

## PET 직물을 매트릭스로 이용한 Fixed Site Carrier Membrane의 금속이온 투과성

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### Fixed Site Carrier Membrane for selective metal ion transport, supported by PET fabric

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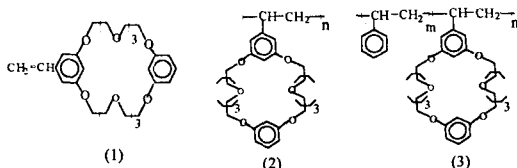
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#### 1. Introduction

Membranes which selectively transport specific metals on an industrial scale is much useful in a number of applications, such as aqueous stream purification, catalyst and recycling of the reactants, the applications in metal ion sensing and so forth. Numerous studies have been already made to use liquid, supported liquid and, emulsion liquid membranes (LM) for selective carriers for metal ion transport. In liquid membrane system, one or more metal ions from the source phase are selectively transported across the membrane and separated into a second aqueous phase. Although extensive studies have been made, there still remains difficulty in the large scale industrial applications in separation metal ions due to the loss of carrier and membrane solvent plague. The fixed site carrier membranes (FCM) which combines the positive aspects of both the solid adsorbent and liquid membrane separation was widely investigated because FCM is much superior to the liquid membrane systems. FCM can prevent not only the loss of solvent or carriers but also realize the elimination of the periodic regeneration the system, eventually, which makes it possible to apply this system for the continuous operation. The reactive site of FCM is required to have certain binding strength in order to capture metal ions, but the binding strength must be appropriate so as to the metal ions enters membranes and irreversibly complexes with the ligand to diffuse in the membranes.

Crown ether have ideal complexation ability for diversified metal ions, so it was widely used as carrier for the LMs, SLMs and PIMs. In this study, the

preparation of FCMs incorporating 32-membered crown ether (structure depicted in Fig. 1) and its capability as a carrier, i.e., the selective behavior in transport of several alkali metal ions is dealt with.



Scheme. 1. Structure of the carriers for FCM

## 2. Experimental section

### 2.1 Extraction metal ions in liquid-liquid system.

The procedure for extraction is similar to that, developed by Pedersen [1]. Equal volumes (10ml) of the methylene chloride solutions of the carriers (1), (2) or (3) and aqueous alkali metal hydroxide solutions containing picric acid were introduced into a stoppered flask, and then shaken for 20min at ambient temperature. After complete phase separation, concentration of picrate in the organic phase was determined by UV spectroscopy ( $\lambda_{\max}$ : 374nm,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\epsilon$ : 18600, in methylene chloride).

### 2.2 Preparation of FCMs

FCMs were prepared using the method reported by Sugiura [2], i.e. in a 9cm diameter flat-bottomed glass petri dish, PET fabric(1.5cm x 1.5cm) was dipped into methylene chloride solution of poly(5-vinyl- *m*-phenylene- *m'*-phenylene-32-crown-10)(PVCE) (depicted in Schem. 1). After evaporation of methylene chloride, a few drops of water were swirled on the top of the FCM to be easily loosed from the glass. FCM was carefully peeled out from the dish, and then dried at room temperature. The % add on of the PVCE is controlled by the number of the operation of repeating to have values of 8~9mg P(VCE)/13.5 mg of PET fabric. The SEM micrographs of the FCM is shown in Fig. 1.

### 2.3 Transport of metal ions via FCMs

The FCMs placed between two 300 ml glass vessels, connected by a glass tube where a sealing parafilm O-ring is placed at the center. Test membrane was installed at the O-ring in order to prevent the leakage. New original membrane was used for each experiment. Source solution was prepared by dissolving the ap-

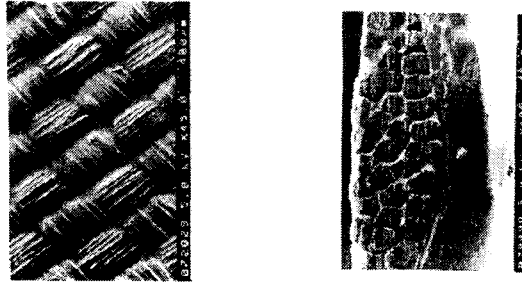


Fig. 1. SEM micrographs of FCM, Top surface (left); Cross Section (right)

appropriate amount of metal ions at one side glass vessel, 150 ml of deionized water was used in both cells and stirred with magnetic bars. samples were periodically taken( once per day) and determined the concentration of metal ions was performed on a AAS spectrometer.

Table 1 Extraction of metal ions in methylene chloride-water system

Samples	Metal ions extraction(%)		
	Na( I )	K( I )	Cs( I )
VCE (1)	1.8	4.0	10.3
P(VCE-co-ST) (3)	4.9	6.9	11.6
P(VCE) (2)	9.4	23.1	63.0

[metal hydroxide]= 0.1M, [picric acid]=  $4.8 \times 10^{-5}$ M, [crown ether unit]= $3.5 \times 10^{-3}$ M  
 Copolymer composition of P(VCE-co-ST): ST/VCE(in molar ratio) = 5/1

### 3. Results and Discussion

Table 1 listed the extraction data of carrier (1), (2) and (3) for the several alkali metal ions from methylene chloride-water system. Comparison of the results reveals that the highest selectivity to Cs<sup>+</sup> ion is observed in P(VCE). The selectivity to Cs<sup>+</sup> ion decreases in the order of P(VCE-co-ST), VCE. The selectivity for metal decreases in the order of Cs<sup>+</sup>, K<sup>+</sup> and Na<sup>+</sup> cation. It is postulated that the highest selectivity of PVCE is probably due to the effective coordinative effect of proximate VCE unit to form a 1 : 2 sandwich type complex with the metal ions. The higher selectivity of Cs<sup>+</sup> ion to other two metal ions is due to the closeness of the diameter of Cs<sup>+</sup> cation to the diameter of proximate

VCE unit.

The selectivity in the transport of the several metal ions through PET supported P(VCE) membrane is shown in Fig. 2 expressed as the salt concentration of the receiving side as a function of operation time. It is evident that the rate of diffusion of metal ions decreases in the order of  $\text{Cs}^+$ ,  $\text{K}^+$  and  $\text{Na}^+$  ion as it was observed in the extraction experiment in the methylene chloride-water system. The concentration of metal ion in the receiving side increases as the operation time increases, particularly, it is interesting to note that the concentration of  $\text{Cs}^+$  ion increases linearly with time, which implies that the ability of the complex formation of the  $\text{Cs}^+$  ion is much higher than those of other metal ions. The transport of the metal ion is taken place via the complex formation of metal ion with crown ether unit, located at the surface of the membrane feed side and followed by the diffusion to the receiving side of membrane by the gradients of chemical potential across the FCM.

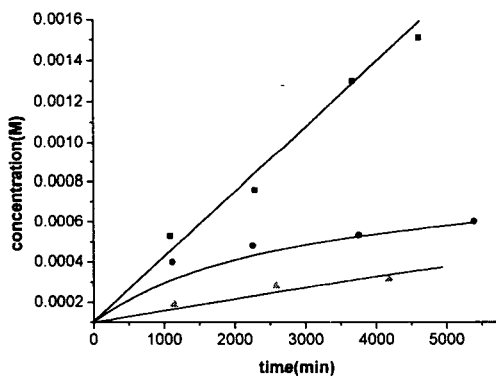


Fig.2. Selective transport of several metal ions through FCM P(VCE) 9-10 mg /PET fabric 13 mg, Concentration of feed solution: 0.05 M concentration: ■ CsCl, ● KCl, ▲ NaCl

#### 4. conclusion

FCM, supported by PET fabric was prepared by dipping of the fabric into the solution of poly(32-membered crown ether). It was found that the FCM is highly selective to  $\text{Cs}^+$  ion over  $\text{Na}^+$  and  $\text{K}^+$  ion and the selectivity of FCM to metal ions is explained in terms of the complex formation of the 32-crown ether unit of FCM with metal ions.

#### 5. References

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