

Pervaporation of Aqueous Alcohol Mixtures Through a Membrane Prepared by Grafting of Polar Monomer onto Nylon 4

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SYNOPSIS

A hydrophilic pervaporation membrane was prepared via a homografting polymerization of *N,N'*-(dimethylamino)ethyl methacrylate (DMAEM) onto nylon 4 backbone, DMAEM-*g*-N4. The water permselectivity was improved by the ammonium quaterization of the pendant *N,N'*-dimethylamino group on the DMAEM-*g*-N4 membrane using dimethyl sulfate, DMAEMQ-*g*-N4. The separation factor and permeation rate for both chemically modified nylon 4 membranes were higher than those of the unmodified nylon 4 membrane. The effects of feed composition, feed temperature, and molar volume of the alcohols on pervaporation performance were investigated. Optimum pervaporation was obtained by a DMAEMQ-*g*-N4 membrane with a degree of grafting of 12.7% for a 90 wt % ethanol feed concentration, giving a separation factor of 36 and a permeation rate of 564 g/m²h. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Separation carried out by membranes is considered to be one of the most promising processes for energy-saving separation technology. The pervaporation technique is one of the potential methods to separate azeotropic mixtures, mixtures having nearly the same boiling point, heat-sensitive compounds, and structural isomers. Membranes incorporating a hydrophilic moiety into the membrane matrix, to increase the hydrophilicity of the membrane, are effective for pervaporation separation. Yoshikawa et al. reported that synthetic polymer membranes having imide groups,¹ *N*-substituted imide groups,² carboxylic acid moieties,³ and ester groups⁴ selectively permeated water from aqueous alcohol solution by the pervaporation technique by making use of hydrogen-bonding interactions. We investigated various ways, such as plasma deposition, homografting, and heterografting by Co⁶⁰ γ -ray irradiation^{6,7} to improve the membrane morphology and pervaporation performance of the nylon 4 membrane. In addition, ion-exchange membranes such as Nafion⁸ and copolymeric membranes containing an ionic group⁹ have also been investigated. The higher permselectivity of water through these membrane is possibly due to the higher hydrophilicity of the ionic group to increase the affinity to water. Furthermore, higher permeation rates are observed due to the greater size of the permeation paths formed by ionic repulsion. In this article, separation of water from a water-alcohol solution was attempted through chemically modified nylon 4 membranes to increase the ester group or ionic sites and enhance the affinity to water molecules by the pervaporation technique. The effects of the monomer concentration, degree of grafting, crystallinity, feed concentration, feed temperature, and the molar volume of the permeating species on the pervaporation performance of prepared membrane were investigated. A comparison of an unquaternized modified nylon 4 membrane and a quaternized modified nylon 4 membrane for the pervaporation separation process was also made.

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EXPERIMENTAL

Materials

The nylon 4 synthesis procedure was carried out as described previously.¹⁰ The molecular weights of the samples, measured by a Cannon Fenske viscometer with *m*-cresol as the solvent at 25°C, was 25,000–30,000. *N,N'*-(dimethylamino)ethyl methacrylate (DMAEM) and 2,2'-azobis(2-methylpropionitrile) (AIBN) were purified before being used. All other reagent-grade chemicals were used directly without further purification. Water was deionized and distilled.

Grafting Procedure

An ampule containing DMAEM (2–12 vol %), AIBN, and nylon 4 polymer solution (10 g/100 mL formic acid) was degassed by three freeze-pump-thaw cycles and sealed off under a high vacuum (< 10⁻⁴ Torr). The sealed tube was then placed in a constant temperature bath at 80°C for 3 h while agitating. The reaction mixture was poured into a large amount of methanol, allowed to stand at room temperature, then was dried at 80°C in vacuum.

The degree of grafting and grafting efficiency of DMAEM onto nylon 4 were calculated according to the following equation, after extraction of homopolymers for 72 h using a Soxhlet with water:

$$\text{Degree of grafting (\%)} = \frac{(A - B)}{B} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{(A - B)}{(C - B)} \times 100$$

where *A* is the weight of grafted nylon 4 (after extraction); *B*, the weight of nylon 4 before grafting; and *C*, the weight of the crude grafted nylon 4.

Membrane Preparation

The membrane of DMAEM-*g*-N4 was prepared from a casting solution of the grafted copolymer in formic acid solvent. The detailed procedure was described in a previous article.¹⁰ The membrane thickness was in the range of 15–25 μm.

Quaternary-Ammonium Ionization

The DMAEM-*g*-N4 membranes were dipped in a 2 wt % solution of dimethyl sulfate in a 50 wt % aqueous ethanol solution at room temperature for

about 30 min. After quaternization, the quaternized membranes, DMAEMQ-*g*-N4, were washed with distilled water. The ammonium ionization was confirmed by FTIR.

Degree of Swelling

The degree of swelling of the membrane was defined by the following equation:

$$\text{Degree of swelling} = \frac{\text{weight of swollen membrane}}{\text{weight of dry membrane}}$$

where the weight of dry membrane and the weight of swollen membrane denote the weight of dry and solvent swollen membranes, respectively.

X-ray Measurement

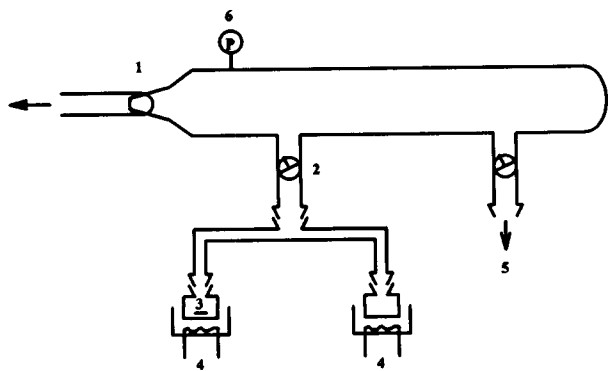
Wide-angle X-ray diffraction pictures were obtained with a Shimadzu XD-5 XRD Model X-ray diffractometer. The X-ray source was used employing CuKα radiation at the following parameters: accelerating voltage 30 kV and anodic current 20 MA. Diffraction pictures were made by continuous scanning over the range of diffraction angle 2θ from 5° to 35° at a rate of 2°/min.

Pervaporation Measurements

Traditional pervaporation and sorption⁵ processes were used. The effective membrane area was 10.2 cm². Most of the experiments were conducted at 25°C. The effects of temperature were studied in the range of 25–45°C. In pervaporation, the permeation rate was determined by measuring the weight of the permeate. The composition of the feed solutions, permeates, and solutions adsorbed in the membrane were measured by gas chromatography (GC, China chromatography 8700T). The separation factor, α, was calculated from the following equation:

$$\alpha_{\text{alcohol}}^{\text{H}_2\text{O}} = \frac{(Y_{\text{H}_2\text{O}}/Y_{\text{alcohol}})}{(X_{\text{H}_2\text{O}}/X_{\text{alcohol}})}$$

For pervaporation, *Y*_{H₂O}, *Y*_{alcohol}, and *X*_{H₂O}, *X*_{alcohol} are the weight fractions of water and alcohol in the permeate and feed, respectively. For sorption, *Y*_{H₂O} and *Y*_{alcohol} are the weight fractions of water and alcohol in the membrane, respectively.



1: Vacuum pump
2: Cock
3: Membrane
4: Cooled trap with LN_2
5: Release
6: Pirani gauge

Figure 1 Schematic presentation of sorption apparatus.

Contact Angle Measurements

The contact angle of water was measured with a FACE contact angle meter CA-D type (Kyowa Tnterface Science Co. Ltd). Sets of droplets (sessile drops, volume ca. $1.8 \times 10 \text{ cm}^3$) of water were placed on a membrane-covered fixing knob. The dimensions of the droplets were measured about 10 s after placing the droplets on the knob. The droplets must be small enough so that their shape can be approximated by a sphere. The contact angle was calculated by the following equation:

$$\text{Contact angle} = 2 \tan^{-1}(h/r)$$

where h is the height of the spherical segment, and r , the radius of the spherical segment.

Preferential Sorption Measurements

The sorption apparatus used in this study is illustrated in Figure 1. A membrane was immersed in ethanol-water mixtures for 24 h. It was subsequently blotted between tissue paper to remove adherent solvent and placed in the left container of a twin tube setup. The system was evacuated while the left container with the swollen membrane was heated to evaporate completely the liquid absorbed in the membrane. The evaporated vapor was trapped in the right one by cooling with liquid nitrogen. The composition of condensed liquid in the right tube was determined by GC.

RESULTS AND DISCUSSION

Influence of the Monomer Concentration on the Chemical Grafting Process

The effects of monomer concentration on grafting are shown in Figure 2. It can be seen that the degree of grafting increases with monomer concentration up to 8 vol %, whereas, beyond this concentration, the degree of grafting decreases. These results might be due to the fact that, at high concentrations, more monomer chains are amenable to removal by washing. However, when the monomer concentration exceeds 8 vol %, homopolymerization is favored more than is grafting polymerization. Additionally, the grafting efficiency decreased gradually, indicating that homopolymerization becomes predominant at higher monomer concentration. Similar results were observed by Nishioka et al.¹¹

FTIR Measurements

The existence of DMAEM grafting onto nylon 4 was confirmed by FTIR spectrophotometrically. Figure 3 shows the spectra of (a) unmodified nylon 4, (b) DMAEM-*g*-N4, and (c) DMAEMQ-*g*-N4 with 12.7% degree of grafting. Comparison between spectra (a) and (b) shows that a new absorption peak at 1730 cm^{-1} , which corresponds to $\text{C}=\text{O}$ stretching in the DMAEM, appeared in spectrum (b). Thus, this peak confirms that grafted chains exist in the nylon 4 matrix. Spectrum (c) is that of the DMAEM-*g*-N4 from treatment with dimethyl sulfate. In the grafted

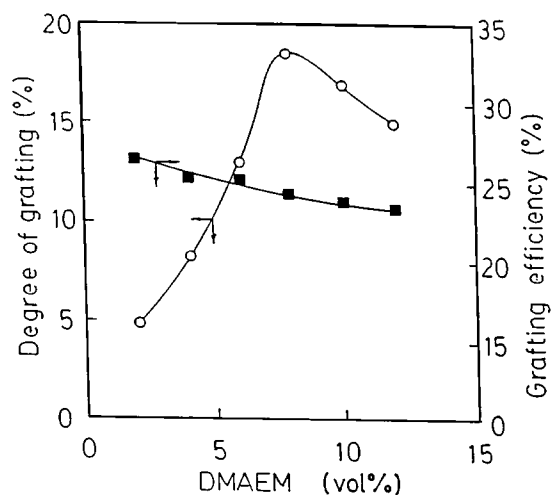


Figure 2 Effect of monomer concentration on the grafting of DMAEM with AIBN. Grafting time: 3 h with shaking; nylon 4 concentration (10 g/100 mL formic acid); 80°C : (○) degree of grafting; (■) grafting efficiency.

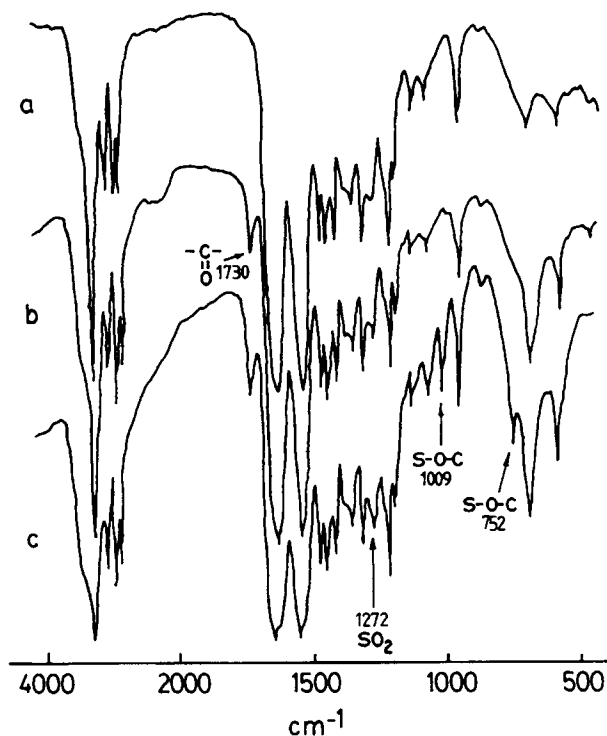


Figure 3 FTIR spectra of (a) unmodified nylon 4 membrane, (b) DMAEM-*g*-N4 membrane, degree of grafting = 12.7%; (c) DMAEMQ-*g*-N4 membrane, degree of grafting = 12.7%.

membranes treated with Me_2SO_4 , several characteristic peaks that indicate the ammonium-ionized form appeared, i.e., the peaks located at 1272 ($\nu_s\text{SO}_2$), 1009, and 752 cm^{-1} were observed.¹² These peaks were not observed at all in the unmodified nylon 4 and DMAEM-*g*-N4. Furthermore, in the FTIR spectra of the DMAEM-*g*-N4, the peak of the carbonyl group in ester was observed at 1730 cm^{-1} , and the position did not change after the ammonium ionization of the terminal *N,N*-dimethylamino group by dimethyl sulfate.

Influence of the Degree of Grafting on Pervaporation Performances

The effect of the degree of grafting on the permeation rates and separation factors for pervaporation of 90 wt % aqueous ethanol solutions through the chemically modified nylon 4 membrane are shown in Table I. The permeation rate increases as the degree of grafting increases for both chemically modified nylon 4 membranes. Furthermore, when the grafted membranes are ammonium-quaternized by dimethyl sulfate, the separation factor and permeation rate increase further with increasing degree

of grafting from 5.0 to 12.7%. These results can be explained from the viewpoint of the hydrophilicity of the quaternized membrane because the hydrophilicity of the DMAEM-*g*-N4 membrane is lower than that of the DMAEMQ-*g*-N4 membrane. However, the separation factor for the DMAEMQ-*g*-N4 membrane, whose degree of grafting was 18.5%, is lower than that of the DMAEM-*g*-N4 membrane. These phenomena might be due to the fact that the swollen membrane of the former is swollen more than is the latter. This facilitates the transport of ethanol molecules along with water, resulting in increased concentration of ethanol in the permeate. In addition, the water contact angles of unmodified nylon 4 membrane, DMAEM-*g*-N4 membrane, and DMAEMQ-*g*-N4 membrane with 12.7% degree of grafting are 78°, 66° and 54°, respectively. This result confirms that the hydrophilicity increases as the DMAEM monomer is grafted onto the nylon 4 backbone, then quaternized on the pendant *N,N*-dimethylamino group on the DMAEM-*g*-N4 membrane. The hydrogen-bonding and ion-dipole interaction between modified nylon 4 membrane (DMAEM-*g*-N4, DMAEMQ-*g*-N4) and water molecules in the feed solution become strong, resulting in a higher permselectivity of water than that of the unmodified nylon 4 membrane. To investigate the effect of the degree of grafting on the structure transition of the grafted membrane, X-ray diffraction studies were made and are shown in Figure 4. The X-ray diffraction diagram of the grafted membrane shows that the intensity of the diffraction at angles $2\theta = 20.5^\circ$ and $2\theta = 24^\circ$ decreases with increasing degree of grafting, due to the crystallinity decrease.⁶

Table I Effect of Degree of Grafting on Pervaporation Performances of Chemical Modified Nylon 4 Membranes

Degree of Grafting (%)	Separation Factor		Permeation Rate ($\text{g}/\text{m}^2\text{h}$)	
	A	B	A	B
0	4.0	—	350	—
5.0	13.7	14.5	385	425
7.6	18.2	19.5	417	485
12.7	28.3	36.0	439	564
18.5	17.5	16.0	688	795

A: DMAEM-*g*-N4.
 B: DMAEMQ-*g*-N4.
 90 wt % ethanol aqueous solution.
 Operation temp.: 25°C.
 Operation pressure: 2 mmHg.
 Membrane thickness: 25 μm .

Thus, the DMAEM monomer grafted onto the nylon 4 backbone results in a relaxation structure of the DMAEM-*g*-N4 membrane. Therefore, the permeation rate increases with increasing degree of grafting.

Influence of Temperature and Feed Composition for DMAEM-*g*-N4 Membrane with a 12.7% Degree of Grafting

The effects of temperature and feed composition on the total permeation rate are shown in Figure 5. The total permeation rate increases with increasing the temperature and the water concentration of the feed solution. According to the free-volume theory,¹³ the thermal motion of polymer chains in the amorphous regions randomly produces a free volume. As temperatures increase, the frequency and amplitude of the chain jumping increase and the resulting free volume becomes larger and the activity of permeating molecules increases at the same time. Thus, the permeation of individual molecules and associated molecules through the DMAEM-*g*-N4 membrane becomes easier, resulting in increased total permeation rate.

In other words, the plasticizing effects of the permeants and the interaction between permeants and polymer can be used to further explain the above phenomena. As the temperature increases, the interactions become weaker, so that the plasticizing effect is enhanced. However, strong interactions can be formed at low temperatures and reduce the plasticizing effect.¹⁴ Moreover, the degree of swelling increases as the feed water concentration increases for both grafted nylon 4 membrane and unmodified nylon 4 membrane, as shown in Figure 6. These results correspond well with the results mentioned above regardless of the temperature, as indicated in Figure 5. The degree of swelling of the DMAEMQ-*g*-N4 membrane with a degree of grafting of 12.7% is much higher than that of the unmodified nylon 4 membrane and the DMAEM-*g*-N4 membrane. These phenomena might be due to the fact that the interaction between the water molecules of the feed solution and the quaternized amino group of the DMAEMQ-*g*-N4 membrane increases with increasing water content in the feed solution.

Effect of Feed Composition on Membrane Performances

The effects of the compositions of the feed mixtures on the pervaporation performances of chemical-modified nylon 4 membranes with 12.7% degree of grafting are shown in Table II. As the ethanol con-

centration in the feed solution increases, the separation factor increases while the permeation rate decreases. These results might be due to the plasticizing effect of water. Generally, hydrophilic membranes, e.g., DMAEM-*g*-N4 and DMAEMQ-*g*-N4, have more polar groups and a strong interaction with water through hydrogen bonding or ion-dipoles and thereby the selectivity of the membrane to water can be enhanced. When the water concentration in the feed solution is higher, the amorphous regions of the membrane are more swollen.¹⁵ Hence, the polymer chains become more flexible, thus decreasing the energy required for diffusive transport through the membrane, resulting in the permeation rate increases with the water concentration in the feed solution. The activation energies of diffusion are calculated according to the Arrhenius plot. The activation energies of ethanol-water permeating through the DMAEM-*g*-N4 membrane were in the range of 3.39–4.45 kcal/mol for ethanol feed concentrations varying from 10 to 90 wt %. Further-

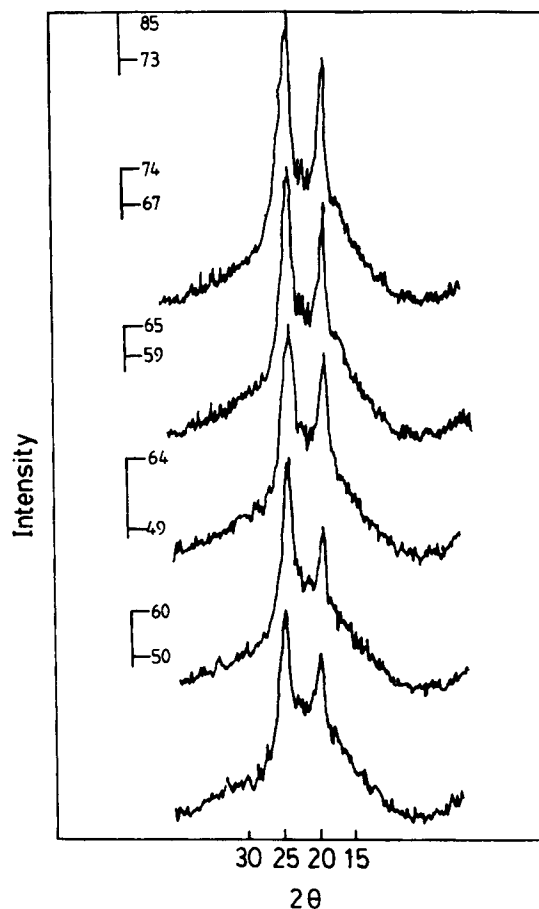


Figure 4 X-ray diffraction patterns of various degree of grafting of DMAEM-*g*-N4 membrane: (a) unmodified N4; (b) 5%; (c) 7.6%; (d) 12.7%; (e) 18.5%.

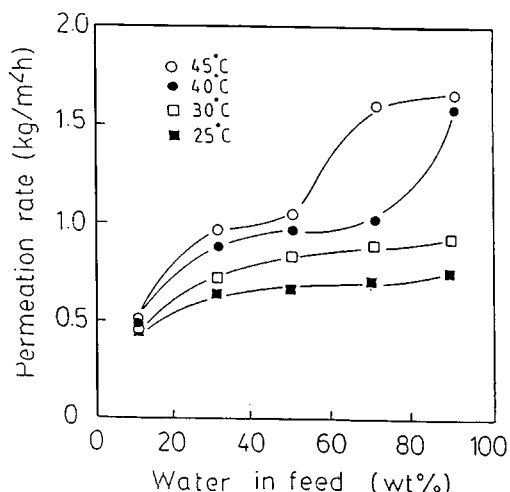


Figure 5 Effect of feed water concentration on the total permeation rate with varying temperature: (○) 45°C; (●) 40°C; (□) 30°C; (■) 25°C.

more, compared with the DMAEM-*g*-N4 membrane for pervaporation performance, the DMAEMQ-*g*-N4 membrane effectively increases both the separation and permeation rate for the aqueous alcohol solution. These phenomena are probably due to the fact that the quaternized ammonium group on the DMAEMQ-*g*-N4 membrane enhances the hydrophilicity of the grafted membrane, and the hydrogen bonding and ion-dipole interaction between ionized groups and water molecules in the feed solution are higher than those of the unquaternized membrane.

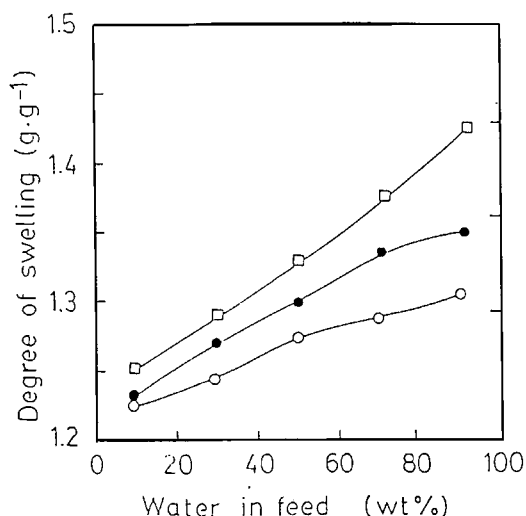


Figure 6 Effect of feed water concentration on the degree of swelling: (○) unmodified nylon 4 membrane; (●) DMAEM-*g*-N4 membrane with 12.7% degree of grafting; (□) DMAEMQ-*g*-N4 membrane with 12.7% degree of grafting.

Table II Permeation Rate and Separation Factor of EtOH/H₂O Mixture Solution Through Modified Nylon 4 Membranes

Feed Ethanol Conc. (wt %)	Separation Factor		Permeation Rate (g/m ² h)	
	A	B	A	B
90	28.3	36.0	439	564
70	17.0	19.5	624	694
50	6.3	7.8	663	792
30	3.3	7.0	718	1073
10	2.4	3.1	767	1350

A: DMAEM-*g*-N4 membrane.
B: DMAEMQ-*g*-N4 membrane.
Degree of grafting: 12.7%.

Thus, the higher separation factor and permeation rate for the DMAEMQ-*g*-N4 membrane were obtained. Similar results were obtained by Hirotsu.¹⁶

Alcohol Sorption of DMAEM-*g*-N4 Membrane

To investigate the effects of solubility and diffusivity on the membrane permselectivity, sorption experiments for DMAEM-*g*-N4 membrane with water feed concentrations varying from 10 to 90 wt % were made. Figure 7 shows the influence of the feed water concentration in the permeate and in the membrane for the DMAEM-*g*-N4 membrane. The water concentration in the membrane is higher than that in the permeate for water feed concentrations in the range of 10–90 wt %. The permeate and sorption

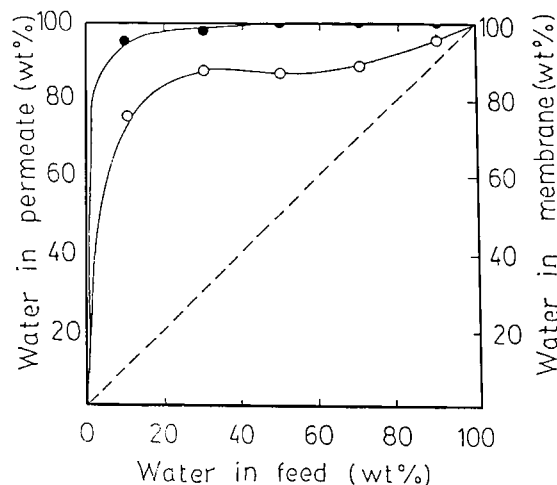


Figure 7 Effect of feed water concentration on composition of the solution adsorbed and permeated with DMAEM-*g*-N4 membrane: (○) permeated; (●) adsorbed.

composition curves lie above the diagonal line, indicating that the water molecules are selectively dissolved into the DMAEM-*g*-N4 membrane which contains hydrophilic groups, e.g., amide groups or ester groups, and are also preferentially diffused through the membrane. Thus, the separation factor for the sorption is higher than that for pervaporation. For example, the separation factors for pervaporation and sorption with the DMAEM-*g*-N4 membrane having a 12.7% degree of grafting, for the 90 wt % aqueous ethanol feed solution, are 28.3 and 123, respectively. In addition, the pervaporation and sorption properties of the DMAEM-*g*-N4 membranes for alcohol-water mixtures are shown in Table III. The data show that an increase in the number of carbon atoms in the alcohol results in an increase in the separation factor for pervaporation and sorption, but gives a decrease in the permeation rate for pervaporation and total sorption. These results can be explained by the molecular size and shape of the alcohol. The separation factor was found to depend on the molecular length for this linear alcohol series; it was also found that the permeation rate of *tert*-butanol is lower than that of the *n*-propanol, which may be due to the steric hindrance of the former being higher than that of the latter.^{5,17}

Table III also shows that the sorption of water increases a little in going from methanol to *tert*-butanol, but that the sorption of the alcohol decreases drastically, resulting in a strong increase in sorption selectivity. When the sorption results are compared with the pervaporation results, it can be seen that both follow the same line qualitatively. It seems that the component is sorbed preferentially and also permeates preferentially.¹⁸ Additionally, Figure 8 shows the individual permeation rates of alcohol and water for a DMAEM-*g*-N4 membrane with a 90 wt % aqueous alcohol solution:

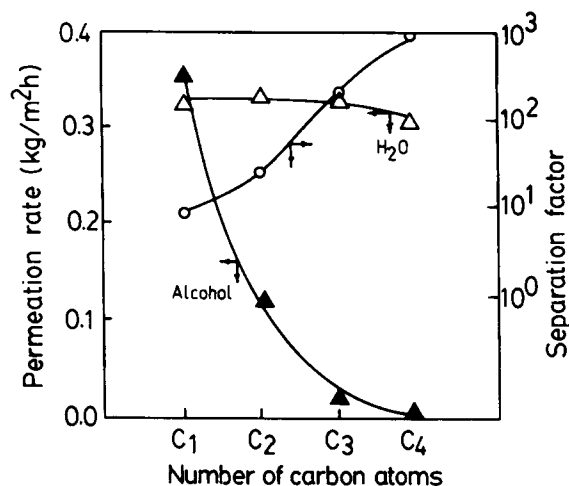


Figure 8 Effect of molecular shape of alcohol on permselectivity of DMAEM-*g*-N4 membrane with 90 wt % aqueous alcohol solution: (Δ) permeation rate of water; (\blacktriangle) permeation rate of alcohol; (\circ) separation factor.

The permeation rate of water is nearly constant, about 320 g/m² h, irrespective of the number of carbon atoms of alcohols, but the permeation rate of alcohol decreases from 356 g/m² h for methanol to 2.78 g/m² h for *tert*-butanol. Similar results were also observed for the plasma deposition⁵ and Co⁶⁰ γ -ray irradiation^{6,7}-modified nylon 4 membranes.

CONCLUSIONS

The pervaporation performances of the DMAEM-*g*-N4 and DMAEMQ-*g*-N4 membrane are significantly improved compared to that of the unmodified Nylon 4 membrane for aqueous ethanol concentrations in the range of 10–90 wt %. The DMAEM-*g*-N4 membrane with a 12.7% degree of grafting gives

Table III Pervaporation and Sorption Properties of Chemical Grafted Nylon 4 Membranes for Alcohol–Water Mixture

Alcohol	Alcohol in Feed (wt %)	<i>L</i> (Å)	Total Sorption (g/g)	Water Sorption (g/g)	Ethanol Sorption (g/g)	Separation Factor		Permeation Rate (g/m ² h)
						A	B	B
Methanol	90	2.9	1.26	1.127	0.132	76.7	8.2	678
Ethanol	90	4.2	1.22	1.136	0.084	123	28.3	439
<i>n</i> -propanol	90	5.4	1.18	1.165	0.015	340	216	345
<i>t</i> -butanol	90	—	1.18	1.174	0.006	1755	955	298

L: molecular length (ref. 17).

A: sorption.

B: pervaporation.

the best results for the separation factor and permeation rate, i.e., 28.3 and 439 g/m² h, respectively. In addition, both the separation factor and the permeation rate of the DMAEMQ-*g*-N4 membrane are higher than those of the DMAEM-*g*-N4 membrane. Water molecules are selectively dissolved into the modified nylon 4 membrane that contain hydrophilic groups, e.g., an ester group, amide group, and quaternized ammonium group, and also are preferentially diffused through the membrane. There are complex interactions between permeants and polymer as well as the plasticizing effect of water which significantly alter permeation and separation properties of the prepared membrane.

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