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Membrane Concentration and Separation of L-Aspartic Acid and L-Phenylalanine Derivatives in Organic Solvents

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ABSTRACT

The concentration and separation of the amino acids *N*-benzyloxycarbonyl L-aspartic acid and L-phenylalanine methyl ester hydrochloride in organic solvents have been investigated using reverse osmosis membranes of two types of cellulose acetate, a nanofiltration membrane of polyamide–polyphenylene sulfone (PA–PPSO) composite and a gas separation membrane of polyimide composite in a stirred batch cell. The organic solvents used included primary, secondary, and tertiary alcohols, an ester, and a ketone. There were significant variations in permeate flux, solute rejection, and membrane stability. Usually the rejection of both amino acids was similar; however, certain membrane-solvent combinations gave significantly different levels of rejection. The highest rejection of amino acids (~0.94) at the lowest pressure of 0.5 MPa was obtained with the PA–PPSO membrane using methanol as a solvent. The cellulose acetate membranes gave reasonable rejection and fluxes but the membrane stability was very poor. The performance of the polyimide composite membrane was good with ethanol but poor with other solvents. The PA–PPSO membrane with methanol as solvent appeared the most promising combination, and the separation performance according to concentration polarization was discussed.

Key Words. Membrane separation; Amino acids; Aspartame; Organic solvent; Reverse osmosis; Nanofiltration

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INTRODUCTION

Many consumers nowadays wish to reduce their dietary intake of sucrose and are therefore using low calorie sweeteners such as aspartame. Aspartame (L-aspartyl-L-phenylalanine methyl ester) is a synthetic, low calorie dipeptide of aspartic acid and phenylalanine with a sweetness 150 to 200 times that of sucrose (1). It has been approved for use as a food additive by the United States Food and Drug Administration but only after extensive safety studies were conducted (2). It is now used in carbonated beverages, powdered food products, chewing gum, yogurt, ice cream, and as a table-top sweetener (3).

Recently there has been much interest in producing aspartame by an enzymatic process in organic solvents. The possible advantages of such a process are stability and temperature tolerance of the enzyme and the absence of pH and water effects on the reaction rate. The enzymatic synthesis of *N*-benzyloxycarbonyl-L-aspartyl-L-phenylalanine methyl ester, a precursor of aspartame, in butyl ethanoate (butyl acetate) and 2-methyl 2-butanol (*t*-amyl alcohol) has been reported by several researchers (4–7). The amino acid derivatives used in the synthesis of this aspartame precursor are *N*-benzyloxycarbonyl L-aspartic acid (Z-Asp) and L-phenylalanine methyl ester hydrochloride (PheOMeHCl). In order to improve the performance of this enzymatic process, it is desirable to be able to concentrate the amino acids so that they can be recycled. The primary objective of this study therefore was to find a suitable method for concentrating Z-Asp and PheOMeHCl in butyl ethanoate or 2-methyl 2-butanol.

The molecular weights of the amino acid derivatives (267.2 and 215.7 Da for Z-Asp and PheOMeHCl, respectively) are in the range that can be separated by reverse osmosis (RO) and nanofiltration (NF). RO and NF have been widely used for seawater desalination and also in the food, fermentation, and wastewater treatment industries as one of the most energy saving technologies (8). The solutions treated have been almost exclusively aqueous and there has been very little published data on the use of RO or NF with organic systems. Sourirajan (9) and Kimura and Sourirajan (10) demonstrated the ability of cellulose acetate RO membranes to separate various hydrocarbon mixtures in an aqueous system. Koseoglu et al. (11) investigated the use of composite RO and NF membranes to concentrate crude vegetable oils in hexane, ethanol, and isopropanol. Hexane damaged several of the membranes and gave negligible flux with some of them. Reasonable results were obtained using a cellulose acetate membrane with ethanol and isopropanol. Koike et al. (12) investigated the separation of fatty acids and mono, di, and triglycerides in hexane and ethanol solvents using a variety of different membranes. They

showed that a cellulose acetate RO membrane (NTR-1698) with ethanol and a gas separation membrane (NTGS-2100) with hexane gave the best results. On the basis of this information in the literature, it was decided to test the ability of two different types of cellulose acetate RO membranes and a gas separation membrane (polyimide composite) to concentrate amino acids. A recently developed polyamide–polyphenylene sulfone composite NF membrane (Toray Industries, Inc., Japan) for organic solvents was also tested as a comparison. The secondary aim of this project was to gain more understanding of the physicochemical parameters that influence the performance of membranes with organic solvents. For this reason various organic solvents were tested for their ability to concentrate amino acids. In addition, the possibility of separating amino acids by a membrane process was investigated.

MATERIALS AND METHODS

Solutions of Amino Acids

Solutions of amino acids (2 mM) were prepared by dissolving *N*-benzyloxycarbonyl L-aspartic acid (Z-Asp) (1 mM) and L-phenylalanine methyl ester hydrochloride (PheOMeHCl) (1 mM) in different organic solvents. The organic solvents used in the experiment include butyl acetate, acetone, hexane, and a group of different alcohols. The alcohols were methanol (M-OH), ethanol (E-OH), 1-propanol (1P-OH), 1-butanol (1B-OH), 2-propanol (2P-OH), 2-methyl 2-propanol (2M2P-OH), 2-butanol (2B-OH), 2-methyl 1-propanol (2M1P-OH), and 2-methyl 2-butanol (2M2B-OH). To minimize the effect of osmotic pressure on membrane performance due to concentration polarization, low concentration solutions were used. PheOMeHCl is insoluble in butyl acetate, so therefore it was first dissolved in acetate buffer at a pH of 6.7 and extracted 4–5 times as L-phenylalanine methyl ester (PheOMe) (adjusting the pH value every time) by saturating with butyl acetate (13). Similar concentrations of aqueous solutions were also prepared using RO permeated water. PheOMeHCl was supplied by Aldrich Chemical Company, Inc., Wisconsin, USA. All other chemicals used were laboratory grade, supplied by Wako Pure Chemical Industries Ltd., Osaka, Japan.

Membranes

The membrane materials were cellulose acetate (CA), polyimide composite (PI-COM), and polyamide–polyphenylene sulfone composite (PA-PPSO). The membranes used in the experiment were obtained from two suppliers. Cellulose acetate (CA1) NTR-1698 and Gas separation (PI-

COM) NTGS-2100 membranes were supplied by the Nitto Denko Corporation, Tokyo, Japan, and the SC-3000 (CA2) and Toray composite NF (PA-PPSO) membranes were supplied by Toray Industries, Inc., Tokyo, Japan.

Equipment and Operating Conditions

The test cell (Fig. 1) was operated at 40°C, using a membrane (with a diameter of 7.5 cm and an exposed surface area of 32 cm^2) backed by a porous Teflon layer. A Teflon-coated O-ring resistant to organic solvents was used on the membrane surface. Mixing was provided at 500 rpm by a magnetic stirrer suspended above the membrane. Before use, the membranes were preconditioned by soaking in the respective pure organic solvent overnight and subjected to pure solvent at a pressure of 4 MPa for 30 minutes using nitrogen gas. Generally 150 mL of feed solution was concentrated to about half of the volume. However, when the permeate flux was below 2×10^{-3} $kg \cdot m^{-2} \cdot s^{-1}$, the experiment was stopped after 3 hours of operation. The permeate flux was continuously recorded with a top-pan balance and a personal computer. For the experiments to determine the mass transfer coefficient in an aqueous system, a CA membrane and a 1-mM solution of Z-Asp were used. The speed of the stirrer was

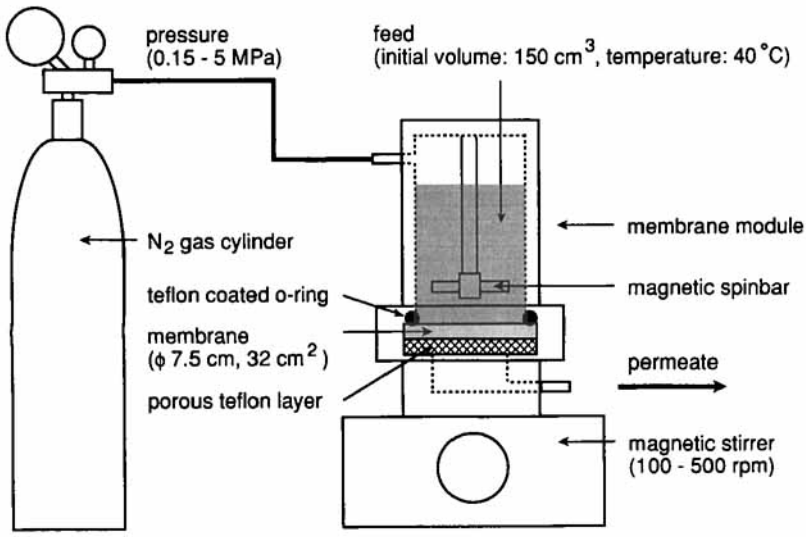

FIG. 1 Filtration system.

varied from 100 to 500 rpm in order to create different shears, and the pressure was kept constant at 1 MPa. All experiments were done in duplicate or more as specified in the results.

Analysis

The concentrations of amino acids in the initial feed, permeate, and retentate solutions were determined by HPLC analysis using a Finepak SIL C18S column with a UV detector (Japan Spectroscopic Co. Ltd., Tokyo) at 220 nm. A mixture of phosphate buffer at pH 2.4 (65%) and acetonitrile (35%) was used as the mobile phase for HPLC. The injected sample volume was 1 μL. The mass balance was checked prior to the calculation of observed rejection (R_{obs}). A very good mass balance for each solute (98.5–101.5%) was observed for all experiments. R_{obs} was calculated using the following equation (14):

$$R_{obs} = \ln(C_s/C_{s0})/\ln(W_0/W) \quad (1)$$

where C_{s0}, C_s, W_0, and W are initial concentration of each solute in the feed ($mol \cdot kg^{-1}$), initial concentration of each solute in the retentate ($mol \cdot kg^{-1}$), initial feed solution weight (kg), and retentate solution weight (kg), respectively.

Surface examination of PA–PPSO and CA membranes was done with a JSM-890 Scanning Electron Microscope (JEOL Ltd., Tokyo, Japan).

RESULTS AND DISCUSSION

Effects of Membrane Type and Solvent on Flux and Rejection of Amino Acids

The four membranes were first tested for their performances with methanol, ethanol, 2-methyl 2-butanol, and butyl acetate solutions. Additionally, the PA–PPSO was tested with acetone. The results of amino acids rejection and permeate flux are presented in Table 1.

Methanol solution gave lower permeate fluxes than ethanol with CA and *PI-COM* membranes but not with the PA–PPSO membrane. A general observation was that the permeate flux declined significantly with CA membranes within each operation and from operation to operation. Continuous use of the membranes for more than 10 hours at 4 MPa resulted in almost negligible flux. However, prolonged soaking of the CA membranes for more than 10 days in solvents before use had no effect on the initial flux. It appears that the membranes swell and undergo compaction in organic solvents when they are subjected to pressure. Scanning electron microscopic (SEM) examination of the CA membranes revealed an exten-

TABLE 1
Observed Rejection of Amino Acids and Flux

Solvent		Membrane[a] CA1	CA2	PI-COM	PA-PPSO
M-OH	R_{obs} of Z-Asp (—)	0.47	0.65	0.08–0.57	0.86[b]
	R_{obs} of PheOMeHCl (—)	0.72	0.85	0.13–0.50	0.86
	$J \times 10^3$ ($kg \cdot m^{-2} \cdot s^{-1}$)	2.1–2.7	1.7–2.4	1.4–9.7	2.3
E-OH	R_{obs} of Z-Asp (—)	0.38	0.19	0.80	0.64
	R_{obs} of PheOMeHCl (—)	0.81	0.38	0.69	0.62
	$J \times 10^3$ ($kg \cdot m^{-2} \cdot s^{-1}$)	7.7–14.7	13.5–16.7	3.4–4.5	4.7–5.7
2M2B-OH	R_{obs} of Z-Asp (—)	0.19	0.53[c]	0.06	0.41[d]
	R_{obs} of PheOMeHCl (—)	0.26	0.57	0.06	0.40
	$J \times 10^3$ ($kg \cdot m^{-2} \cdot s^{-1}$)	5.4–5.5	3.4	7–8	0.06
Butyl acetate	R_{obs} of Z-Asp (—)	0.34	0.00	0.00	0.53[d]
	R_{obs} of PheOMe (—)	0.00	0.00	0.00	0.04
	$J \times 10^3$ ($kg \cdot m^{-2} \cdot s^{-1}$)	1.4–4.4	5.3	>40	0.56
Acetone	R_{obs} of Z-Asp (—)	—	—	—	0.35[e]
	R_{obs} of PheOMeHCl (—)	—	—	—	0.18
	$J \times 10^3$ ($kg \cdot m^{-2} \cdot s^{-1}$)	—	—	—	5.1

[a] Pressure = 4 MPa except as noted.
[b] Pressure = 0.2 MPa.
[c] Membrane failed after 60 minutes.
[d] Pressure = 0.5 MPa.
[e] Pressure = 0.15 MPa.

sive swelling effect. If the stability of the CA membranes is improved, there is a possibility to separate the amino acids since rejection of PheOMeHCl was about twice that of Z-Asp. PA–PPSO membrane performance was best with ethanol and methanol solutions. The stability of the membrane was good, and it gave high rejection of both solutes (0.62–0.86) and more stable permeate flux compared to other membranes. The stability of the PA–PPSO membrane was further confirmed by SEM examination of the surface of new and used membranes. There was no appreciable

change in the micro structure of the membrane skin layer. Slight fouling was only observed on the membrane surface. PI-COM membrane could also give a stable flux and a high rejection with ethanol solution; however, it was damaged by methanol solution.

The 2-methyl 2-butanol solution gave lower rejections of amino acids than methanol or ethanol solution with all membranes except the CA2 membrane which failed after 60 minutes of operation. Butyl acetate solution gave no rejections with CA2 and PI-COM membranes. With the other membranes, significant differences were observed in rejection between the two amino acids. With CA1 and PA–PPSO membranes, the rejection of Z-Asp was 0.34 and 0.53, respectively, while that of PheOMeHCl was almost zero (0–0.04). Similar to the cases with CA membranes for methanol or ethanol solution; it is also possible to separate the amino acids in which rejection of Z-Asp is higher, in contrast to the CA membrane case. The permeate flux of acetone solution with PA–PPSO membrane was high (5.1×10^{-3} kg·m^{-2}·s^{-1} at 0.15 MPa pressure) and stable. However, the solute rejections were poor.

In conclusion, the performance of the PA–PPSO membrane appeared promising. The membrane was stable for all of the solvents and could be used to concentrate Z-Asp and PheOMeHCl.

Determination of the Mass Transfer Coefficient by Velocity Variation Method

The mass transfer coefficient is described by the concentration polarization equation (10)

$$J/\rho = k \ln[(C_m - C_p)/(C_b - C_p)] \quad (2)$$

where J, ρ, K, C_m, C_p, and C_b are solvent flux (kg·m^{-2}·s^{-1}), solvent density (kg·m^{-3}), mass transfer coefficient (m·s^{-1}), solute concentration at the membrane surface (mol·kg^{-1}), solute concentration in the permeate (mol·kg^{-1}), and solute concentration in the bulk feed (mol·kg^{-1}), respectively. The equation can be written using real rejection and observed rejection:

$$\ln[(1 - R_{obs})/(R_{obs})] = \ln[(1 - R)/(R)] + J/(\rho k) \quad (3)$$

where R and R_{obs} are real rejection (—) and observed rejection (—), respectively. The mass transfer coefficient, k, is usually a function of the Reynolds number, Re (—), which is given from the flow velocity for a thin channel module (15):

$$k = A^* u^{\alpha} \quad (4)$$

in which A^* and α are constants and u is flow velocity ($m \cdot s^{-1}$). For the stirred batch cell, the mass transfer coefficient, k, is also a function of the Reynolds number (16):

$$Re = \omega^* r^2/\nu \tag{5}$$

$$kr/D = a^* Re^{\beta} Sc^{1/3} \tag{6}$$

where a^* and β are constants and ω^*, r, ν, D, and Sc are stirrer speed ($rad \cdot s^{-1}$), radius of the stirring batch cell (m), kinetic viscosity ($m^2 \cdot s^{-1}$), diffusion coefficient ($m^2 \cdot s^{-1}$), and Schmidt number (—), respectively. The value of β is variable with the flow regime (16–18).

Turbulent flow:

$$\beta = 0.75 \qquad (32{,}000 < Re < 82{,}000) \tag{7}$$

Transition from laminar to turbulent flow:

$$\beta = 0.567 \qquad (8000 < Re < 32{,}000) \tag{8}$$

When Re is below 20,000, the boundary layer is laminar (18). For the laminar flow system the following value is used based on the Lévêque equation (19).

Laminar flow:

$$\beta = 1/3 \qquad (Re < 20{,}000) \tag{9}$$

Equations (3), (4), and (6) can be rewritten as

$$\ln\{(1 - R_{obs})/(R_{obs})\} = \ln\{(1 - R)/(R)\} + J_v/(A\omega^{\beta}) \tag{10}$$

$$k = A\omega^{\beta} \tag{11}$$

$$A = aD^{2/3}\nu^{1/3-\beta} \tag{12}$$

where J_v and ω are permeate volume flux ($m^3 \cdot m^{-2} \cdot s^{-1}$) and stirrer speed (rpm), respectively, and a is a constant derived from cell design.

When the flux is constant the real rejection is regarded as constant and the mass transfer coefficient can be obtained by the velocity (stirrer speed) variation method (15, 20). With variation of the stirrer speed, ω, from 100 to 500 rpm, 1 mM Z-Asp aqueous solution was filtered with the CA membrane (NTR-1698) at 1 MPa. The observed rejection of Z-Asp varied from 0.121 to 0.282, and the volume flux was almost constant. Figure 2 shows the linear relationship between $\ln\{(1 - R_{obs})/(R_{obs})\}$ and $J_v/\omega^{1/3}$. Although Re varied from 11,080 (stirrer speed: 100 rpm) to 55,400 (500 rpm) in the aqueous system at 40°C in this study, the laminar flow value of 1/3 showed the best linear relationship among the β values of 0.75, 0.567, and 1/3. The stirring effect was relatively weak compared to previ-

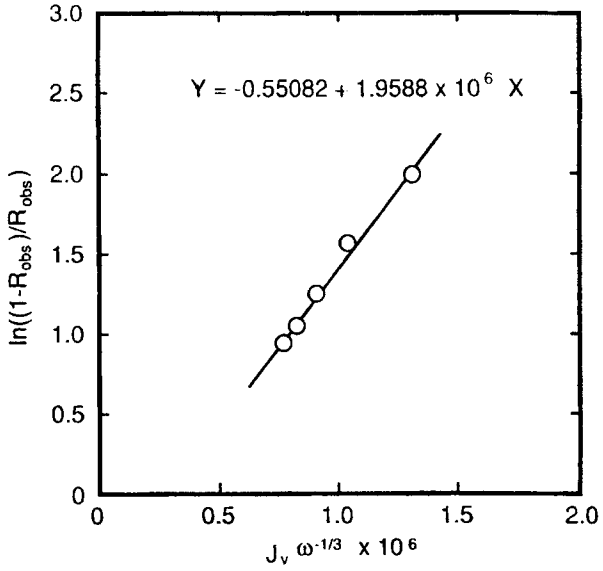

FIG. 2 Estimation of mass transfer coefficient and real rejection by the velocity (stirrer speed) variation method.

ous studies. The mass transfer coefficient was calculated from the slope and determined as 4.05×10^{-6} m·s^{-1} at a stirrer speed of 500 rpm. The real rejection, R, was 0.634, which was calculated from the intercept of the plot. For a dilute solution, diffusion coefficient, D (m^2·s^{-1}), can be estimated by the modified Wilke–Chang equation as follows (21):

$$D = 6.6 \times 10^{-15}(\phi M)^{1/2}\, T/(\mu V^{0.6}) \qquad (13)$$

where M, T, μ, and V are molecular weight of the solvent (g·mol^{-1}), absolute temperature (K), viscosity (Pa·s), and molar volume of the solute (cm^3·mol^{-1}), respectively. The ϕ value is the association coefficient of the solvent, which is 2.6 for water and 1.9 for methanol. Physicochemical parameters such as the viscosities of water and methanol at 40°C were obtained from data books (22), and the molar volume of Z-Asp could be calculated as 293.7 cm^3·mol^{-1} using the method of Le Bas (23). The diffusion coefficients of Z-Asp in aqueous and methanol solution were calculated as 4.87×10^{-10} and 8.05×10^{-10} m^2·s^{-1}, respectively. Finally, with the use of Eqs. (11) and (12) the mass transfer coefficient of Z-Asp methanol solution was calculated as 5.66×10^{-1} at a stirrer speed of 500 rpm.

Pressure Effect on Flux and Rejection with PA–PPSO Membrane for Aqueous and Methanol Solutions

The effect of pressure on flux and rejection of amino acids for aqueous and methanol solutions is shown in Figs. 3 and 4. The observed rejection of amino acids in aqueous solution was in the 0.85–0.94 range. The flux increased linearly with an increase in applied pressure, which suggests that the osmotic pressure development on the membrane surface from concentration polarization is negligible compared to the applied pressure. It is interesting to note that the flux was reasonable even at very low pressures. For a new PA–PPSO membrane, the initial flux drop due to pressure compaction was about 20% at 4 MPa pressure for 30 minutes. Flux drop within any operation or between operations was negligible, indicating good stability of the membrane with methanol solution. The rejection trend for Z-Asp and PheOMeHCl was generally similar. The highest rejection (~0.94) was observed at the lowest pressure (0.5 MPa), and the lowest rejection (~0.70) was observed at the highest pressure (4 MPa). The variation between replicates was less than 3%. The decrease in rejection of solute at higher flux was attributed to the phenomenon of concentration polarization. Figure 5 shows the observed and the real

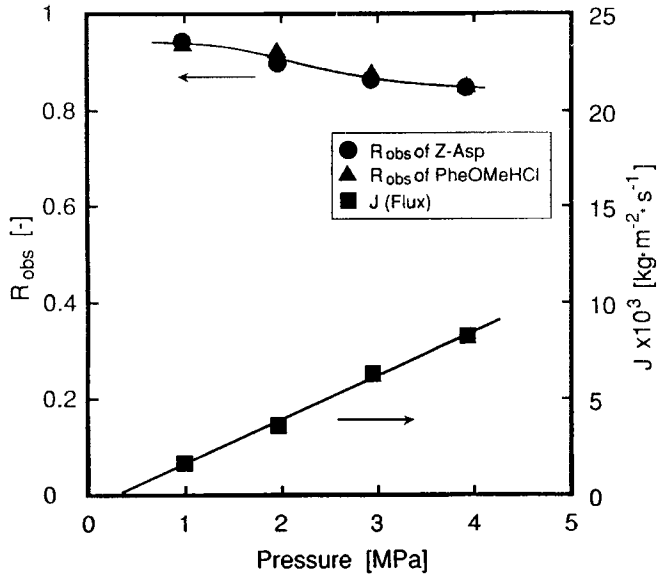

FIG. 3 Effect of pressure on observed rejection (R_{obs}) and flux for aqueous solution using PA–PPSO membrane.

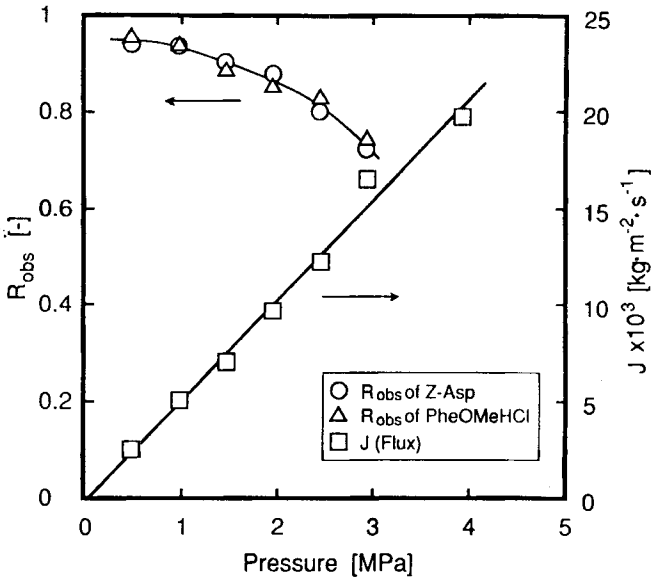

FIG. 4 Effect of pressure on observed rejection (R_{obs}) and flux for methanol solution using PA–PPSO membrane.

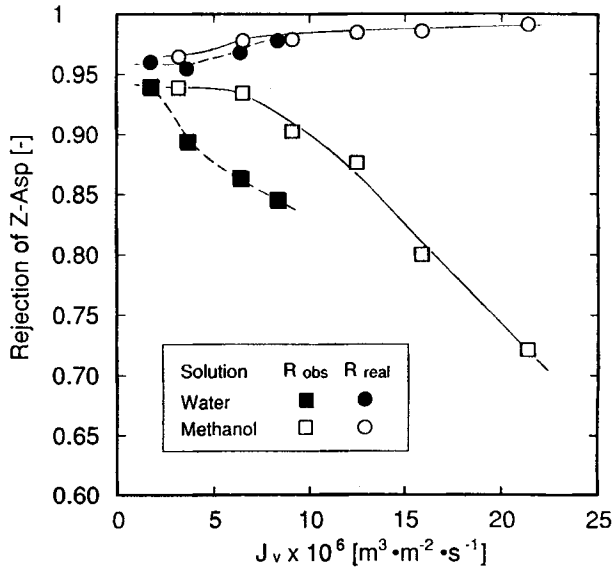

FIG. 5 Effect of volume flux (J_v) on observed rejection (R_{obs}) and real rejection (R_{real}) of Z-Asp for methanol and aqueous solution using PA–PPSO membrane.

rejections of Z-Asp against the volume flux using the mass transfer coefficients 4.05 $\times$ 10^{-6} $m \cdot s^{-1}$ in aqueous solution and 5.66 $\times$ 10^{-6} $m \cdot s^{-1}$ in methanol solution obtained in the previous section. Higher flux with methanol solution may create higher concentration at the membrane surface than in the bulk solution. The real rejection is not changed so much in the range of flux and it is similar to the observed rejection for the volume flux below 5 $\times$ 10^{-6} $m^3 \cdot m^{-2} \cdot s^{-1}$. The stability of the membrane used with methanol solution was tested by concentrating a similar concentration of amino acids in aqueous solution. Comparison of the results of aqueous solution with new and used membranes showed no significant variation.

Performance of PA–PPSO Membrane for Alcoholic and Other Solutions

The results of normalized flux of alcoholic solutions are presented in Fig. 6. Normalized flux (flux per unit operating pressure) of primary alcohols decreased substantially with an increase in their molecular weight.

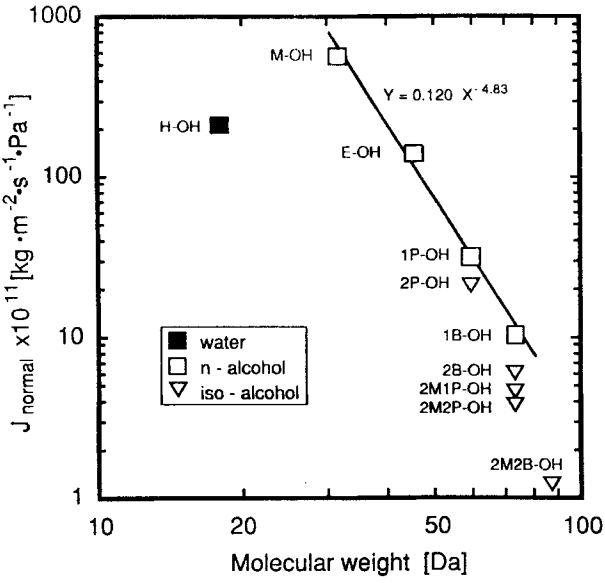

FIG. 6 Effect of molecular weight of alcohols on normalized flux (J_{normal}) using PA–PPSO membrane.

The fluxes of secondary alcohols were lower than those of the corresponding primary alcohols. There have several reports on RO/NF separations for organic substances in aqueous solution. Matsuura and Sourirajan (24, 25) reported that a good correlation was observed between the permeation of alcohols as solute and hydrogen bonding ability of alcohols by using cellulose acetate RO/NF membranes. It is clear from the results that permeability of alcohols is influenced by the molecular weight and hydrophobicity.

The solution-diffusion model (26) predicts that the normalized flux, J_{normal} ($kg \cdot m^{-2} \cdot s^{-1} \cdot Pa$), of a nonporous membrane is proportional to the diffusion coefficient in the membrane, D_m ($m^2 \cdot s^{-1}$), and the solubility of a solvent in the membrane, S_m ($kg \cdot m^{-3}$):

$$J_{normal} = B^* D_m S_m \tag{14}$$

where B^* is a constant. Among the solvents used in the experiment, differences can be seen in the solubility parameter, δ ($cal^{1/2} \cdot cm^{-3/2}$). The δ_p, δ_h, and δ_d are the polar, hydrogen bonding, and dispersive contributions to the solubility parameter of a solvent ($cal^{1/2} \cdot cm^{-3/2}$) (27):

$$\delta^2 = \delta_p^2 + \delta_h^2 + \delta_d^2 \tag{15}$$

It is considered that the solubility of a solvent to a membrane is described as

$$S_m = b/\{(\delta_p - x)^2 + (\delta_h - y)^2 + (\delta_d - z)^2\} \tag{16}$$

where x, y, and z are the polar, hydrogen bonding, and dispersive contributions to the solubility parameter of the membrane and b is a constant. The following equation is obtained from Eqs. (14)–(16).

$$D_m/J_{normal} = B\{(\delta_p - x)^2 + (\delta_h - y)^2 + (\delta_d - z)^2\} \tag{17}$$

in which B is a constant. In order to investigate effects of the solubility parameter of solvents on the normalized flux and to seek the solubility parameter of the membrane, each contribution for the solubility parameter of the solvents was plotted against D_s/J_{normal} as shown in Fig. 7. It was assumed that the self-diffusion coefficient, D_s ($m^2 \cdot s^{-1}$), obtained from data books (22, 28, 29) could be applied to the diffusion coefficient in the membrane, D_m. In consideration of particular data with water and hexane, it seems difficult to find a obvious tendency for the relationship between D_s/J_{normal} and each contribution of the solubility parameter of the solvents. However, the solubility parameter of the membrane could be estimated from the intercept of the Y-axis as $x = 4.71$ (δ_p), $y = 9.27$ (δ_h), and $z = 7.47$ (δ_d).

The results of amino acids rejection in different alcohols are presented in Fig. 8. The solute rejection in primary alcohol solutions decreased as the chain length increased up to propanol, but butanol gave higher solute rejection. The possibility of a concentration polarization effect on solute rejection was negligible using the data at a low volume flux below 5×10^{-6} $m^3 \cdot m^{-2} \cdot s^{-1}$. The solute rejection appears to decrease with the molecular weight of solvents up to a certain stage (~60 Da), but beyond that the rejection increased with molecular weight. Primary alcohols gave higher solute rejection compared to their corresponding secondary alcohols. The differences in diffusion coefficient between solvent and solutes may decrease the rejection of solute up to 60 Da. Above 60 Da, the solvent may interfere with the solute membrane interaction and enhance the rejection of solutes. Methanol appeared to be the best solvent to obtain higher solute rejection using the PA–PPSO membrane than any other alcohol.

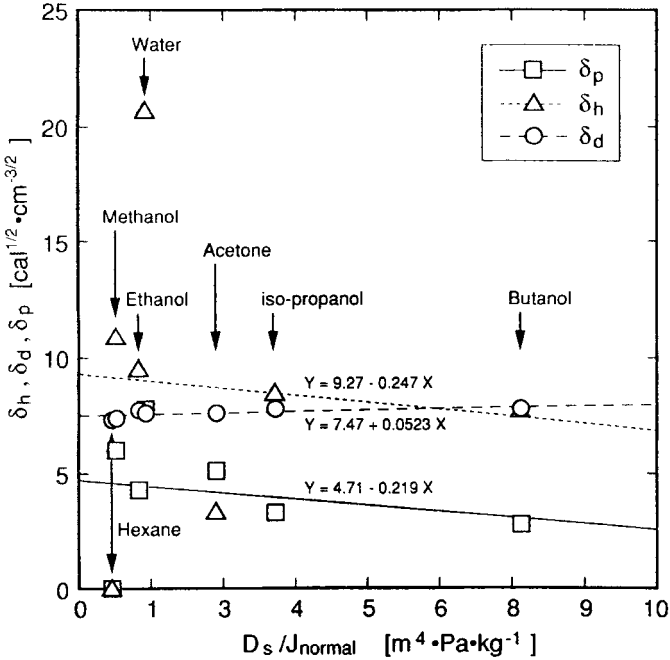

FIG. 7 Relationship between D_s/J_{normal} and the solubility parameter of the solvents, and estimation of the solubility parameter of PA–PPSO membrane: $x = 4.71$ (δ_p), $y = 9.27$ (δ_h), $z = 7.47$ (δ_d).

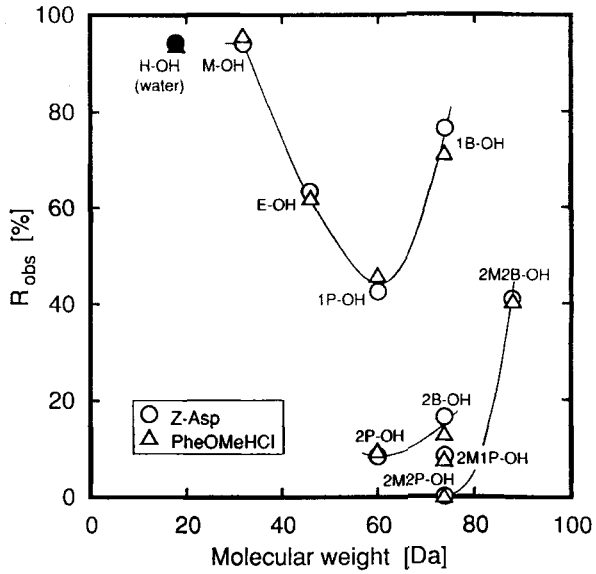

FIG. 8 Effect of molecular weight of alcohols on observed rejection (R_{obs}) of Z-Asp and PheOMeHCl using PA–PPSO membrane.

CONCLUSIONS

The solute rejection and permeate flux are both significantly influenced by the organic solvents and the type of membrane. Membrane concentration data of Z-Asp and PheOMeHCl in different organic solvents using three RO/NF membranes and one gas separation membrane showed that the PA–PPSO membrane performed well with methanol and ethanol solvents. Increase in the molecular weight and branching of alcohols decreased the permeate flux and solute rejection using the PA–PPSO membrane. Higher solute rejection and permeate flux were observed at low operating pressures due to the concentration polarization phenomenon. The PA–PPSO membrane was stable with methanol even after more than 25 hours of operation at pressures up to 4 MPa. The Pl-COM membrane gave greater rejection with ethanol solution; however, the long-term stability of the membrane needs to be investigated. CA membranes were not stable with regard to flux and solute rejection. The difference in rejection between Z-Asp and PheOMeHCl with certain solvent–membrane combi-

nations is promising for the separation of amino acids. Future work should be directed toward developing more permeable and dissolution-resistant membranes to organic solvents.

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NOMENCLATURE

a	constant
A	constant
a^*	constant
A^*	constant
b	constant
B	constant
B^*	constant
C_b	solute concentration in bulk feed ($mol \cdot kg^{-1}$)
C_m	solute concentration at the membrane surface ($mol \cdot kg^{-1}$)
C_p	solute concentration in permeate ($mol \cdot kg^{-1}$)
C_s	concentration of each solute in the retentate ($mol \cdot kg^{-1}$)
C_{s0}	initial concentration of each solute in the feed ($mol \cdot kg^{-1}$)
D	diffusion coefficient ($m^2 \cdot s^{-1}$)
D_m	diffusion coefficient in a membrane ($m^2 \cdot s^{-1}$)
D_s	self-diffusion coefficient ($m^2 \cdot s^{-1}$)
J	flux ($kg \cdot m^{-2} \cdot s^{-1}$)
J_{normal}	normalized flux ($kg \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)
J_v	volume flux ($m^3 \cdot m^{-2} \cdot s^{-1}$)
k	mass transfer coefficient ($m \cdot s^{-1}$)
M	molecular weight of a solvent ($g \cdot mol^{-1}$)
r	radius of the stirring batch cell (m)
R	real rejection (—)
R_{obs}	observed rejection (—)
Re	Reynolds number (—)
S_m	solubility of a solvent in a membrane ($kg \cdot m^{-3}$)
Sc	Schmidt number (—)
T	absolute temperature (K)

u	flow velocity ($m \cdot s^{-1}$)
V	molar volume of the solute ($cm^3 \cdot mol^{-1}$)
W	retentate solution weight (kg)
W_0	initial feed solution weight (kg)
x	polar contributions to the solubility parameter ($cal^{1/2} \cdot cm^{-3/2}$)
y	hydrogen bonding contributions to the solubility parameter ($cal^{1/2} \cdot cm^{-3/2}$)
z	dispersive contributions to the solubility parameter ($cal^{1/2} \cdot cm^{-3/2}$)

Greek

α	constant
β	constant
δ_p	polar contributions to the solubility parameter ($cal^{1/2} \cdot cm^{-3/2}$)
δ_h	hydrogen bonding contributions to the solubility parameter ($cal^{1/2} \cdot cm^{-3/2}$)
δ_d	dispersive contributions to the solubility parameter ($cal^{1/2} \cdot cm^{-3/2}$)
ϕ	association coefficient of the solvent
μ	viscosity (Pa·s)
ν	kinetic viscosity ($m^2 \cdot s^{-1}$)
ρ	solvent density ($kg \cdot m^{-3}$)
ω	stirrer speed (rpm)
ω^*	stirrer speed ($rad \cdot s^{-1}$)

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