Lanthanoid Element Recognition on Surface-Imprinted Polymers Containing Diolelyphosphoric Acid as a Functional Host

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Surface-imprinted polymers have been newly developed for the separation of lanthanoid elements: *i.e.* La(III), Ce(III), and Dy(III). The imprinted polymers were prepared by surface template polymerization with diolelyphosphoric acid, which exhibits a high affinity to lanthanoids, as a functional host molecule. Separation behavior of La(III), Ce(III) and Dy(III) was investigated with the imprinted polymers, and the imprinting effect of the polymers was evaluated in comparison with that of the unimprinted polymers and also with a conventional solvent extraction method for the same lanthanoid ions. The results indicate that the increase of selectivity for Dy(III) compared to the rest of the ions by the surface-imprinted polymers originated from a synergistic effect of both the affinity with the functional host molecule in nature and the size exclusion by the cavity formed on the polymer surface.

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Introduction

An efficient separation process for lanthanoid elements has been actively studied for the production of novel advanced materials for various electronic, optical, and magnetic devices. Conventional solvent extraction is well-known as an effective method for the separation and concentration of lanthanoid elements on an industrial scale. However, the extraction process requires a large number of stages for a series of mixer-settlers to obtain high-purity products, because these elements behave almost identically due to the similarity of the chemical and physical properties among the lanthanoids. Liquid surfactant membranes have been investigated as an advanced solvent-extraction method for separating and concentrating lanthanoids to a high degree.^{1,2} Meanwhile, a column-separation process using an appropriate stationary phase has a great advantage of high concentration efficiency and simplicity with respect to the equipment and operation. For purifying lanthanoid elements, the separation processes have been widely carried out with the combination of a cation exchanger as a stationary phase and a solution containing a chelating reagent as a selective mobile phase. However, when highly selective materials are available as the stationary phase in the column system, diluted mineral acids can be used as eluents in place of expensive chelating reagents.

Molecular imprinting is a technique used for preparing polymeric materials that are capable of high molecular recognition.³⁻⁶ This method usually involves the cross-linking of functional monomers in the presence of template organic molecules or ions by radical polymerization, followed by removal of the target molecules. The imprinted polymers selectively rebind with the template molecules or ions in a mixture of chemical species. The great advantage of this self-assembly approach to form specific recognition sites stems from its generality and relative simplicity. Molecular imprinting has now been successfully applied to create recognition sites in synthetic polymers for a variety of molecules: *e.g.*, nucleotide bases,^{7,8} steroid hormones,⁹ and dipeptide derivatives.¹⁰⁻¹²

We have developed a novel molecular imprinting technique, called "surface template polymerization" (Fig. 1). The method allows one to overcome the following fundamental drawbacks of conventional imprinted polymers that stem from the formation of recognition sites within the hydrophobic polymer matrix: *i.e.* (1) rebinding kinetics is very slow; (2) it is difficult to handle water-soluble templates, such as metal ions and biological components like proteins. Surface-imprinted polymers are prepared by emulsion polymerization utilizing a functional host molecule, an emulsion stabilizer, a polymer matrix-forming monomer, and a print molecule. A functional host molecule, which is amphiphilic in nature, forms a complex with a print molecule at the interface of emulsions, and thus-formed complex remains at the reaction surface. After the matrix is polymerized, the coordination structure is eventually "imprinted" on the polymer surface. We succeeded to prepare

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Fig. 1 Schematic illustration of surface template polymerization with W/O emulsions.

surface-imprinted polymers for transition-metal ions,^{13–15} lanthanoid elements,¹⁶ amino acid derivatives,¹⁷ nucleotides,¹⁸ and artificial enzyme.^{19,20} The zinc-ion surface-imprinted microspheres presented an advantage for column separation between zinc and copper ions, compared to the conventional chelating resin.²¹ Furthermore, we clarified that the requirements for designing functional hosts are a strong binding ability with a target molecule and high interfacial activity.^{13–15} We also showed that another important criteria is the rigidity of the polymer matrix to strictly immobilize the functional host molecules on the polymer surface,¹³ and investigated the essential factors that affect the characteristics of the polymer matrix in detail. Consequently, an appropriate choice of the preparation conditions, such as a buffer solution, has made it possible to show the imprinting effect with dioleoyl phosphoric acid without γ -ray irradiation.²²

In the present study, we prepared surface-imprinted polymers for La(III), Ce(III) and Dy(III) with dioleoylphosphoric acid as a functional host molecule, which has an effective functional group in lanthanoid separation. Separations of La(III), Ce(III) and Dy(III) with imprinted polymers were performed, and the imprinting effect of the polymer was evaluated in comparison with an unimprinted polymer, and also with a conventional solvent-extraction method for the same metal ions. We also discuss the recognition mechanism of lanthanoid(III)-imprinted polymers.

DOLPA

2C₁₈Δ⁹GE

Fig. 2 Structures of dioleoylphosphoric acid (DOLPA) and L-glutamic acid dioleylester ribitol (2C₁₈Δ⁹GE).

Experimental

Materials

The syntheses of dioleoylphosphoric acid (DOLPA) and L-glutamic acid dioleylester ribitol (2C₁₈Δ⁹GE) were reported previously.^{23,24} Divinylbenzene (DVB, Wako Pure Chemical Industries, Ltd.) was used after a treatment with silica gel to remove the inhibitor. Other reagents were of reagent grade. The structures of the functional host and the surfactant are shown in Fig. 2. Since 2C₁₈Δ⁹GE is easily dissolved in the organic phase, and its interfacial activity is very high, the surfactant is a suitable emulsion stabilizer for surface template polymerization.

Preparation of lanthanoid(III)-imprinted polymer

DOLPA (2.9 g, 4.8 mmol) and 2C₁₈Δ⁹GE (0.15 g, 0.18 mmol) were dissolved in a 60 mL toluene-DVB (1:2, v/v) solution. An aqueous solution (30 mL) of 0.010 M lanthanoid(III), whose pH was adjusted with hydrochloric acid, was added. The mixture was sonicated for 3 min to give a water-in-oil (W/O) emulsion. After the addition of 0.36 g (1.4 mmol) of 2,2'-azobis(2,4-dimethylvaleronitrile) and 36.56 g (28 mmol) of DVB, emulsion polymerization was carried out at 55°C for 2 h under a flow of nitrogen. The bulk polymer was dried *in vacuo* and ground into particles, which were washed with 4.0 M nitric acid to remove the lanthanoid(III), and filtered off. This procedure was repeated until the lanthanoid(III) concentration in the filtrate could not be detected. The lanthanoid(III)-imprinted polymer was dried *in vacuo*. A reference polymer was prepared similarly, but in the absence of lanthanoid(III). The swelling percentage of the polymers was determined by a volumetric measurement.²⁵ Toluene was employed as a swelling solvent.

Solvent extraction of La(III), Ce(III) and Dy(III) by DOLPA

The organic solution was of 10 mM DOLPA in toluene. The aqueous solution was a mixture of 0.10 mM lanthanoid(III) chlorides (LaCl₃, CeCl₃, DyCl₃). Its pH was adjusted to a desired value of between 1 and 5 with hydrochloric acid. A mixture of 10 mL each of the organic and aqueous solutions was shaken in a thermostatted water bath at 303 K for 24 h. After phase separation, the equilibrium concentration of lanthanoid(III) in the aqueous phase was determined by ICP atomic emission spectroscopy (Shimadzu, ICPS-5000).

Table 1 Swelling ratio of polymers in toluene

Polymer	Swelling ratio, %
Unimprinted polymer for La(III) and Ce(III)	15
Unimprinted polymer for Dy(III)	26
La(III)-imprinted polymer	17
Ce(III)-imprinted polymer	22
Dy(III)-imprinted polymer	19

Adsorption of lanthanoid(III) on surface-imprinted polymers

The equilibrium adsorption of lanthanoid(III) by the imprinted polymers was determined batchwise. To the polymer (0.1 g) was added 5.0 mL of a 0.10 mM lanthanoid(III) chloride solution. The pH was adjusted to the desired value between 1 and 5 with hydrochloric acid. The mixture was shaken in a thermostatted water bath at 30°C for 24 h. The obtained polymers were filtered with a cellulose nitrate membrane (DISMIC-25, Toyo Roshi Kaisha, Ltd.). The amounts of lanthanoids(III) adsorbed on the polymers were calculated from the decrease in the lanthanoid(III) concentration in the material source, as measured by ICP atomic emission spectrophotometry.

Results and Discussion

Optimum pH condition in the aqueous phase

The pH condition in the aqueous phase is one of the dominant factors when preparing highly selective metal ion-imprinted polymers successfully. At a lower pH (< 1.0), recognition sites on the imprinted polymers were not created, due to poor interaction between the functional host molecules and the template lanthanoid ions. At a higher pH, the selectivity of the imprinted polymers decreased due to an increase of the random distributed functional host molecules. Since the optimum pH condition is dependent on the stability of the metal ion-functional host complex, we used the solvent-extraction behavior as the criterion for the desirable pH value during polymerization. The extractability also indicates the degree of interaction between lanthanoid(III) and DOLPA under the minimum geometric constraint. Figure 3 shows the solvent-extraction behavior of La(III), Ce(III) and Dy(III) with DOLPA. Dy(III) was extracted more than La(III) and Ce(III); the extraction behavior of La(III) was similar to that of Ce(III). The pH during polymerization was adjusted to the value at 90% extraction in a similar way for Zn(II)-imprinted polymers, *i.e.* 1.5 for Dy(III); 2.3 for La(III) and Ce(III).

Rigidity of the polymer matrix

The rigidity of the polymer matrix is also important to firmly immobilize the functional hosts. We evaluated the rigidity by utilizing the swelling ratio of the soaked polymer in toluene. Based on the results of Zn(II)-imprinted polymers,¹⁵ the minimum requirement to obtain a high template effect is that the swelling ratio of the imprinted polymer is below 30%. The swelling ratios of lanthanoid(III)-imprinted polymers are summarized in Table 1. All swelling ratios of imprinted and unimprinted polymers are below 30%, while the ratio of Zn(II)-imprinted polymers with DOLPA is much higher than that of unimprinted polymers.¹³ Therefore, the matrix of the lanthanoid(III)-imprinted polymers possesses an appropriate rigidity to strictly fix the functional host molecules. This is due to much fewer inhibitors, such as sodium ions in the buffer

Fig. 3 Solvent-extraction behavior of La(III), Ce(III), and Dy(III) with DOLPA.

Fig. 4 Adsorption behavior of La(III), Ce(III), and Dy(III) with unimprinted polymers using DOLPA.

solution for surface template polymerization.²²

Separation of lanthanoid(III) with surface-imprinted polymers

Most organophosphate-lanthanoid(III) complexes have a nonacoordination structure, *i.e.* tricapped trigonal prism coordination in a series of lanthanoids(III).²⁶ Thus, size recognition is required to prepare surface-templated polymers for accomplishing an effective separation of lanthanoid elements.

Figure 4 shows the adsorption behavior of La(III), Ce(III) and Dy(III) with unimprinted polymers under different pH conditions. The pH values during polymerization were 1.5 for Dy(III) and 2.3 for La(III) and Ce(III). No difference between unimprinted polymers prepared at pH 1.5 and 2.3 was observed. Since the pH value during polymerization does not affect the adsorption ability of unimprinted polymers, the functional host distribution was almost the same in both unimprinted polymers within this pH range. The selectivity of unimprinted polymers was similar to that of solvent extraction with DOLPA. This poor selectivity is due to the random distribution of functional hosts on the polymer surface.

Figure 5 exhibits the pH dependence of the adsorption of La(III), Ce(III) and Dy(III) on the Dy(III)-imprinted polymer. The percent adsorption was enhanced with increasing the pH for all lanthanoid(III) ions. This result suggests that the adsorption behavior proceeds through an ion-exchange mechanism. The

Fig. 5 Adsorption behavior of La(III), Ce(III), and Dy(III) with Dy(III)-imprinted polymers using DOLPA.

Fig. 7 Adsorption behavior of La(III), Ce(III), and Dy(III) with Ce(III)-imprinted polymers using DOLPA.

Fig. 6 Adsorption behavior of La(III), Ce(III), and Dy(III) with La(III)-imprinted polymers using DOLPA.

imprinted polymer, however, adsorbed Dy(III) much more effectively than Ce(III) and La(III) over the entire pH range. In the case of adsorption by the unimprinted polymer, prominent selectivity for Dy(III) was not observed compared to that by the imprinted polymer (Fig. 4). The ionic radii of Dy(III), Ce(III) and La(III) in nonacoordinate are 1.083, 1.196 and 1.216 Å, respectively;²⁷ the selectivity for Dy(III) is controlled by the size of the cavity that functional host molecules have created on the surface of the polymers. On the other hand, no imprint effect was observed in an adsorption test using the La(III)-imprinted polymer (Fig. 6). This indicates that Ce(III) and Dy(III) can invade into the La(III)-fitted cavity and adhere to the recognition sites, because their ionic radii are smaller and their affinity with the functional host molecules in nature is higher than that of La(III). The imprinted polymer for Ce(III), whose ion radius is intermediate between La(III) and Dy(III), showed an intermediate selectivity among three metal ions; *i.e.* Dy(III) was still significantly adsorbed, while the adsorption of La(III) decreased on the Ce(III)-imprinted polymers (Fig. 7). This result also supports the effect of ion size exclusion. When the smallest ion Dy(III) was imprinted on the polymer surface, La(III) and Ce(III), which have a larger ionic size than Dy(III), cannot invade the cavity due to the size-exclusion effect. Therefore, the Dy(III)-imprinted polymer showed the highest template effect in the lanthanoid separation test. Based on the results, the improvement of selectivity for lanthanoid(III) by

surface-imprinted polymers originates from a synergistic effect of the affinity with a functional host molecule in nature, and the size exclusion by the cavity formed on the polymer surface.

Conclusions

We have developed lanthanoid ion-imprinted polymers by surface template polymerization for the separation of lanthanoid elements, *i.e.* La(III), Ce(III), and Dy(III). A Dy(III)-imprinted polymer was shown to exhibit a tremendously high selectivity towards Dy(III) ions over La(III) and Ce(III) ions. We found that there are two important factors to obtain high selectivity and an imprint effect towards a target lanthanoid: a high affinity to the target ion and a size-exclusion effect, which stems from imprinted sites formed by functional molecules. A high selectivity was observed by an imprinted polymer in which the above two factors were satisfied for the preparation.

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