

## 養成技術者の研究・研修成果等

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2. 養成カリキュラム名 : 分子認識化合物の多機能集積膜へ応用
3. 養成カリキュラムの達成状況

当該フェローは養成カリキュラムに従って順調に研究を遂行し、期待通りの成果をあげた。具体的には、シクロデキストリン含有ポリマーを合成するとともに、それで表面修飾した高分子膜においてブタノール及びキシレン異性体分離能を発現させた。これらの研究を通して、所期の研修項目である「分子認識化合物の合成技術」及び「分子認識化合物の分離技術への応用についての知見と技術」を習得している。更に、この分離膜の高度化のために安定性の高い無機多孔膜の作製についても研究し、ナノメートルレベルの孔を有するアルミナ/シリカ膜の作製に成功した。また、高機能性膜として有機ゲル膜についても研究し、分機能だけでなく濃縮機能を有する膜の開発にも成功している(「膜の微細加工技術」を習得)。  
本養成カリキュラムで得られた成果は非常に多く、それらは以下に記されているように、多数の口頭発表としてだけでなく、多数の特許や一流誌への論文として報告されている。

4. 成果 (A4版3枚程度)

### **4.1 Development of macrocyclic host compound-containing membranes for separation of organic isomer mixtures**

#### **4.1.1 Introduction**

The separation of isomers is an important but difficult process in the chemical and pharmaceutical industries. The separation of isomer mixtures using supported liquid membrane (SLM) is an attractive method because of its high selectivity. However, SLMs are unstable owing to the dissolution of the solvent and the carrier in the surrounding solution. For the industrial application, the immobilization of the carrier in a polymer membrane is expected to overcome the instability problem. Here, we focus on the development of polyion complex (PIC) membranes containing macrocyclic host compound. The formation of such membrane is expected to be effective for the separation of isomer mixtures since the host compound serves as a selective fixed carrier, whereas the PIC serves as a barrier for the permeation of organics. In the first step of this work, we explored a method to convert the surface of a base membrane into an ultrathin PIC, and used the membrane for the separation of water-organic mixtures by pervaporation technique. In the second step, we incorporated  $\beta$ -cyclodextrin ( $\beta$ -CD) as a host compound into a PIC membrane and investigated the pervaporation characteristic of the membrane for butanol isomer mixtures as a model for organic isomers. Further, polyacrylic acid (PAA) was used instead of PIC, and PAA membranes containing CDs ( $\alpha$ -,  $\beta$ - or  $\gamma$ -CD) were prepared and tested for the pervaporation of xylene isomer mixtures.

#### **4.1.2 Experimental**

##### **Preparation and characterization of PIC membranes based on CA :**

A solution of cellulose acetate (CA) in 1,4-dioxane was cast onto a clean glass plate, and dried at a room temperature for one day. The CA membrane was then exposed to oxygen plasma at various radio frequency (RF) powers of 20-100 W and exposure times of 30-180 s. To prepare a single PIC layer, the plasma-treated membrane was dipped into an aqueous solution of polyallylamine (PALA) and rinsed with distilled and deionized water. Multilayer PIC was obtained by dipping the plasma-treated membrane into the aqueous solutions of PALA as the polycation and polyacrylic acid (PAA) as the polyanion alternately. Finally, the membranes were annealed at 80°C for 1 h. The membranes were tested for the pervaporation

of water-ethanol mixture at a feed concentration of 90 wt% ethanol, a feed temperature of 298 K and a permeate pressure of 25 Pa. The permeate concentration was determined using gas chromatography. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR), electron spectroscopy for chemical analysis (ESCA) and contact angle measurements were carried out to characterize the membrane surfaces.

#### Preparation and characterization of $\beta$ -CD-containing PIC membrane :

A positively charged copolymer containing  $\beta$ -CD was synthesized through a radical copolymerization of 2-hydroxy-3-methacryloyl- $\beta$ -CD monomer and allylamine using ammonium peroxydisulfate as an initiator (Figure 1). This copolymer is abbreviated as PALA- $\beta$ -CD. Nafion 117 membrane was used as the base membrane for the preparation of  $\beta$ -CD-containing PIC membrane. First, the Nafion membrane was immersed in boiling water, dipped into an aqueous solution of PALA- $\beta$ -CD, and finally rinsed with distilled deionized water. The membrane was tested for the pervaporation of butanol isomers mixtures at a feed temperature of 25°C and a permeate pressure of 25 Pa. Surface analysis using ATR-FTIR and ESCA was carried out to characterize the membranes.

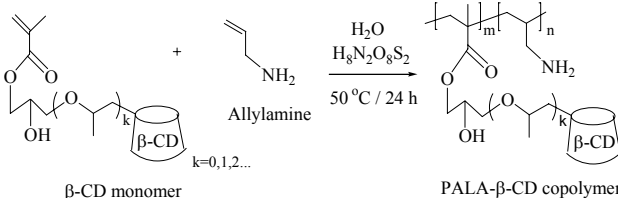


Fig. 1 Synthesis of PALA- $\beta$ -CD copolymer.

#### Preparation and characterization of CD-containing PAA membrane :

PAA and CDs ( $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD) with different weight ratios were dissolved in distilled and deionized water at a room temperature. The solutions were filtered and cast onto an ultrafiltration membrane as a supporting material. After being dried at a room temperature for one day, the membranes were used for the pervaporation of *o*-/p-xylene mixture (1:1) at a feed temperature of 25°C and a permeate pressure of 25 Pa.

### 4.1.3 Results

#### PIC membranes based on CA :

The analysis using ESCA showed an increase in the concentration of carboxyl group in the CA membrane surface after the oxygen plasma treatment. This indicated that the surface of the CA membrane was converted to a negatively charged polyion layer. Dipping of the oxygen plasma-treated CA membrane into an aqueous solution of PALA led to the formation of an ultrathin PIC layer because of the electrostatic interaction between the carboxyl group of the plasma-treated CA and the amine group of PALA. Figure 2 shows the pervaporation performance of the CA/PIC membranes for water-ethanol as a function of energy for plasma treatment. It can be seen that the permeate flux shows a minimum with increasing applied energy, and consequently the separation factor shows a maximum. An optimum energy to achieve a high selectivity was found at 2400 J. In order to improve the selectivity of the PIC membrane, multilayer PIC membranes were developed. Figure 3 shows the effect of number of layer pairs on pervaporation performance. It can be seen that the ethanol flux decreased sharply with increasing number of the layer pairs, while the water flux decreased slightly. As a result, the separation factor of the membrane increased sharply. This result showed that several layer pairs are effective to seal remaining leakages of the PIC layer.

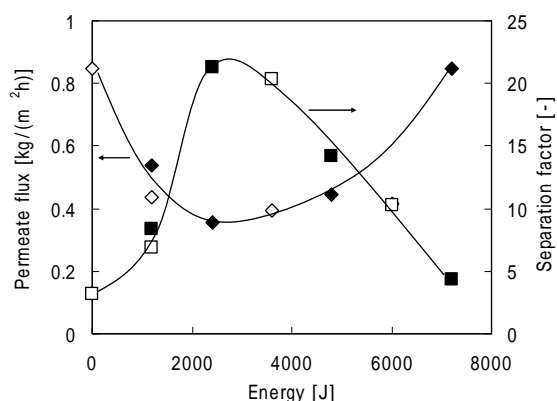


Fig. 2 Effect of energy for plasma treatment on pervaporation performance for water-ethanol.

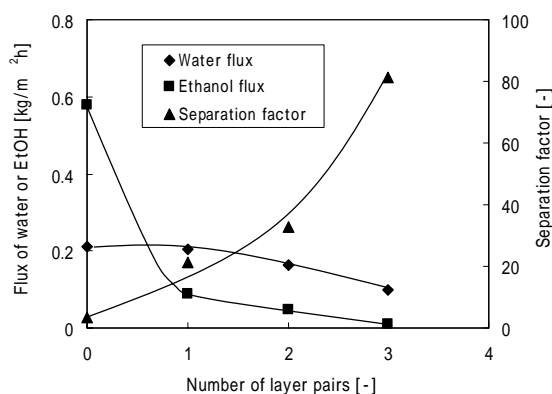


Fig. 3 Effect of number of layer pairs on pervaporation performance for water-EtOH.

#### $\beta$ -CD-containing PIC membrane based on Nafion :

Based on the previous result that organic substances such as ethanol was rejected by the PIC layer,  $\beta$ -CD was incorporated into the PIC layer by the formation of Nafion/PALA- $\beta$ -CD membrane. The result of the ESCA analysis showed that an ultrathin PALA- $\beta$ -CD layer with a thickness of lower than 5 nm was

attached on the Nafion membrane by the formation of PIC.

The pervaporation performance of the unmodified and modified Nafion membranes for the *n*-/*tert*-butanol mixture is listed in Table 1. We found that the unmodified Nafion membrane showed almost no separation selectivity. After the surface of the Nafion membrane was converted to a PIC layer by dipping into an aqueous solution of PALA, the permeate flux decreased to a very low value, but the separation selectivity was only slightly changed, indicating that the PIC layer effectively blocked the diffusion of both *n*- and *tert*-butanol. Interestingly, after the modification with PALA- $\beta$ -CD, *n*-butanol preferentially permeated through the Nafion/PALA- $\beta$ -CD membrane, and a separation factor of 2.0 was achieved. This result showed that  $\beta$ -CD selectively facilitated the transport of the butanol molecules through the PIC membrane. The structure of the membrane can be schematically illustrated in Figure 4.

Table 1 Pervaporation performance of unmodified and modified Nafion membranes for an *n*-/*tert*-butanol mixture (feed conc.: 45 wt % *tert*-butanol)

Membrane	Permeate flux [kg/(m <sup>2</sup> h)]	Separation factor [-]
Nafion	0.066	0.93
Nafion/PALA	0.002	1.16
Nafion/PALA- $\beta$ -CD	0.016	2.0

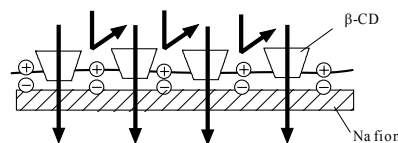


Fig. 4 Structural model of  $\beta$ -CD-containing PIC membrane for isomer separation.

### CDs-containing PAA membranes :

Here, PAA was used instead of PIC, and PAA membranes containing CDs ( $\alpha$ -,  $\beta$ - or  $\gamma$ -CD) were prepared and tested for the pervaporation of xylene isomer mixtures. The blend solutions of PAA and CDs were homogeneous, showing the good compatibility between PAA and CDs, and clear films were obtained by the casting method. Figure 5 shows the effect of the incorporation of  $\alpha$ -CD on the pervaporation *o*-/*p*-xylene. As seen, the permeate flux of xylenes through the PAA membrane without  $\alpha$ -CD was extremely low and not measurable by the applied means. The permeate flux was still almost zero at  $\alpha$ -CD concentrations below the threshold concentration. Interestingly, above the threshold concentration the permeate flux was measurable and increased with increasing  $\alpha$ -CD concentration. This result indicated that the PAA matrix served as a barrier for the permeation of xylenes, whereas  $\alpha$ -CD served as fixed carriers, which facilitated the transport of xylenes. The permeate flux increased linearly with the increase in the  $\alpha$ -CD content above the threshold concentration, and constant separation factors of about 1.5 (*o*-xylene selectivity) were achieved for enough  $\alpha$ -CD contents. Further, it was found that the PAA membranes containing different types of CDs had different pervaporation performance as listed in Table 2. This result suggest that the different inclusion strengths between CDs and xylene isomers governed the permeate flux and the selectivity.

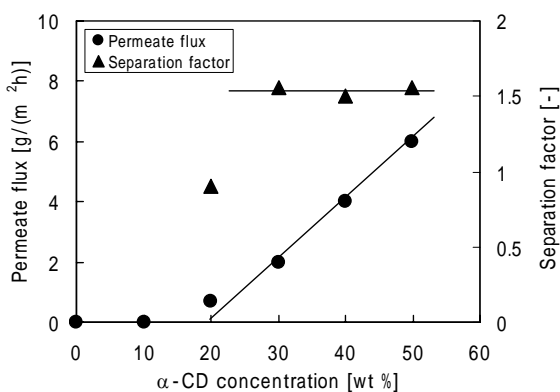


Fig. 5 Effect of  $\alpha$ -CD concentration on pervaporation performance (feed: *o*-/*p*-xylene, 50 wt% *o*-xylene)

Table 2 Pervaporation performance of PAA membrane containing different types of CDs (CDs concentration: 30 wt%, feed: *o*-/*p*-xylene, 50 wt% *o*-xylene,)

Membrane	Permeate flux [g/(m <sup>2</sup> h)]	Separation factor [-]
PAA	0	-
PAA/ $\alpha$ -CD	2	1.56
PAA/ $\beta$ -CD	7	0.98
PAA/ $\gamma$ -CD	5	0.86

As a conclusion, it has been shown that the PIC and polyelectrolyte membranes containing CDs were effective for the separation of organic isomer mixtures. We believe the findings in this work have a great potential for the development of solid membranes not only for isomer separation but also for other applications such as biochemical and molecular recognition processes.

## 4.2 Development of polymer inclusion membranes for treatment of nuclear wastewater

### 1. Introduction

The use of supported liquid membranes (SLMs) for the removal of radioactive elements from nuclear liquid wastes is very attractive. However, lack of stability is a common limitation of SLMs and hinders their commercial application in the industries. In this work, in order to develop stable membranes, we prepared polymer inclusion membranes (PIMs) based on cellulose triacetate (CTA) using 2-nitrophenyl n-octyl ether (NPOE) as a solvent. The carriers used to develop the PIMs were octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (CMPO), N,N,N',N'-tetraoctyl-3-oxapentane-diamide (TODGA), and acyclic ligands having diphenylphosphonylacetamide group (DPA). An aqueous acidic solution containing cerium(III)nitrate was used as a model for the low level radioactive wastewater, and the transport of cerium(III) ions through the PIMs was investigated experimentally.

### 2. Experimental

To prepare a PIM, NPOE and a solution of CTA in  $\text{CHCl}_3$  were mixed with a weight ratio of NPOE:CTA = 3:1. Then, the carrier (CMPO, TODGA or DPA) was added and the solution was stirred for 2 h at room temperature. The solution was then cast onto glass petri dishes, and chloroform was allowed to evaporate slowly for one day. Finally, the membranes were carefully peeled off the dishes. The resulted PIMs were completely clear and showed a good mechanical strength although they contained a high amount of NPOE solvent. Transport experiments were performed using a permeation cell. The feed compartment was filled with 20 ml of an aqueous feed solution containing 100-1800 ppm  $\text{Ce}(\text{NO}_3)_3$ , 0.05 M  $\text{HNO}_3$  and 2.95 M  $\text{NaNO}_3$ . The receiving (strip) compartment was filled with 20 ml of distilled and deionized water. Both compartments were stirred at 600 rpm. For sampling, samples of feed and strip were periodically taken, and analyzed by inductively coupled plasma (ICP) spectroscopy.

### 3. Results and discussion

The result of the transport experiment using the PIM without carrier showed that in the absence of carrier no transport of cerium from the feed phase to the strip phase was detected. This result established that the PIM without carrier served as an effective barrier to ion permeation. Figure 6 shows the results of the transport experiment using the PIMs containing 15 wt% CMPO and TODGA. The feed solution was an aqueous solution of 200 ppm  $\text{Ce}(\text{NO}_3)_3$  in 0.05 M  $\text{HNO}_3$ / 2.95 M  $\text{NaNO}_3$ . As can be seen, cerium ions were completely transported from the feed phase to the strip phase within 5 h through both the PIM containing CMPO and the PIM containing TODGA. The transport rate of the PIM containing CMPO was found to be higher than that of the PIM containing TODGA. This difference should be related to the different extraction capabilities of the carriers. This suggestion was confirmed by the result of the extraction experiment which showed that the distribution ratio of CMPO was higher than that of TODGA.

Figure 7 shows the results of the transport experiment using the PIMs containing 15wt% DPA carriers. The carrier DPA-1, which contains a phenylene group as a spacer, showed a low transport rate. On the other hand, higher transport rates were obtained using the carriers DPA-2, 3 and 4, indicating that the ethylene or propylene groups as a spacer effectively increased the diffusivity of the carriers in the PIMs. It was observed that the order of the transport rate was DPA-3>DPA-2>DPA-4>DPA-1. Compared with the PIM containing TODGA, the transport rate of the PIM containing DPA-3 is higher.

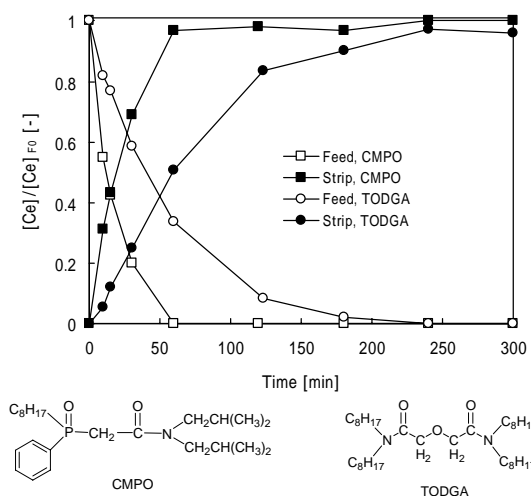


Fig. 6 Transport of cerium(III) ions through PIMs containing CMPO and TODGA carriers.

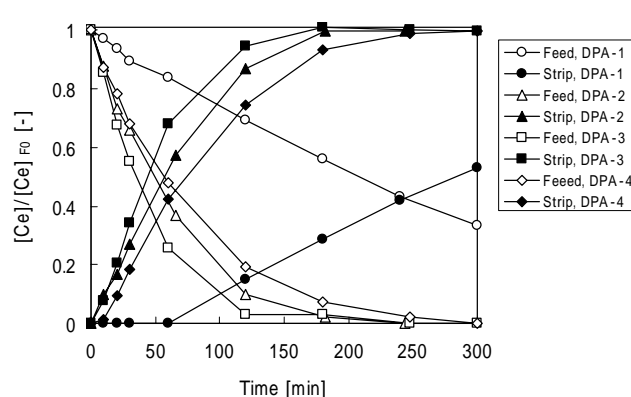


Fig. 7 Transport of cerium(III) ions through PIMs containing DPA carriers.

As a conclusion, the present PIMs are very effective for the facilitated transport of cerium ions, and are promising an attractive method applicable for the treatment of radioactive wastewater.

## 5 . 成果の対外的発表等

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( 3 ) 特許等 : 3 件

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