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Preparation of Aliquat 336-impregnated porous membrane

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Abstract

Aliquat 336, tri-*n*-octylmethylammonium chloride, was impregnated into the polymer chain grafted onto a porous hollow-fiber membrane. 6-Aminohexanoic acid and octadecylamine were introduced into the epoxy group of the graft chain. The amount of impregnated Aliquat 336 was 1.2 mol/kg of the GMA-grafted porous hollow-fiber membrane. The coexistence of 6-aminohexanoic acid and octadecylamino groups enabled the high-density and stable impregnation of Aliquat 336 to the graft chain. Palladium chloride (100 mg-Pd/L) dissolved in 1 M hydrochloric acid was forced to permeate through the pores of the Aliquat 336-impregnated porous hollow-fiber membrane. The binding efficiency, defined as the ratio of number of moles of palladium adsorbed to half the number of moles of impregnated Aliquat 336, was found to be 69%.

Keywords: Extractant; Aliquat 336; Impregnation; Porous hollow-fiber membrane; 6-Aminohexanoic acid group; Octadecylamino group

1. Introduction

The analysis of radioactive species in radioactive wastes is essential to the safe and economical disposal of such wastes. Among radioactive species, actinides such as uranium and plutonium should be purified prior to various radiometric determinations. Solid samples containing actinides are dissolved in strong mineral acids. Actinide elements can be purified using anion exchangers because they exist as complex anions in a strongly acidic medium such as concentrated hydrochloric and nitric acids.

Horwitz and co-workers suggested extraction chromatography using the resin beads into which extractants designated for liquid–liquid extraction were impregnated [1–3]. The extractants are classified into three categories: acidic, neutral, and basic extractants; respective representatives are HDEHP (bis(2-ethylhexyl)phosphate), TBP (tri-*n*-butyl phosphate), and Aliquat 336(tri-*n*-octylmethylammonium chloride). For example, the Aliquat 336-impregnated resin is capable of efficiently collecting plutonium and neptunium in concentrated hydrochloric and nitric acids [3]; therefore, the resin is applicable to the separation of various actinides in radioactive wastes and environmental samples. However, a bed charged with extractant-impregnated beads has a disadvantage in that it takes a long time for metal ions to diffuse into the interior of the beads. This lowers the degree of recovery and preconcentration.

To overcome the disadvantage of the separation technique using the bead-charged bed, we have proposed functional porous hollow-fiber membranes that achieve a high-rate collection of molecules or ions during the permeation of the target molecule/ion-containing solution through the pores of the functional porous hollow-fiber membranes [4,5]. The high collection rate is explained by the negligible diffusional mass-transfer resistance of the molecule/ion to the functional groups, aided by convective flow through the pores. Functional groups include anion or cation exchange groups [6,7], chelate-forming groups [8,9], hydrophobic ligands [10], and affinity ligands [11]. The functional groups were introduced into the polymer chain grafted onto the pore surface of a flat-sheet [12] or hollow-fiber form [4–11].

Domon et al. [13] prepared an HDEHP-impregnated porous hollow-fiber membrane and demonstrated high-speed separation of yttrium ion. In addition, Asai et al. [14] experimentally verified high stability for repeated adsorption-elution cycles of the HDEHP-impregnated porous hollow-fiber membrane.

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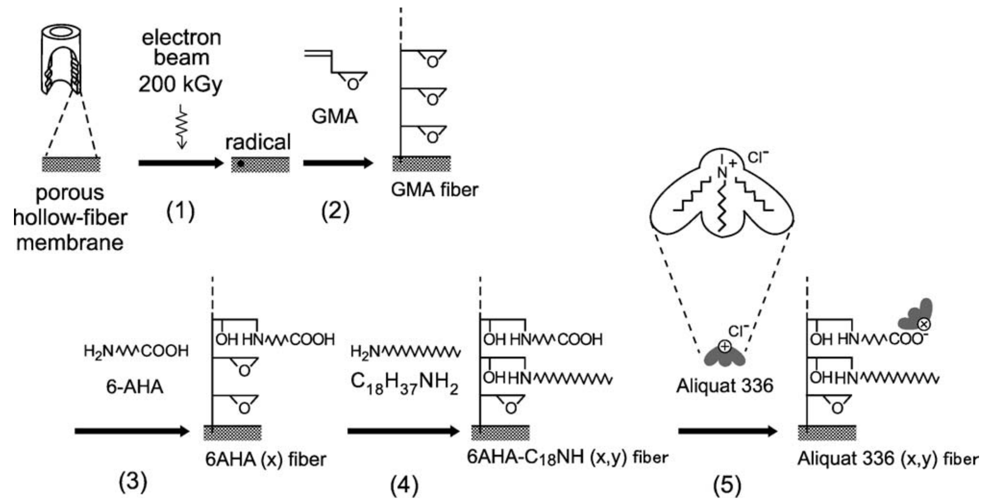

Fig. 1. Scheme for impregnation of Aliquat 336 into the polymer chain grafted onto a porous hollow-fiber membrane.

Aliquat 336-impregnated porous hollow-fiber membranes are useful for the high-performance analysis of actinide elements dissolved in acidic media. The objective of this study was twofold: to impregnate Aliquat 336 into a porous membrane of the hollow-fiber form and to demonstrate the collection of anions during the permeation of a solution across an Aliquat 336-impregnated porous hollow-fiber membrane. In this study, $PdCl_4{}^{2-}$ was used as a model complex anion, which has a high affinity for Aliquat 336 [15]. In addition, this anion can be conveniently used in experiments in a non-radiation-controlled area because it is not radioactive.

2. Experimental

2.1. Materials

A porous hollow-fiber membrane was used as the trunk polymer for grafting. This membrane made of high-density polyethylene had inner and outer diameters of 1.8 and 3.1 mm, respectively, with an average pore diameter of 0.4 μm and a porosity of 70%. An epoxy-group-containing monomer, glycidyl methacrylate (GMA, $CH_2=CCH_3COOCH_2CHOCH_2$), was purchased from Tokyo Kasei Co. and used without further purification. 6-Aminohexanoic acid (6-AHA, $NH_2C_5H_{10}COOH$) and octadecylamine ($C_{18}H_{37}NH_2$) were obtained from Nakalai Tesque Co. and Wako Pure Chemical Industries, respectively. Aliquat 336 with a purity of 100% was purchased from Avocado Research Chemicals Ltd., and used. The palladium solution ($PdCl_2$ in 1 M HCl) was acquired from Nacalai Tesque Inc. Other chemicals were of analytical grade or higher.

2.2. Impregnation of Aliquat 336 into graft chain

The impregnation scheme for Aliquat 336 into the porous hollow-fiber membrane is shown in Fig. 1. This scheme consists of five steps: (1) irradiation with an electron beam. The polyethylene porous hollow-fiber membrane (PE fiber) was irradiated with an electron beam to produce radicals onto the PE fiber [16]; (2) graft polymerization of GMA. The poly-GMA chain was grafted onto the PE fiber uniformly across the membrane thickness; (3) introduction of the 6AHA group into the graft chain. Some of the epoxy groups of the poly-GMA chain were

Table 1
Preparation conditions for Aliquat 336 fiber

Grafting of glycidyl methacrylate (GMA)	
GMA concentration (vol.%)	10
Solvent	Methanol
Reaction temperature	313 K
Introduction of 6-aminohexanoic acid (6AHA) group	
6AHA concentration (vol.%)	6AHA/water/dioxane = 5/45/50 (w/w/w)
pH	13 (adjusted with 0.4 M NaOH)
Reaction temperature	353 K
Introduction of octadecylamino (C_{18}NH) group	
C_{18}NH concentration (vol.%)	100
Reaction temperature	353 K
Impregnation of tri-*n*-octylmethylammonium chloride (Aliquat 336)	
Aliquat 336 concentration (wt.%)	10
Solvent	Ethanol/water = 2/1 (v/v)
Reaction temperature	Ambient temperature