

Pervaporation Separation of Water/Alcohol Mixtures Through Hydroxypropylated Chitosan Membranes

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ABSTRACT: The present study investigated the pervaporation performance of novel hydroxypropylated chitosan (HPCS) membranes to separate water from an aqueous alcohol solution. Hydroxypropylated chitosan was prepared from the reaction of chitosan and propylene oxide. The results show that the separation factor decreases and the flux increases with increasing of the substitution degree of the hydroxypropylated chitosan membrane. Crosslinking with glutaraldehyde or treatment with Cu^{2+} can improve the pervaporation performance of modified chitosan membrane greatly. The performance data indicate that the crosslinking hydroxypropylated chitosan membrane treated with Cu^{2+} is an excellent pervaporation membrane for the separation of alcohol–water mixtures, and one-stage separation is attainable for some alcohol–water mixtures such as an *n*-propanol–water and an isopropanol–water system, which has a good separation factor of 220 for the *n*-PrOH/water system and 240 for the *i*-PrOH/water system using 85 wt % alcohol concentration at 60°C. The flux for both cases is around $0.5 \text{ kg m}^{-2} \text{ h}^{-1}$. At the same time, the structure of the chemically modified chitosan membranes and their separation characteristics for aqueous alcohol solutions are also discussed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2035–2041, 1998

Key words: pervaporation; water–alcohol mixture; modified chitosan membrane; dehydration; separation

INTRODUCTION

The pervaporation process has been of much interest because of the energy saving in the separation of azeotropic, close-boiling, or aqueous organic mixtures. In recent years, separation of water–ethanol has attracted much attention and greater efforts have been made to develop a more effective membrane. It is well known that for water permselective membranes, more hydrophilicity of the membrane is favorable to the perm-

selective separation of water; therefore, the incorporation of a group in the membrane structure that may cause a strong interaction such as hydrogen bonding is effective in increasing the permselectivity of water.^{1,2} Novel membrane materials can be developed by different methods. Among these, the modification of existing polymers or polymeric membrane, especially those available commercially, is one promising route toward new membrane material.

Chitosan is similar in its chemical structure to cellulose and is one of the most abundant organic materials which can be easily obtained in nature, but its uses and applications have not yet been realized as much as those of cellulosic materials. Because of having active groups of $-\text{NH}_2$, chitosan membrane and some of its modifications have

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Scheme 1

been recently investigated as membrane materials,²⁻⁵ the results showed that it is a more promising polymer material for application in pervaporation. In this article, we report the preparation of hydroxypropylated chitosan (HPCS) and its crosslinking with glutaraldehyde membranes and their pervaporation performance for aqueous alcohol solution separation. At the same time, the effects of treating the two kinds of membrane with Cu^{2+} on their pervaporation performance were also studied.

EXPERIMENTAL

Membrane Materials

Chitosan (CS) has a degree of deacetylation of 83.5% and a viscosity average molecular weight of 5.2×10^5 .

Characterization

An infrared spectrophotometer (Shimadzu IR-470), a differential scanning calorimeter (Perkin-Elmer DSC-7), and elemental analysis (Carlo Erba 1106) were used for structural determination.

Preparation of Hydroxypropylated Chitosan

The modified chitosan was prepared by the reaction of chitosan with propylene oxide. The general experimental procedure was as follows: Thirty grams of chitosan was swollen in water for 5 days; then, the appropriate amount of propylene oxide was added and stirred. The reaction proceeded at 25°C for 48 h. After the reaction, the product was poured into a large amount of acetone and the precipitate was filtered. The product was washed with acetone several times, then dried at room temperature under reduced pressure. Samples were obtained by varying the mol ratio of propylene oxide to chitosan.

Membrane Preparation

The membrane was prepared by casting 3 wt % HPCS in a 1 wt % acetic acid aqueous solution onto a glass plate, drying at 40°C, and treating in a 3 wt % NaOH solution. Crosslinked HPCS membrane was prepared by casting the solution, which was made from a mixture of modified chitosan, in 1 wt % acetic acid and 0.54 wt % glutaraldehyde. The thickness of these membranes was about 20 μm .

Pervaporation Experiment

A detailed procedure for performing the pervaporation experiment can be found in our previous article.⁴

RESULTS AND DISCUSSION

Separation of Water-Alcohol Mixtures by Pervaporation Through Hydroxypropylated Chitosan Membrane

Effect of Hydroxypropylation

Reaction of chitosan with epoxides results in nucleophilic substitution and opening of the epoxide

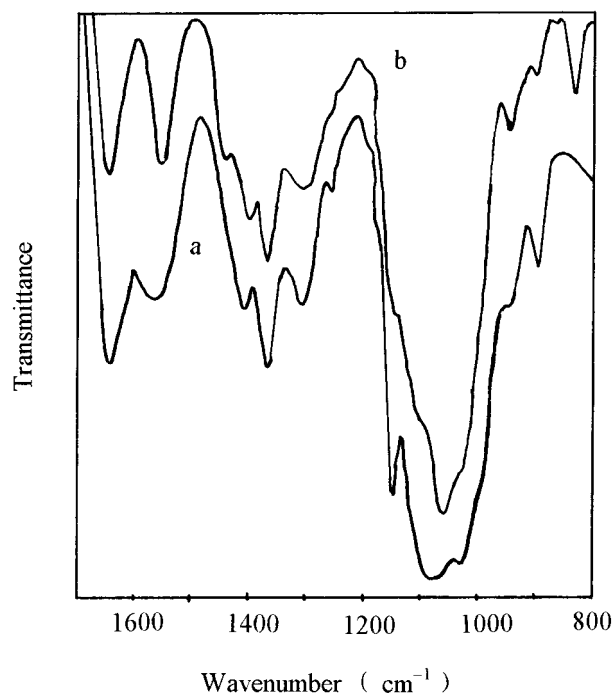


Figure 1 Infrared spectra for (a) chitosan and (b) hydroxypropylated chitosan membrane.

Table I Elemental Analysis of Chitosan and Hydroxypropylated Chitosan

Sample	Amount of Epoxide (mL)	Elemental Analysis			DS ^a
		C%	H%	N%	
CS	0	45.09	6.80	8.26	0
R-1	10	45.64	6.92	8.09	11.3%
R-2	15	46.08	7.05	7.80	20.5%
R-3	20	46.80	7.16	7.30	38.6%
R-4	25	47.05	7.30	7.25	43.4%
R-5	30	47.27	7.36	7.23	46.2%

^a Degree of substitution.

ring. The most favorable nucleophilic center of chitosan is the amino group, but the other nucleophilic center, the hydroxyl group, could also react with the epoxide ring. But which group in chitosan reacts with propylene oxide, hydroxyl in the C-6 position of the glucosamine unit, or —NH_2 in C-2 position? There is a different opinion about the reacting with epoxides⁶ and two kinds of product may be formed as shown in Scheme 1.

To solve this question, infrared spectra of chitosan and hydroxypropylated chitosan was investigated (Fig. 1). The results show that new absorption bands at 830, 940, and 1440 cm^{-1} appear after hydroxypropylation, and the intensity of the peak at 830 cm^{-1} becomes stronger with increasing the amount of propylene oxide. At the same time, the absorption bands at 1150, 1030, and 1250 cm^{-1} disappeared. In comparison with chitosan, the band at 2900 cm^{-1} of the modified chitosan split into two peaks. It is well known that the absorption bands at 1150 and 1250 cm^{-1} are attributed to the —NH_2 group and the stretching vibration of the C—N of primary amine, respectively.⁷ From the results above, propylene oxide did react with the —NH_2 group in chitosan. This

corresponds well to the reaction of chitosan with glycidyl trimethylammonium chloride.⁶

Table I shows the effect of the amount of epoxide on the degree of substitution in chitosan. With increase of the amount of propylene oxide, the degree of substitution increases, which is identical to the results of the infrared spectra.

The pervaporation performance of the modified CS membrane tested with 90 wt % ethanol feed at 60°C is shown in Table II. Compared with the chitosan membrane, the permeation rate increased with the degree of substitution, but the separation factor decreased sharply, which may be due to the increasing of the swelling degree of the modified chitosan membrane. The swelling degree of the HPCS membrane increased with increase of the substitution degree. An increase in flux and decrease in the separation factor after hydroxypropylation is believed to be due to the formation of the side chain, which made the structure of the modified chitosan membrane looser. This also could be proved from the DSC curves (Fig. 2). The endothermic peak at about 250°C which was attributed to the crystal structure of the chitosan membrane⁸ shifted to a lower temperature and became weak. This result implies that the increase in the substitution degree of the HPCS membrane decreases the crystallinity of the membrane.

Effect of Treatment with Cu^{2+}

The above result reveals that the modified chitosan membrane has a better flux but a lower separation factor. To improve this defect, the pervaporation properties of the HPCS membrane treated with CuCl_2 was investigated (seen in Tables III and IV). The results show that by treating the modified CS with CuCl_2 the separation factor increases from 18 to 54 for a 90 wt % ethanol aqueous solution and from 31 to 74 for a 85 wt

Table II Effect of Degree of Substitution on Pervaporation Separation Ability of Modified Chitosan

Membrane	Swelling Degree	Total Flux ($\text{g m}^{-2} \text{h}^{-1}$)	Water Flux ($\text{g m}^{-2} \text{h}^{-1}$)	Ethanol Flux ($\text{g m}^{-2} \text{h}^{-1}$)	Separation Factor
Chitosan	32.5%	127	127	0.1	8991
R-1	39.8%	358	258	127	18.4
R-2	42.7%	470	298	171	17.4
R-3	46.4%	537	282	255	9.0
R-4	49.2%	835	366	469	7.3
R-5	54.7%	1150	445	705	6.5

Feed ethanol concentration 90 wt %; operating temperature: 60°C.

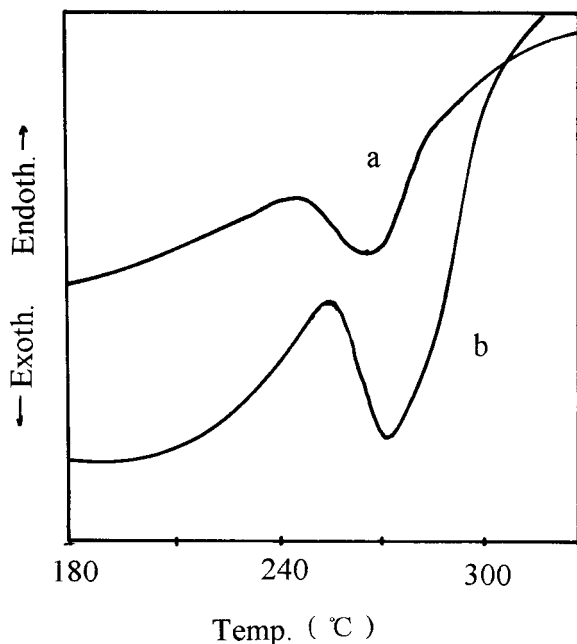


Figure 2 DSC thermogram for (a) R-1 film and (b) chitosan film.

% *n*-propanol aqueous solution at 60°C, but the permeation rate decreases. At the same time, both the separation factor and the flux increase with increase in the operating temperature for the HPCS membrane treated with CuCl_2 . This kind of separation behavior is very useful for the industrial separation of alcohol–water mixtures.

Some behaviors of the HPCS membrane treated with Cu^{2+} can be explained by the specific structure of the membrane. According to Eyring's theory, the thermal motion of a polymer chain in the amorphous regions randomly produces the

Table III Effect of Pervaporation Performance on Operating Temperature (Feed Concentration: 90 wt % Ethanol)

Operating Temperature (°C)	Membrane R-1		Membrane R-1 Treated with CuCl_2	
	α	Flux ($\text{g m}^{-2} \text{h}^{-1}$)	α	Flux ($\text{g m}^{-2} \text{h}^{-1}$)
30	23	94	29	28
40	20	156	37	41
50	19	262	45	71
60	18	385	54	105

^a Membrane R-1 treated with 80 wt % ethanol solution containing $3.7 \times 10^{-2} \text{ CuCl}_2$.

Table IV Effect of Pervaporation Performance on Operating Temperature

Operating Temperature (°C)	Membrane R-1		Membrane R-1 Treated with CuCl_2	
	α	Flux ($\text{g m}^{-2} \text{h}^{-1}$)	α	Flux ($\text{g m}^{-2} \text{h}^{-1}$)
50	35	315	57	72
60	31	497	74	125

Feed concentration: 85 wt % *n*-PrOH. α stands for the separation factor.

“holes” through which the permeating molecules can diffuse.² Therefore, the HPCS membrane treated with an aqueous ethanol solution containing a small amount of the metal salt CuCl_2 could, via the property of the $-\text{OH}$ groups or $-\text{NH}_2$ groups on the modified membrane, induce chelation. This results in conformational changes in the HPCS molecules, thereby reducing the number of “holes” on the membrane. This contraction of the “hole” hardly affects the diffusivity of the water molecules, but affects the diffusivity of the larger alcohol molecules to a significant degree, after which only the small water molecules can pass through the membrane. Thus, the membrane treated with CuCl_2 decreases the diffusivity of the alcohol and increases the separation factor (seen in Tables III and IV).

As the temperature increases, the frequency and amplitude of chain jumping increase and the resulting “holes” become larger, and the diffusion rate of individual permeating molecules and associated permeating molecules are high, so that the total flux increases and the separation factor de-

Table V Effect of Operating Temperature on Flux of Membrane R-1 Treated with CuCl_2

Operating Temperature (°C)	Feed: 90 wt % EtOH		Feed: 90 wt % <i>n</i> -PrOH	
	Water Flux	EtOH Flux	Water Flux	<i>n</i> -PrOH Flux
30	22	7	20	4
40	33	8	27	4
50	59	12	39	5
60	90	15	60	6

Feed: 90 wt % ethanol, 90 wt % *n*-propanol. Flux ($\text{g m}^{-2} \text{h}^{-1}$).

Table VI Effect of Crosslinking Agent Amount on Pervaporation Properties of Crosslinking HPCS Membrane

Membrane	Crosslinking Agent (mL)	Alcohol in Permeate (wt %)	Separation Factor	Flux (g m ⁻² h ⁻¹)
R-1	0	33	18	385
GR-1	0.3	42	12	434
GR-2	0.6	36	16	420
GR-3	0.9	17	42	430

Feed temperature: 60°C; feed composition: 90 wt % ethanol solution.

creases. The HPCS membrane follows Eyring's theory (shown in Tables III and IV). However, the HPCS membrane treated with CuCl₂ cannot be explained as above.

The reason may be that the mobility of the HPCS molecule is strongly controlled because of the chelation. Therefore, only a small increase of the motion of the HPCS molecule will be allowed with increasing the temperature, that is, the expansion of the "hole" will be controlled to a certain average. So, the increase of the temperature hardly causes expansion of the "holes," and the large increase of the permeation rate of ethanol is not brought about. With respect to the permeation of water, the "holes" will be large enough for water molecules to diffuse through, so its permeation rate increases with enhancing the operating temperature. Thus, the separation factor increases as shown in Tables III and IV. This explanation corresponds well to the changing of the alcohol and water permeation with operating temperature (see Table V).

Separation of Water–Alcohol Mixtures by Pervaporation Through Crosslinking HPCS Membrane

Effect of Crosslinking on HPCS Membrane

Good dimensional stability of these membrane systems was achieved by crosslinking with glutar-

aldehyde which reacts with the hydroxyl or —NH₂ group in the HPCS membrane, so we subjected the HPCS membrane to crosslinking and report some properties of the crosslinked membrane. The results of the pervaporation separation of the crosslinking membranes for alcohol–water mixtures are listed in Tables VI and VII. The performance data show that both the selectivity and flux increased with increasing crosslinking agent and the crosslinked membrane is a good pervaporation membrane for the separation of alcohol–water mixtures and the separation factor is 366 for the isopropanol/water mixture.

The effects of operating temperature on pervaporation performance of the GR-3 membrane is shown in Figure 3. The data indicate that for the crosslinking HPCS membrane the separation factor decreases and the flux increases with increase of the temperature as in most membranes.

Effect of Treatment with Cu²⁺

The separation characteristics of the crosslinking HPCS membrane treated with CuCl₂ are shown in Table VIII. The result indicates that the separation factors of all membranes treated with Cu²⁺ are higher than those of the untreated ones. Especially for *n*-PrOH–water and *i*-PrOH–water systems, the separation factors are more than 220

Table VII Pervaporation Properties of Crosslinking HPCS Membrane for Alcohol–Water Mixtures

Membrane	Separation Factor			Flux (g m ⁻² h ⁻¹)		
	EtOH/Water	<i>n</i> -PrOH/Water	<i>i</i> -PrOH/Water	EtOH/Water	<i>n</i> -PrOH/Water	<i>i</i> -PrOH/Water
R-1	18	24	89	385	227	197
GR-1	12	27	106	434	337	276
GR-2	16	29	216	420	421	300
GR-3	42	69	366	430	420	312

Feed concentration: 90 wt % alcohol; *T* = 60°C.

Table VIII Pervaporation Properties of Crosslinking Membrane Treated with Cu²⁺ for Alcohol–Water Mixtures

Membrane Treated with Cu ²⁺	Separation Factor			Flux (g m ⁻² h ⁻¹)		
	EtOH/Water	<i>n</i> -PrOH/Water	<i>i</i> -PrOH/Water	EtOH/Water	<i>n</i> -PrOH/Water	<i>i</i> -PrOH/Water
GR-1	15	700	5000	483	340	187
GR-2	58	520	1411	236	460	386
GR-3	64	220	240	220	485	470

$T = 60^{\circ}\text{C}$. EtOH–water system: 90 wt % ethanol; PrOH–water system: 85 wt %.
Membranes were soaked at $3.5 \times 10^{-2} \text{ M}$ CuCl₂ in 80 wt % ethanol solution at room temperature.

and the fluxes are about $0.5 \text{ kg m}^{-2} \cdot \text{h}^{-1}$ for an 85 wt % alcohol solution at 60°C .

The effect of the *i*-PrOH concentration of the feed mixture on the permselectivity of the cross-linked HPCS membrane and one treated with Cu²⁺ was investigated. The results are shown in Figure 4. This figure indicates that the permselectivity of the two kinds of membrane is highly influenced by the feed composition. The permeation rate decreased and separation factor increased with increasing *i*-PrOH concentration from 70 to 90 wt %. At the same time, treating with Cu²⁺ can improve the pervaporation performance of the GR-2 membrane greatly in the range of experimental concentration. The separation factor increased from 246 to 10^5 for the 90 wt % *i*-PrOH/water mixture at 50°C after treatment with Cu²⁺ and one-stage separation was attainable.

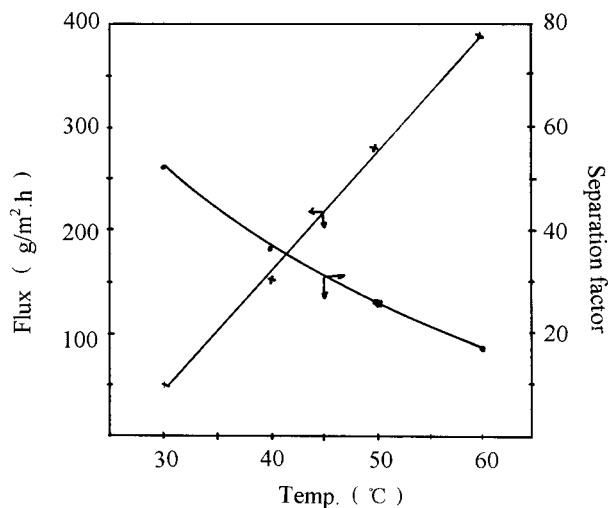


Figure 3 Dependence of separation factor and flux on operating temperature for 96 wt % ethanol solution. GR-3 membrane.

CONCLUSIONS

Hydroxypropylated chitosan (HPCS) membranes were prepared from the reaction of propylene oxide and chitosan. IR spectra results show that propylene oxide reacts mainly with the —NH₂ group in chitosan. After hydroxypropylation, the separation factor decreases and the flux increases with increasing of the substitution degree. Crosslinking with glutaraldehyde or treating with Cu²⁺ can improve the pervaporation performance of the HPCS membrane greatly. The crosslinking HPCS membrane treated with Cu²⁺ has a better pervaporation performance of the separation factors of more than 240 and permeation rates of about 0.5

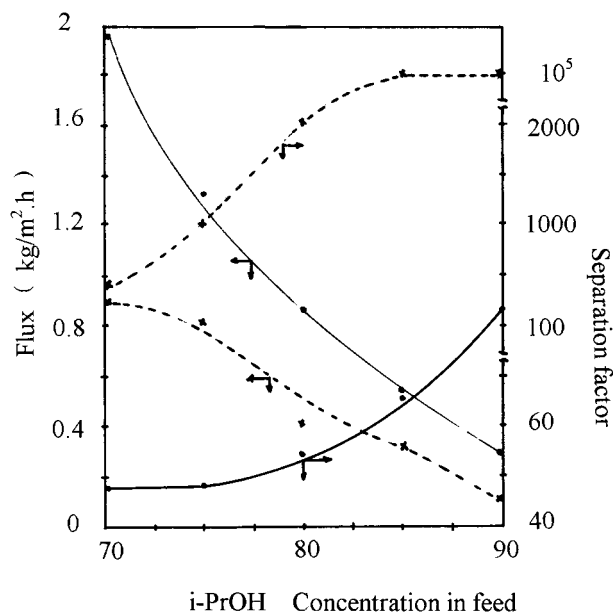


Figure 4 Effect of *i*-PrOH concentration on permselectivity of (—) GR-2 membrane and (· · · · ·) GR-2 treated with Cu²⁺; $T = 50^{\circ}\text{C}$.

kg m⁻² h⁻¹ for 85 wt % *n*-PrOH and *i*-PrOH aqueous solutions.

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