

Separation of Aqueous Phenol through Polyurethane Membranes by Pervaporation

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ABSTRACT: The separation of a phenol-water mixture using a polyurethane membrane by a pervaporation method was investigated. Polyurethane was selected as a membrane material because its affinity for phenol was considered to be high. Polyurethane was prepared by the polyaddition of 1,6-diisocyanatohexane and polytetramethyleneglycol. The polyurethane layer was sandwiched with a porous polypropylene membrane (Celgard® 2500). Pervaporation measurement was carried out under vacuum on the permeate side, and the permeate vapor was collected with a liquid nitrogen trap. The phenol concentration in the permeate solution increased from 0 to 65 wt % with increasing feed concentration of phenol from 0 to 7 wt %. The total flux also increased up to 930 g m⁻² h⁻¹ with increasing phenol partial flux. In the sorption measurement at 60°C, the concentration of phenol in the membrane was 68 wt %, which was higher than that of the permeate solution. Therefore, it was considered that the phenol selectivity was based on high solubility in the polyurethane membranes. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 469–479, 1997

Key words: pervaporation; phenol; polyurethane; solubility selectivity

INTRODUCTION

It is important to separate organic compounds from industrial waste for the prevention of environmental pollution and for the reuse of the organic compounds. To remove and recover the organics, chemical, biological, and physical chemical methods are used.

Membrane separation, which is one of the physical chemical methods, is an effective way with a low-energy consumption. In the membrane separation, microfiltration, ultrafiltration, reverse osmosis, and pervaporation (PV) are utilized for the prevention of water pollution by the organics and

for their recovery from the waste water. PV with the organic permselective membrane is effective for the separation of organics from dilute aqueous solutions.

Polydimethylsiloxane and poly(1-trimethylsilyl-1-propyne) were reported to be organic solvent permselective membranes in organic aqueous solutions.^{1–3} In recent years, poly(ether-block-amide), polyurethane, and silicone-polycarbonate copolymer have been reported as other organophilic membranes.^{4–8}

We reported good performance of the polyacrylate and polymethacrylate membranes for the separation of chlorinated hydrocarbons and esters from dilute aqueous solution.^{9,10} A large quantity of chlorinated hydrocarbons are used for detergents, resulting in these organics creating problems in the disposal of waste water and the pollu-

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tion of underground water. It is expected that the disposal of waste water using the membrane will be put to practical use by the development of high-performance membranes.

In this study, phenol was chosen as the object of separation; it is a raw material used for phenolic resin, bisphenol-A, and other chemicals.¹¹ The phenolic resin is manufactured by a condensation reaction. A large quantity of water containing phenol is produced, and the effective disposal of that is desired.

In order to separate phenol from dilute aqueous solution, the membrane materials were selected according to the following idea. The separation by PV is carried out on the basis of a difference in the dissolution, diffusion, and vaporization process of each component. In these processes, the dissolution and diffusion processes are concerned with the membrane. As a result of the previous work, the solubility selectivity contributed to the high permselectivity of organics. On the other hand, the diffusivity selectivity was favorable for water. In the case of the separation of organics from dilute aqueous solution, the polymer materials, which have a high affinity for the organics, are therefore suitable for the membrane materials. For example, the organics are good solvents of the polymer. The use of a polymer which has a low glass transition temperature should be effective for the reduction of diffusion resistance.

As a result of the investigation of various polymers, good phenol permselectivity was observed with the polyurethane, which was synthesized from 1,6-diisocyanatohexane and polytetramethyleneoxyglycol. It is considered that the high permselectivity is derived from the high phenol affinity, the hydrophobicity of polytetramethyleneoxyglycol, and the structure of the polyurethane.

THEORY

The solution-diffusion theory is used in which a concentration difference of each penetrant between both sides of the membrane is a driving force for the diffusion process.^{9,12,13} In the theory, (1) the concentration difference is derived from the chemical potential difference, and (2) the activity is a product of the activity coefficient and the concentration. From (1) and (2), the general permeation equation can be written as

$$J_i = \frac{D_i}{l} \{K_{i1}C_{i1}^s - K_{i2}C_{i2}^s\} \times \exp[-V_i(P_1^s - P_2^s)/RT] \quad (1)$$

or

$$J_i = \frac{D_i K_{i1}}{l} \left\{ C_{i1}^s - \frac{K_{i2}}{K_{i1}} C_{i2}^s \right\} \times \exp[-V_i(P_1^s - P_2^s)/RT] \quad (2)$$

Assuming that the activity coefficient is constant in the membrane, hence

$$\frac{K_{i2}}{K_{i1}} = \frac{\gamma_{i2}}{\gamma_{i1}} \quad (3)$$

The vapor pressure, which in equilibrium is set up between liquid and vapor, is described as follows:

$$\frac{p_{i1}^s}{p_i^*} = \gamma_{i1} \cdot C_{i1}^s \quad (4)$$

$$\frac{p_{i2}^s}{p_i^*} = \gamma_{i2} \cdot C_{i2}^s \quad (5)$$

Eq. (2) can be rewritten as

$$J_i = \frac{P_i C_{i1}^s}{l} \left\{ 1 - \frac{p_{i2}^s}{p_{i1}^s} \exp[-V_i(P_1^s - P_2^s)/RT] \right\} \quad (6)$$

where

$$P_i = D_i \cdot K_{i1} \quad (7)$$

In the case of PV, the feed side of the membrane is at atmospheric pressure, and the permeate side of the membrane is under vacuum. The molar volume, V_i , is considered to be close to that of the liquid. Then, $[-V_i(P_1^s - P_2^s)/RT]$ becomes very small, and the exponential term becomes nearly equal to 1. By this approximation, eq. (6) can be written as

$$J_i = \frac{P_i C_{i1}^s}{l} \left(1 - \frac{p_{i2}^s}{p_{i1}^s} \right) \quad (8)$$

Further, p_{i2}^s becomes nearly equal to 0 when the pressure of the permeate side is close to 0; hence, eq. (8) becomes

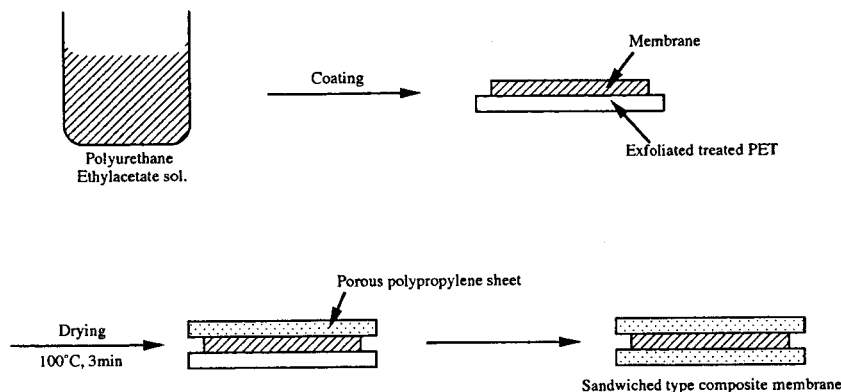


Figure 1 Membrane preparation.

$$J_i = \frac{P_i}{l} C_{i1}^s \quad (9)$$

EXPERIMENTAL

Synthesis of Polyurethane

Into a 300 cm³ flask equipped with a stirrer and a reflux condenser with a drying tube, polytetramethyleneglycol (PTMG, Aldrich, USA, $M_n = 2,900$) was placed in an oil bath at 50°C under nitrogen atmosphere. 1,6-Diisocyanatohexane (HMDI, Tokyo Kasei, Japan) and dibutyltindilaurate (Tokyo Kasei, Japan) as a catalyst were added, and the mixture was stirred for 1 h. Ethylacetate and a triisocyanate compound were added, and stirring was continued for 3 h at the same temperature. Thus, crosslinked polyurethane [HMDI-PTMG(2900)] was obtained. PTMG, HMDI, and other reagents were used without further purification. The molecular weight of HMDI-PTMG(2900) was measured by size exclusion chromatography (standard : polystyrene), and the remnant isocyanate was confirmed by Fourier transform infrared spectrometer (FTIR).

Preparation of Membrane

The ethylacetate solution containing 20 wt % of HMDI-PTMG(2900) was coated on an exfoliated treated polyethylene telephthalate film (PET) and then dried at 100°C for 3 min. The HMDI-PTMG(2900) membrane was laminated with a porous polypropylene sheet, Celgard® 2500 (Daicel Chemical Industries, Japan), and the PET film was displaced with Celgard®. Thus, a sandwiched-type composite membrane was prepared. Figure 1 shows the preparation method for this type of membrane.

PV Measurement

A schematic diagram of the PV apparatus is shown in Figure 2. The effective area of the membrane was 19.6 cm². Feed liquid (1,000 cm³) was circulated with a microtube pump. The permeation measurement was carried out under vacuum on the downstream side of the membrane, and the upstream pressure was maintained at atmospheric pressure. The permeate vapor was collected in a cold trap with liquid nitrogen. The concentration of phenol and water in the permeate liquid and the flux were determined by gas chromatographic analysis and by measurement of the weight of the collected sample, respectively. The concentration of phenol in the permeate liquid was high, so that the permeant separated into two phases. The gas chromatographic measurement was then carried out by adding 2-propanol to make a uniform solution.

The flux was calculated from the following equation:

$$\text{Flux (g m}^{-2} \text{ h}^{-1}) = \frac{Q}{A \cdot t} \quad (10)$$

The separation factor of PV, α_P , was expressed as follows.

$$\alpha_{P(i/j)} = \frac{C_{i2}^s / C_{j2}^s}{C_{i1}^s / C_{j1}^s} \quad (11)$$

Sorption and Degree of Swelling

The HMDI-PTMG(2900) membrane pieces, the weight of which was previously measured, were immersed in the aqueous phenol solution for 48 h. The solution on the membrane surface was

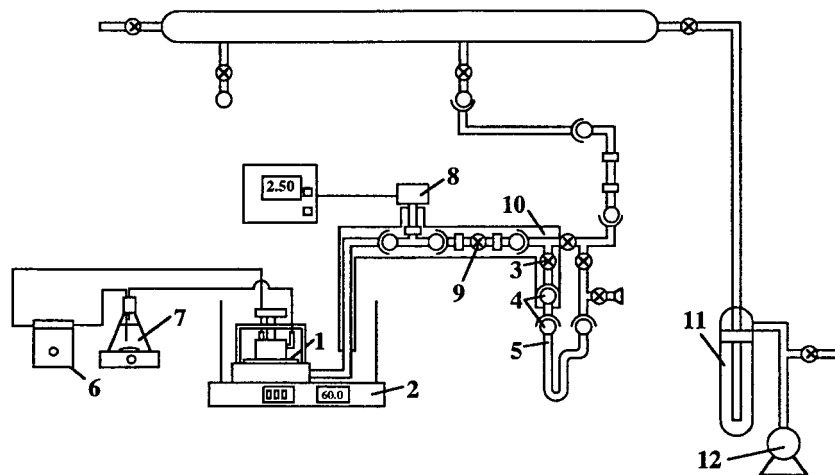


Figure 2 PV apparatus. (1) PV cell, (2) constant temperature bath, (3) greaseless cock, (4) ball joint, (5) cold trap for collecting sample, (6) microtube pump, (7) feed solution, (8) pressure transducer, (9) bellows valve, (10) ribbon heater, (11) cold trap, (12) vacuum pump.

wiped off, and the weight of the membrane was measured. The degree of swelling was calculated as follows:

$$\text{Degree of swelling (\%)} = \frac{W_w - W_D}{W_D} \times 100 \quad (12)$$

The membrane piece was then frozen under vacuum in a glass vessel. The membrane piece was then heated, and the adsorbate was vaporized and collected in the cold trap with liquid nitrogen. The concentrations of phenol and water were determined in the same way as PV.

In the case of PV, the permeability coefficient represents the product of the partition coefficient and the diffusion coefficient.^{14,15} Consequently, it is considered that the α_P is expressed as the product of partition, α_K , and diffusion, α_D , as follows:

$$\alpha_{P(ij)} = \alpha_{K(ij)} \cdot \alpha_{D(ij)} \quad (13)$$

The $\alpha_{K(ij)}$ can be written as

$$\alpha_{K(ij)} = \frac{K_i}{K_j} = \frac{C_{i3}^s / C_{i1}^s}{C_{j3}^s / C_{j1}^s} \quad (14)$$

RESULTS AND DISCUSSION

Synthesis of Polyurethane

The number-average molecular weight and weight-average molecular weight values of

HMDI-PTMG(2900) were 8.06×10^4 and 2.82×10^5 , respectively. The FTIR spectra of HMDI-PTMG(2900), HMDI, and PTMG(2900) are shown in Figure 3. The strong absorption in the 2260–2280 cm^{-1} region (asymmetric $-\text{N}=\text{C}=\text{O}$ stretch) of HMDI disappeared. The peak

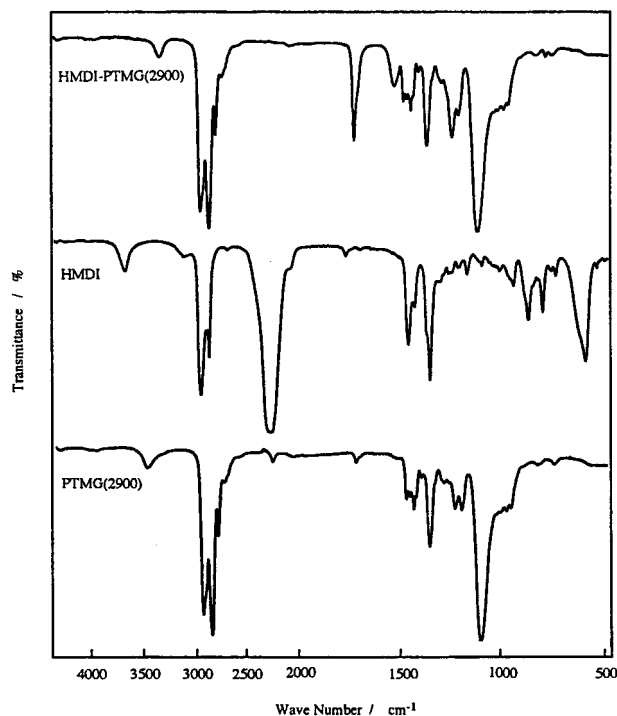


Figure 3 FTIR spectrum of HMDI-PTMG(2900), PTMG, and HMDI.

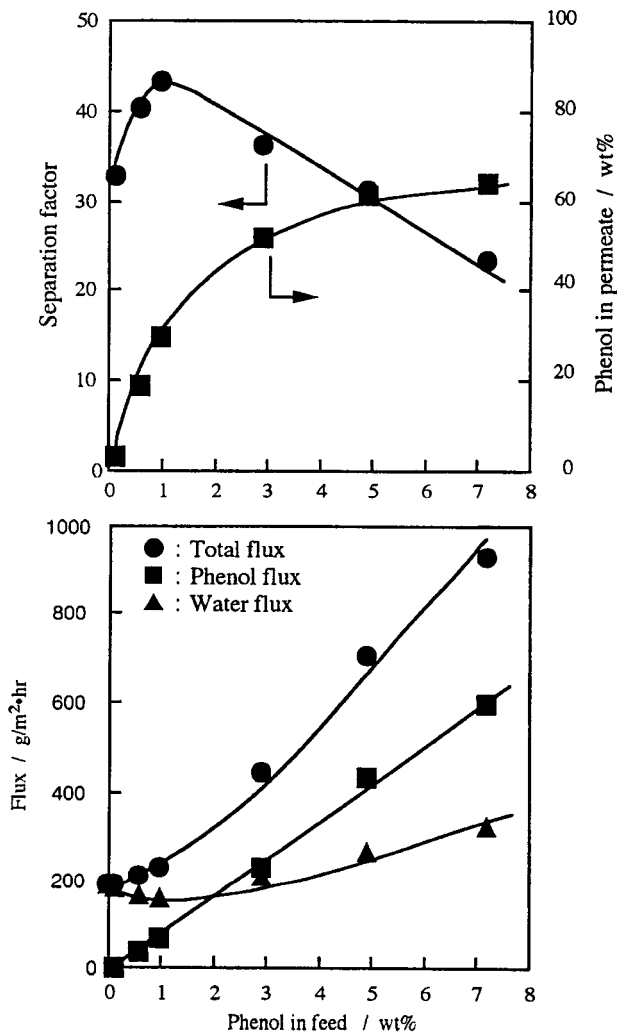


Figure 4 Effect of feed composition on the separation of phenol through HMDI-PTMG(2900) membrane. PV conditions: temperature, 60°C; downstream pressure, 2.50 mmHg.

near 1,720 cm^{-1} ($\text{C}=\text{O}$ stretch or Amide I), which was not observed on HMDI and PTMG(2900), was observed.¹⁶ Thus, it seems that the polyaddition reaction progressed sufficiently.

Effect of Phenol Concentration

The effect of feed concentration on the separation of a phenol-water mixture through an HMDI-PTMG(2900) membrane is shown in Figure 4. The phenol concentration in the permeate liquid increased from 0 to 65 wt % with increasing feed concentration of phenol from 0 to 7 wt %. The total flux also increased up to 930 $\text{g m}^{-2} \text{h}^{-1}$ with increasing phenol partial flux. On the other hand,

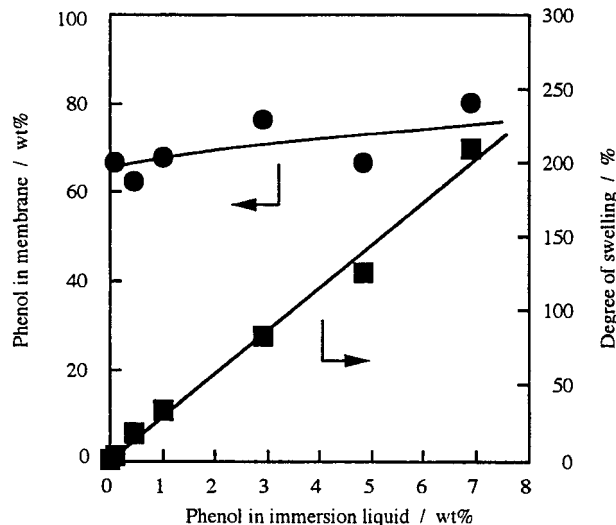


Figure 5 Effect of phenol concentration on the sorption and swelling for HMDI-PTMG(2900) membrane at 60°C.

the augmentation of the water partial flux was very slight.

The effect of the phenol concentration in the immersion liquid on the sorption and the degree of swelling is shown in Figure 5. The degree of swelling changed remarkably from 1.25 to 211%. The phenol concentration in the membrane increased from 63 to 81 wt % and was always higher than those of the immersion and permeation liquids.

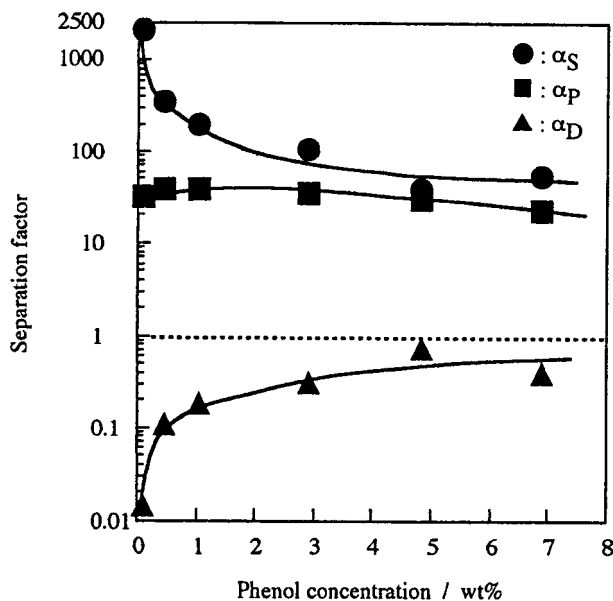


Figure 6 Effect of phenol concentration on α_P , α_D , and α_S for HMDI-PTMG(2900) membrane at 60°C.

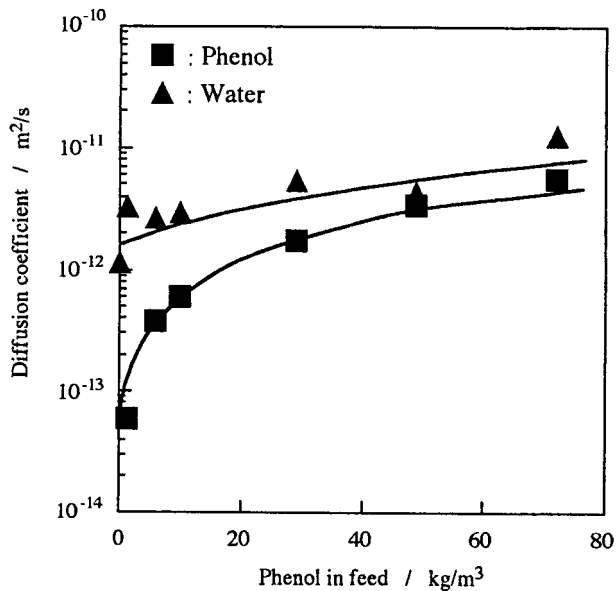


Figure 7 Effect of phenol concentration on the diffusion coefficient for HMDI-PTMG(2900) membrane at 60°C.

Each separation factor for permeation, diffusion, and partition, which was calculated using eqs. (7), (9), and (10), is plotted in Figure 6. Comparing α_P with α_K , the former was lower than the latter, and the diffusivity selectivity was less than 1. Therefore, it is considered that the phenol selectivity is based on the high solubility of phenol in the HMDI-PTMG(2900) membranes.

In general, the diffusion coefficient, D , can be written as the following equation, which includes the exponential term of the concentration²:

$$D = D_0 \exp(\beta C^s) \quad (15)$$

As a result of the sorption measurement, it seems that the value of β for phenol is large due to its high affinity for the membrane. Thus, the concentration dependence of the diffusion coefficient is large, too. In contrast, the value of β for water is small. The phenol flux should consequently depend on the concentration, and the water flux will not change drastically.

The diffusion coefficient is calculated from the following equation:

$$P_i = D_i \cdot K_{i1} \quad (7)$$

$$J_i = \frac{P_i}{l} C_{i1}^s \quad (9)$$

$$K_i = \frac{C_{i3}^s}{C_{i1}^s} \quad (16)$$

Figure 7 shows the effect of the phenol concentration on the diffusion coefficient, which was calculated from the results of the PV and the sorption measurement using the above relation.

The diffusion coefficient of phenol increased drastically from 6.20×10^{-14} to $5.80 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ with increasing the phenol concentration; that of water slightly increased. In the low phenol concentration region, the diffusivity of water was larger than that of phenol. In spite of the solubility of phenol being very high, it is considered that the phenol partial flux was smaller than that of water by the low phenol diffusivity. On the other hand, the diffusivity of phenol was the same as that of water in the high phenol concentration region. Therefore, the phenol partial flux was larger than that of water by the high solubility and the high diffusivity.

Temperature Dependence

The temperature dependence of the flux and the separation factor are shown in Figure 8. The partial flux of phenol and water, respectively, increased from 38.4 to 174 $\text{g m}^{-2} \text{ h}^{-1}$ and from 114 to 452 $\text{g m}^{-2} \text{ h}^{-1}$ with increased temperature.

The overall and partial fluxes as functions of the reciprocal of absolute temperature are shown in Figure 9.

In general, the temperature dependence of the flux can be described by the Arrhenius expression [eq. (17)].^{1,17}

$$J = J_0 \exp(-E_a/RT) \quad (17)$$

Figure 9 shows good linearity, so that the increase in flux is expressed by the above equation. The temperature dependence of the sorption and the degree of swelling are shown in Figure 10.

The degree of swelling decreased from 41 to 26 wt %. This suggests that the solubility of each component in the membrane decreased. The phenol concentration in the membrane increased slightly from 63 to 70 wt %. Comparing the temperature dependence of the phenol solubility in the membrane with that of water, the former was smaller than the latter. Therefore, it is considered that the phenol concentration in the membrane increased relatively.

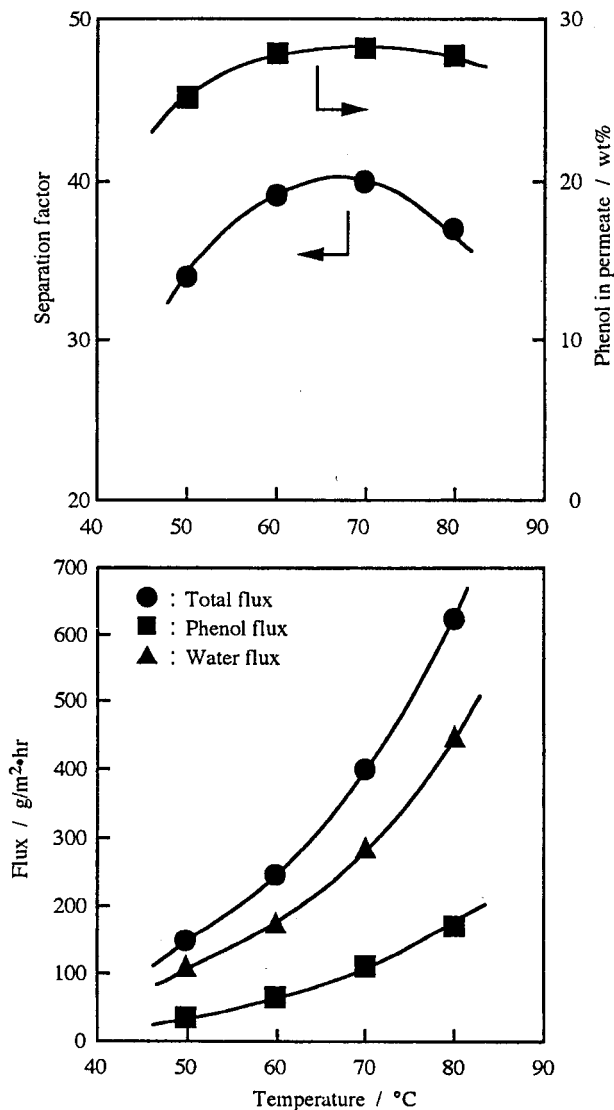


Figure 8 Temperature dependence on the separation of phenol through HMDI-PTMG(2900) membrane. PV conditions: feed solution, 1 wt % phenol aqueous solution; downstream pressure, 2.50 mmHg.

Effect of Downstream Pressure

The effect of downstream pressure on the separation of the phenol-water mixture is shown in Figure 11. When the downstream pressure was increased from 0.5 to 30 mmHg, the phenol and water flux decreased from 73.9 to 8.75 $\text{g m}^{-2} \text{h}^{-1}$ and that of water changed from 194 to 126 $\text{g m}^{-2} \text{h}^{-1}$, respectively. The decrease in flux was slow at low pressure (below 5 mmHg) but became more drastic at higher pressure. The water partial flux was relatively constant above 5 mmHg. In contrast, that of phenol decreased over the range studied. The phenol concentration in the perme-

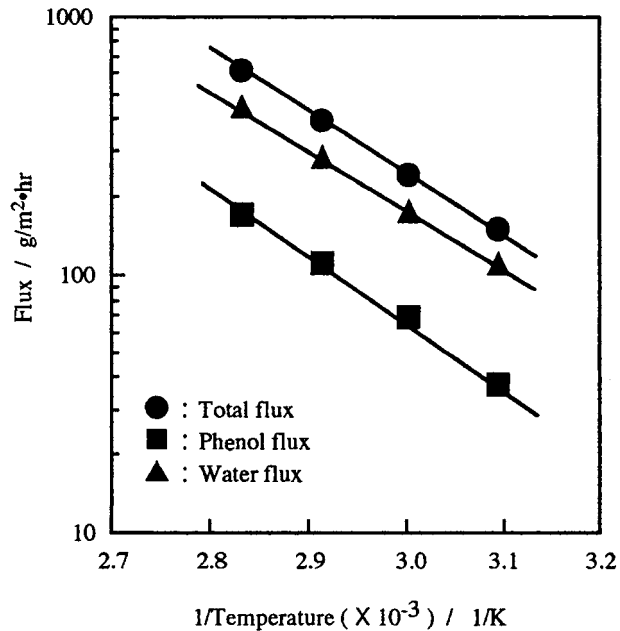


Figure 9 Temperature dependence on the separation of phenol through HMDI-PTMG(2900) membrane. PV conditions: feed solution, 1 wt % phenol aqueous solution; downstream pressure, 2.50 mmHg.

ate liquid and the separation factor consequently decreased with the increase in downstream pressure. It seems that this behavior is affected by the saturated vapor pressure of phenol and water at 60°C.

The behavior of the flux could be explained as

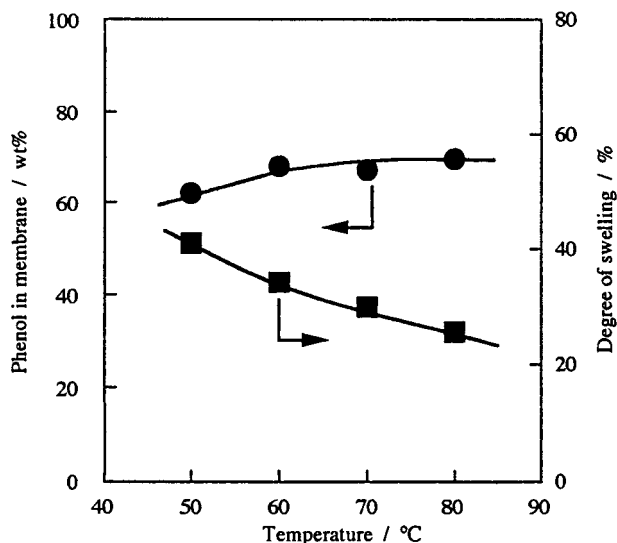


Figure 10 Temperature dependence on the sorption and the degree of swelling of HMDI-PTMG(2900) membrane in 1 wt % phenol aqueous solution.

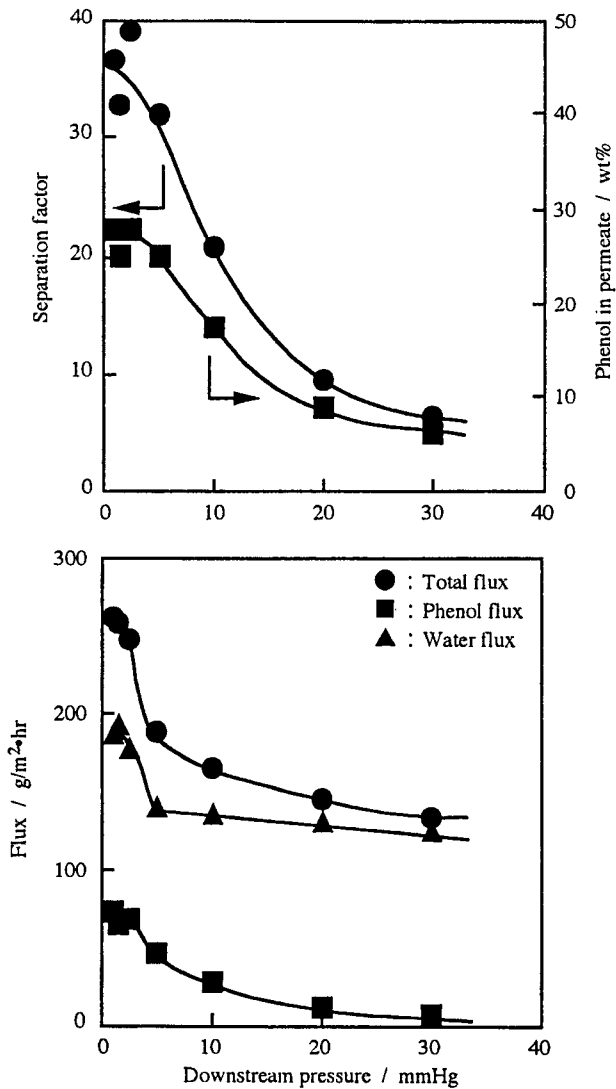


Figure 11 Effect of downstream pressure on the separation of phenol through HMDI-PTMG(2900) membrane. PV conditions: temperature, 60°C; feed solution, 1 wt % phenol aqueous solution.

follows. In the case of a downstream pressure close to zero, the flux can be written as eq. (9). When the downstream pressure increases, particularly over the saturated vapor pressure, the pressure term in eq. (9) cannot be ignored. The flux can be thus described by eq. (8). In this study, the upstream pressure was constant, so that the value of $1 - p_{2i}/p_{1i}$ was reduced with the increase in downstream pressure. Therefore, it is considered that the flux of both phenol and water decreased.

Effect of Membrane Thickness

The effect of membrane thickness on the separation of a phenol-water mixture through an HMDI-

PTMG(2900) membrane is shown in Figure 12. The water flux decreased from 680 to 223 $\text{g m}^{-2} \text{h}^{-1}$ with increasing dry membrane thickness. Meanwhile, the phenol flux was relatively constant over the range studied. The concentration of phenol in the permeate liquid increased from 10.9 to 20.6 wt % and the separation factor increased from 11.7 to 25.6 with the increase in the dry membrane thickness. Based on these results, a model for the concentration profile in the membrane was derived according to Figure 13.

The membrane under a steady-state condition

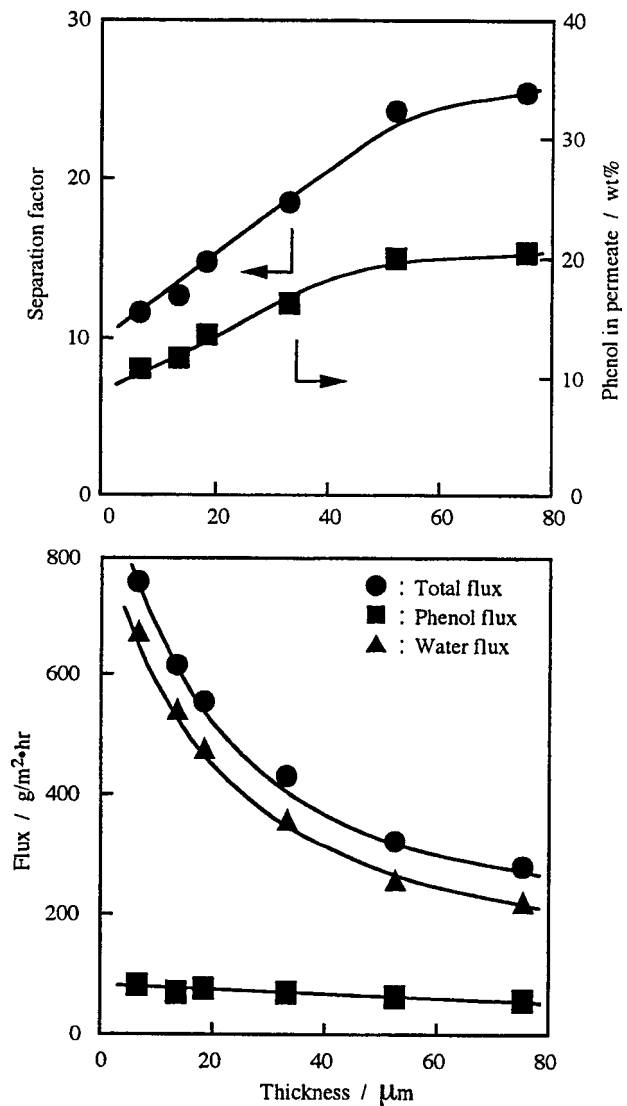


Figure 12 Effect of dry membrane thickness on the separation of phenol through HMDI-PTMG(2900) membrane. PV conditions: feed solution, 1 wt % phenol aqueous solution; temperature, 60°C; downstream pressure, 2.50 mmHg.

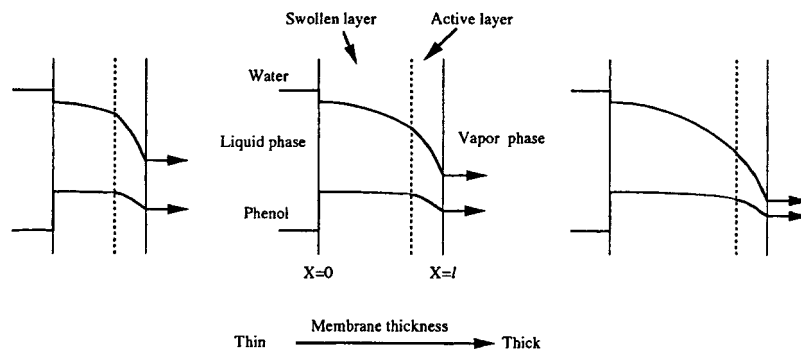


Figure 13 Concentration gradient of phenol and water in the polyurethane membrane under PV conditions.

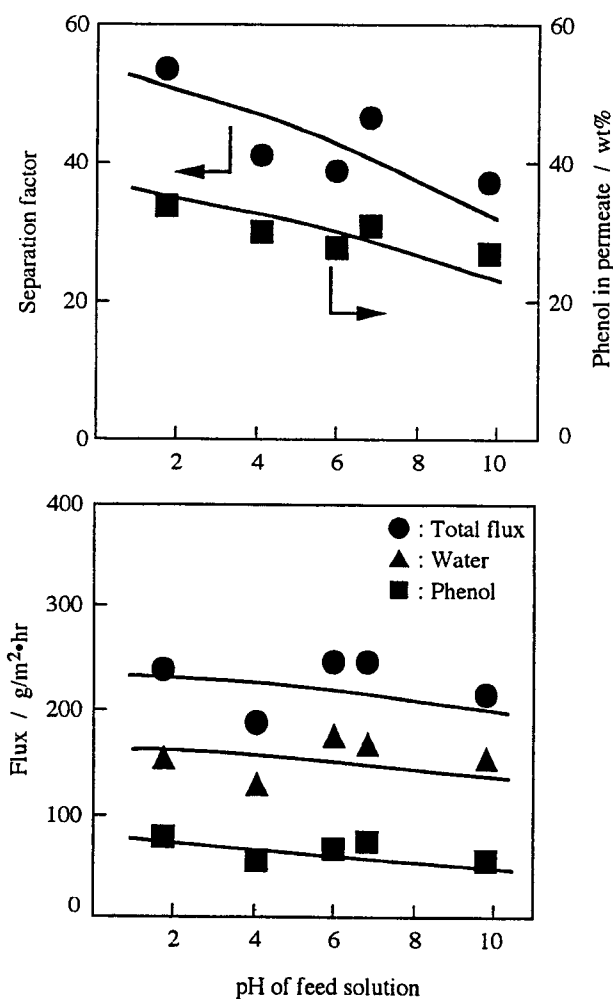


Figure 14 Influence of pH of feed solution on the phenol-water mixture separation through HMDI-PTMG(2900) membrane. PV conditions: feed solution, 1 wt % phenol aqueous solution; temperature, 60°C; downstream pressure, 2.50 mmHg.

of PV could be regarded as two layers; one is the active layer, the other is the swollen layer.^{15,18} The solubility of phenol in the membrane was very high as a result of the sorption, so that the concentration gradient of phenol in the swollen layer was very small. This layer had little effect on the permeation and separation of phenol. The active layer therefore affected the permeation and separation. It seems that the thickness of the active layer was constant because of the behavior of the phenol partial flux and that the increase in the dry membrane thickness contributed to the increase in the swollen layer thickness.

The affinity of water for the membrane was low based on the result of the sorption measurement. It is assumed that a concentration gradient should be developed in the swollen layer. The water partial flux thus decreased with increasing membrane thickness.

Effect of pH of the Feed Liquid

The effect of the pH of the feed liquid is shown in Figure 14, and the composition of the buffer solution is summarized in Table I. The phenol selectivity and flux, respectively, decreased from 54 to 37 and from 240 to 220 g m⁻² h⁻¹ with the rise

Table I Composition of Buffer Solution

pH (at 60°C)	Composition of Buffer Solution
1.72	0.04961 mol/dm ³ KH ₃ (C ₂ O ₄) ₂ ·2H ₂ O
4.09	0.05 mol/dm ³ C ₆ H ₄ (COOK)(COOH)
6.84	0.025 mol/dm ³ KH ₂ PO ₄ + 0.025 mol/dm ³ Na ₂ HPO ₄
9.80	0.02490 mol/dm ³ NaHCO ₃ + 0.02491 mol/dm ³ Na ₂ CO ₃

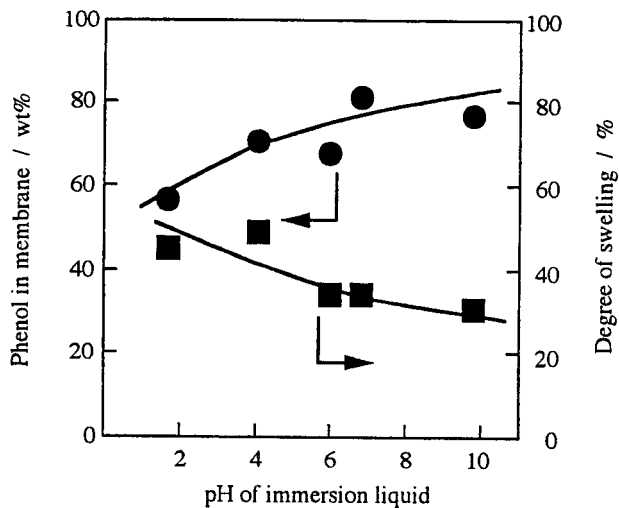


Figure 15 Effect of pH of immersion liquid on the sorption and swelling of HMDI-PTMG(2900) membrane at 60°C.

in pH. The reduction in the flux was mainly due to that of the phenol partial flux.

Figure 15 shows the result of the sorption and swelling measurement. The phenol concentration in the membrane increased from 57 to 81 wt % and the degree of swelling decreased from 46 to 31% with the rise in pH.

Phenol transforms into a phenolate compound, which dissolves in water in the basic region. It is considered that the affinity for the membrane, namely, the solubility in the membrane, is lower than that in the acidic region. The lowered solubility led to the decrease in the flux, the concentration of phenol in the permeate liquid, and the degree of swelling. The intermolecular spacing becomes narrow with the decrease in the degree of swelling. The solubility of the water molecule therefore becomes lower. It is considered that the phenol concentration in the membrane increases relatively.

CONCLUSIONS

The separation of phenol from aqueous liquid through a polyurethane membrane by PV was found to be viable. High phenol selectivity was obtained due to the high solubility of phenol in the HMDI-PTMG(2900) membrane. The diffusivity selectivity was favorable for water. The phenol concentration in the permeate liquid and the phenol flux increased remarkably with increasing phenol concentration in the feed liquid. On the

other hand, the water flux was slightly increased. The phenol and water flux increased with the rise in temperature. The temperature dependence of the separation factor was small. With the increase in downstream pressure, the flux of each component decreased. The decrease in the phenol flux was exceptional. The phenol flux was relatively constant with the variation in the dry membrane thickness. In contrast, the water flux decreased with the increase in the dry membrane thickness. Good separation of phenol was achieved in the low pH region.

NOMENCLATURE

A	effective membrane area
C^s	concentration
D	diffusion coefficient
D_0	infinite dilution diffusion coefficient
J	flux per unit time and per area
J_0	flux in standard state
K	partition coefficient
l	membrane thickness
P	permeability coefficient
P^s	total pressure
p^s	vapor pressure
p^*	saturated vapor pressure
Q	weight of permeate liquid
R	gas constant
T	absolute temperature
t	measuring time
V	partial molar volume
W_D	dried membrane weight
W_w	swollen membrane weight
α_D	separation factor of diffusion
α_K	separation factor of partition
α_P	separation factor
β	plasticization coefficient
γ	activity coefficient
Subscript i	component i
Subscript j	component j
Subscript 1	quantities concerning the bulk feed solution
Subscript 2	quantities concerning the downstream side of the membrane
Subscript 3	quantities concerning the membrane interior

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