

Pervaporation of organic mixtures using modified cellulose acetate membrane

Takayuki Ichikawa^{1,2}, Samuel P. Kusumocahyo¹, Toshio Shinbo¹,
Takashi Iwatsubo¹, Mitsuyoshi Kameda¹, Katsuhide Ohi¹,
Yasuo Yoshimi², Toshiyuki Kanamori¹

¹*National Institute of Advanced Industrial Science and Technology (AIST)
Central 5th, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565, Japan*

²*Shibaura Institute of Technology
3-9-14 Shibaura, Minato-ku, Tokyo, 108-8548, Japan*

1. Introduction

Many studies have examined the use of liquid membranes for various processes such as separations of isomers, gas, organic mixtures, and removal of specific ions. It has been reported that liquid membranes show high selectivity. However, it is difficult to apply the liquid membranes to practical industrial processes because of the low stability of the liquid membranes. The instability is caused by the loss of carrier and solvent, which are usually impregnated in a porous membrane, into the surrounding solutions. The development of fixed-carrier membranes are expected to overcome this instability problem.

In this work, we developed a fixed-carrier membrane using cellulose acetate (CA) as a base polymer and dinitrophenyl (DNP) group as a carrier. It is known that DNP group has different interactions with various organic substances such as benzene, cyclohexane, and xylene isomers. On the other hand, the separations of benzene/cyclohexane mixture and xylene isomer mixtures are very important processes in chemical and petrochemical industries. However, the separations of these mixtures using conventional methods such as distillation are very difficult due to the close boiling points. Thus, we tested the CA membrane modified with DNP group (CA-DNP) to separate benzene/cyclohexane mixture and xylene isomer mixtures by pervaporation technique.

2. Experimental

2.1 Membrane preparation

CA-DNP polymer was synthesized using a synthetic route as shown in Figure 1. One gram of CA (Aldrich, MW: 50,000, 39.7 wt% acetyl content) was dissolved in 10 ml pyridine at room temperature for 2 h, and then one gram of 3,5-dinitrobenzoyl

chloride (Merck) was added. Then, 5.0 mg of dimethylamino pyridine was added, and the solution was stirred for 24 h at 40°C. The solution was concentrated using an evaporator, diluted with chloroform, and then dropped into diethylether for precipitation of the polymer. The obtained polymer was sufficiently washed in water, and re-precipitation was performed using diethylether. Finally, the polymer was dried *in vacuo* at room temperature for one day. The product was analyzed using NMR, to confirm the modification of CA with DNP. Elemental analysis of the CA-DNP polymer was carried out, and it was found that the value of m: n was 4.5: 1.

To prepare a membrane, the CA or CA-DNP polymer was dissolved in dioxane to obtain a 2 wt% polymer solution. The solution was cast onto a glass dish, and dried at room temperature for three days under nitrogen atmosphere. A membrane thickness of about 40 μm was obtained.

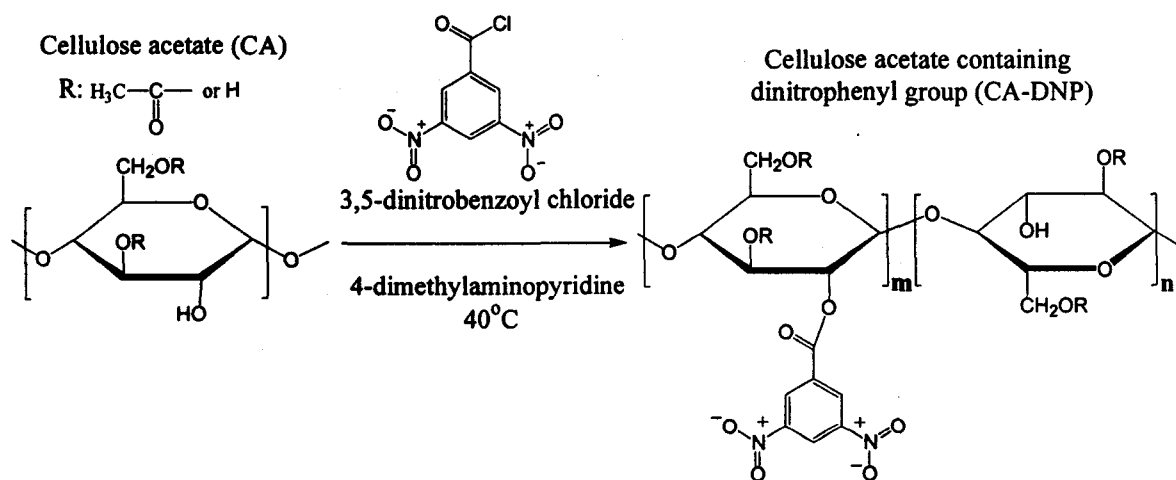


Fig. 1 Synthesis of CA-DNP

2.2 Pervaporation experiment

Pervaporation (PV) experiment was conducted on the following condition. Benzene/cyclohexane (Bz/Chx) mixture or xylene isomer mixtures (*p*-/*o*-, *p*-/*m*-, *m*-/*o*-xylene) were used as a feed solution, and were circulated using a pump through a PV membrane cell having an effective surface area of 13.7 cm^2 . The feed temperature was kept at 70°C, while the permeate pressure was lowered using a vacuum pump in the range of 5-10 Pa. The permeate was collected in a cold trap using liquid nitrogen. The permeate flux [$\text{kg}/(\text{m}^2 \text{ h})$] was determined from the weight of the collected permeate, and the concentration was measured using gas chromatograph (Shimadzu GC-8A) equipped with BX-10 glass column (GL Sciences) for benzene/cyclohexane mixture and bentone stainless column (GL Sciences, Uniport HP 80/100) for xylene isomers. The

separation factor α was calculated using the equation described below:

$$\alpha_{A/B} = \frac{Y_A/Y_B}{X_A/X_B}$$

where X and Y are concentrations of components in feed and permeate, respectively, and A and B subscripts denote the two components to be separated.

3. Results & Discussion

3.1 Pervaporation characteristic for benzene/ cyclohexane mixture

The result of the pervaporation of benzene/cyclohexane mixture (weight ratio of 1:1) using the CA and CA-DNP membranes is shown in Table 1. The difference in the separation factors, $\alpha_{Bz/Chx}$, of both membranes can be clearly seen. The modification of CA with DNP resulted in an increase in the selectivity for benzene with a very high separation factor of 103. On the other hand, the permeate fluxes of both membranes were almost the same. From this result, we suggest that DNP served as a barrier for the permeation of cyclohexane, and thus improved the benzene selectivity.

Further, pervaporation using the CA-DNP membrane was performed for various feed concentrations. The result is shown in Figure 2. The permeate flux increased with increasing the benzene concentration in the feed. On the other hand, the permeate concentrations were about 99 wt% benzene for all feed concentration ranges. This result shows that the CA-DNP membrane is applicable to the separation of benzene/cyclohexane mixture.

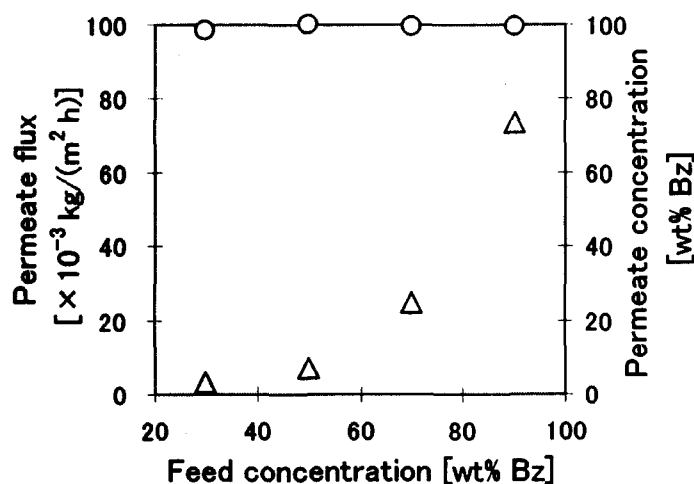


Fig. 2 Effect of feed concentration on pervaporation performance of CA-DNP membrane for benzene/cyclohexane mixture

Table 1 Result of pervaporation of benzene/cyclohexane mixture (1:1)

Membrane	Permeate flux [$\times 10^{-3}$ kg/(m ² h)]	$\alpha_{Bz/Chx}$ [-]
CA	10	65
CA-DNP	10	103

3.2 Pervaporation characteristic for xylene isomers

Pervaporation of single component of xylene isomers was performed using the

CA-DNP membrane. The result is shown in Table 2. The permeate flux decreased in the order of *p*-xylene > *m*-xylene > *o*-xylene. Further, pervaporation of binary mixtures of xylene isomers (weight ratio of 1:1) was performed using the unmodified CA and the CA-DNP membranes. The result is shown in Table 3. When pervaporation of *p*-/*o*-xylene mixture was performed using the unmodified CA membrane, the permeate flux was extremely low and could not be measured. On the other hand, when pervaporation of *p*-/*o*-xylene mixture was performed using the CA-DNP membrane, *p*-xylene selectivity was obtained. This result indicated that DNP served as a selective carrier to facilitate the transport of xylene isomers. As listed in Table 3, the order of the preferentially permeating component for the binary mixtures of xylene isomers was *p*-xylene > *m*-xylene > *o*-xylene. This order is in agreement with that in the case of the pervaporation of pure component of xylene isomers. We suggest that this result is related to the different interactions between the DNP carrier with the xylene isomer molecules.

Table 2 Result of pervaporation of xylene using CA-DNP membrane

Component	Permeate flux [$\times 10^{-3}$ kg/(m ² h)]
<i>p</i> -xylene	8.6
<i>m</i> -xylene	6.7
<i>o</i> -xylene	3.3

Table 3 Result of pervaporation of binary mixtures of xylene isomers (1:1) using unmodified CA and CA-DNP membrane

Membrane	Feed (A/B)	Permeate flux [$\times 10^{-3}$ kg/(m ² h)]	$\alpha_{(A/B)}$ [-]
CA	<i>p</i> -/ <i>o</i> -xylene	0.0	-
	<i>p</i> -/ <i>o</i> -xylene	5.2	1.7
CA-DNP	<i>p</i> -/ <i>m</i> -xylene	7.3	1.3
	<i>m</i> -/ <i>o</i> -xylene	5.3	1.2

4. Conclusion

We prepared a fixed-carrier membrane by modifying a CA membrane with DNP group, and investigated its pervaporation performance for benzene/cyclohexane mixture and xylene isomer mixtures. The result of the pervaporation of benzene/cyclohexane mixture showed that the modification of CA with DNP was effective to increase the benzene selectivity. In the case of the pervaporation of xylene isomers, the order of the preferentially permeating component was *p*-xylene > *m*-xylene > *o*-xylene.