NOVEL METAL ION-IMPRINTED RESINS PREPARED BY SURFACE TEMPLATE POLYMERIZATION WITH W/O EMULSION

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Introduction

In recent years, rare earth metals have been noted as resources in the field of the electronic or magnetic products. Therefore, the development of new materials for highly selective separation of rare earth metals has been strongly demanded. The molecular imprinting technique^{1, 2, 3)} is a promising way to prepare metal ion-selective resin. This method is practical because the metal ion-binding function is easily introduced in the resin.

Recently, we proposed a novel molecular imprinting technique for a metal ion-selective resin ("surface template polymerization")⁴⁾. A surface-templated resin is prepared by an emulsion polymerization using a metal ion-binding (host) monomer, a resin matrix-forming comonomer and a target (guest) metal ion. A host monomer which has amphiphilic nature forms a complex with a metal ion at the interface of an emulsion, and the complex remains as it is. After the matrix is polymerized, the coordination structure is "imprinted" at the resin interface.

The goals of our study are (1) to prepare a metal ion-imprinted resin with W/O emulsion for rare earth metals, and (2) to select a suitable metal ion-binding monomer for each metal. In this study as a preliminary part, a heavy metal ion was adopted as a target metal, and dioleoyl phosphoric acid and di(2-ethylhexyl) phosphoric acid were selected as the metal ion-binding monomers. Adsorption of metal ion onto the imprinted resin was examined and the imprinting effect was characterized.

1. Experimental

1.1 Reagent

Dioleoyl phosphoric acid (abbreviated as DOLPA) and 1-glutamic acid dioleylester ribitol (abbreviated as 2C₁₈Δ⁹GE) were synthesized according to the procedure described in our previous work^{5, 6)}. Reagent-grade di(2-

ethylhexyl) phosphoric acid (abbreviated as D2EHPA, Tokyo Chemical Industry Co., Ltd.) was used without further purification. **Figure 1** indicates the structures of DOLPA and D2EHPA. Divinylbenzene (abbreviated as DVB, Wako Pure Chemical Industries, Ltd.) was used after treatment with silica gel to remove an inhibitor. Other reagents were of commercially available grades.

1.2 Resin preparation

Metal ion-imprinted resin was prepared according to **Fig. 2**. First stage: A 40 cm³ solution of DVB, in which 2.9 g of DOLPA (or 1.55 g of D2EHPA) and 0.25 g of 2C₁₈Δ⁹GE were dissolved, was mixed with 20 cm³ of toluene. A 30 cm³ aqueous solution of 10 mol/m³ Zn (CH₃COO)₂ (pH 3.5, buffered with 100 mol/m³ acetic acid-sodium acetate) was added and the mixture was sonicated for 3 min to give a W/O emulsion. Second stage: With the addition of 0.36 g of powder initiator (2,2'-azobis (2,4-dimethylvaleronitrile), Wako Pure Chemical Industries, Ltd.), the mixture was stirred at 45°C for 2 h under a nitrogen atmosphere. Third stage: After being ground, the resins were washed with 1000 mol/m³ hydrochloric acid solution to remove zinc ion and then filtered. This procedure was repeated until zinc ion in the filtrate became negligible. Finally, Zn-imprinted resins were dried in vacuo. A reference resin (unimprinted resin) was prepared similarly but without zinc ion.

1.3 Adsorption of zinc ion

The adsorption equilibrium of zinc ion onto the resins was determined in a batchwise method. A quantity of 0.1 g of resin was immersed in 5 cm³ solution of 0.1 mol/m³ Zn(CH₃COO)₂. The pH was adjusted to a desired value between 1 and 5 with 50 mol/m³ acetic acid-sodium acetate and 1000 mol/m³ nitric acid. The mixture was shaken in thermostated water at 303 K for 24 h. The resins were filtered through a cellulose nitrate membrane (DISMIC-25, Toyo Roshi Kaisha, Ltd.). The amount of zinc ion bound on the resins was calculated from the decrease in zinc ion concentration in the filtrate. Zinc ion concentration was analyzed by an atomic

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DOLPA

D2EHPA

Fig. 1 Structures of dioleoyl phosphoric acid (DOLPA) and di (2-ethylhexyl) phosphoric acid (D2EHPA)

Fig. 2 Schematic illustration of surface template polymerization with W/O emulsion

absorption spectrophotometer (SAS 760, Seiko Instruments Inc.).

2. Results and Discussion

Metal ion-imprinted resin was prepared by surface template polymerization with W/O emulsion. DVB, toluene, DOLPA (or D2EHPA) and $2\text{C}_{18}\Delta^9\text{GE}$ were used as cross-linking agent, diluent, metal ion-binding amphiphile and emulsion stabilizer, respectively. After the polymerization, the resin was ground into particles whose average diameter was ca. $10\ \mu\text{m}$ in all experiments. Zinc ion was completely removed from the resins with $1000\ \text{mol/m}^3$ hydrochloric acid. Then the resins were dried. The yield was ca. 70 %.

Figure 3 shows the pH dependence of the adsorption of zinc ion on Zn-imprinted and unimprinted resins with DOLPA. Imprinted resins adsorbed zinc ion much more effectively than did the reference resins over the entire pH range. With increasing pH the adsorption percentages increased for both resins. This indicates that DOLPA on the resins binds zinc ion in ionized phosphate forms. The comparison of a half-adsorption pH, $\text{pH}_{1/2}$, between the two resins suggests that Zn-imprinted resins have an ability of zinc ion binding more than 100 times that of unimprinted resins. These results clearly verify the effect of Zn ion imprinting; DOLPA was implanted on the Zn-imprinted resins in a structure advantageous for zinc ion-coordination (probably in the

Fig. 3 pH dependence of the adsorption of zinc ion on Zn-imprinted and unimprinted resins with DOLPA

Fig. 4 pH dependence of the adsorption of zinc ion on Zn-imprinted and unimprinted resins with D2EHPA

tetrahedral configuration), while DOLPA on unimprinted resins was randomly distributed.

Figure 4 shows the pH dependence of the adsorption of zinc ion on Zn-imprinted and unimprinted resins with D2EHPA. No differences were observed between Zn-imprinted and unimprinted resins. These results mean that D2EHPA was not reorganized desirably on the surface of W/O emulsion during contact with zinc ion. The contrast between DOLPA and D2EHPA is due to interfacial activity. The concentration of D2EHPA in the emulsion does not seem high enough to realize implantation on the resin surface.

Conclusion

Novel metal ion-imprinted resins were prepared by surface template polymerization with W/O emulsion. Zn-imprinted resins with DOLPA manifested the effect of zinc ion imprinting. A comparison between DOLPA and D2EHPA suggests that interfacial activity is a substantial key for choosing a metal ion-binding amphiphile.

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