

STUDIES ON REVERSE OSMOSIS SEPARATION OF AQUEOUS ORGANIC SOLUTIONS BY PAA/PSF COMPOSITE MEMBRANE

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Abstract The reverse osmosis (RO) separation of aqueous organic solutions, such as alcohols, amines, aldehydes, acids, ketones, and esters etc., by PAA (polyacrylic acid)/PSF (polysulfone) composite membrane has been studied. It was found that the separation results for aliphatic alcohols, amines and aldehydes are satisfactory, the solute rejection (R_a) and the volume fluxes of solutions (J_v) for 1000 ppm ethanol, ethylamine and ethyl aldehyde are 66.2%, 61.0%, 84.0% and 0.90×10^{-6} , 0.35×10^{-6} , $0.40 \times 10^{-6} \text{ m}^3/\text{m}^2 \cdot \text{s}$, respectively, at 5.0 MPa and 30°C. R_a increased with increasing molecular weights of alcohols, amines and aldehydes, and the R_a for *n*-amyl alcohol, *n*-butylamine and *n*-butyl aldehyde reached 94.3%, 88.6% and 96.0%, respectively. Satisfactory separation results ($R_a > 70\%$) for ketones, esters, phenols and polyols have been obtained with the PAA/PSF composite membrane. The effect of operating pressure on the properties of reverse osmosis has also been investigated. Analysis of experimental data with Spiegler-Kedem's transport model has been carried out and the membrane constants such as reflection coefficient σ , solute and hydraulic permeabilities ω and L_p for several organic solutes have been obtained.

Keywords PAA/PSF composite membrane, Reverse osmosis, Separation of aqueous organic solution

INTRODUCTION

Reverse osmosis (RO) separation has been demonstrated to be a reliable and economical technique in seawater and brackish water desalination during the past decades. With the development of new polymer membranes, especially the composite membranes, the reverse osmosis technique has been widely applied in a lot of fields. Although primarily developed for seawater desalination, the applicability of reverse osmosis membranes has extended to the separation of solvent-containing water. This feature is of great interest in many applications, such as the treatment of solvent-containing waste water, the recovery of valuable organic compounds from their aqueous solutions and the harvesting of organic substances from fermentation broths. However, the RO separation of aqueous organic solutions is less developed compared with the separation of inorganic solutions. Matsuura and Sourirajan^[1-4] studied such separations for alcohols, phenols, organic acids, and hydrocarbons in aqueous solutions using porous cellulose acetate membranes. Some physicochemical criteria for RO separation of organics were discussed. However, the rejections of cellulose acetate membrane for aqueous solution of organics are relatively low, especially for low molecular weight organics. Some polymer membranes have better separation properties for organics than those of cellulose membranes. The solute rejections (R_a) of the main commercial RO composite membranes, such as NS-100^[5], HR-95^[6], HR-98^[6], SC-200^[6], SC-1000^[6] and PEC-1000^[7], for aqueous ethanol solution could reach above 60%. It was found that the RO separation mechanism for organics was different from and more complicated than that for inorganic ions^[8, 9]. The separation properties of organics were mainly controlled by the physicochemical properties of organic molecules, the structure and physicochemical properties of membrane and the interaction between membrane material and organic solute^[10].

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In this work, crosslinked PAA/PSF composite membrane was prepared by a TDI crosslinking method. This membrane has been used to study the reverse osmosis (RO) separation properties for alcohols, amines, aldehydes, acids, ketones, and esters *et al.* The effect of operating pressure on the properties of reverse osmosis has also been investigated and it was found that the solute rejections and the fluxes of solution increased with the increasing of the operating pressure in the experiment. An analysis of experimental data with Spiegler-Kedem's transport model has been carried out and the membrane constants such as reflection coefficient σ , solute and hydraulic permeabilities ω and L_p for several organic solutes were obtained.

EXPERIMENTAL

Membrane Preparation

Materials

Polyacrylic acid (PAA) and polysulfone (PSF) were obtained from Alderich Chemicals. Their M_w were 250,000 and 30,000; and their glass transition temperature were 106°C and 109°C, respectively. The non-woven polyester fabric (No. K0100), used as the substrate in the fabrication of the support layer, was supplied by the Kanai Juyo Ind. Co. (Japan). All the solvent used was analytical grade and obtained from Wako Chemicals (Japan).

Support layer

The PSF asymmetric membrane support layer was made by a phase inversion process. The PSF dope solution (10 wt% PSF in *N,N*-dimethylformamide) was cast onto a non-woven polyester fabric fixed on a glass plate. The glass plate was subsequently immersed in a gelation bath consisting of ice-cold water (0~2°C). After a specific period of time, the support membrane was removed from the glass plate. It was then rinsed with water for several hours and then immersed in a solution of 80 wt% ethanol in water for one day at room temperature to remove the residual solvent. The support membrane was finally dried under vacuum at room temperature.

Composite membrane

The PAA coating solution was poured on the surface of the PSF support layer. The coating solution consisted of a certain amount of PAA in water with ethylene glycol as crosslinking agent and with aluminium nitrate [Al(NO₃)₃] which increased the hydrophilicity of the layer by exerting an electric charge on the carboxyl groups. The concentration of [Al(NO₃)₃] in the coating solution was 0 to 1 wt%. After being dried at room temperature, the membrane was immersed in tolylene-2,4-diisocyanate (TDI) solution (1 wt% TDI in hexane) for 3 min. The PAA-PSF crosslinked composite membrane was finally obtained by thermally treating the membrane in a clean oven at 150°C for 120 min. The thickness of the PAA layer was set at 2~10 μm .

Reverse Osmosis (RO) Experiment

The experimental apparatus for RO was the same as that reported in earlier papers^[11, 12]. The effective membrane area used was 12.69 cm² in all cases. All tests were conducted at 5.0 MPa, 30°C and a feed flow rate of 800 mL/min. All membranes were tested with single-solute solution. The concentration of organic solute in the feed solution was 1000±50 ppm. Each test solution was circulated over the membrane surface under test conditions for at least 3 h prior to collecting the permeate samples. In each experiment, the percentage of solute separation, was defined as:

$$R_a (\%) = \frac{\text{solute ppm in feed} - \text{solute ppm in permeate}}{\text{solute ppm in feed}} \times 100\%$$

A Shimadzu total carbon analyzer, Model TOC-500, equipped with an automatic sample injector, Model ASI-502, was used to measure the concentration of organic solutes in both permeate and feed solutions.

RESULTS AND DISCUSSIONS

Membrane Preparation

Some research using polyacrylic acid (PAA) as a membrane component to prepare pervaporation membranes with preferential water permeation characteristic has been reported recently^[13~15]. PAA membranes possess

excellent selectivity and permeability in dehydration of alcohol-water mixtures, but they will loss their selectivity in solutions containing large amount of water because of the swelling of membranes. In order to use the PAA composite pervaporation membrane to separate aqueous organic solutions by RO, a TDI crosslinking method was used to control the swelling of the membranes and improve their separation properties.

The influence of TDI crosslinking structure on the membrane properties is shown in Table 1. It could be seen that the membrane uncrosslinked with TDI has no separation characteristics for aqueous alcohol solutions and its volume flux of solution (J_V) is relatively high. After being crosslinked with TDI, the J_V of the membrane decreased, but the solute rejection (R_a) increased notably, the R_a of aqueous ethanol solution reached 66.2%. This indicated that the TDI crosslinked structure in the membrane not only can restrict the swelling of the membrane, but also has some repulsion action to alcohol molecules.

Table 1. The effect of TDI crosslinking structure on membrane properties

Sample	Membrane	R_a (%)	$J_V \times 10^6$ (m ³ /m ² ·s)
1	Uncrosslinked with TDI	3.2	1.44
2	Uncrosslinked with TDI	2.5	1.93
3	Uncrosslinked with TDI	2.8	1.76
4	Crosslinked with TDI	61.36	0.648
5	Crosslinked with TDI	64.58	0.625
6	Crosslinked with TDI	66.2	0.607

Ethanol: 1000, 5.0 MPa, 30°C, Al(NO₃)₃: 0.5 wt%

Table 2 shows that Al(NO₃)₃ additive plays an important role in membrane preparation. The Al(NO₃)₃ concentration in coating solutions apparently affects the membrane properties. It could be seen that the Al(NO₃)₃ additive not only can restrict the swelling of the membrane by forming the crosslinking structure with Al³⁺, but also increases the hydrophilicity of the layer as a result of coupling of the aluminium with carboxyl groups in PAA (see Fig. 1^[16, 17]), which causes the decrease of J_V and the increase of R_a for organics (i.e. permselective for water). The suitable concentration of Al(NO₃)₃ in PAA coating solutions is around 0.5 wt%. We speculate that the subsequent decrease in R_a and the increase in J_V at higher concentrations of Al(NO₃)₃ (≥0.7 wt%) are resulted from the inorganic particles and defects in the surface layer.

Table 2. The effect of Al(NO₃)₃ additive on membrane properties

Al(NO ₃) ₃ (wt%)	R_a (%)	$J_V \times 10^6$ (m ³ /m ² ·s)
0	2.39	5.30
0.1	31.26	3.54
0.3	62.57	0.691
0.5	69.28	0.681
0.7	48.72	1.293
1.0	20.13	0.795

Ethanol: 1000, 5.0 MPa, 30°C

Separation Properties of *n*-Alkyl Organics

The separation properties of crosslinked PAA/PSF composite membranes for *n*-alkyl alcohols, amines and aldehydes are shown in Fig. 2, Fig. 3 and Fig. 4, respectively. It can be seen that R_a increases with the increase of M_w of *n*-alkyl alcohols, amines and aldehydes. The R_a values for ethanol, ethylamine and ethyl aldehyde are 66.2%, 61.0% and 84.0%, respectively, and those for *n*-amyl alcohol, *n*-butylamine and *n*-butyl aldehyde reach 94.3%, 88.6% and 96.0%, respectively. The volume fluxes of solution (J_V) maintained in 0.8~1.1×10⁻⁶, 0.30~0.45×10⁻⁶ and 0.20~0.40×10⁻⁶ m³/m²·s for *n*-alkyl alcohols, amines and aldehydes, respectively. This is mainly due to the increase of hydrophobicity and steric effects of organics with the increase of their molecular weight, which causes the decrease of distribution and permeability in the membrane, therefore the increase of R_a . While the permeability of water through the membrane is unchanged, so the J_V values are relatively stable with the change of M_w of the organic solutes.

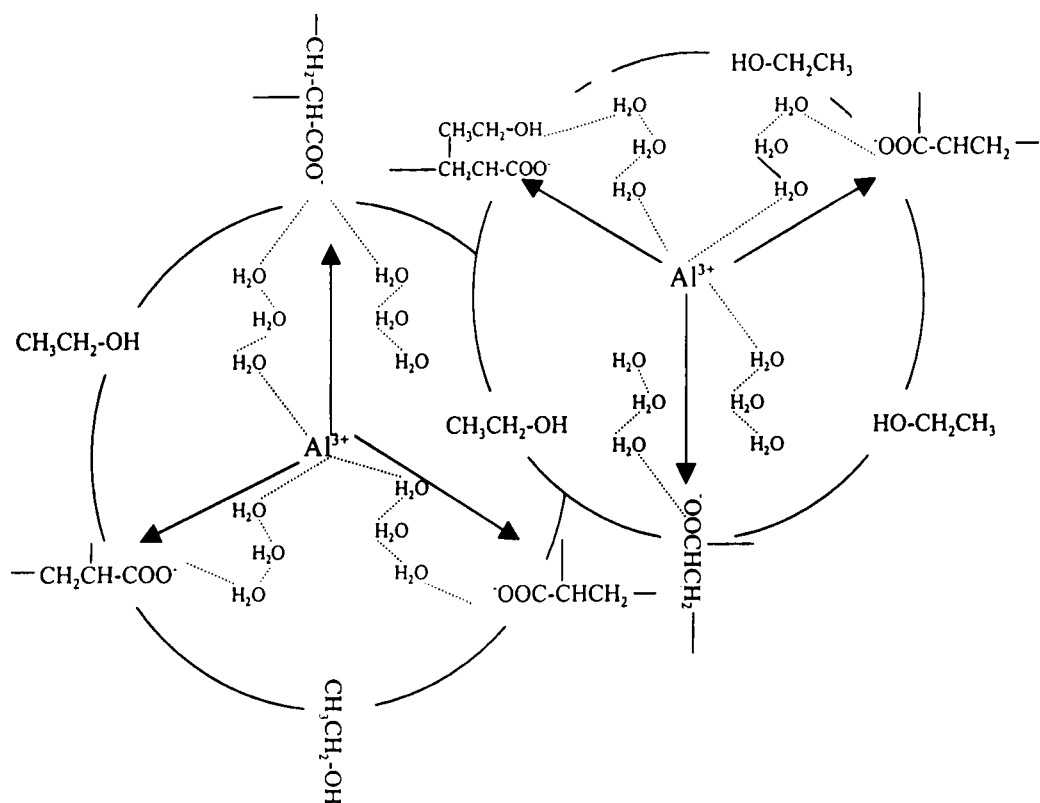


Fig. 1 Schematic model of water and ethanol transport-channel in crosslinked PAA membranes

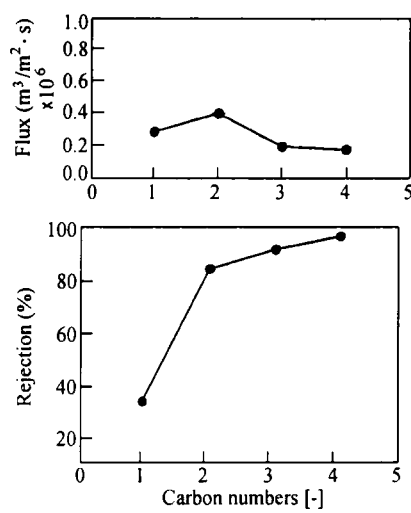


Fig. 2 The separation properties for *n*-alkyl alcohols

It can be found from Fig. 2, Fig. 3 and Fig. 4 that the solute rejections (R_a) follow the order of aldehydes > alcohols > amines. This may be mainly due to the hydrophilicity of the crosslinked PAA layer. As the order of hydrophilicity of the solutes is aldehydes < alcohols < amines, therefore, the attraction action between the solute and the crosslinkd PAA layer has the same order. The attraction effect can cause the increase of the distribution of the solute on the membrane surface and its solubility in the membrane and hence the decrease of R_a .

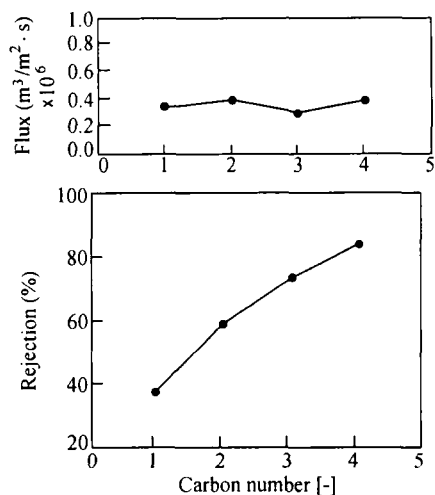


Fig. 3 The separation properties for *n*-alkyl amines

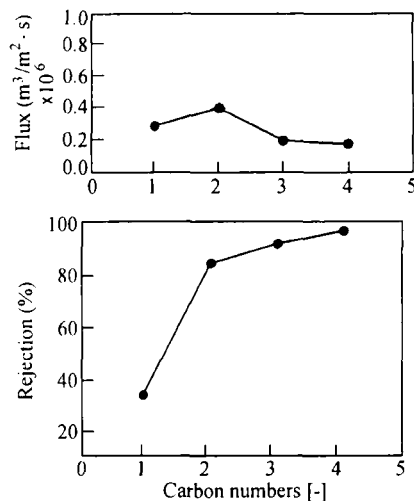


Fig. 4 The separation properties for *n*-alkyl aldehydes

Figure 5 shows the separation properties of crosslinked PAA composite membrane for *n*-alkyl aliphatic acids. It can be seen that the R_a s of the membrane for aliphatic acids are relatively low. R_a for acetic acid is only 27.8%, while R_a for *n*-butyric acid is 45.6%. The R_a increase with the molecular weight of aliphatic acids may be caused mainly by the decrease of the degree of dissociation and the steric hindrance effect. We can speculate that the low separation properties for aliphatic acids are probably due to the hydrophilicity of acids and the ester bond

($\text{—}\overset{\text{O}}{\parallel}\text{C—O—}$) and the acid group ($\text{—}\overset{\text{O}}{\parallel}\text{C—OH}$) in the crosslinked PAA layer, which can cause the increase of distribution of aliphatic acid on the membrane surface and the solubility of aliphatic acid in the membrane, as mentioned by Zheng *et al.*^[6].

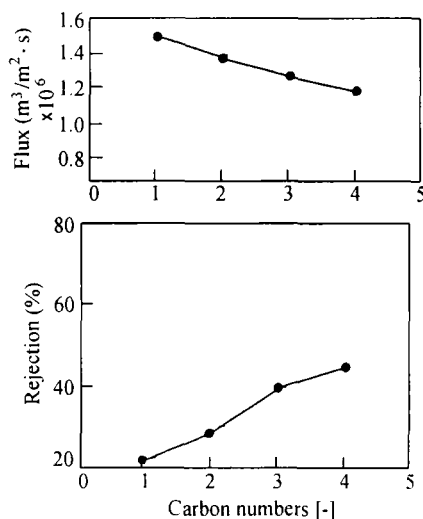


Fig. 5 The separation properties for *n*-alkyl aliphatic acids

The Separation Properties for Some Other Organics (Table 3)

Table 3. The reverse osmosis separation properties for some organic solutes		
Solutes	Solute rejection	
	R_a (%)	Volume flux of solution $J_v \times 10^6 \text{ m}^3/\text{m}^2 \cdot \text{s}$
Methyl acetate	94.79	0.291
Ethyl acrylate	94.90	0.363
Phenol	89.68	0.217
Aniline	90.42	0.293
Acetone	84.36	0.526
Ethylene glycol	74.51	0.238
Glycerin	71.25	0.403

Concentration of solute: 1000, 5.0 MPa, 30°C

Effect of Operating Pressure

The effect of operating pressure on the RO properties of PAA/PSF composite membranes for methanol, ethanol, *n*-propyl alcohol, *n*-butyl alcohol, and *n*-amyl alcohol are shown in Fig. 6. Both the solute rejections and the fluxes of the solutions increase with the increase of the operating pressure.

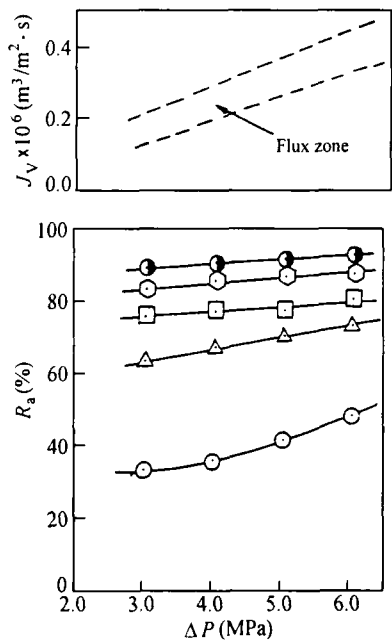


Fig. 6 The effect of operating pressure on RO properties of PAA/PSF
○ methanol, △ ethanol, □ *n*-propyl alcohol,
○ *n*-butyl alcohol, ● *n*-amyl alcohol

ANALYSIS OF EXPERIMENTAL DATA

Transport Equation

The relation between concentration of solute at the membrane surface (C_2) and concentration in the bulk solution (C_1) can be expressed by Eq. (1)^[18]:

$$(C_2 - C_3)/(C_1 - C_3) = \exp(J/k) \tag{1}$$

where C_3 is the concentration of the solute in the permeate solution, k is the mass transfer coefficient at membrane surface. In this RO system and cells used, k can be obtained by the following equation as reported earlier^[19]:

$$S_h = 1.77R_c^{0.734}S_c^{0.33} \tag{2}$$

where $S_h = k_d/D$, $S_c = v/D$, $R_c = U_d/v$. The concentration of solute at the membrane surface (C_2) can be obtained from Eq. (1).

The process of permeation of any binary solution through a membrane is described by the following Spiegler-Kedem transport Eqs. (3) and (4)^[20]:

$$J_V = L_p (\Delta P - \sigma \Delta \pi) \tag{3}$$

$$J_s = \omega \Delta \pi + (1 - \sigma) J_V C_s \tag{4}$$

Spiegler and Kedem^[20] divided the membrane into differential elements in the direction of its thickness and applied Eq. (3) to it in the form of a differential equation, integrating the equation to give the following intrinsic rejection (R_{int}).

$$R_{int} = 1 - SP = (C_2 - C_3) / C_2 = \sigma (1 - F) / (1 - \sigma F) \tag{5}$$

where

$$F = \exp[-(1 - \sigma) J_V / (\omega RT)] \tag{6}$$

By extrapolating J_V to infinite value, the value of R_{int} in Eq. (5) approaches the reflection coefficient σ as the value of F approaches zero.

Estimation of σ , L_p and ω

As mentioned above, the reflection coefficient σ can be obtained by extrapolating the intrinsic rejection R_{int} to infinite flux J_V or zero value of $1/J_V$ on the ordinate. Therefore, we can plot R_{int} versus $1/J_V$ and get the reflection coefficient σ by extrapolating R_{int} to zero value of $1/J_V$ as described earlier^[20].

By using σ estimated as above, the hydraulic and solute permeabilities L_p , ω can be obtained from Eqs. (3) and (4) where C_s is the logarithmic averaged molar concentration of C_2 and C_3 , and $\Delta \pi$, the osmotic pressure was estimated using the van't Hoff equation as follows:

$$\Delta \pi = RT \Delta C \tag{7}$$

Analysis Results and Discussions

The values of σ , L_p and ω obtained by the method mentioned above for several organic solutes are shown in Table 4. It can be seen that the hydraulic permeability hardly changed with the carbon number of organic molecules having the same functional group, while the solute permeability decreased with increasing carbon numbers because of the steric hindrance.

Table 4. Membrane constants of crosslinked composite membrane for alcohol solutes

Solutes	σ [-]	L_p [m ³ /m ² · Pa · s]	ω [mol/m ² · Pa · s]
Methanol	0.57	5.58	10.73
Ethanol	0.77	6.26	3.61
<i>n</i> -Propyl alcohol	0.84	7.02	1.87
<i>n</i> -Butyl alcohol	0.92	6.94	1.53
<i>n</i> -Amyl alcohol	0.99	7.23	0.85

CONCLUSIONS

1) In the present study, the TDI crosslinking method was used to prepare PAA/PSF composite membrane for the separation of aqueous organic solutions. The experiments indicated that the crosslinked structure with TDI in the surface of PAA coating solution is the main factor which controls the RO separation properties of the membrane for organic solutes. It was found that the suitable concentration of Al(NO₃)₃ in PAA coating solutions was around 0.5 wt%. 2) The PAA-PSF crosslinked composite membrane possesses suitable RO separation properties for low molecular organic aqueous solutions. The R_a for ethanol, ethylamine and ethyl aldehyde could reach 66.2%, 61.0% and 84.0%, respectively. And R_a increases with increasing the molecular weight of the organics. The R_a values for *n*-amyl alcohol, cursive-butylamine and *n*-butyl aldehyde reach 94.3%, 88.6% and 96.0%, respectively. R_a values of above 70% for some organic solutes, such as ketones, esters, phenols and polyols, were also obtained with PAA-PSF crosslinked composite membranes. 3) The low R_a for aliphatic acids indicates that

the PAA-PSF crosslinked composite membrane is unsuitable for the separation of aliphatic acid aqueous solutions by the RO process. 4) Both the solute rejections and the solution fluxes increase with increasing the operating pressure. 5) An analysis of experimental data with Spiegler-Kedem's transport model has been carried out and some membrane constants such as reflection coefficient σ , solute and hydraulic permeabilities ω and L_p have been obtained for several organic solutes. It was found that the hydraulic permeability L_p remains almost unchanged with the carbon numbers of the organics having the same functional group, while the solute permeability ω decreases with increasing the carbon numbers because of the steric effects coming from the molecular size.

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