PET Fabric Supported Fixed Site Carrier Membrane for Selective Metal Ion Transport

Long Yi Jin and Soukil Mah*

Department of Textile Engineering, Inha University, Yonghyun-dong 253, Nam-ku, Incheon 402-751, Korea

Abstract: Development of a novel fixed site carrier membrane (FCM), supported by PET fabric for metal ion separation is reported. The membranes were prepared by dipping PET fabric into the methylene chloride solution of Poly(5-vinyl-m-phenylene-m'-phenylene-32-crown-10) (P(VCE)), a polymeric metal ion carrier. It was found that the flux of mono-valent metal ion transported across the membrane is significantly differed from each other and the flux decreases in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ irrespective to the anion except perchlorate anion. It was explained in terms of the stability of the complex, formed by crown ether unit of the P(VCE) and the various metal ions, meanwhile, the lower rate of transport in the presence of perchlorate anion was ascribed to its low hydrophilicity.

Keywords: Fixed site carrier membrane, PET fabric, Poly(vinyl crown ether), Selective transport, Metal ion

Introduction

Development of the membranes, capable of separating the metal ions in aqueous phase 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. Membranes having the selective transport of specific metal ions are expected to be utilized in the number of industrial applications, such as aqueous stream purification, catalyst and recycling of the reactants, the applications in metal ion sensing and so forth[1,2]. Although liquid membranes including supported liquid, and emulsion liquid membranes (LM) were developed for the selective metal ion transport from aqueous source phase into a receiving aqueous phase across the membrane[1,3], there still remains difficulty in application to large industrial scale due to the problems in the solvent plague and the loss of the carrier[4].

Polymer supported or inclusion fixed site carrier membranes (FCM), where the carriers are fixed into the porous solid membrane have been developed in order to avoid the loss of carrier and assure the continuous operation by the elimination of the periodic regeneration of the membrane system[5-7].

The carrier of FCM is required to bind with metal ions at source phase, but its binding strength with metal ions is appropriate so as to release the metal ions at receiving phase[8]. Crown ethers have been known the ideal carrier for the complexation with diversified metal ions[9-12], therefore, crown ethers have been widely used as carriers for various LM, supported liquid membrane (SLM) and polymer inclusion membrane (PIM)[3-5].

In this study, complexation capability of the VCE, P(VCE), and P(VCE-co-ST) and selective metal transport behavior of

*Corresponding author: simah@inha.ac.kr

FCM, prepared from poly(5-vinyl-m-phenylene-m'-phenylene-32-crown-10) are investigated (Refer to Figure 1).

Experimental

Materials

Picric acid, all chloride salts, LiOH, RbOH, and CsOH purchased from Aldrich Chemical were used as received, other chemicals were received from Oriental Chemical Industries (Korea). PET fabric (100 ends/inch, 80 picks/inch; 5.85 mg/cm^2) is treated with methanol and dried under reduced pressure at room temperature.

5-vinyl-m-phenylene-m'-phenylene-32-crown-10 (VCE) has been synthesized in accordance with the procedures given elsewhere[13].

Preparation of the Polymers Containing the Crown Ether Unit

5-vinyl-m-phenylene-m'-phenylene-32-crown-10 (VCE), P(VCE), and P(VCE-co-ST) were prepared according to the method given in the literature[13]. For the homopolymerization of P(VCE), toluene (0.26 m*l*) solution containing 50 mg of VCE and 0.89 mg AIBN in a Pyrex ampoule was degassed and sealed off on a vacuum line. The ampoule was allowed to stand for 24 hr at 60°C for the polymerization and
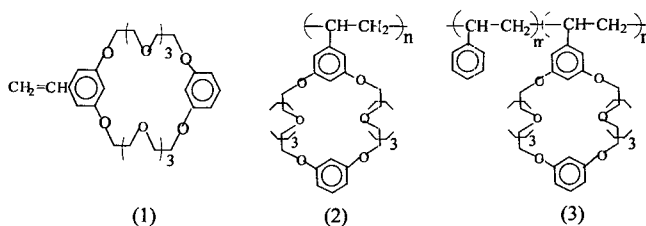

Figure 1. Structure of various ligands, containing 32-membered crown ether unit: (1) VCE, (2) P(VCE), (3) P(VCE-co-ST).
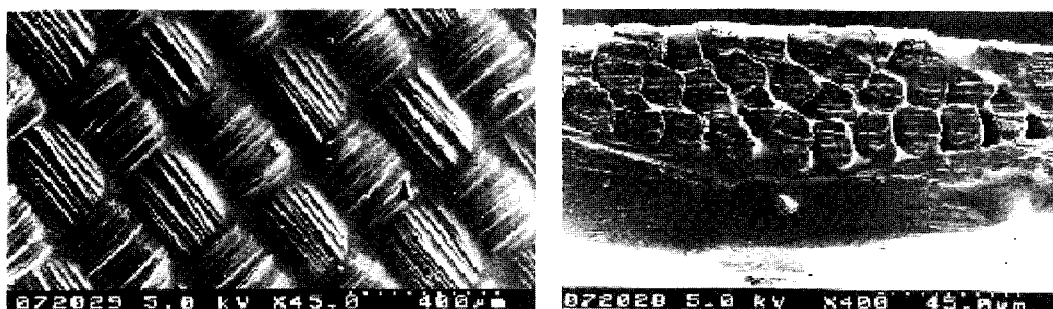
Figure 2. SEM micrographs of FCM, surface (left); Cross Section (right).

then terminated by the addition of methanol. The precipitated polymer was purified by reprecipitation in methanol and dried overnight under reduced pressure at room temperature. The yield was 23 mg (46% conversion). Styrene (ST) was used as a second monomer in the copolymerization.

Preparation of FCM on PET Fabric

FCM, supported by PET fabric was prepared by similar procedures which was reported by Sugiura and Kikkawa [14]. In a 5 cm diameter flat-bottomed glass petri dish, PET fabrics (1.5 cm ×1.5 cm) was dipped into methylene chloride solution of P(VCE). Few drops of water were swirled on the top of the FCM after evaporation of the solvent for the easy removal of the FCM from petri dish and dried at room temperature. The % add on the PET fabric was controlled by the number of the dipping operation to have values of 8-9 mg P(VCE) on to the 13.5 mg of PET fabric. Then was obtained nonporous density membrane. The SEM micrographs of the FCM is shown in Figure 2.

Extraction of Metal Ion from Aqueous Phase

The effect of crown ether unit on the extraction of various metal ions from the aqueous phase was performed in accordance with the procedures developed by Perdersen[15]. 10 m*l* of the methylene chloride solutions of VCE, P(VCE) or P(VCE-co-ST) is mixed together with the equal volume of aqueous alkali metal hydroxide solutions containing picric acid in a stoppered flask and agitated for 20 min at ambient temperature. The metal picrate concentration in methylene chloride phase was determined by UV spectroscopy (λ_{max}: 378 nm, ε_{max}: 1.8×10^4, in methylene chloride) after complete separation of water and the organic phase.

Transport of Metal Ions across FCM

Transport of mono-valent metal ion in the aqueous phase across the FCM was determined by the concentration of metal ion of the receiving side, filled with 150 m*l* deionized water, which is connected to the same volume of the source aqueous solution of metal ion by 1 cm diameter tube. FCM 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. Newly prepared membrane was always used in every test. Source solution was prepared by dissolving the appropriate amount of metal salts in deionized water. The concentration of metal ion in receiving side was determined periodically (once a day) using atomic absorption spectrometer (AAS) for Cs, K, Na cations and inductively coupled plasma-mass spectrometer (ICP-MS) for Rb and Li ions.

Results and Discussion

Extraction Capability of the Ligands Containing VCE Unit

The extraction of the various mono-valent metal ions from the aqueous phase by three types of the ligands containing VCE unit has been performed. The results are summarized in Table 1. The extraction capability of the three types of the ligands containing VCE to various mono-valent aqueous metal ions, were estimated by the determination of the concentration of the picrate transferred to methylene chloride from the aqueous phase with metal ions where the ligands such as VCE, P(VCE), and P(VCE-co-ST) is present and is expressed as the extraction constant, defined by equation (1) assuming that VCE unit and metal ion forms 2:1 type complex[10].

$$K_e = \frac{\alpha}{\alpha^+(1-\alpha)([Cr]_0/[A]_0 - 2\alpha)[A]_0} \tag{1}$$

Table 1. Extraction constant (K_e) of various ligands containing 32-membered crown ether unit to the mono-valent aqueous metal ions

Ligands	$K_e \times 10^{-3}$ M^{-2}				
	Li (I)	Na (I)	K (I)	Rb (I)	Cs (I)
VCE	0.46	0.52	1.41	2.39	3.72
P(VCE-co-ST)	0.67	1.27	2.01	2.59	3.91
P(VCE)	1.0	2.85	8.51	21.3	45.4

[metal hydroxide]=0.01 M, [picric acid]=4.8×10^{-5} M, [crown ether unit]=3.5×10^{-3} M, composition of P(VCE-co-ST): ST/VCE(in molar ratio)=5/1, P(VCE) number average molecular weight: 36 kg/mol.

Where α^+ denotes the metal ion activity in the aqueous phase, $[Cr]_o$ and $[A]_o$ are the initial concentrations of crown ether unit and picric acid in the aqueous phase, respectively, and α denotes the mole fraction of metal picrate transferred from the aqueous phase to the methylene chloride. It is evident that Cs^+ is the most highly extractable than other metal ions used in this investigation and the extraction capability of the ligand containing VCE to Cs^+ decreases in the order P(VCE) > P(VCE-co-ST) > VCE. The higher extraction capability of the polymeric ligand is ascribed to the polymeric effect. Meanwhile, the value of the extraction constant decreases in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, irrespective to the type of the ligand used. It is postulated that the higher extraction capability of the polymers than that of monomeric VCE is probably due to the effective coordinative effect of proximate VCE unit to form a sandwich-type 2:1 crown ether ring-to-cation complexes with the metal ions[16] and the highest extraction constant of VCE unit to Cs^+ among the mono-valent metal ions is due to the closeness of the ionic radius of the metal ion to that of proximate VCE unit[10] to result in a complex which has a high stability constant.

Transport of Metal Ions across FCM

The metal ion transported across the FCM was estimated by the detrmination of the concentration in receiving side. The amount of metal ion transferred across the FCM for several mono-valent metal ions across the PET supported P(VCE) membrane is shown in Figure 3. The concentration of metal ion (in type of the metal chlordie) in the receiving side increases almost linearly as the operation time increases. The flux which is determined by the slope of the curve decreases in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ which is similar to that observed in extraction experiment
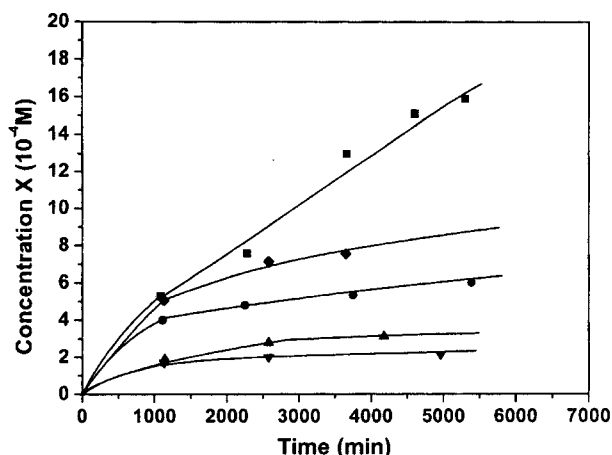
carried out in water-methylene chloride system. This implies that the stability of the inclusion compound of crown ether unit and metal ion is major factor in determination of the rate of metal ion transfer across the membrane. It is postulated that the concentration of the complex formed between Cs^+ and 32-membered crown ether unit at the surface of the membrane contacted with the source solution is the higher than other mono-valent metal ions due to the closeness the cavity size of crown ether ring and the ionic radius of the Cs^+, therefore, it is also believed that the diffusion of the metal ion in the membrane by corcentration gradient across the FCM is minor in this metal transport system.

The effect of the concentration of the various mono-valent metal ions of the source solution on the flux across the membrane was also investigated and the results are shown in
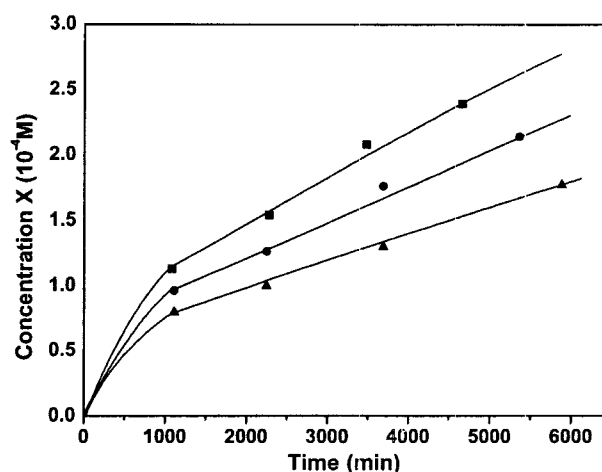

Figure 4. Receiving side concentration versus operating time for transport of metal ions (metal chloride). Concentration of source solution: 0.02 M, Cs ■, K ●, Na ▲.

Figure 3. Receiving side concentration versus operating time for transport of metal ions (metal chloride). Concentration of source solution: 0.05 M, Cs ■, Rb ◆, K ●, Na ▲, Li ▼.
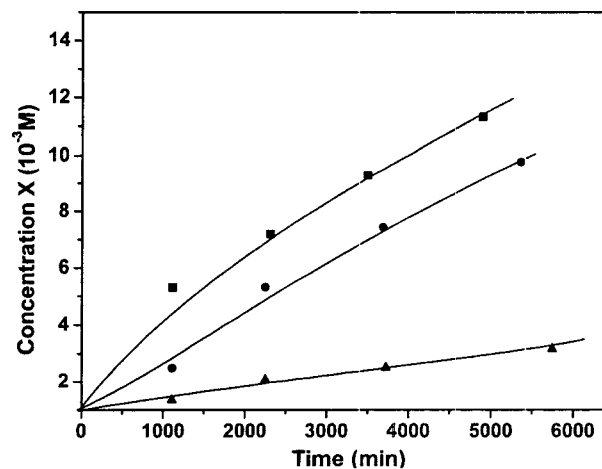

Figure 5. Receiving side concentration versus operating time for transport of metal ions (metal chlordie). Concentration of source solution: 0.1 M. Cs ■. K ●. Na ▲.
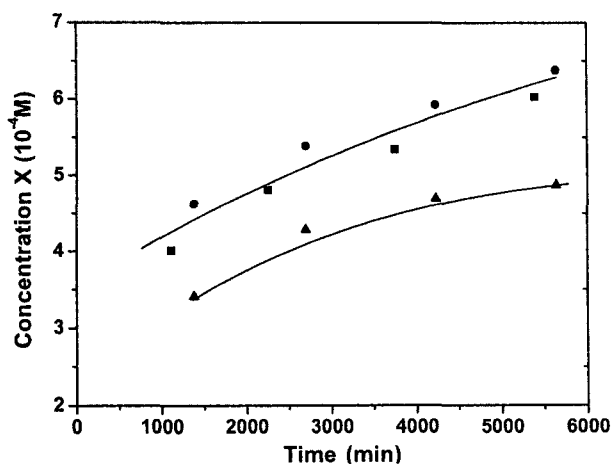
Figure 6. Effect of anion on the flux of potassium ion transport across FCM. Concentration of source solution. 0.05 M, Anion: NO_3^- ●, Cl^- ■, ClO_4^- ▲.

Figures 4 and 5, respectively. Although the flux of the metal ion increases as metal ion concentration of the source solution increases, however, the reverse in the order of the flux in metal ions is not observed, i.e., the flux across the membrane decreases in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.

The dependence of K^+ flux on the type of anion was also investigated and the results are shown in Figure 6, demonstrating that the flux is almost independent on the type of the anion except in the case where perchlorate anion is used. A significant decrease in the flux is observed when perchlorate anion is used, which is contradictory with the results reported in LM. It has been reported that the flux in LM, increases with increasing hydrophobicity of anions [6,17]. This contradiction, however, is explainable in terms of hydrophilicity of the membrane. LM is hydrophobic since the carrier is soluble in organic phase, on the contrary, it is believed that the flux of metal ion increases as the hydrophilicity of the anion increases in the FCM containing crown ether unit which exhibits the hydrophilic behavior, therefore the flux of metal ion is higher when nitrate or chloride anion is used which is more hydrophilic than perchlorate anion[6].

Conclusions

PET fabric supported FCM containing 32-membered crown ether unit was prepared by dipping of the PET fabric into the solution of the homopolymer incorporating 32-membered crown ether unit. It was found that the polymers containing the crown ether unit is useful in the extraction of various metal ions from the aqueous phase and the FCM can be also utilized as a selective transport of mono-valent metal ion by membrane separation process. The FCM shows preferential selectivity to Cs^+ and the flux across the membrane decreases in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. The selectivity of FCM to metal ions is explained in terms of the stability of the complex formed between the 32-crown ether unit and metal ions. The higher flux of the polymer than monomer ligand was ascribed to the polymer effect in the formation of 2:1 sandwich tape complex of crown ether unit and metal ion and the highest selectivity to Cs^+ was attributed to the closeness of ionic radius of metal ion and the cavity size of crown ether ring. Lower flux in the presence of perchlorate reveals the hydrophilic nature of FCM.

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