Template-Dependent Metal Adsorptivity of Dialkyl Phosphate-Type Resins Prepared by Surface Template Polymerization Technique

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Many classes of organo-oxy phosphorus moieties form stable complexes with the so-called "hard" or "class a" metal ions including lanthanides and actinides, among which uranyl ion has been of particular importance in relation to nuclear energy. Therefore, polymeric resins carrying these groups have attracted much attention for the past three decades.^{1,2} In fact, the resins adsorbed uranyl ion quite effectively, though they have a common problem that more than two phosphate coordinating groups must be placed appropriately to form a stable complex with the metal ion; the random introduction of the groups in the resin does not create a favorable placement of resin-anchored metalophilic groups for multidentate coordination.

On the other hand, macrocyclic compounds having coordinating groups have been employed for uranyl-selective chelating agents, since the macrocyclic "template"s should allow an arrangement of the coordinating groups in the appropriate position and orientation to fit the ion spatially.³ However, synthetic procedures for such compounds are time- and labor-consuming.

Recently, we proposed a facile preparation method for a metal ion-selective resin: a surface-templated resin was prepared by an emulsion polymerization using oleic acid as a host monomer, divinylbenzene as a resin matrix-forming comonomer and Cu^{2+} ion as the target metal.⁴

Since the amphiphilic host monomer functions at the same time as a surfactant, the complexation of the metal with the host monomers is conducted at an interface between water and oil (*i.e.*, the matrix-forming comonomer). In addition, the resultant metal complex is expected to be not totally lipophilic nor hydrophilic, *i.e.*, the chemical structure around the complexed metal ion likely remains also amphiphilic. Therefore, the complexes are expected to be placed at the water-oil interface. The coordination structure is thus implanted or "imprinted" at the resin surface after the matrix-forming comonomer is polymerized to "cement" the complex entity. The template effect was demonstrated

by the highly-effective binding of the Cu^{2+} -imprinted resin to Cu^{2+} ion as compared with that of a reference (unimprinted) one. However, the ion-binding selectivity to other metals of this surface- Cu^{2+} -templated resin has not yet been clarified.

In the present study, the imprinting method was applied to the preparation of organo-phosphate-carrying resins by using dioleoyl phosphoric acid as an amphiphilic host monomer, in the presence or in the absence of Cu^{2+} or Zn^{2+} ion (Fig. 1). As a result, the Cu^{2+} -imprinted resin adsorbed Cu^{2+} ion much more effectively than did the unimprinted one, while the Zn^{2+} -imprinted one showed an adsorption ability to Cu^{2+} as small as the unimprinted. The metal ion-selective feature of the surface templated resins to the target ion was successfully, though indirectly, demonstrated for the first time. This study also indicated that the present type of imprinted resin preparation is not limited to carboxylate (oleate) but also includes phosphate coordinating groups. The results suggest that the phosphoric acid-carrying resin thus prepared with the aid of the "surface template technique" would be promising as selective adsorbents for other metal ions such as uranyl and lanthanide ions.

Experimental

Reagents and apparatus

Dioleoyl phosphoric acid (1) and L-glutamic acid dioleylester ribitol (2) were synthesized according to the literature.⁵ Divinylbenzene (DVB) purchased from Nacalai Tesque, Inc. was used after treatment with silica gel to remove an inhibitor. Pure water obtained by means of a Milli-Q Water Purification System (Nippon Millipore Ltd.) was used throughout the work. A metal-ion standard solution (Wako Pure Chemical Industries Ltd., for atomic absorption analysis) was used for atomic absorption analysis. The other reagents were of commercially available grades.

Fig. 1 Schematic illustration of surface template polymerization using dioleyl phosphoric acid as an amphiphilic host monomer, divinylbenzene as a resin-forming monomer (oil phase) and Cu^{2+} ion as a target.

Scheme 1 Structures of dioleyl phosphoric acid (1) and L-glutamic acid dioleylester ribitol (2).

A particle grading analysis was made on a Microtrac instrument, CM-type (Nikkiso). The metal-ion concentration was determined by an SAS 760 Atomic Absorption Spectrophotometer (Seiko Instruments Inc.).

Resin preparation

A 10 cm³ solution of DVB containing 0.4 mmol of 1 and 0.2 mmol of 2 was combined with 100 cm³ aqueous solution of 2 mM $\text{Cu}(\text{CH}_3\text{COO})_2$ (pH 5.6, buffered with 100 mM acetic acid–sodium acetate). Then the mixture was sonicated for 3 min to give a stable emulsion. With the addition of 0.09 g of 2,2'-azobis(2,4-dimethylvaleronitrile) (Wako Pure Chemical Industries Ltd.), the mixture was stirred at 45°C for 6 h under nitrogen atmosphere. To the mixture was added a hydrochloric acid solution (1 M), and the precipitated resin was filtered.

This resin was washed with 1 M hydrochloric acid solution in order to exchange the bound metal ion with a proton, and then filtered again. This procedure was repeated three times until Cu^{2+} ion in the filtrate became negligible, as estimated by atomic absorption. Finally, the obtained resin was dried *in vacuo*. A reference resin was synthesized similarly but without Cu^{2+} . A Zn^{2+} -imprinted resin was prepared by using $\text{Zn}(\text{CH}_3\text{COO})_2$ instead of $\text{Cu}(\text{CH}_3\text{COO})_2$. The yield of the resin was in typical cases *ca.* 50%.

Measurement

The adsorption equilibrium of Cu^{2+} ion onto the resins was examined in the following way. The resin (0.1 g) was placed in a plastic tube (10 cm³ volume), to which was added a 5 cm³ solution of $\text{Cu}(\text{CH}_3\text{COO})_2$ (0.1 mM). The pH was adjusted to a desired value between 2 and 7 with 50 mM acetic acid–sodium acetate. The mixture was shaken at 25°C for 12 h. The equilibrated mixture was centrifuged (5000 rpm, 5 min), and the supernatant solution was filtered with a cellulose nitrate membrane (Dismic 25, Toyo Roshi Kaisha, Ltd.). The filtrate was analyzed for Cu^{2+} ion by atomic absorption spectrophotometry. The adsorption percentage defined as the percentage of the amount of Cu^{2+} ion adsorbed to that initially added was calculated from the data.

Results and Discussion

The phospho-diester-carrying resins were prepared from divinylbenzene (DVB) by using dioleyl phosphoric acid (1) as a metal ion-binding amphiphile in the presence

Fig. 2 pH dependence of the adsorption of Cu^{2+} ion on the Cu^{2+} -imprinted ($\circ$), the Zn^{2+} -imprinted ($\square$) and the unimprinted (reference, $\bullet$) resins. Conditions: 0.1 g of resin and 5 cm^3 of aqueous solution of $\text{Cu}(\text{CH}_3\text{COO})_2$ (0.1 mM), at 25°C for a shaking period of 12 h.

of Cu^{2+} ion. However, with 1 alone, the mixture emulsion was not stable and became phase-separated in 30 min. Therefore, L-glutamic acid dioleylester ribitol (2) was employed as a co-surfactant; 0.2 mmol of 2 was used to stabilize an emulsion from 100 cm^3 of water containing 0.2 mmol of $\text{Cu}(\text{CH}_3\text{COO})_2$ and 10 cm^3 of DVB containing 0.4 mmol of 1. After a short sonication (3 min), the mixture kept its emulsion state for at least 12 h, which is much longer than the polymerization period (7 h).

After the polymerization, the resin was isolated and washed with 1 M hydrochloric acid solution repeatedly. We confirmed that, with the procedure, there was practically no Cu^{2+} in the resin, since the total amount of Cu^{2+} recovered in the washings was more than 97% of the amount of Cu^{2+} initially added. The particle grading analysis of the Cu^{2+} -imprinted and the unimprinted resins indicated that their volume-averaged diameters were 6.5 and 7.1 μm , respectively.

Figure 2 shows the pH dependence of the adsorption of Cu^{2+} ion on Cu^{2+} -imprinted, Zn^{2+} -imprinted and unimprinted (reference) resins. The resin prepared in the presence of Cu^{2+} was clearly shown to adsorb Cu^{2+} ion much more effectively than does the reference resin which was prepared in the absence of Cu^{2+} . The adsorption percentages increased with increasing pH on both the resins. This means that the dioleyl phosphoric acid groups on the resins play a predominant role in the metal ion binding in their ionized phosphate forms. The comparison of a half-adsorption pH ($\text{pH}_{1/2}$) for the two resins suggest that the Cu^{2+} -imprinted resin has 100-times higher ability of Cu^{2+} binding than the unimprinted one.

On the other hand, the resin prepared in the presence of Zn^{2+} did not show any characteristic binding to Cu^{2+} ion, but only a profile similar to that of the reference resin.

These results clearly verify the effect of Cu^{2+} imprinting; the dioleyl phosphoric acid groups are implanted on the Cu^{2+} -imprinted resin in such a way that they can match a desirable coordination (probably the square planar one) around the Cu^{2+} ion when they interact with the Cu^{2+} ion. On the other hand, in the reference resin, dioleyl phosphoric acid groups are randomly distributed on the resin as determined by such conditions as pH and counter ion (Na^+) concentration. Zn^{2+} imprinting may have served to place the groups appropriately for the coordination with Zn^{2+} ion (probably in the tetrahedral configuration), but such placements did not favor the accommodation of Cu^{2+} ion.

In conclusion, it was confirmed not only for oleic acid in the previous work⁴ but also for dioleyl phosphate in the present one that our surface template technique can fix coordinating groups on the surface of a resin so as to be arranged spatially for the target metal ion. As discussed previously⁴, this should endorse the rapid, reversible and unusually strong complexation with the target ion. In addition, it was clarified in the present work that this technique gives the resin metal ion-selective features for the target ion. The dialkyl phosphoric acid-carrying resin prepared with the aid of the present template technique would be promising as selective adsorbent for uranyl ion as well as for lanthanides. The experiments in this direction are now under way.

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