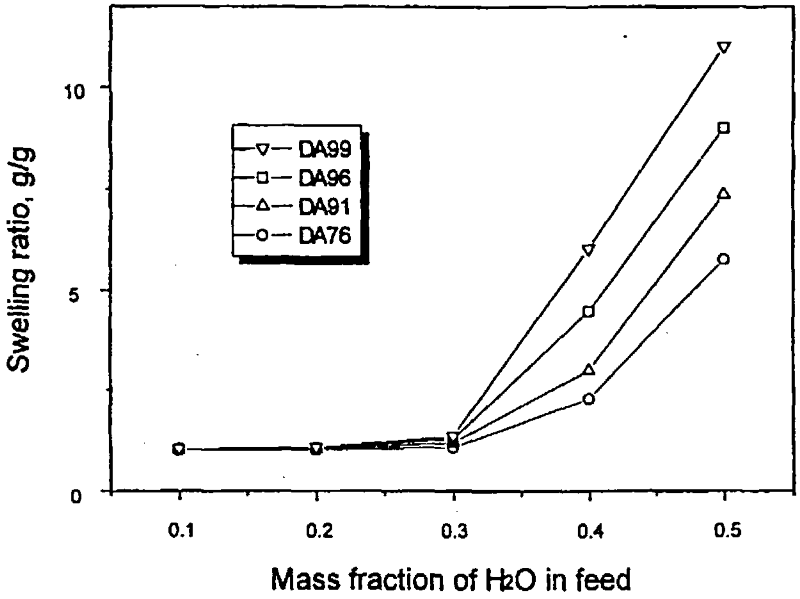

FIG. 6 Swelling ratio of different deacetylated chitosans in ethanol/water solutions at 37°C.

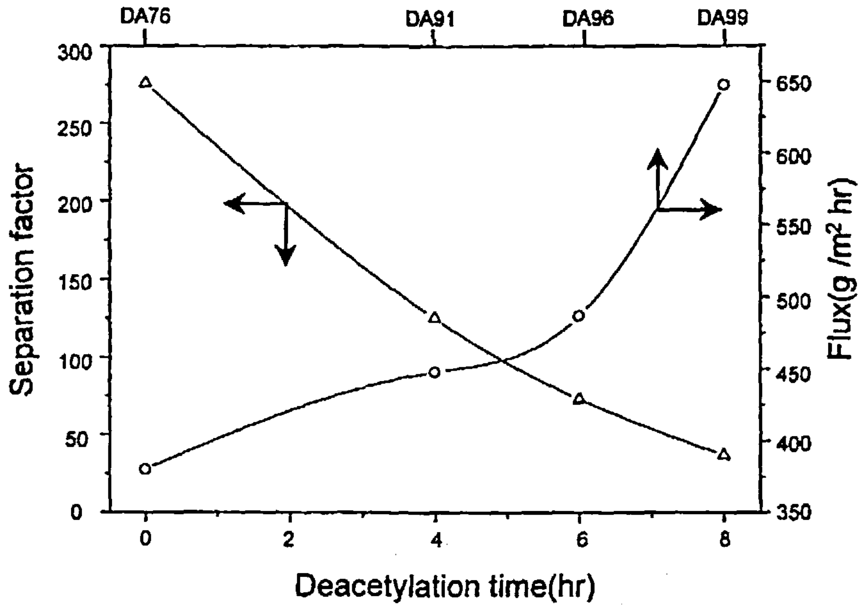

FIG. 7 The effect of deacetylation of chitosan on pervaporation performance. Operation temperature, 70°C; downstream pressure, 3 torr; feed concentration, 95 wt% ethanol solution.

the free volume of chitosan available for permeation and therefore result in high permeation flux.

Effect of Deacetylation on Pevaporation Performance

Figure 7 shows the pervaporation performance of the different deacetylated chitosan composite membranes. The total permeation flux and separation factor are represented as a function of deacetylation time while the feed concentration has been fixed to 95 wt% ethanol concentration. With an increase of deacetylation time, the total flux of the chitosan membranes increases and the separation factor decreases. Generally, diffusion of penetrants in a polymer depends on the mobility of penetrants within the polymer and also on the free volume in the polymer. More deacetylation of chitosan enlarges the proportion of free volume by removing relatively large acetyl groups. This increases the free volume elements, which are considered to be micropores, and are available for the diffusion of permeating species. As the degree of deacetylation in a chitosan membrane increases, if the same degree of cross-

TABLE 2
Viscometric Molecular Weight of Different Deacetylated Chitosans after Alkali Treatment; $[\eta] = KM^{\alpha}$ ($K = 8.93 \times 10^{-4}$, $\alpha = 0.71$); Viscometry Measurement Temperature, 25 ± 0.05 °C; Solvents, 0.2 M Acetic Acid/0.1 M NaCl/4 M Urea Aqueous Solution

Degree of deacetylation (%)	$[\eta]$ (dL/g)	Molecular weight (M)
76	11.50	6.14×10^5
91	9.64	4.79×10^5
96	8.30	3.88×10^5
99	6.82	2.94×10^5

linking is considered, the chitin properties gradually vanish, the solubility of water increases, and the diffusivity, which is governed by the free volume, increases.

Additionally, the molecular weight of chitosan can be reduced by strong alkali treatment during the deacetylation process. Reduction of the molecular weight of chitosan decreases the viscosity of the chitosan casting solution, as shown in Table 2. This results in an increase of the number of micropores due to reduction of the size of long chitosan chains. Therefore, more diffusional transport of the penetrants can be achieved. Consequently, the total permeation flux increases and the separation factor decreases. From the results of pervaporation performance, the total permeation fluxes were found to increase considerably with deacetylation while the selectivities decrease. Hence, it may be assumed that increased swelling of chitosan results in increased polymer segmental motions due to the reduction of molecular weight. This facilitates the diffusion of ethanol molecules along with water, increasing the fluxes and decreasing the selectivities.

Effect of Operating Temperature

Figure 8 shows the effects of feed temperature on the membrane performance of different deacetylated chitosans. In an entire temperature range the total permeation flux of a chitosan membrane with a high degree of deacetylation is greater than that of a chitosan membrane with a relatively lower degree of deacetylation and the separation factor declines, suggesting that the penetration of ethanol molecules should increase. The permeation flux increases drastically compared with the decrease of the separation factor. It is well known that the thermal motions of polymer chains increase as the temperature is raised, leading to activation of polymer chains motion. This thermal behavior of polymers should enable ethanol molecules as

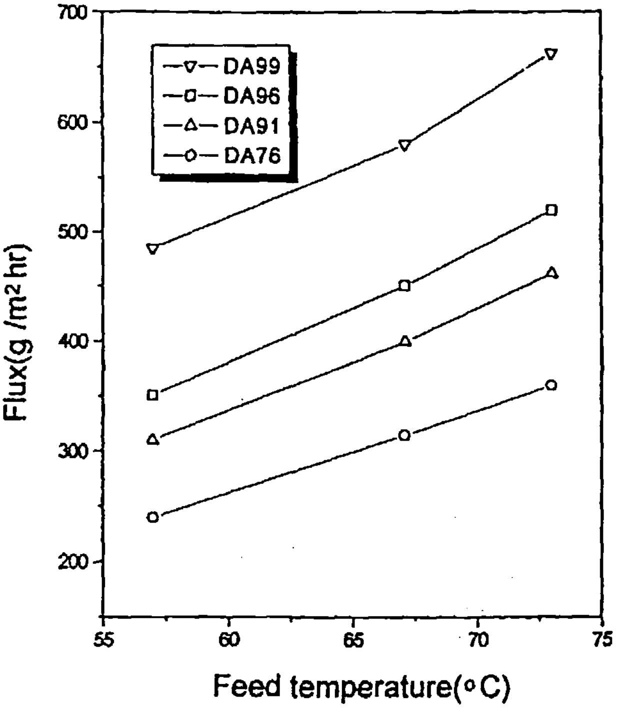

FIG. 8 The effect of feed temperature on pervaporation performance of different deacetylated chitosan membranes. Downstream pressure, 3 torr; feed concentration, 95 wt% ethanol solution.

well as water molecules to diffuse through the larger free volume in the membrane.

Figure 9 illustrates the Arrhenius plots, ln(flux) vs $1/T$ (K), used to calculate the activation energy. They show good linearity in the given temperature range. The temperature dependence of the permeation rate can be represented by the following Arrhenius-type relationship.

$$\ln(J_t/A) = -(E_p/RT) \qquad (7)$$

where J_t is the total permeation flux, A is a constant, E_p is the effective activation energy for permeation, and T is the absolute temperature. The activation energy for permeation is obtained by using E_p calculated from the slope of each plot in Fig. 8, and the values are given in Table 3. The activation energy of each chitosan membrane decreased with an increase of deacetylation

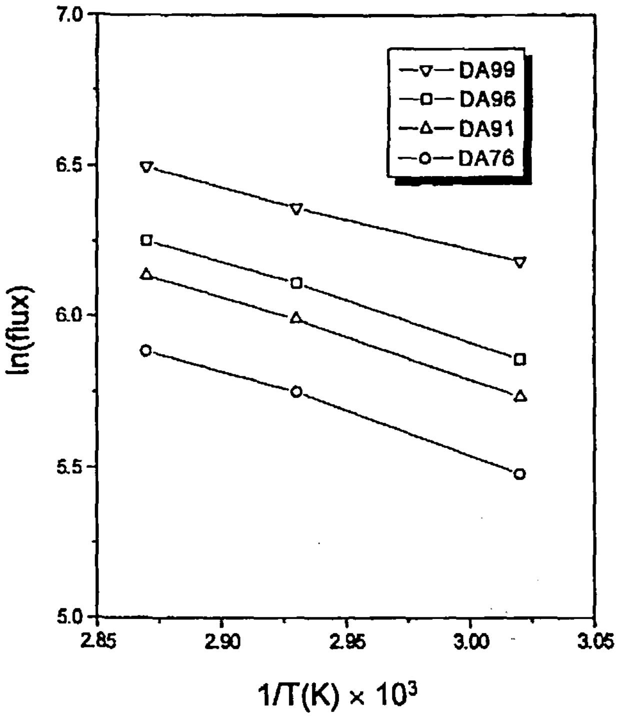

FIG. 9 Arrhenius plots of Fig. 8 illustrating total permeation flux vs reciprocal of absolute temperature (K^{-1}).

in that chitosan. It may be assumed that increased swelling of chitosan due to deacetylation results in increased polymer segmental motions. This facilitates the transport of diffusing species, thus reducing the separation factor and increasing permeation rates.

TABLE 3

Activation Energy for Permeation on Different Deacetylated Chitosan/Polyether Sulfone Composite Membranes; Feed Concentration, 95% Ethanol; Downstream Pressure, 3 Torr

Degree of deacetylation (%)	*E* (kJ/mol)	Temperature range *t* (°C)
91	24.5	>55
96	22.7	>55
99	19.9	>55

CONCLUSIONS

Commercial chitosan with 76% deacetylation was treated by strong alkali treatment for different reaction times, and the degree of acetylation of chitosans obtained was 91, 96, and 99%, respectively. The deacetylation values were measured by both an infrared spectrometric method and by elemental analysis. The two methods produced good agreement. With an increase of deacetylation in chitosan, the total permeation flux of chitosan membranes increases and the separation factor decreases because deacetylation of chitosan enlarges the proportion of free volume of the chitosan polymer by removing relatively large acetyl groups, thus increasing the diffusing rates of permeating species. In an entire operating temperature range the total permeation flux of a chitosan membrane with a high degree of deacetylation is greater than that of a chitosan membrane with a relatively lower degree of deacetylation. On the assumption that Arrhenius's law is valid for pervaporation mixtures, the activation energies of pervaporation, E_p, were estimated. With an increase of deacetylation in chitosan, the apparent activation energies decreased, suggesting that a reduction of molecular weight by the deacetylation process results in increased segmental motions of chitosan chains and promotes the diffusion rates of permeating molecules.

ACKNOWLEDGMENTS

We gratefully acknowledge the Research and Development Center for Energy (RaCER) under the Korean Ministry of Trade and Industry for support of this work. H.B.P. and S.Y.N. are grateful to the Graduate School of Advanced Materials and Chemical Engineering, Hanyang University, for fellowships.

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Received by editor May 8, 1997
Revision received September 1997