

Separation of benzene/cyclohexane by pervaporation through chelate poly(vinyl alcohol)/poly(allyl amine) blend membrane

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SUMMARY

Chelate poly(vinyl alcohol)/poly(allyl amine) blend membrane was prepared and used for the separation of benzene/cyclohexane mixture by pervaporation processes. The coordination of benzene in the feed with cobalt in the membrane plays a major role in the separation of the mixture. Chelate poly(vinyl alcohol)/poly(allyl amine) blend membrane showed a preferential sorption toward benzene and was found to be more effective for permeating benzene in the benzene/cyclohexane mixture than an original Schiff base poly(vinyl alcohol)/poly(allyl amine) membrane.

INTRODUCTION

Several studies on the separation of benzene/cyclohexane mixture by pervaporation have recently been reported and are summarized in Table 1. Olefinic polymers such as polyethylene and polypropylene are easily available and have been applied on separating benzene/cyclohexane mixture(1,2). M. Kucharski *et al.* investigated the effect of orientation of polypropylene membrane on the separation capacity and reported that the biaxial orientation could increase the separation factor toward benzene. The improvement of separation factor toward benzene could be also acquired by adding swelling agents such as dimethylsulfoxide(DMSO) in the feed(3,4). Cellulosic polymer membranes were widely used in this application, too(5-7). Cabasso *et al.*(7) reported the separation factor toward benzene of 19 and permeation rate of 0.48 kg- $\mu\text{m}^2/\text{m}^2\text{hr}$ through cellulose acetate membrane.

The separation of olefins from olefins/paraffins or aromatics from aromatics/aliphatics using coordinating agents has generated considerable research interests in the chemical industries(8,9). It is based on the chemisorption of olefin by a metal complex between coordinating agents and permeating compounds. The use of coordinating agents can be classified into three forms: the solution, the solid adsorbent and the membrane. Using the solution form, Walker(10) reported a reversible coordination of ethylene and propylene with the solutions of cuprous aluminum cyanotrichloride($\text{CuAl}(\text{CN})\text{Cl}_3$) in aromatic solvents. In the use of solid adsorbents containing coordinating agents, Hirai *et al.*(11) reported an ethylene-selective adsorbent based on cuprous chloride and polystyrene resin containing amino groups. Upon an incorporation of coordinating agents in the membrane form, Hughes *et al.*(12) reported an olefin separation via the supported liquid membranes of aqueous AgNO_3 solutions dispersed in porous cellulose acetate/nitrate materials. These studies were based on the coordination effects for separating unsaturated hydrocarbons and saturated hydrocarbon.

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Table 1. Results on the separation of benzene/cyclohexane mixtures by pervaporation

Membrane	Membrane thickness [μm]	Conc. of benzene in feed [wt %]	Operating temperature [$^{\circ}\text{C}$]	Permeation rate [$\text{kg}\cdot\mu\text{m}/\text{m}^2\text{hr}$]	Separation factor ^{e)}	Ref.
LDPE ^{a)}	25	50	25	10.8	1.60	1
Polypropylene (double oriented)	40	55	25	10.4	2.37	2
Polypropylene (oriented)	40	55	25	15.8	1.32	2
Polypropylene (unoriented)	40	55	25	34.6	1.10	2
PVDF ^{b)} + 23% 3-methylsulfolene	16	53	56	1.49	5.45	3
PVDF + 5% DMSO in feed	16	53	60	1.60	6.20	4
PPOBrP ^{c)} /CA ^{d)}	20	51	53.5	3.95	9.70	5
Modified cellulose ester	16	53	80	50.3	5.20	6
CA	20	55	77.8	0.48	19.00	7

a) Low density polyethylene

b) Poly(vinylidene fluoride)

c) Poly(bromophenylene oxide dimethylphosphonate ester)

d) Cellulose acetate

e) Toward benzene

On these grounds, we prepared chelate polymer membrane containing cobalt and used for the separation of benzene from benzene/cyclohexane mixture in this study. Chelate membranes have been used for separating gases(13-15), metal ions(16,17), optical isomers(18) and so on. However, no other studies have been reported for the separation of benzene/cyclohexane mixture using chelate membrane by pervaporation processes.

EXPERIMENTAL

Material

Poly(vinyl alcohol)(PVA, Mw : 66,000) and poly(allyl amine) (PAAm, Mw : 100,000) were purchased from Shin Yo Pure Chemicals(Japan) and Aldrich Chemicals Co.(U.S.A), respectively. Distilled and deionized water treated with Milli-Q(Millipore Co., USA) were used as a blending solvent. Salicylaldehyde, methanol, dimethylformamide(DMF), $\text{Co}(\text{acetate})_2\cdot 6\text{H}_2\text{O}$ and triethylamine (TEA) were used for the preparation of chelate membrane. All reagents were from Junsei Chemicals(Japan, GR grade).

Membrane preparation

PVA and PAAm were dissolved separately in water by 5wt%. Then, each polymer solution was blended to become PVA : PAAm = 4 : 1 by weight. The polymer blend solution was filtered with glass filter and cast onto a framed acrylic plate. The casting solution was dried in a vacuum oven at 40°C under 10mmHg for two days. Schiff base type membrane was prepared by treating the blend membrane with salicylaldehyde solution composed of salicylaldehyde, water and methanol(1:1:4 by volume). Chelate membrane was prepared by dipping the Schiff's base membrane into the vessel filled with cobalt acetate(5.6g), TEA(3cc) and DMF(50cc) for one day. The chemical structure of chelate membrane is shown in Fig. 1.

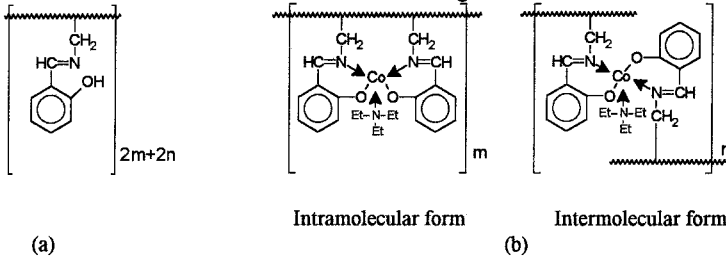


Fig. 1. Schematic of the structure of PAAm in (a) Schiff base form and (b) chelate form.

Degree of swelling

Chelate PVA/PAAm membrane samples were dipped into test tubes filled with benzene, cyclohexane and benzene/cyclohexane mixtures, respectively. The degree of swelling was determined after the test tubes were placed in an incubator kept at 30°C for 30, 90, 150, 870 and 1320 minutes, respectively. The following equation was used,

$$\text{Degree of swelling(\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

where W_w and W_d represent the weights of the membrane in wet and dry states, respectively.

Pervaporation

The equipment and procedures used to conduct the pervaporation experiments were identical to those described previously by Lee et al.(19). The effective membrane area in contact with liquid was about 25.98cm² and the membrane thickness was 28 μm. The downstream pressure was maintained at 5 torr and the operating temperature was 25°C.

The separation analysis was carried out by Shimadzu GC-14A equipped with a 3m long glass column packed with PEG-1000 and with thermal conductivity detector. Separation factor(a) and permeate flux(J) are defined as follows,

$$a = \frac{Y_b / Y_c}{X_b / X_c} \quad (2)$$

$$J = \frac{Q}{A \times t} \quad (3)$$

where Y_i is the weight fraction in permeate and X_i is that in feed. Subscripts b and c denote benzene and cyclohexane, respectively. Q , A and t represent the weight of permeant(g), effective membrane area(m²) and operating time(hr), respectively.

RESULTS AND DISCUSSION

FT-IR spectra analysis

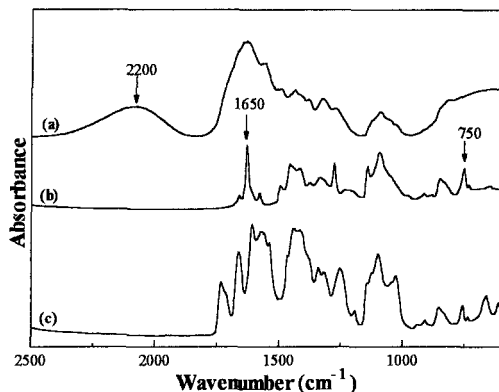


Fig. 2. FT-IR spectra of (a) PVA/PAAm blend, (b) PVA/PAAm Schiff base, (c) PVA/PAAm Co(II) chelate membrane.

Fig. 2 shows the FT-IR spectra of membranes prepared at each modification step. First, the absorption band at 2200 - 2000 cm^{-1} is shown in PVA/PAAm blend membrane (a), which is typical for antisymmetric deformation band of $-\text{NH}_3^+$. Poly(allyl amine) possesses amino group in the side chain that acts as Lewis base, and poly(vinyl alcohol) has hydroxyl group which are known to be weak acidic. The compatibility of PVA/PAAm blend is possible from acid-base interaction between $-\text{NH}_2$ and $-\text{OH}$. In PVA/PAAm Schiff base membrane (b), new bands at 1650 and 750 cm^{-1} indicate the overtone and combination band and out-of-plane $-\text{CH}-$ deformation band of aromatic ring in Schiff base, respectively. No distinctive bands are observed between Schiff base and chelate membranes (c). About 10.56wt% Co(II) content in the membrane was determined by TGA heated to 900 $^{\circ}\text{C}$.

Coordination

Fig. 3 is a schematic diagram for describing the coordinating interaction of benzene in the feed and cobalt in the membrane. Metals are in the low oxidation state and often form a complex with π acceptor ligands because of the opportunity they provide to lessen the electron density on the central metal atom. In this case, the interaction by a coordination can only be occurred between the orbitals of the same symmetry and similar energies(20). Therefore, the π orbitals of benzene can coordinate with $3d$ orbitals of cobalt. However, the coordination between cyclohexane and cobalt is not rather possible to occur not only because cyclohexane has no π orbitals to coordinate with cobalt, but because the energy difference between them is too large to form a bond

The coordinating interaction of benzene with the cobalt in the membrane is identified by FT-IR (see Fig. 4). The coordinated sample of benzene with the cobalt in the membrane is prepared by dipping Co(II) chelate membrane in benzene for 1 day, and drying in vacuum oven at 40 $^{\circ}\text{C}$ for 1 day. This sample is named as Co(II)-Bz chelate membrane. Co(II)-Bz chelate membrane shows a $-\text{CH}-$ stretching vibration band of benzene at 3010 cm^{-1} and in-plane $-\text{CH}-$ deformation band in benzene at 1270 cm^{-1} (see Fig. 4 (b)), whereas these two characteristic peaks of benzene are not shown in Co(II) chelate membrane(see Fig. 4(a)). Therefore, we can say that there exists an interaction between benzene and cobalt in Co(II)-Bz chelate membrane.

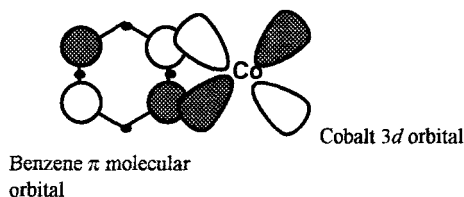


Fig. 3. Schematic diagram of cobalt-benzene coordination.

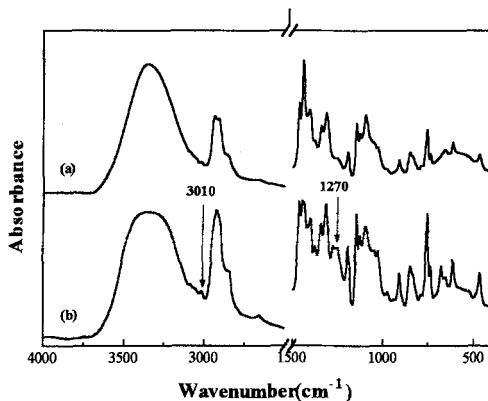


Fig. 4. FT-IR spectra of (a) Co(II) chelate and (b) Co(II)-Bz chelate membranes

Swelling behavior

Fig. 5 shows the time-dependent swelling behavior of the chelate PVA/PAAm membrane measured at 25°C. Both benzene and cyclohexane are non-polar molecules and their chemical and physical properties are similar. However, benzene shows higher affinity toward chelate membrane than that cyclohexane does. The degree of swelling of the membrane at equilibrium for benzene and cyclohexane was 6.74 and 1.76%, respectively. The reason why the degree of swelling in benzene was greater than that in cyclohexane is due to the easy access of benzene to coordinate with cobalt. Fig. 6 shows the degree of swelling of chelate and Schiff base membranes in benzene/cyclohexane mixture as a function of its composition. As shown in Fig. 6, the degree of swelling of chelate membrane increases with benzene in the mixture, attributed to the affinity or coordination of benzene with cobalt.

Pervaporation

The comparison of pervaporation capacity between Schiff base and chelate membrane is given in Table 2. Both chelate and Schiff base type membrane showed a selectivity toward benzene. Cobalt containing chelate membrane exhibited the total permeation flux (J) of 80.7 g/m²hr while the Schiff base membrane had only $J = 20.6$ g/m²hr. The fourfold increase of permeation flux by introducing cobalt in the Schiff base membrane is attributed to the coordination effect of cobalt with benzene as explained above.

We conducted further investigation about the effect of the concentration of benzene in the feed on the separation factor and the permeation flux through chelate membrane (see Fig. 7). Total permeation flux (J) increased with the concentration of benzene in the feed, C_b^f , and ranged between 59.6 and 122.8 g/m²hr. However, cyclohexane flux (J_c) was in the range of 15.2 ~ 5.4

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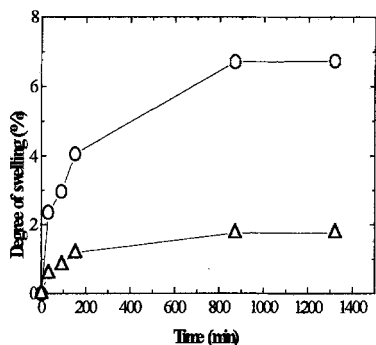


Fig. 5. The time-dependent swelling behavior of chelate PVA/PAAm membrane in benzene(O) and cyclohexane(Δ).

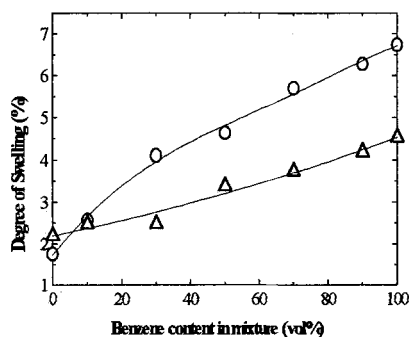


Fig. 6. Effect of benzene content in benzene/cyclohexane mixture on the degree of swelling for Schiff base (Δ) and Co(II) chelate membrane (O), measured at 30°C.

g/m²hr and gradually decreased with the C_b^f . Chelate membrane showed the separation factor ranging between 2.5 ~ 26.4.

In general, when one of the solute in the feed has an affinity with a carrier site in the membrane, the membrane selectivity toward a permeate should increase in case that the increased solubility outpass the decreased diffusivity due to the reversible binding to carrier sites in the membrane(21). In the present chelate membrane, however, the degree of swelling of benzene in chelate membrane is about 1.5 times greater than that of Schiff base membrane as shown in Fig. 6. Therefore the binding of benzene with cobalt may be easier than their dissociation. Furthermore, the swelling in chelate membrane may cause the feed mixture to penetrate through the membrane, resulting in the increased flux, but constant separation factor for chelate membrane compared with Schiff base membrane.

Fig. 8 shows the permeate composition in pervaporation of benzene/cyclohexane mixture through chelate membrane as a function of feed composition. Above 50wt% of concentration of benzene in the feed, the concentration of benzene in the permeate was above 92wt%. In a low benzene

benzene in the feed, the concentration of benzene in the permeate was above 92wt%. In a low benzene concentration range, the concentration of benzene in the permeate was above 70wt%. The chelate membrane showed high benzene selectivity over the entire range and no azeotropic point existed.

Table 2. Comparison of pervaporation capacity

Membrane	Separation factor	$\frac{J}{J_b} \frac{J_c}{J_c}$ [g/m ² ·hr]		
Schiff base	11.0	20.6	18.9	1.7
Chelate	11.9	80.7	74.3	6.4

* Conc. of benzene in feed : 50wt% ; Temp. : 25°C ;
Membrane thickness : 28μm

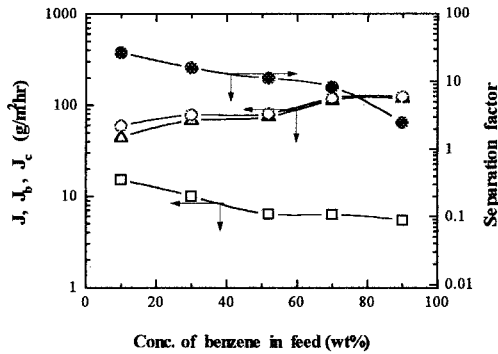


Fig. 7. Effect of concentration of benzene in feed on separation factor(●), total flux, J (○), benzene flux, J_b (Δ) and cyclohexane flux, J_c (□) using chelate PVA/PAAm membrane with $l = 28\mu\text{m}$ and measured at 25°C.

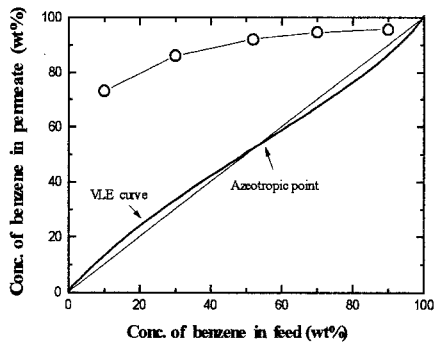


Fig. 8. X-Y graph of the result of pervaporation through PVA/PAAm chelate membrane.

CONCLUSION

In the present study, we prepared chelate PVA/PAAm membrane containing cobalt for the separation of benzene from benzene/cyclohexane. As the cobalt is coordinating with benzene in the feed rather than with cyclohexane, the degree of swelling of chelate membrane in benzene was 2.5 times greater than in cyclohexane. Chelate membrane showed the separation factor of 2.5 ~ 26.4 toward benzene and the permeation flux of 59.6 ~ 122.8 g/m²hr. It is found that the coordination between cobalt in the membrane and benzene in the feed plays a major role in improving permeation flux and selectivity toward benzene.

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