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Preparation of an extractant-impregnated porous membrane for the high-speed separation of a metal ion

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Abstract

A novel impregnation method of extractants into a porous polymeric support is described. Bis(2-ethylhexyl)phosphate (HDEHP) was impregnated onto an *n*-octadecylamino group of the polymer chain grafted onto the pore surface of a porous hollow-fiber membrane. First, an epoxy-group-containing polymer chain was appended onto the porous membrane by radiation-induced graft polymerization of glycidyl methacrylate (GMA). Second, *n*-octadecylamine was added to the graft chain via an epoxy-ring opening reaction to yield a hydrophobic group density of 3.0 mmol/g of the GMA-grafted fiber. Finally, HDEHP was impregnated to the *n*-octadecylamino group. The amount of impregnated HDEHP of 2.1 mmol/g of the GMA-grafted fiber was attained while retaining the liquid permeability of the porous membrane. An yttrium solution was forced to permeate through the pores of the HDEHP-impregnated porous hollow-fiber membrane. The higher permeation rate of the yttrium solution led to the higher adsorption rate of yttrium because of a negligible diffusional mass-transfer resistance. In addition, a high stability of impregnated HDEHP was observed after the repeated use of adsorption with 50 mg-Y/L yttrium solution and elution with 7 M nitric acid.

Keywords: Porous hollow fiber; Graft polymerization; Hydrophobic interaction; Impregnation; HDEHP; Yttrium separation

1. Introduction

Adsorption methods based on chelate formation for separating and purifying target ions and molecules are advantageous over solvent extraction because of the solvent-free and highly selective operation. Various adsorbents selective and specific for metal ions have been developed for the analysis of radionuclides in environmental samples and radioactive wastes. Commercially available adsorbents include chelate-forming resins and extractant-impregnated resins in bead form: the former contains chelating groups, that is, chelate-forming moieties, immobilized to a polymeric support via covalent bonding, whereas the latter holds extractants in the polymeric support via hydrophobic and intermolecular interactions. Representative chelating group and reagent are the iminodiacetate group [1–3] and organophosphorus extractants [4,5], respectively.

These resins in bead form are packed into a bed for applications such as liquid chromatography (LC) and solid-phase extraction (SPE). These beads allow a target ion to diffuse into the bead interior where the chelating groups are immobilized and extractants are impregnated. The bead-packed bed has a trade-off relationship between mass transfer and hydrodynamic considerations: a longer time is required for the ion to reach the functional group immobilized and the extractant impregnated to the interior of larger-size beads. On the other hand, the bed packed with smaller-size beads demands a

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higher operational pressure to force the liquid to flow through the bed interstices.

In order to overcome the disadvantage of the bead-packed bed, porous supports have been extensively studied, Brandt et al. [6] prepared a porous affinity membrane for the purification of proteins and demonstrated that the convective transport of proteins minimizes the diffusional path to the affinity ligand. Afeyan et al. [7] prepared a functionalized bead having pores through which a protein can be transported by convection and showed that diffusional mass-transfer resistance in the bead-packed bed could be reduced. These two convection-assisted methods of chromatography were termed membrane chromatography and perfusion chromatography, respectively.

To date we have proposed novel porous hollow-fiber membranes containing chelating [8,9] and ion-exchange groups [10–13], and hydrophobic [14] and affinity [15] ligands, by radiation-induced graft polymerization. These porous membranes exhibited excellent mass-transfer characteristics in a permeation mode due to the negligible diffusional mass-transfer resistance of a target ion or molecule to the functional group of the polymer chain grafted onto the pore surface of the porous membrane.

Extractant impregnation to the porous membranes can satisfy the requirements of speed and capacity for the adsorption of metal ions. The objective of our study was two-fold: (1) to impregnate the extractant at a high density to the hydrophobic ligand of the polymer chain grafted onto the pore surface of the porous hollow-fiber membrane and (2) to demonstrate a high-speed adsorption of a metal ion to the extractant-impregnated porous hollow-fiber membrane in the permeation mode. In this study, bis(2-ethylhexyl)phosphate (HDEHP) was impregnated to an *n*-octadecylamino ($C_{18}NH$) group as a hydrophobic group to form the chelation with yttrium ion as a model metal ion.

Previous studies [16–18] demonstrated that HDEHP as an extractant for liquid–liquid extraction exhibits a high selectivity for yttrium ions in coexisting elements, such as strontium, cobalt, nickel, and technetium in an acidic medium. The separation of yttrium ions using an HDEHP-impregnated porous hollow-fiber membrane is applicable to the determination of ^{90}Sr, one of the extremely hazardous fission products in radioactive wastes because ^{90}Sr is measured by counting its daughter nuclide ^{90}Y in radioactive equilibrium by radiometry.

2. Experimental

2.1. Materials

A porous hollow-fiber membrane supplied by Asahi Kasei Chemicals Co., was used as a base membrane for grafting. This hollow-fiber membrane made of polyethylene had inner and outer diameters of 1.8 and 3.1 mm, respectively, with an average pore size of 0.4 μm and a porosity of 70%. Glycidyl methacrylate ($CH_2{=}CCH_3COOCH_2CHOCH_2$, GMA) and HDEHP were purchased from Tokyo Kasei and used without further purification. Yttrium oxide (Y_2O_3) was acquired from Wako. Methanol, ethanol and octadecylamine were of analytical grade and obtained from Wako.

2.2. Preparation of hydrophobic porous membranes

A scheme for the impregnation of HDEHP onto the pore surface of the porous hollow-fiber membrane is shown in Fig. 1. The scheme consists of the following four steps: (1) electron beam irradiation to the base membrane to produce radicals, (2) graft polymerization of an epoxy-group-containing monomer GMA onto the pore surface of the porous hollow-fiber membrane, (3) introduction of an $C_{18}NH$ group as a hydrophobic ligand into the graft chain, and (4) impregnation of HDEHP to the $C_{18}NH$ group of the graft chain.

Preparation procedures of hydrophobic porous membranes are described briefly: the base membrane was irradiated with an electron beam using a cascade-type accelerator (Dynamitron IEA 3000-25-2, Radiation Dynamics). The

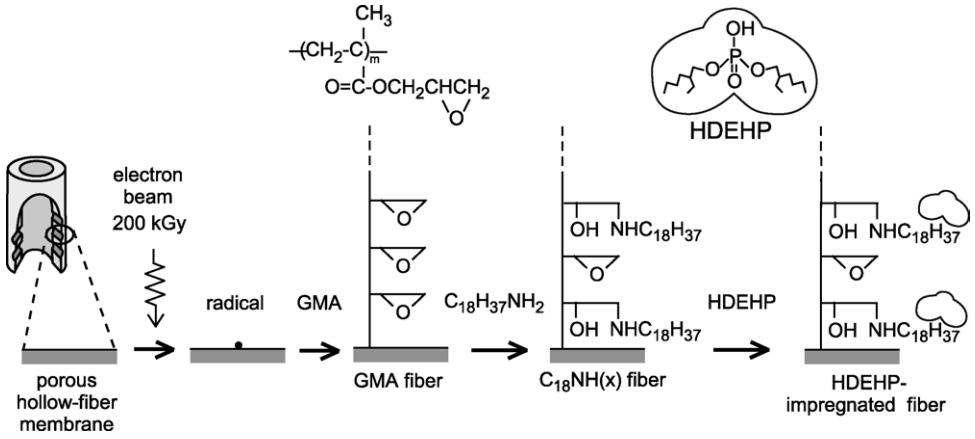

Fig. 1. Impregnation scheme of HDEHP to the polymer chain grafted onto a porous hollow-fiber membrane.

dose was 200 kGy. The irradiated porous hollow-fiber membrane was immersed in 10% (v/v) GMA/methanol at 313 K. The degree of GMA grafting, defined below, was set at 200% by adjusting the reaction time to be 15 min.

$$\text{Degree of GMA grafting (\%)} = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

where W_0 and W_1 are the masses of the base and GMA-grafted porous hollow-fiber membranes, respectively. The resultant porous hollow-fiber membrane is referred to as a GMA fiber.

The GMA fibers with a length of 4 cm of 0.09–0.11 g were immersed in 20 g of pure octadecylamine in liquid form at 353 K. The reaction time was up to 5 h. The hollow fiber was removed, washed with ethanol for 2 h, dried at 333 K and weighed. The molar conversion of the epoxy group into the $C_{18}NH$ group and the $C_{18}NH$ group density were calculated as

$$\text{Molar conversion (\%)} = \frac{(W_2 - W_1)/\text{MW}_{\text{octa}}}{(W_1 - W_0)/\text{MW}_{\text{GMA}}} \times 100 \quad (2)$$

$$C_{18}NH \text{ group density (mmol/g)} = \frac{(W_2 - W_1)/\text{MW}_{\text{octa}}}{W_1} \times 1000 \quad (3)$$

where W_2 is the mass of the hydrophobic porous hollow-fiber membrane. MW_{octa} and MW_{GMA} denote the molecular masses of octadecylamine and GMA, respectively. The resultant porous hollow-fiber membrane is referred to as a $C_{18}NH$ (x) fiber, where x indicates the molar conversion.

2.3. Impregnation of HDEHP to the hydrophobic porous membranes

The $C_{18}NH$ (x) fiber was immersed in 5% (v/v) HDEHP-ethanol solution at an ambient temperature for 2 h. The hollow fiber was taken out and dried at 333 K for 2 h to evaporate the ethanol. The resultant porous hollow-fiber membrane is referred to as an HDEHP-impregnated fiber. The amount of impregnated HDEHP and molar impregnation ratio were evaluated from the weight gain as follows:

$$\text{Amount of impregnated HDEHP (mmol/g)} = \frac{(W_3 - W_2)/\text{MW}_{\text{HDEHP}}}{W_1} \times 1000 \quad (4)$$

$$\text{Molar impregnation ratio (unitless)} = \frac{\text{mole number of impregnated HDEHP}}{\text{mole number of } C_{18}NH \text{ group}} \quad (5)$$

where W_3 is the mass of the HDEHP-impregnated fiber and MW_{HDEHP} is the molecular mass of the HDEHP.

After the HDEHP-impregnated fiber was freeze-dried, the cross-section of the hollow fiber was observed by scanning electron microscopy (SEM, JSM-6700F JEOL).

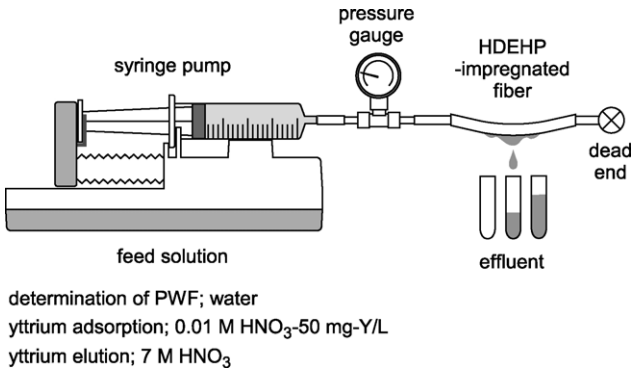

Fig. 2. Experimental apparatus for permeation of pure water, yttrium solution, and nitric acid through the porous membrane.

2.4. Flux determination of the HDEHP-impregnated porous membranes

The porous hollow-fiber membrane with an effective length of 1.5 cm was positioned in a dead-end mode, as illustrated in Fig. 2. Pure water was forced to permeate from the inside surface of the hollow fiber outward at a constant transmembrane pressure of 0.05 MPa. Pure water flux (PWF) of the hollow fiber was determined by dividing the permeation rate of pure water by the inside surface area of the hollow fiber.

The swelling of the hollow fiber induced by a series of graft polymerization, introduction of $C_{18}NH$ group, and impregnation of HDEHP was evaluated by a volume ratio such as V_2/V_1 and V_3/V_2. For example,

$$\frac{V_3}{V_2}(\text{dimensionless}) = \frac{(d_{o,3}^2 - d_{i,3}^2)\, L_3}{(d_{o,2}^2 - d_{i,2}^2)\, L_2} \quad (6)$$

where V, d_i, d_o, and L are the volume, inner and outer diameters, and length of the hollow fiber, respectively. The subscripts 1–3 indicate the GMA-grafted, $C_{18}NH$-group-containing, and HDEHP-impregnated fibers, respectively.

2.5. Yttrium adsorption during the permeation of the solution through the pores of the HDEHP-impregnated porous membranes

A 50 mg-Y/L yttrium solution dissolved in 0.01 M nitric acid was forced to permeate outward from the inside surface of the HDEHP-impregnated fiber at a constant permeation rate, using an experimental apparatus shown in Fig. 2. The permeation rate of the yttrium solution ranged from 30 to 120 mL/h using a syringe pump. The effluent penetrating the outside surface was continuously collected. The yttrium concentration was determined by ICP-AES (HITACHI P-4000). Subsequently, 7 M nitric acid was permeated to elute the yttrium adsorbed.

3. Results and discussion

3.1. n-Octadecylamino group density of porous membranes

The epoxy group of the graft chain onto the pore surface of the porous hollow-fiber membrane was converted into a $C_{18}NH$ group as a hydrophobic ligand to impregnate extractants. Time course of the molar conversion of the epoxy group into the $C_{18}NH$ group is shown in Fig. 3(a) along with the $C_{18}NH$ group density. The molar conversion increased with increasing reaction time and leveled off at 63% after 3 h. The swelling ratio V_2/V_1, defined by dividing the volume of the $C_{18}NH$ (x) fiber by that of the GMA fiber, increased linearly increasing molar conversion, as shown in Fig. 3(b). This is indicative of the swelling induced by the incorporation of the $C_{18}NH$ group to the graft chain via the epoxy ring opening with octadecylamine.

3.2. Amount of impregnated HDEHP

HDEHP was impregnated to the $C_{18}NH$ group in an immersion mode. The amount of impregnated HDEHP onto

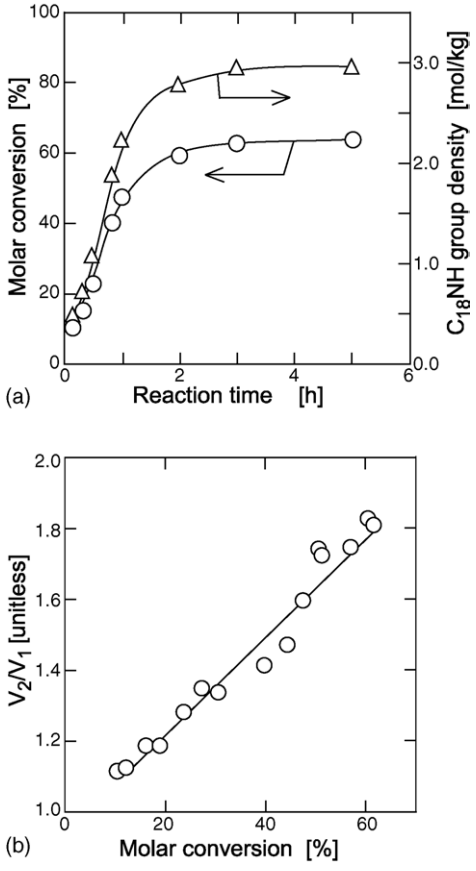

Fig. 3. n-Octadecylamino group density and swelling ratio of the porous membrane. (a) Time course of a molar conversion of the epoxy group into the $C_{18}NH$ group and (b) Swelling ratio vs. molar conversion.

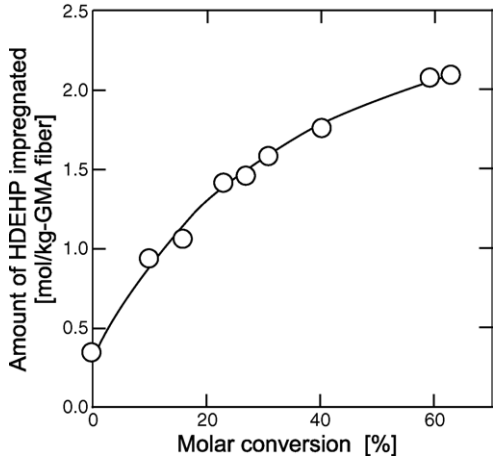

Fig. 4. Amount of HDEHP impregnated vs. molar conversion.

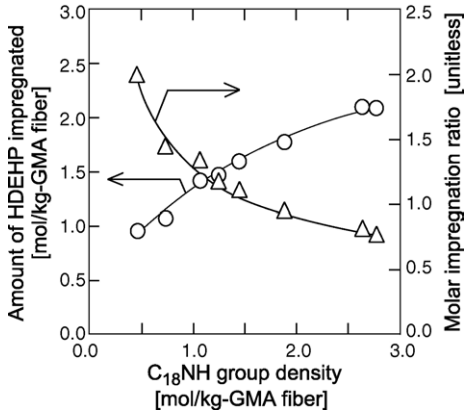

Fig. 5. Molar impregnation ratio vs. $C_{18}NH$ group density.

the $C_{18}NH$ (x) fiber is shown in Fig. 4 as a function of the molar conversion. The amount of impregnated HDEHP increased with increasing molar conversion. The maximum amount of impregnated HDEHP reached 2.1 mmol/g of the GMA fiber at a molar conversion of 63%. The amount of HDEHP impregnated to the porous hollow-fiber membrane was 56–70% that of extractants impregnated to various matrices (Table 1).

The molar impregnation ratio for HDEHP defined by Eq. (5) is shown in Fig. 5. With an increasing $C_{18}NH$ group density, the amount of impregnated HDEHP increased, whereas the molar impregnation ratio decreased. This can be explained by the fact that an increase in the $C_{18}NH$ group density allows the graft chain to extend itself due to electrostatic repulsion originating from the amino moiety in the $C_{18}NH$ group, while increasing steric hindrance by the $C_{18}NH$ group.

SEM images of the cross-sections of the porous hollow-fiber membranes are shown in Fig. 6. SEM revealed that the pore structure of the HDEHP-impregnated fiber was retained when compared to that of the $C_{18}NH$ (63) fiber. The pore size of the porous hollow-fiber membrane increased due to the swelling induced by the introduction of the $C_{18}NH$ group into the graft chain. Furthermore, the pore surface became

Table 1
Previous studies on extractant-impregnated adsorbent

Extractants	Matrix	Impregnation amount	Capacity	Target metal ions	Reference
DAAP[a]	Amberchrom CG-71[b] or Amberlite XAD-7	40% (w/w)	0.40 mmol-U/g[c]	U(VI)	[4]
Mixture of CMPO[d] and TBP[e]	Amberchrom CG-71 or Amberlite XAD-7	40% (w/w)	0.076 mmol-Am/g[c]	An(III, IV, VI), Ln(III)	[5]
Aliquat336[f]	Amberchrom CG-71	40% (w/w)	0.64 mmol-Cl/g[c]	Th(IV), Np(IV), Pu(IV), Tc(VII)	[19]
TBP	XAD-4[g]	50% (w/w)	0.64–0.71 mmol-U/g	U(VI), Pu(IV), Np(V),Am(III)	[20]
HT18C6TO[h]	Empore extraction disk[i]	10 mg/disk	0.0012 mmol-Hg/disk	Hg(II)	[21]
DMG[j]	Silica (sol–gel material)	–	0.009 mmol-Ni/g	Ni(II)	[22]
HDEHP	Octadecylamino group containing porous-hollow fiber membrane	28% (w/w)	0 38 mmol-Y/g-GMA fiber	Y(III)	This study

[a] Diamyl amylphosphonate.
[b] Macroreticular acrylic polymer from Rohm and Haas Company.
[c] Experimentally measured capacity.
[d] *n*-Octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide.
[e] Tri-*n*-butyl phosphate.
[f] Tri-*n*-octylmethylammonium chloride.
[g] Macroreticular aromatic polymer from Rohm and Haas Company.
[h] Hexathia-18-crown-6-tetraone.
[i] C_{18} bonded silica from 3 M Co.
[j] Dimethylglyoxime.

smooth via the impregnation of HDEHP. The pore sizes of the HDEHP-impregnated fiber observed by SEM ranged from 0.4 to 0.8 μm. The increase in pore size was evaluated by calculating the pore radius ratio r_3/r_1 using

$$\frac{r_3}{r_1}(\text{dimensionless}) = \left[\left(\frac{F_3}{F_1}\right)\left(\frac{d_{i,3}L_3}{d_{i,1}L_1}\right)\left(\frac{D_{T,3}}{D_{T,1}}\right)\right]^{1/4} \quad (7)$$

where F and D_T are the pure water flux and the thickness of the porous hollow-fiber membrane, respectively [23]. The pore size of the HDEHP-impregnated fiber, calculated using Eq. (7), was 0.6 μm. This value was in good agreement with the pore size observed from the SEM image in Fig. 6.

After the impregnation of HDEHP, pure water was forced to permeate through the pores of the HDEHP-impregnated fiber. No leakage of HDEHP was directly observed in the effluent penetrating the outside surface of the HDEHP-impregnated fiber.

3.3. Flux of the HDEHP-impregnated porous membranes

The pure water flux of the HDEHP-impregnated fiber versus the molar conversion is shown in Fig. 7 along with the swelling ratio V_3/V_2, defined as the volume ratio of the HDEHP-impregnated fiber to the $C_{18}NH$ (x) fiber. The pure water flux increased up to 1.5 m/h at a transmembrane pressure of 0.05 MPa with increasing the molar conversion.

The graft chain, that is, the polymer chain grafted onto the porous hollow-fiber membrane made of polyethylene, is formed in two regions: (1) the graft chain extended from the pore surface toward the pore interior, thereby narrowing the pore size, and (2) the graft chain embedded in the depth of the polyethylene matrix, thereby swelling the entire membrane. The liquid permeability through the pores of the grafted porous hollow-fiber membrane is determined by these two competing factors. In this case, the swelling over the membrane induced by the impregnation of the extractant to the hydrophobic ligand of the graft chain overwhelmed the pore size reduction by the graft chain extended from the pore surface.

3.4. Yttrium adsorption during permeation through the pores

An yttrium solution (50 mg-Y/L in 0.01 M HNO_3) was forced to permeate through the pores of the HDEHP-impregnated fiber at various permeation rates of the solution. The breakthrough curves of the HDEHP-impregnated fiber with a molar conversion of 29% and the amount of impregnated HDEHP of 1.4 mmol/g of the GMA fiber are shown in Fig. 8. In this figure, the abscissa is a dimensionless effluent volume defined by dividing the effluent volume by the membrane volume excluding the lumen part; the ordinate is a relative yttrium concentration of the effluent to the feed. The breakthrough curves overlapped irrespective of the permeation rate of the yttrium solution. This denotes that the higher permeation rate of the yttrium solution across the extractant-impregnated fiber led to the higher overall adsorption rate of yttrium to the impregnated extractant because of negligible diffusional mass-transfer resistance of yttrium ion in the pore interior to the extractant. These phenomena were observed in other combinations such as cobalt ion captured by the chelating porous hollow-fiber membrane [24] and lysozyme captured by the cation-exchange porous hollow-fiber membrane [10].

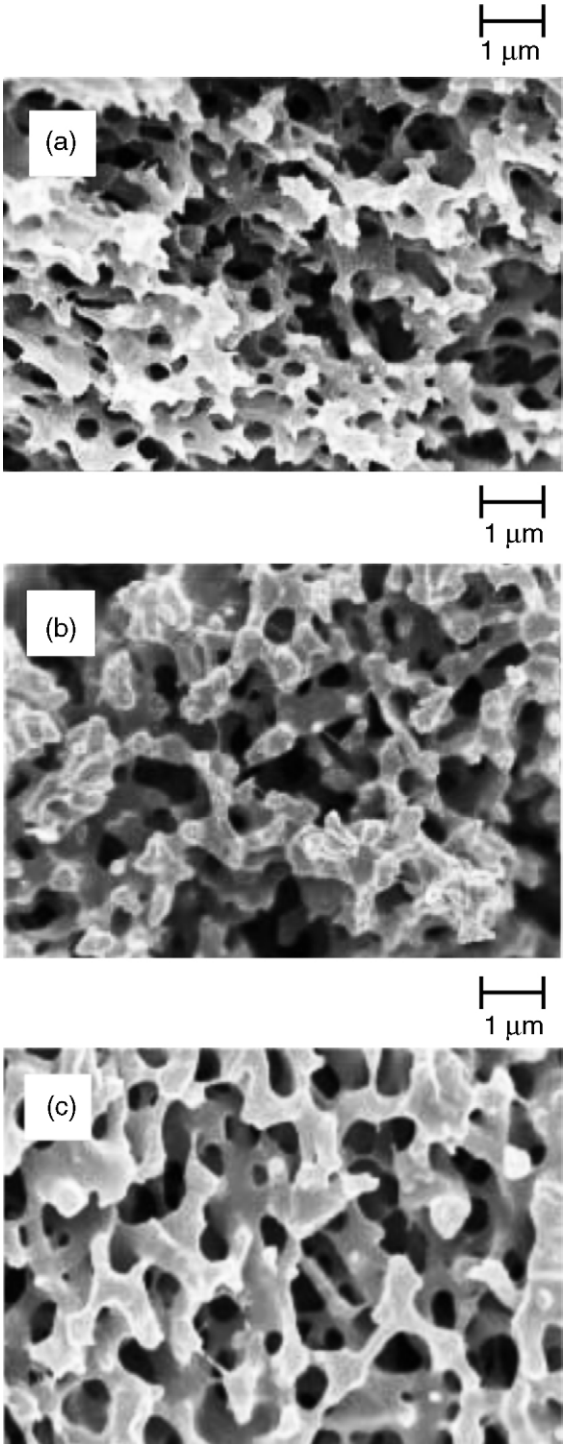

Fig. 6. SEM images of the cross-sections of the porous membranes. (a) GMA fiber, (b) C_{18}NH (63) fiber, and (c) HDEHP-impregnated fiber.

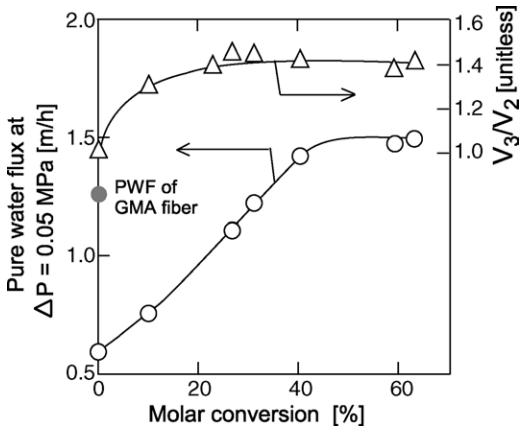

Fig. 7. Pure water flux vs. molar conversion along with the swelling ratio V_3/V_2.

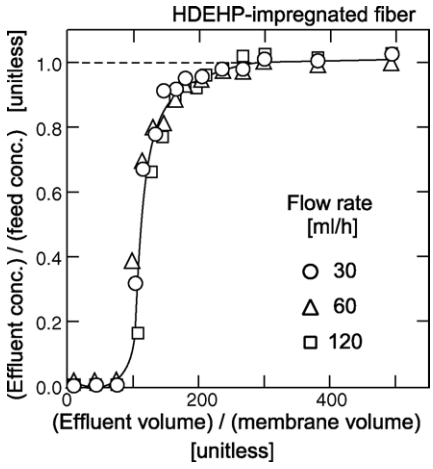

Fig. 8. Breakthrough curves of yttrium during the permeation of 50 mg-Y/L yttrium solution through HDEHP-impregnated fiber.

The equilibrium adsorption capacity for yttrium of the HDEHP-impregnated fiber was calculated as 0.38 mmol/g of the GMA fiber. This demonstrated that assuming a complex ratio of yttrium to HDEHP of 1:3 [25], 82% of impregnated HDEHP contributed to the binding of yttrium. In addition, the amount of adsorbed yttrium was quantitatively eluted with 7 M nitric acid in the permeation mode. After the four cycles of adsorption and elution, no deterioration of the adsorption capacity for yttrium was observed.

Previous studies [4,5,19–22] of the capacities of metal ions of the extractant-impregnated adsorbents are summarized in Table 1. A high capacity of the metal ion of the HDHEP-impregnated fiber comparable to that of previous extractant-impregnated matrices while retaining the pure water flux of the porous hollow fiber membrane at a feasible level was achieved.

4. Conclusions

The epoxy-group-containing polymer chain was grafted onto the pore surface of a porous hollow-fiber membrane by radiation-induced graft polymerization. Subsequently, *n*-octadecylamino group was introduced into the polymer chain to impregnate HDEHP as a representative organophosphorous extractant. The liquid permeability of the HDEHP-

impregnated porous hollow-fiber membrane was retained at a feasible level after the HDEHP impregnation to the polymer chain. The amount of impregnated HDEHP onto the porous hollow-fiber membrane was 56–70% of that of impregnated extractants onto various matrices. Convective transport of an yttrium solution through the pores enabled a negligible diffusional mass-transfer resistance of yttrium ion to the impregnated HDEHP. The HDEHP-impregnated porous hollow-fiber membrane exhibited a high stability during repeated adsorption-elution cycles. In order to apply yttrium separation using the HDEHP-impregnated porous hollow-fiber membrane to the determination of ^{90}Sr by counting its daughter nuclide ^{90}Y, the difference in the selectivity between HDEHP impregnated onto the polymer chain and that dissolved in the organic solvents will be discussed in a later publication.

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