

**Poly(4-vinyl-benzo-15-crown-5-co-di(ethylene glycol) ethyl ether acrylate)
Carrier-Facilitated Transport Membrane의 선택적 금속이온 투과성**

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**Selective transport of aqueous metal ions of carrier-facilitated transport
membrane prepared from poly(4-vinyl-benzo-15-crown-5-co-Di(ethylene glycol)
ethyl ether acrylate)**

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1.Introduction

Development of the membranes, capable of selective separation of the metal ions in aqueous solution has been the subject of extensive study since the membrane is much advantageous not only in the promotion of the efficiency of the process but also in the energy saving. Although liquid membrane systems including supported liquid(SLM), and emulsion liquid membranes (ELM) were developed for the selective metal ion transport from aqueous source phase into a receiving aqueous phase across the membrane, there still remains difficulty in application to large industrial scale due to the problems in the solvent plague and the loss of the carrier(1,2). Therefore, it has been attempted to develop a polymeric nonporous density carrier facilitated transport membrane (CFM) in order to avoid the loss of carrier and assure the continuous operation by the elimination of the periodic regeneration of the membrane system(3-4).

The carrier used in CFM has a capability of binding with metal ions at surface of aqueous metal ion source phase, however, its binding strength with metal ions is appropriate so as to release the metal ions inside of the membrane and at the surface of receiving side phase. Crown ethers have been known as an ideal carrier for this purpose, such as carrier for liquid membranes and polymer inclusion membranes because of their potentiality to form complex with diversified metal ions(4).

In this study, synthesis of 4-vinyl-benzo-15-crown-5(VCE) and the preparation of the CFM from the copolymer of VCE and di(ethylene glycol) ethyl ether acrylate, supported by PET non-woven fabric has been attempted and its selective metal ions transport properties of PET non-woven fabric supported CFM has been also investigated.

2.Experimental

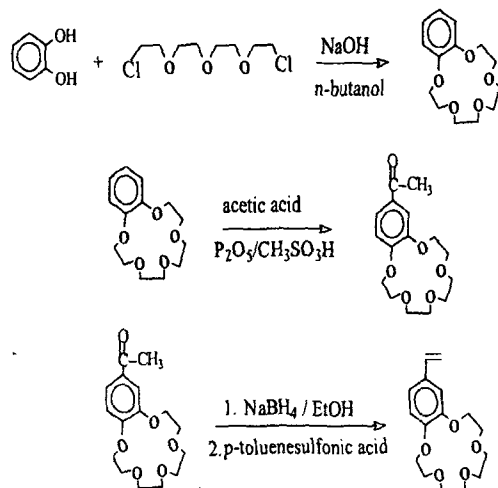
Materials

PET non-woven fabric sheet was used as received from Clean & Science CO., Ltd.(Korea) with mean thickness of 236 μm . All chemical reagents were purchased from Aldrich or Han Jin Co. Ltd. Di(ethylene glycol) ethyl ether acrylate (Aldrich) was purified by distillation under reduced pressure just before use.

Synthesis of 4-vinylbenzo-15-crown-5

4-vinylbenzo-15-crown-5 has been prepared in accordance with procedures given in the literature(5), using tetra(ethylene glycol), catechol, methanesulfonic acid, sodium borohydride, p-toluenesulfonic acid monohydrate via tetra(ethylene glycol) dichloride, Benzo-15-crown-5, 4-acetylbenzo-15-crown-5, 4-(1-hydroxy ethyl) benzo-15-crown-5 as shown in scheme 1 and was identified by $^1\text{H-NMR}$ spectroscopy.

$^1\text{H-NMR}$ (CDCl_3) δ (ppm): 3.75(m, 8H), 3.89(m, 4H), 4.12(m, 4H), 5.11(d, d 1H) 5.57(d, d 1H), 6.61(m,1H), 6.9(m, 4H).



Scheme 1. synthetic route of VCE monomer

Preparation of Carrier-Facilitated Transport Membrane (CFM), supported by non-woven PET fabrics

PET non-woven fabric supported CFM was synthesized by Photo-induced copolymerization of VCE, DEGEAA and hexamethylene diacrylate(HMDA) using MMMP(I-907) as a photoinitiator in n-hexanol solution, i.e., PET non-woven fabric was dipped into two monomers and MMMP in n-hexanol. After the sample was fixed in Pyrex glass tube, air was driven out by bubbling the nitrogen gas for 20 min. A 500W high press mercury lamp(Ushio UI-501-C) was used for the photopolymerization for 1 h. The thickness of the membrane was controlled by the number of the repeated dipping and irradiation to have thickness ranging from 285 to 295 μm including thickness of non-woven PET fabrics. The nonporosity of the CFM was confirmed using SEM micrographs as shown in Figure 1

Transport of metal ions across CFM

Transport of mono-valent metal ion in the aqueous phase across the CFM was determined by the

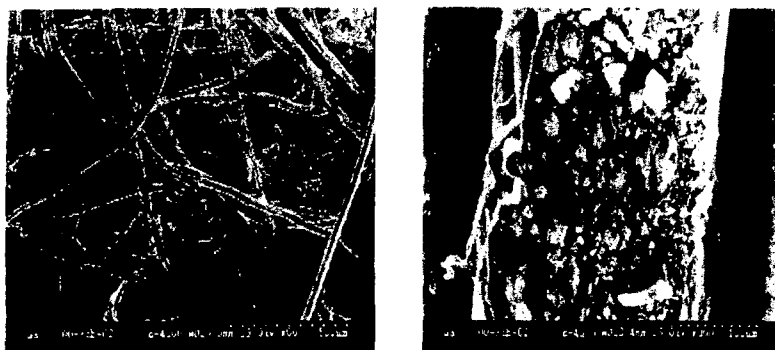


Figure 1. SEM micrographs of CFM: original sample(left) ; Cross section of CFM(right)

concentration of metal ion of the receiving side, filled with 150ml deionized water, which is connected to the same volume of the source aqueous solution of metal ion by 1 cm diameter tube. CFM is installed on O-ring, located at the center of the glass tube. Parafilm was used in sealing of the O-ring in order to prevent the leakage. Source solution was prepared by dissolving the appropriate amount of metal carbonate in aqueous picric acid solution. The concentration of metal ion in the receiving side was determined by UV-visible spectrophotometer(UV-1601PC, Shimadzu).

3.Results and Discussion

PET non-woven fabric supported CFM was prepared by photo-induced copolymerization of VCE, DEGEEA in the presence of trace amount of HMDA, a crosslinking agent. The role of crosslinking agent is to prevent the loss of carrier and assure the continuous operation by the elimination of the periodic regeneration of the membrane system.

Figure 2 shows time-concentration curves of transport of metal picrate across CFM. The copolymer composition is fixed DEGEEA/VCE/HMDA=7/3/1 in molar ratio. It is found that flux of metal picrate decreases in the order of $Cs^+ > Na^+ > K^+$ ion without any exception irrespective to the composition or thickness of the membrane and the selectivity of the membrane to various metal ion leads us to a conclusion that the flux is remarkably dependent on the stability of the complex formed between crown ether and each metal ion. The preferential transport of Cs^+ is due to the formation of 2/1 sandwich type VCE and metal picrate complex at the surface of CFM at the source solution. No significant transport of metal ion was observed when membrane, prepared from poly(DEGEEA).

Figure 3 shows plot of %content VCE in copolymer versus the flux of metal picrate, revealing that the maximum flux is obtained from the membrane having the composition of VCE/DEGEEA=7/3 and the effect of hydrophilicity of the membrane on the flux was also discussed in this phenomenon.

4.Conclusion

PET non-woven fabric supported nonporous density Carrier-Facilitated Transport Membrane was successfully prepared from the poly(VCE-co-DEGEEA), synthesized by photo-induced radical copolymerization of VCE, and DEGEEA in the presence of trace amount of HMDA. It was found that the flux of various metal ions against the membrane decrease in the order of $Cs^+ > Na^+ > K^+$ ion.

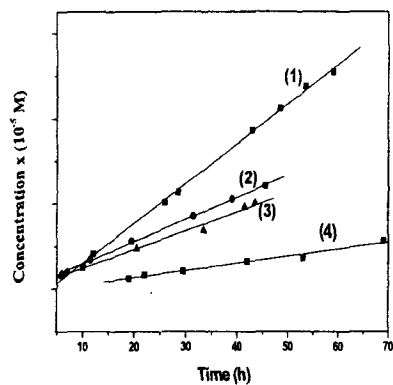


Figure 2. Receiving side concentration versus operating time for transport of metal picrate CFM composition: DEGEEA/VCE=7/3, HMDA mole %=1. (1) Cs⁺, (2) Na⁺, (3) K⁺ (4) Cs⁺ (transported against crosslinked opoly (DEGEEA) membrane).

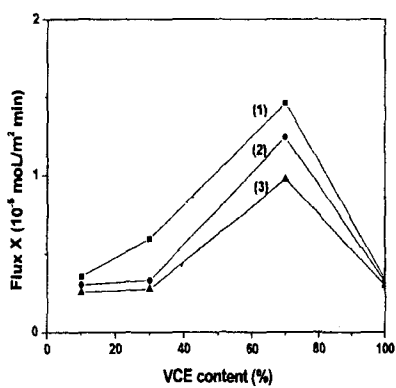


Figure 3. Dependence of Flux on mole % of VCE unit in the copolymer. (1) Cs⁺, (2) Na⁺, (3) K⁺.

5. References

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