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Abstract: Poly-glycidyl methacrylate (GMA) was appended onto a porous membrane of a hollow-fiber form with an epoxy group density of 14 mol per kg of the starting porous membrane. Octadecylamine was added to the epoxy group of the polymer brush at a maximum molar conversion of the epoxy group into the octadecylamino group of 59%. An acidic extractant, bis(2,4,4,-trimethylpentyl)phosphinic acid (Cyanex 272), was impregnated on the octadecylamino group by immersion of the octadecylamine-added porous membrane in Cyanex 272/ethanol solution. The amount of impregnated extractant was 1.4 mol per kg of the GMA-grafted porous membrane at a molar conversion of 59%. The phosphinic acid moiety of

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Cyanex 272 was attracted by the amino part of the octadecylamino group of the polymer brush to swell the entire volume of the porous membrane. This swelling compensated for the pore volume reduction caused by grafting the charged polymer brush to the pore surfaces of the porous membrane. The impregnated Cyanex 272 was repositioned on the charged polymer brush in response to the properties of surrounding liquids. The hydrophobic interaction enables the hydrophobic moiety of Cyanex 272 to associate with the octadecyl part of the octadecylamino group of the polymer brush to capture zinc ions. The binding efficiency of the Cyanex 272-impregnated polymer brush for zinc ion was as high as 93%.

Keywords: Porous hollow fiber, graft polymerization, hydrophobic interaction, extractant impregnation, cyanex 272, Zn adsorption

INTRODUCTION

A charged polymer brush is defined as a pack of polymer chains containing ionizable groups grafted onto an interface of organic or inorganic material (1). Positively and negatively charged or ionizable groups correspond to anion- and cation-exchange groups, respectively. Diethylamino and sulfonic acid groups are representative charged groups. A remarkable character of the charged polymer brush is its extension and shrinkage in response to the pH and ionic strength of surrounding liquids. Kawai et al. (2) demonstrated that the extension or shrinkage of a charged polymer brush is induced by protein binding. Sasagawa et al. (3) demonstrated that the expansion of the charged polymer brush is restricted by crosslinking with bivalent ions such as magnesium and calcium.

The charged polymer brush was attached uniformly across the thickness of a porous membrane using radiation-induced graft polymerization of a precursor monomer and subsequent chemical modifications. (4–6) The modified porous membranes enable high-throughput separation and reaction because the convective flow through the pores driven by transmembrane pressure minimizes the diffusion path of the ions to the charged groups of the polymer brush (7). This convection-aided separation has a distinct advantage over the conventional separation based on a diffusion-restricted process in that a higher flow rate of the target solution across the modified porous membranes leads to a higher collection rate of target ion by the charged group.

To date we have prepared a porous hollow-fiber membrane immobilizing the charged polymer brush to capture proteins in multilayers. For example, diethylamino (8) and sulfonic acid (3) groups of the polymer brush held bovine serum albumin and hen egg lysozyme in 11 and 38 layers onto the pore surface, respectively. Moreover, because a group of proteins representative of albumin exclusively recognizes L-amino acids and a set of proteins (enzymes) specifically produce useful products, materials incorporating protein bound in multilayers to a charged polymer brush are applicable to chiral separations (9, 10) and enzymatic reactions (11).

Radionuclides in radioactive waste and environmental samples have been analyzed by radiometry and mass spectrometry. As a pretreatment before the analysis, the radionuclides are purified by combined solvent extraction and ion-exchange (12–16). However, these methods have drawbacks: solvent extraction generates large amounts of organic solvent and ion-exchange resins exhibit lower selectivity for some elements than various extractants do. To overcome these disadvantages, extraction chromatography using extractant-impregnated beads was suggested by Horwitz in 1992 (17–19).

We suggested a novel method using a porous polymeric membrane as a supporting material for the impregnation of the extractants (20): the extractant was impregnated on the polymer brush grafted to the pore surface and into the polymer matrix, and then a metal solution was forced to permeate through the pores to minimize the diffusional path of the metal ion to the extractant. However, the interactions among charged polymer brush, extractants, and metal ions have not yet been elucidated.

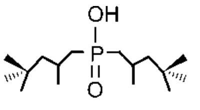
The objective of our study is twofold:

i. to impregnate various extractants for metal ions on the charged polymer brush containing an octadecylamino group grafted onto a porous hollow-fiber membrane, and
ii. to elucidate the interactions among the charged polymer brush, extractant, and metal ion. In this study, three extractants, i.e., bis(2,4,4,-trimethylpentyl)phosphinic acid (Cyanex 272), tri-*n*-butylphosphate (TBP), and tri-*n*-octylmethylammonium chloride (Aliquat 336), were selected as acidic, neutral, and basic extractants, respectively.

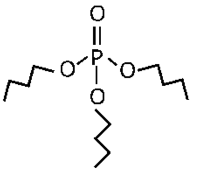
EXPERIMENTAL

Materials

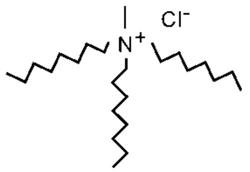
A commercially available porous membrane of a hollow-fiber form was used as the starting membrane for grafting. This hollow fiber made of polyethylene had inner and outer diameters of 1.8 and 3.0 mm, respectively, with an average pore diameter of 0.4 μm and a porosity of 70%. Glycidyl methacrylate ($CH_2 = CCH_3COOCH_2CHOCH_2$, GMA) was purchased from Tokyo Kasei Co. and used without further purification. Three extractants, i.e., Cyanex 272, TBP, and Aliquat 336, the chemical structures of which are shown in Fig. 1, were obtained from CYTEC Industries Inc., Wako Pure Chemical Industries, and Avocado Research Chemicals Ltd., respectively. Standard zinc solution ($ZnCl_2$, 1 g-Zn/L in 1 M HCl) was acquired from Nacalai Tesque Inc. Other reagents were of analytical grade or higher.



Bis(2,4,4,-trimethylpentyl)phosphinic acid; Cyanex 272



Tri-*n*-butyl phosphate; TBP



Tri-*n*-octylmethylammonium Chloride; Aliquat 336

Figure 1. Chemical structures of extractants

Preparation of Octadecylamino-Group-Containing Polymer Brush on Porous Membrane

A hydrophobic porous membrane for the impregnation of the extractants was prepared via following the three steps shown in Fig. 2.

i. Irradiation of an electron beam to produce radicals: the starting porous membrane was irradiated with an electron beam in a nitrogen atmosphere at ambient temperature using a cascade-type accelerator (Dynamitron IEA 3000-25-2, Radiation Dynamics Inc.). The dose was 200 kGy.
ii. Graft polymerization of an epoxy-group-containing monomer (GMA): the irradiated porous membrane was immersed in 10 (v/v) % GMA/methanol solution at 313 K for 15 min. The degree of GMA grafting, defined below, was 200%, which is equivalent to 14 mol of the epoxy group introduced onto the polymer brush per kg of the starting porous membrane.

$$\text{degree of GMA grafting } (\%) = 100(W_1 - W_0)/W_0 \qquad (1)$$

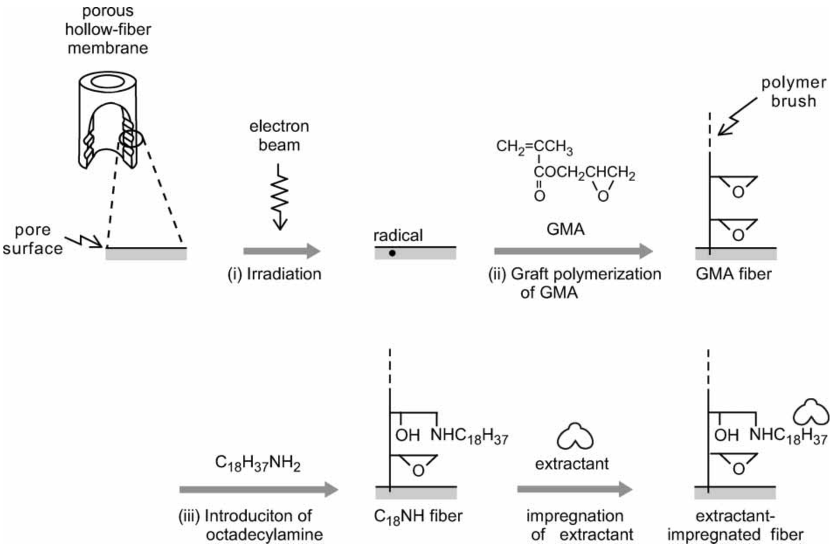


Figure 2. Impregnation scheme of extractants to octadecylamino-group-containing polymer brush grafted onto the pore surface of a porous hollow-fiber membrane.

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

iii. Introduction of an octadecylamino ($C_{18}H_{37}NH$-) group onto the polymer brush: the GMA fiber was reacted with octadecylamine at 353 K. The reaction time ranged from 1 to 5 h. The porous membrane was taken out and washed with ethanol at 353 K to remove residual octadecylamine. The molar conversion of the epoxy group into the octadecylamino group was evaluated from the weight gain as follows:

$$\text{molar conversion}(\%) = 100\ [(W_2 - W_1)/270]/[(W_1 - W_0)/142] \qquad (2)$$

where W_2 is the mass of the octadecylamino-group-containing porous membrane. The numbers 270 and 142 are the molecular masses of octadecylamine and GMA, respectively. The resultant porous membrane was designated as a $C_{18}NH$ fiber.

Impregnation of Extractants onto Octadecylamino-Group-Containing Polymer Brush

Three extractants, i.e., Cyanex 272, TBP, and Aliquat 336, were impregnated onto the $C_{18}NH$ fibers with various molar conversions. Each extractant was dissolved in ethanol to yield a concentration of 5 (v/v)%. The $C_{18}NH$ fiber was immersed in the extractant/ethanol solution at ambient temperature for 2 h. The extractant-impregnated porous hollow-fiber membrane was taken out and dried at 333 K for 2 h to evaporate the ethanol. The resultant porous membrane was referred to as a Cyanex 272, TBP, or Aliquat 336 fiber. The amount of impregnated extractant was calculated as

$$\begin{aligned}&\text{amount of impregnated extractant (mol/kg-GMA fiber)}\\&\quad = 1000\ (W_3 - W_2)/M_r/W_1\end{aligned} \tag{3}$$

where W_3 is the mass of the extractant-impregnated fiber and M_r is the molecular mass of Cyanex 272, TBP, or Aliquat 336 in a dissociated form, respectively.

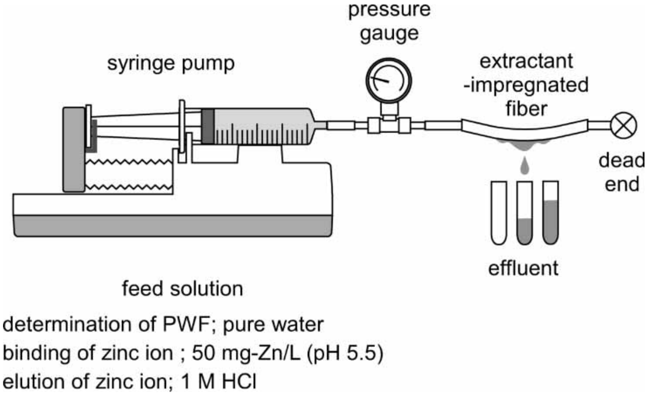
The swelling of the hollow fiber induced by the impregnation of the extractant was described by the swelling ratio as follows:

$$V_3/V_2(-) = [(d_{o,3}^2 - d_{i,3}^2)L_3]/[(d_{o,2}^2 - d_{i,2}^2)L_2] \tag{4}$$

where V_3 and V_2 are the volumes of the extractant-impregnated fiber and $C_{18}NH$ fiber, respectively. The terms d_i, d_o, and L are the inner and outer diameters, and length of the hollow fiber, respectively. The subscripts 1, 2, and 3 denote the GMA, $C_{18}NH$, and extractant-impregnated fibers, respectively.

Determination of Pure Water Flux of Extractant-Impregnated Porous Membranes

The permeability of pure water through the pores of the porous membrane of a hollow-fiber form was measured using the experimental apparatus illustrated in Fig. 3. The porous membrane was positioned in a dead end mode.



determination of PWF; pure water
binding of zinc ion ; 50 mg-Zn/L (pH 5.5)
elution of zinc ion; 1 M HCl

Figure 3. Experimental apparatus to measure the permeation of pure water, zinc solution, and hydrochloric acid through the porous membrane.

Pure water was forced to permeate from the inside surface of the porous membrane radially outward to the outside surface. The transmembrane pressure was maintained at 0.05 MPa. The permeation rate of pure water was measured at 298 K to evaluate pure water flux (PWF) as

$$\begin{aligned}\text{PWF (m/h)} &= (\text{permeation rate of pure water})/\\ &\quad(\text{inside surface area of the hollow fiber}) \qquad (5)\end{aligned}$$

The extractant-impregnated fiber was freeze-dried in liquid nitrogen, and the cross-section of the hollow fiber was observed by scanning electron microscopy (SEM, JSM-6700F JEOL).

Binding and Elution of Zinc Ion during Permeation

A solution of 50 mg-Zn/L, the pH of which was adjusted to 5.5 with HCl and NaOH, was allowed to permeate through the pores of the extractant-impregnated fiber at a permeation rate of 120 mL/h using the same apparatus as shown in Fig. 3. The effluent penetrating the outside surface of the extractant-impregnated fiber was continuously collected in vials and its zinc concentration was determined by ICP-AES (HITACH P-4000). After equilibration with the feed concentration, or after the effluent concentration reached the feed concentration, 1 M HCl was fed to elute the bound zinc.

The amount of zinc bound in equilibrium with the feed concentration, q, and the elution percentage of zinc were calculated as

$$q = \int_0^{Ve} (C_0 - C)dV/W_1 \qquad (6)$$

$$\begin{aligned}\text{elution percentage(\%)} &= 100(\text{amount of zinc eluted})/\\ &\quad(\text{amount of zinc bound}) \qquad (7)\end{aligned}$$

where C_0 and C are the zinc concentrations of the feed and effluent, respectively. The terms V and V_e are the effluent volume and the effluent volume where C reaches C_0, respectively.

RESULTS AND DISCUSSION

Impregnation of Extractants on Polymer Brush

Acidic, neutral, or basic extractant, i.e., Cyanex 272, TBP, or Aliquat 336, respectively, was impregnated on the octadecylamino group ($C_{18}H_{37}NH$-) of the polymer brush grafted onto a porous hollow-fiber membrane. The amounts of impregnated extractants are shown in Figure 4 as a function of the molar conversion of the epoxy group into the octadodecylamino group.

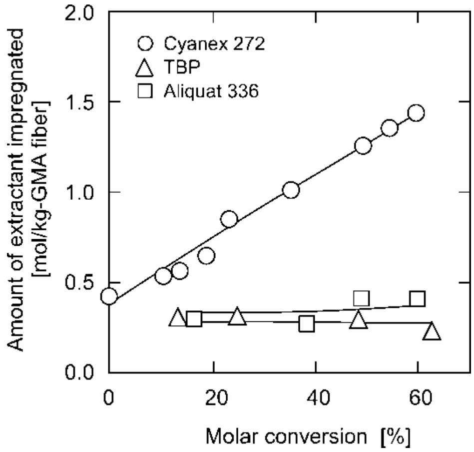


Figure 4. Amount of impregnated extractant as a function of the molar conversion of the epoxy group into an octadecylamino group.

The amount of impregnated Cyanex 272 increased linearly as the molar conversion increased. An amount of impregnated Cyanex 272 of 1.4 mol per kg of GMA fiber was attained at a molar conversion of 59%, whereas the amounts of impregnated TBP and Aliquat 336 were constant irrespective of the molar conversion. The positively charged group of the polymer brush having the opposite charge to the extractant was found to be suitable for the impregnation of the extractant up to a feasible level.

The swelling ratio defined by Eq. (4) is shown in Figure 5 as a function of the molar conversion. A similar dependence of swelling ratio as a function of the amount of impregnated extractant on the molar conversion was

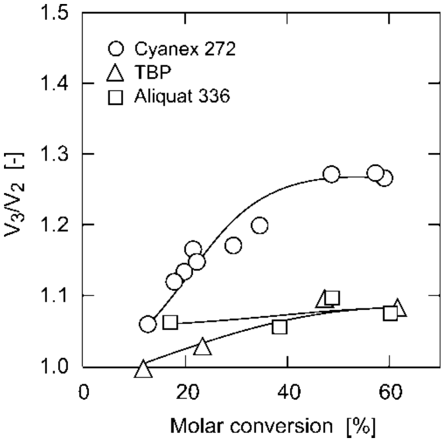
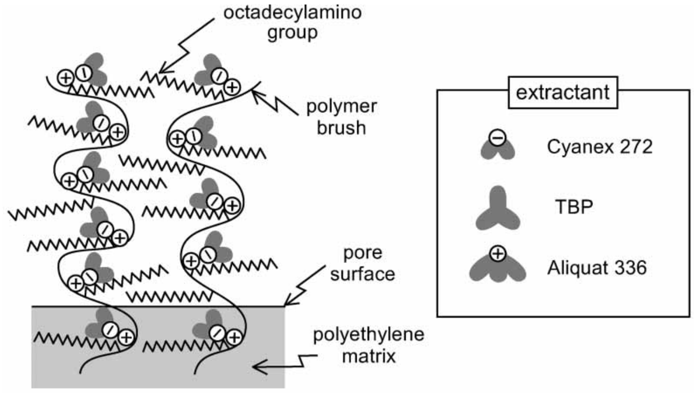


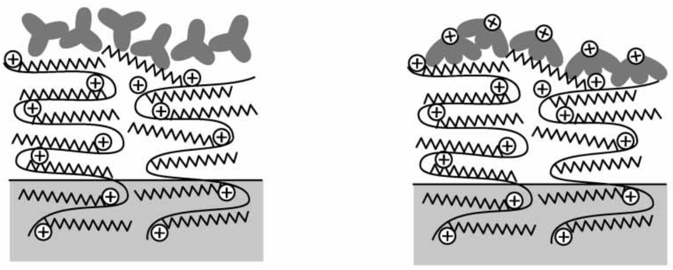
Figure 5. Swelling ratio of the Cyanex 272 fiber.

observed: the swelling ratio of the Cyanex 272 fiber to the $C_{18}NH$ fiber increased as the molar conversion increased, whereas the swelling ratios of the TBP and Aliquat 336 fibers to the $C_{18}NH$ fiber increased slightly as the molar conversion increased.

The amino part of the octadecylamino group introduced into the polymer brush attracts the phosphinic acid moiety of Cyanex 272 electrostatically. Because the positively charged or octadecylamino-group-containing polymer brush is appended both onto the pore surface and into the polymer matrix, the impregnation of Cyanex 272 to the charged polymer brush allows the entire volume of the porous membrane to swell, as illustrated in Fig. 6 (a), whereas neither neutral TBP nor basic Aliquat 336 can invade the positively charged polymer brush grafted onto the pore surface and embedded in the polymer matrix. The TBP and Aliquat 336 exclusively



(a) Cyanex 272 (acidic extractant)



(b) TBP (neutral extractant) (c) Aliquat 336 (basic extractant)

Figure 6. Possible structures of impregnated extractants.

adsorb onto the upper part of the charged polymer brush, as illustrated in Figs. 6 (b) and (c), respectively. Constant amounts of impregnated TBP and Aliquat 336 demonstrate that the impregnation of TBP and Aliquat 336 is ascribed to the hydrophobic interaction between the octadecyl part of the polymer brush and the hydrophobic moieties of TBP and Aliquat 336.

Liquid Permeability of Extractant-Impregnated Porous Membrane

The pure water flux (PWF) of Cyanex 272 fiber is shown in Fig. 7 as a function of the molar conversion. The PWF increased as an the molar conversion increased. In this figure, the pore radius ratio of the Cyanex 272 fiber to the starting porous hollow-fiber membrane is also inserted. Here, the pore radius ratio was evaluated using Eq. (8) in an analysis based on the Hagen-Poiseuille equation based on the assumption that the pore structure consists of a set of uniform, straight pores throughout the membrane. In Eq. (8), F, L and D_T denoted PWF, effective length and thickness of a porous hollow-fiber membrane. The pore radius ratio increased as molar conversion increased.

$$r_3/r_1(-) = [(F_3/F_1)(di_3L_3/di_1L_1)(D_{T,3}/D_{T,1})]^{1/4} \tag{8}$$

SEM images of the cross sections of the C_{18}NH and Cyanex 272 fibers are shown in Figs. 8 (a) and (b), respectively. The porous structure of the membrane remained sponge-like after the impregnation of Cyanex 272. The increase in the pore size accompanied by the impregnation of Cyanex 272 observed by SEM agreed with the results of the pore radius ratio.

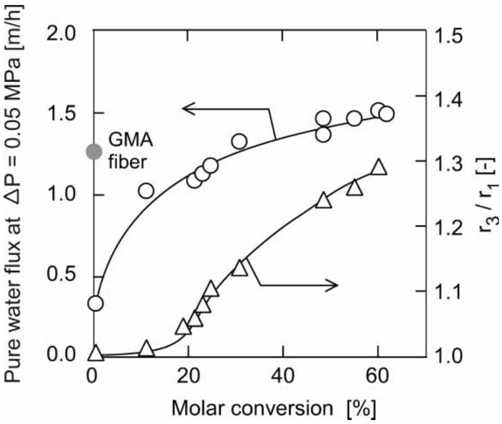
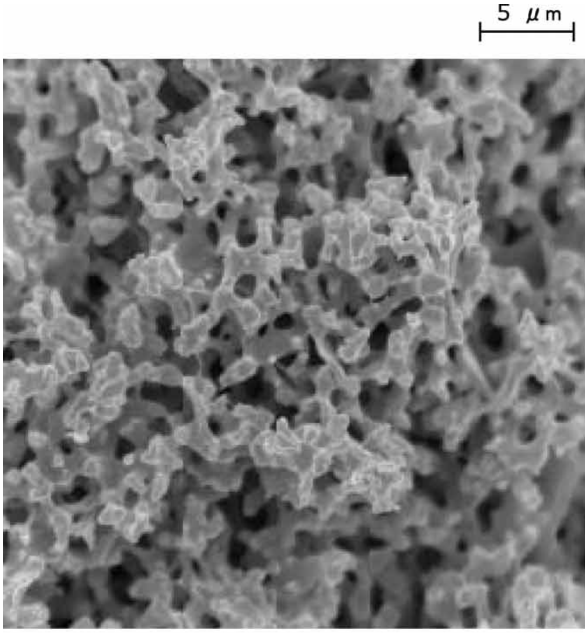
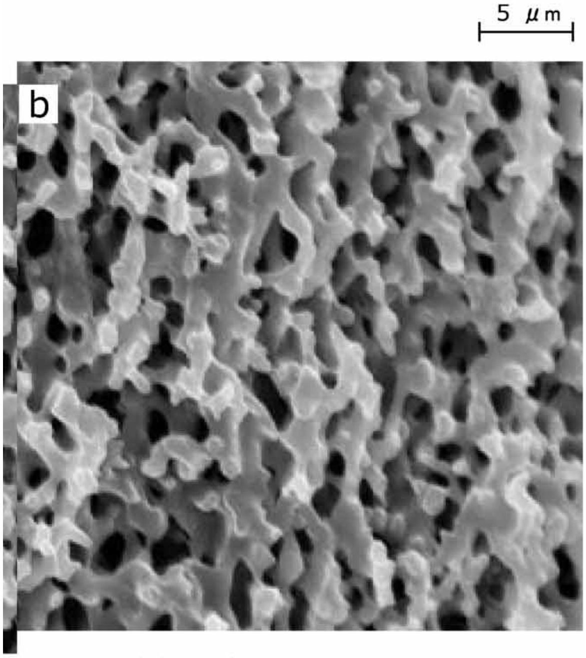


Figure 7. Pure water flux of the Cyanex 272 fiber and the pore radius ratio r_3/r_1 as a function of molar conversion.



(a) the C_{18}NH fiber



(b) the Cyanex 272 fiber

Figure 8. Scanning electron microscopy of a cross-section of the porous membrane.

As a result, an acidic extractant Cyanex 272 was impregnated on the octadecylamino group of the polymer brush grafted onto the porous hollow-fiber membrane mainly by electrostatic interaction. The swelling induced by the impregnation of Cyanex 272 to the charged polymer brush embedded in the polymer matrix compensated for the pore volume reduction caused by the polymer brush extending from the pore surface toward the pore interior and improved the PWF of the Cyanex 272 fiber.

Binding of Zinc Ion to Impregnated Extractant

A zinc solution was forced to permeate through the pores of the Cyanex 272 fiber at a constant rate. The properties of the Cyanex 272 fiber used for zinc ion capture are shown in Table 1. Zinc ion was captured by the extractant impregnated on the charged polymer brush grafted onto the porous hollow-fiber membrane. A breakthrough curve of the Cyanex 272 fiber is shown in Fig. 9. In this figure, the ordinate is the zinc ion concentration of the effluent relative to the feed, while the abscissa is the dimensionless effluent volume defined by dividing the effluent volume by the membrane volume excluding the lumen of the hollow fiber. The equilibrium binding capacity of the Cyanex 272 fiber for zinc ion, defined by Eq. (6), was calculated as 0.61 mol of zinc ion per kg of the GMA fiber; the binding efficiency of zinc ion to impregnated Cyanex 272, defined as follows, was 93%.

$$\text{Binding efficiency (\%)} = 100\ (\text{number of moles of bound zinc})/ [(\text{number of moles of impregnated Cyanex 272})/2] \quad (9)$$

The zinc ion bound to impregnated Cyanex 272 was quantitatively eluted with 1M HCl in a permeation mode. No leakage of Cyanex 272 during the adsorption and elution procedures was directly observed. As a result, a high binding efficiency and absence of leakage indicate that the phosphinic acid moiety of Cyanex 272 departs from the amino moiety of the octadecylamino group introduced into the polymer brush to contribute to the binding of zinc

Table 1. Properties of the Cyanex 272 fiber

Outer diameter	4.7 mm
Inner diameter	2.7 mm
Pure water flux	1.4 M/H[a]
Amount of impregnated Cyanex 272	1.3 mol/kg-GMA fiber
Equilibrium binding capacity	0.61 mol-Zn/kg-GMA fiber
Binding efficiency of Zn ion[b]	93%

[a] $\Delta P = 0.05$ MPa, Temp. 297 K.
[b] defined by Eq. (9).

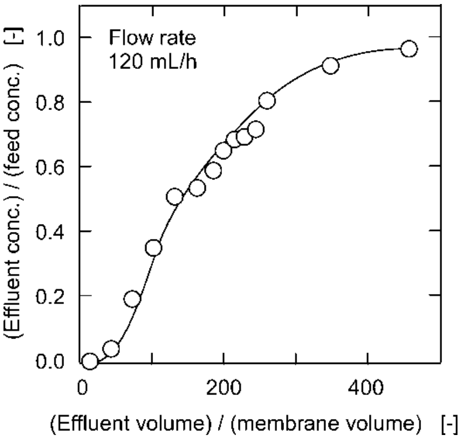
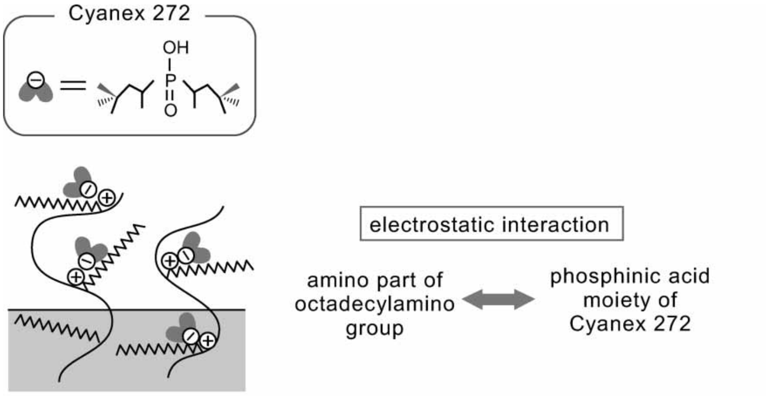


Figure 9. Breakthrough curve of the Cyanex 272 fiber for zinc ion.

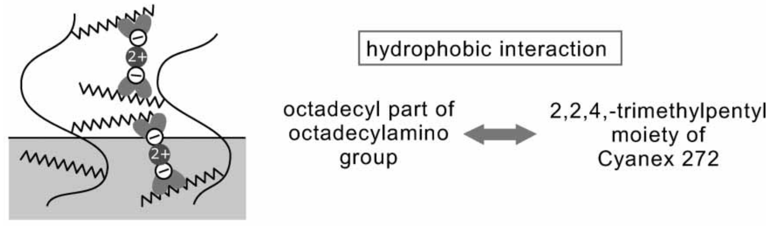
ion and that the 2,4,4,-trimethylpentyl moiety of Cyanex 272 associates with the octadecyl moiety of the octadecylamino group mainly due to the hydrophobic interaction. In other words, ethanol used in the impregnation of Cyanex 272 sustains the elctrostatic interaction between the amino part of octadecyamino group and the phosphinic acid moiety of Cyanex 272 (Fig. 10 (a)), whereas the zinc solution used to collect zinc ion enhances the hydrophobic interaction between the octadecyl part of octadecyamino group and the bis(2,4,4,-trimethylpentyl) moiety of Cyanex 272 (Fig. 10 (b)). Repositioning of Cyanex 272 on the polymer brush containing the octadecylamino group favors the impregnation of Cyanex 272 and the collection of zinc ion.

CONCLUSIONS

Elucidation of the interactions among extractants, charged polymer brush, and metal ion is essential to design extractant-impregnated materials. An organophosphinic extractant Cyanex 272, representative of acidic extractants, was impregnated on the octadecylamino group of a polymer brush grafted onto the porous membrane of a hollow-fiber form. Cyanex 272 was impregnated on the octadecylamino group mainly based on the electrostatic attraction between the phosphinic acid moiety of Cyanex 272 and the amino group of the octadecylamino group, because the amount of impregnated Cyanex 272 increased as the density of the octadecylamino groups increased. In contrast, the amounts of impregnated TBP and Aliquat 336 were constant irrespective of the molar conversion. Impregnation of Cyanex 272 on the octadecylamino-group-containing polymer brush induced swelling of the porous membrane, compensating for the pore volume reduction in the



(a) in Cyanex 272/ethanol solution



(b) in zinc solution

Figure 10. Repositioning of Cyanex 272 on the charged polymer brush.

porous membrane. The phosphinic acid moiety of Cyanex 272 departs from the amino group of the octadecylamino group and contributes to capturing the zinc ions. Each charged group of Cyanex 272 and polymer brush attracts in the Cyanex 272/ethanol solution, whereas each hydrophobic part of Cyanex 272 and polymer brush attracts in the zinc solution. By applying the fact that extractants are impregnated via the interactions between extractants and functional groups of the polymer brush, novel designs for neutral and basic extractants will be discussed on the future publications.

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