Template-Dependent Selectivity in Metal Adsorption on Phosphoric Diester-Carrying Resins Prepared by Surface Template Polymerization Technique

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The surface templated resins for three different metal ions such as Cu^{2+}, Zn^{2+} or Cd^{2+} as the template guest were prepared by emulsion polymerization using oleyl phenyl hydrogenphosphate as a host surfactant, sodium dodecyl sulfate (SDS) as a co-surfactant and divinylbenzene as a resin matrix-forming monomer. The Cu^{2+}-imprinted resin adsorbed Cu^{2+} much more effectively than did the nonimprinted, the Zn^{2+}- and Cd^{2+}-imprinted ones. On the other hand, the Cd^{2+}-imprinted resin showed a more highly effective binding to Cd^{2+} than those of the Cu^{2+}-imprinted, Zn^{2+}-imprinted, and nonimprinted resins. In fact, the Cu^{2+}-imprinted resin did not adsorb any significant amount of Cd^{2+}. The selective feature of the surface templated resins to the target ion was thus successfully demonstrated. The template-dependent selectivity should be ascribed to a favorable placement of the surface-anchored metallophilic groups for multidentate coordination to the specific metal ion.

Chelating resins which show selective adsorption capability for metal ions have attracted extensive attention, since they can achieve readily and efficiently the separation, recovery and purification of valuable metal ions in a variety of matrices.[1] In general, the selectivity of the resins has been governed primarily by the inherent nature of a ligand which is fixed on the resins. Polymeric resins carrying phosphoric acid moieties, for instance, show strong binding with the so-called "hard" metal ions including uranium and rare earth metals.[2] However, selectivity based on an individual ligand is rather limited. The chelating resin would become of much more practical significance if it has specific metal recognition sites which are formed cooperatively by some functional groups.

Recently, we proposed the "surface template polymerization" technique which allows an easy production of polymeric materials for molecular recognition.[3—6] This technique relies on a cooperative interaction of multiple functional groups with a target: The approach involves a preorganization of functional surfactants (amphiphilic host monomers) on oil–water emulsion surface by interacting cooperatively with the target (template guest) in aqueous phase. The organized structure involving the template and the functional surfactants is then immobilized by polymerization of the oil phase which is made from a vinyl monomer. Removal of the template results in polymeric resins which carry the functional groups spatially arranged on their surface, giving recognition sites with preferential rebinding ability for the template molecule.

The preliminary example of the surface-templated resin was prepared for metal ions by an emulsion polymerization using potassium oleate as an amphiphilic coordinating monomer, divinylbenzene as a resin matrix-forming monomer and Cu^{2+} as a target metal.[3] The template effect was demonstrated by the highly-effective binding of the Cu^{2+}-imprinted resin to Cu^{2+} as compared with that of a reference (nonimprinted) one. This novel imprinting method was extended to the preparation of organophosphate-carrying resins by using dioleyl hydrogenphosphate as an amphiphilic host, in the presence or in the absence of Cu^{2+} or Zn^{2+}.[4] As a result, the Cu^{2+}-imprinted resin adsorbed Cu^{2+} 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 nonimprinted one, indicating the dependence of selectivity on the template. However, the metal ion-selective feature of the surface templated resins with respect to the targeted metal and the un-targeted metals has not been clearly demonstrated.

In the present paper, we prepared surface templated resins for three different metal ions including Cu^{2+}, Zn^{2+}, and Cd^{2+} as the template guest (Fig. 1). A host surfactant employed here was oleyl phenyl hydrogenphosphate (**1**) (Fig. 2), while sodium dodecyl sulfate (SDS) was used as a co-surfactant so as to stabilize the emulsion during the template polymerization. As a result, imprinted resin, which had been prepared in the presence of Cu^{2+}, adsorbed Cu^{2+} much more effectively than did the nonimprinted one. We also found that the Cd^{2+}-imprinted resin showed a more highly effective binding to Cd^{2+} than the nonimprinted resin. However, the Cu^{2+}-imprinted resin did not adsorb any significant amount of Cd^{2+}, and vice versa. These results clearly demonstrate the selective feature of the surface templated resins to the target ion as

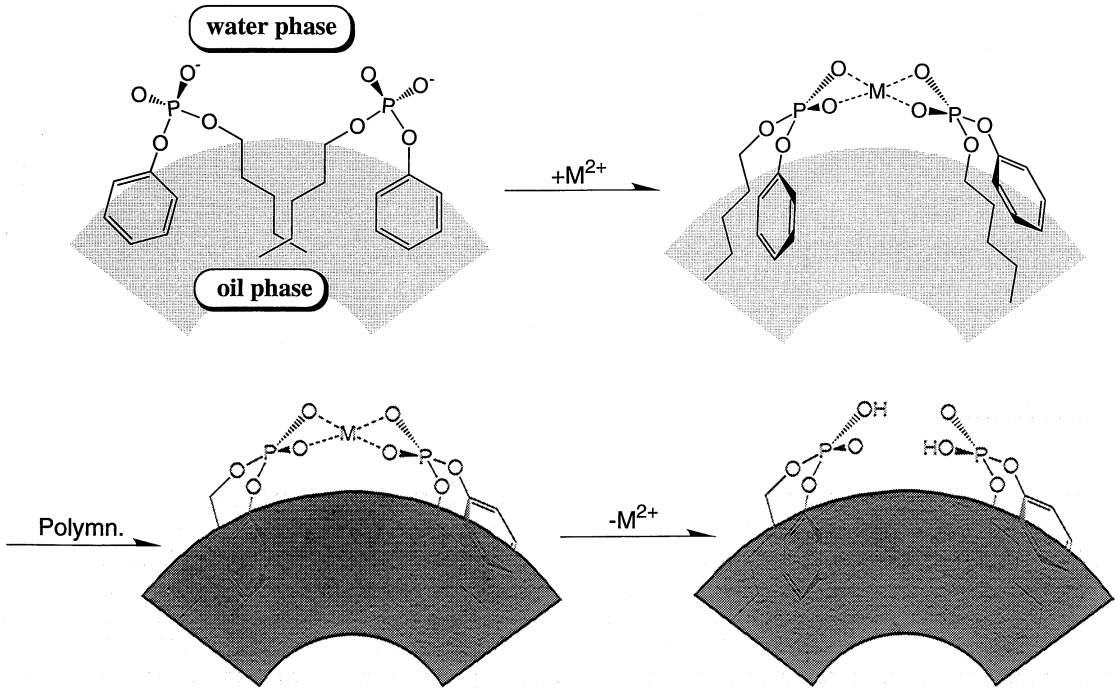


Fig. 1. Schematic illustration of surface template polymerization using oleyl phenyl hydrogenphosphate as an amphiphilic host monomer, divinylbenzene as a resin-forming monomer (oil phase) and divalent metal ion as a target.

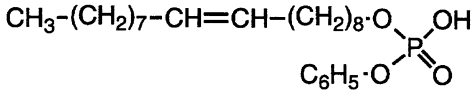


Fig. 2. Structure of oleyl phenyl hydrogenphosphate (**1**).

compared to the un-targeted ions. The surface template polymerization thus attains a favorable placement of the surface-anchored metallophilic groups for multidentate coordination to the template ion.

Experimental

Reagents and Apparatus. Oleyl phenyl hydrogenphosphate (**1**) as a functional surfactant was synthesized as follows: Oleyl alcohol (63.5 g, 0.237 mol) was added dropwise in 90 min to phenyl phosphorodichloridate (50 g, 0.237 mol) with vigorous stirring at room temperature, and the mixture was continuously agitated for further 60 min. Then, the temperature was raised to 50 °C and maintained at this temperature with stirring overnight. The reaction mixture was poured dropwise into 300 cm^3 of cold water, which was stirred overnight at room temperature. The organic phase was extracted with ether (3×100 cm^3), and the combined organic phase was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was recrystallized twice from hexane in a refrigerator. Yield, 50%. Found: C, 68.04; H, 9.58%. Calcd for $C_{24}H_{41}O_4P$: C, 67.90; H, 9.73%. The product was a viscous liquid at room temperature.

Divinylbenzene (DVB) was a generous gift from Sankyo Chemical Industries Ltd. and 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. SDS and other reagents were of commercially available grades. Scanning electron microscopic study was done by an ABT-32 type instrument from Akaishi Beam Technology.

Resin Preparation. The preparation conditions are summarized in Table 1. As a typical example, a Cu^{2+}-imprinted resin was prepared as follows: 0.426 g (1 mmol) of **1** and 0.364 g (1.18 mmol) of 2,2′-azobis(2,4-dimethylvaleronitrile) (Wako Pure Chemical Industries Ltd.) were dissolved in 20 cm^3 of DVB, which was then combined with an aqueous solution (35 cm^3) containing a prescribed amount of SDS (pH 6, buffered with 50 mM MES-sodium hydroxide). Then the mixture was treated by a probe-type sonicator for 3 min to give a stable emulsion. After the addition of 5 cm^3 aqueous solution of 0.1 M $Cu(CH_3COO)_2$ (1 M = 1 mol dm^{-3}), polymerization was carried out with stirring at 50 °C for 7 h under nitrogen atmosphere. The pH value of the emulsion before and after polymerization was around 4.2—4.9. To the mixture was added a hydrochloric acid solution (1 M, 300 cm^3), and the precipitated resin was filtered. The resin was washed in a 1 M hydrochloric

Table 1. Preparation Conditions of the Templated Resins[a)]

Polymer code	Template	SDS/g (mmol)
P1-non	None	0.5 (1.7)
P1-Cu	Cu(II)	0.5 (1.7)
P1-Zn	Zn(II)	0.5 (1.7)
P1-Cd	Cd(II)	0.5 (1.7)
P2-non	None	1.0 (3.5)
P2-Cu	Cu(II)	1.0 (3.5)
P2-Zn	Zn(II)	1.0 (3.5)
P2-Cd	Cd(II)	1.0 (3.5)
P3-non	None	2.0 (6.9)
P3-Cu	Cu(II)	2.0 (6.9)
P3-Zn	Zn(II)	2.0 (6.9)
P3-Cd	Cd(II)	2.0 (6.9)

a) Total aqueous solution, 40 cm^3; divinylbenzene, 20 cm^3; **1**, 0.4 g (1.0 mmol).

acid solution (300 cm^3) in order to exchange the bound metal ion with a proton, and then filtered again. This procedure was repeated three times until Cu^{2+} in the filtrate became negligible, as estimated by atomic absorption. Finally, the obtained resin was dried in vacuo. A reference resin (nonimprinted resin) was synthesized similarly but using pure water (5 cm^3) in place of the copper acetate solution. The Zn^{2+}- and Cd^{2+}-imprinted resins were prepared by using $Zn(CH_3COO)_2$ and $Cd(CH_3COO)_2$, respectively, instead of $Cu(CH_3COO)_2$. The gravimetric yields of resins were varied from 70 to 105% (based on **1** and DVB as starting compounds). Resins were obtained as globular particles having a diameter of 0.1—2 μm as determined by scanning electron microscopic observations. Figure 3 shows a typical view of Cu^{2+}-imprinted resins.

Potentiometric Study. The adsorption of divalent metal ions (Cu^{2+} or Cd^{2+}) to the resins was evaluated by a potentiometric titration procedure at 25 °C that used an ion-selective electrode, which is commercially available for Cu^{2+} and Cd^{2+}, but not for Zn^{2+}. The titration system consisted of an auto piston buret (Kyoto Electronics APB410) and an ion meter (Orion 720A), both being connected to and controlled by a computer. The free divalent metal ion concentrations of the test solution were determined by measuring the emf of a cell constructed with a metal ion-selective electrode (Orion cupric electrode, Model 94-29 or Orion cadmium electrode, Model 94-48) and a reference electrode (Orion double-junction reference electrode, Model 90-02), both of which were connected to the ion meter. All of the titration procedures were carried out as follows: The acid-type (protonated) resin (0.5 g) was placed in the titration cell, to which was added a 2 cm^3 solution of potassium hydroxide (0.1 M) and 20 cm^3 solution of potassium nitrate (0.1 M). After treatment by a sonicator (probe type) for 3 min, the pH of the mixture was adjusted to 5.6 with nitric acid (0.1 M). The mixture was titrated with a 0.01 M copper nitrate or cadmium nitrate solution containing 0.1 M potassium nitrate. A constant emf value was obtained within 2 min for each emf measurement, indicating that the complexation equilibria were accomplished immediately after mixing of the metal ion with the resin dispersion. Just before and after the titration procedures, the emf measurement systems were calibrated; the Nernstain slopes of the calibration measurements for the respective electrode systems were satisfactory.

Results and Discussion

The organophosphate-carrying resins were prepared from DVB by the surface template polymerization using **1** as a metal ion-binding amphiphile in the presence of metal ions (Fig. 1). However, with **1** alone, the emulsion mixture was not stable, and consequently the yields of the microparticulate resin were very low (in typical cases, ca. 30%). This is probably due to the decrease in charge of the emulsion surface by complexation of functional surfactants with metal ions. Therefore, SDS was added to the emulsion: SDS was adopted as a co-surfactant because of its high surface activity and low ability to complex with most metal ions. As a result, the resin yields were improved considerably. All the resins consisted of globular particles with somewhat broad particle size distribution.

Figure 4 shows the Cu^{2+} binding behavior of the resins. The logarithms of the free Cu^{2+} concentrations (log [Cu]) are plotted against the logarithms of the total Cu^{2+} concentrations (log C_{Cu}). The downward deviations from the calibration line (log [Cu] = log C_{Cu}, dotted line) indicate the binding of Cu^{2+} to the resins. The binding curve which falls on the calibration line indicates no metal binding affinity. The upward deviations, on the other hand, should not happen since this violates the mass balance of added metal ions. However, such cases sometimes take place in the region where high metal ion concentrations are involved because of the difficulty in accurate emf calibration (e.g., Figs. 4a and 4c). These experimental errors are not of major importance to our discussion of template-dependent metal absorptivity, since we focus our concern to the metal absorption data obtained in low metal concentration regions free from such ambiguity; the deviation of the absorption curve from the calibration line is much more prominent in these concentration regions.

As seen from Figs. 4a and 4b, it is clear that the P1-Cu and P2-Cu adsorbed their own template ion (i.e., Cu^{2+}) much more effectively than did other resins including the

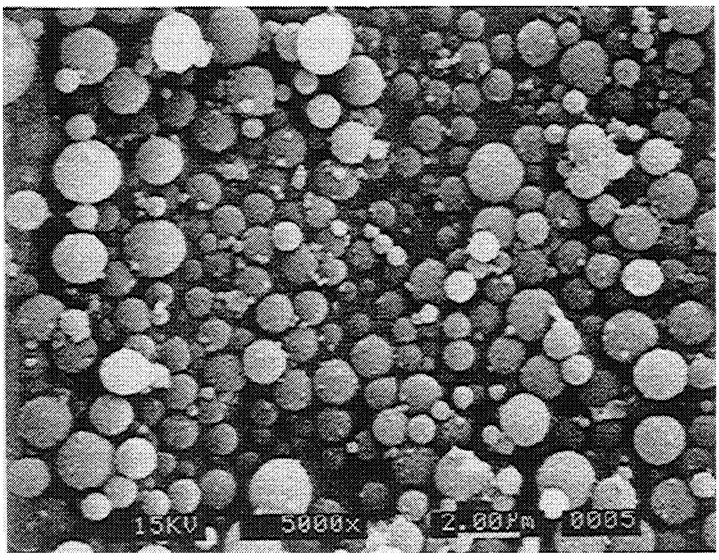
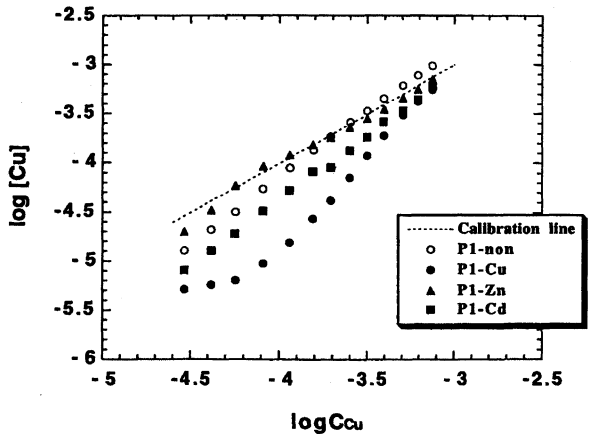
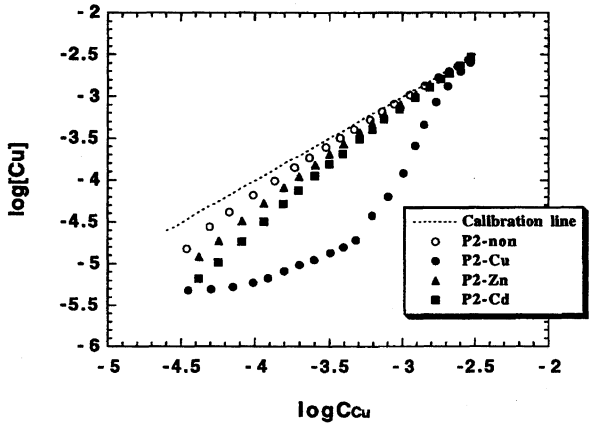


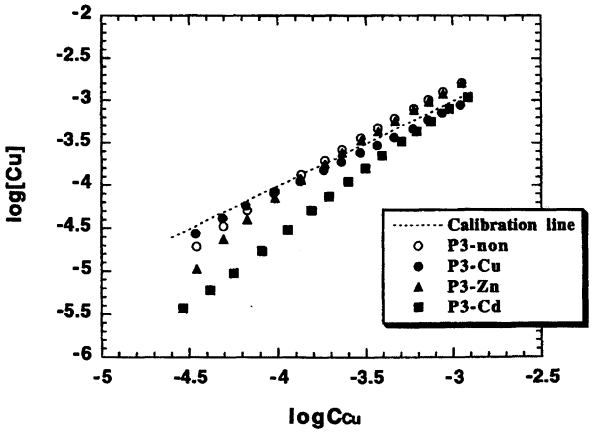
Fig. 3. Scanning electron micrograph of P2-Cu photographed at 5000× magnification.



a) SDS 0.5 g



b) SDS 1.0 g



c) SDS 2.0 g

Fig. 4. Plots of log [Cu] vs. log C_{Cu} for the resins. (a) P1 resins; SDS as a co-surfactant, 0.5 g. (b) P2 resins; SDS, 1.0 g. (c) P3 resins; SDS, 2.0 g. ○, nonimprinted resin; ●, Cu^{2+}-imprinted resin; ▲, Zn^{2+}-imprinted resin; ■, Cd^{2+}-imprinted resin. Conditions; 0.5 g of resin and $C_{KNO_3} = 0.1$ mM, at 25 °C for a potentiometric titration. Dotted line refers to a calibration line.

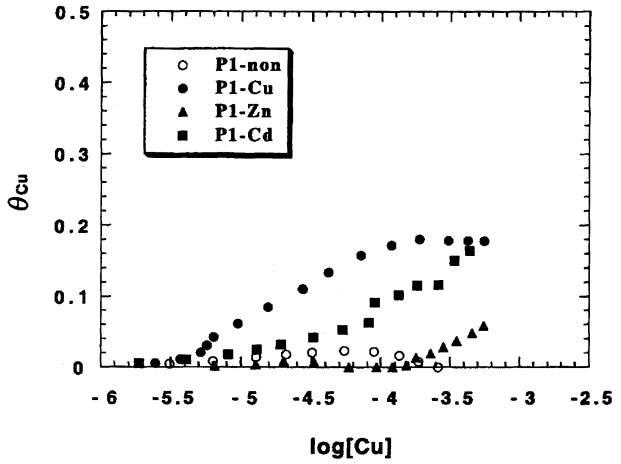
Zn^{2+}-imprinted, Cd^{2+}-imprinted and nonimprinted resins. In particular, P2-Cu which was prepared with using 1 g of SDS as a co-surfactant could rebind prominently with Cu^{2+} in a series of P2 resins over the entire concentration range investigated. In addition, adsorptivity to Cu^{2+} of P2-Cu was much better than that to P1-Cu. On the other hand, P3-Cu which was prepared with using 2 g of SDS showed a much lower binding ability to Cu^{2+}. The reason for this bell-shaped dependency on the amount of SDS is not clear. However, these results suggest that the surface structure of the resins was influenced by the addition of SDS during the polymerization.

A more quantitative way to evaluate the complexation abilities of these chelating resins is to plot the average number of bound metal ions per phosphate group (θ_M), which is calculated using the equation

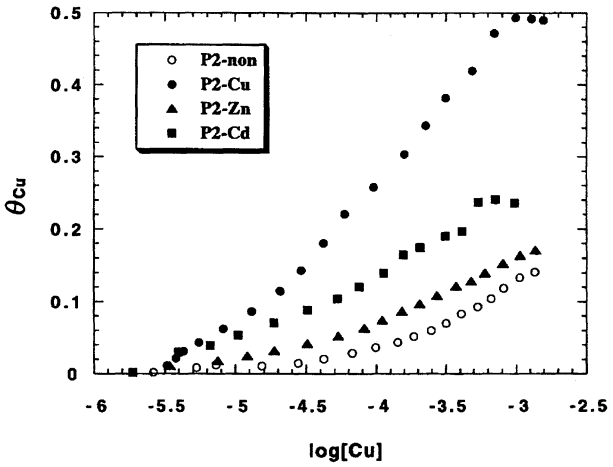
$$\theta_M = (n_M)_{bound}/n_{ex} = (C_M - [M]) \times V/n_{ex},$$

where $(n_M)_{bound}$ indicates the amount of bound metal ions (calculated by $(C_M - [M])$ multiplied by the total solution volume (V; dm^3)) and n_{ex} is the amount of phosphate groups in the resin (mol) as calculated from the amount originally fed to the emulsion. Figure 5 shows the Cu^{2+} binding isotherms obtained for the series of P1 and P2 resins, respectively. The two Cu^{2+}-imprinted resins (P1-Cu and P2-Cu) showed more preferential Cu^{2+}-binding than other resins over the entire [Cu] region. In both resins, the maximal value of θ_M is in the order of the Cu^{2+}-imprinted, Cd^{2+}-imprinted, Zn^{2+}-imprinted, and nonimprinted resins. In particular, the maximum θ_M value for P2-Cu reached almost 0.5. Assuming that the binding mode was due to a 2 : 1 complex (phosphate : Cu^{2+}), almost all the phosphate groups used in the polymerization functioned as preferential Cu^{2+}-binding sites on the resin surface.

The Cd^{2+} binding isotherms for the series of P1 and P2 resins were examined similarly (Fig. 6). As expected, P1-Cd and P2-Cd resins prepared in the presence of Cd^{2+} were clearly shown to adsorb Cd^{2+} much more effectively than did other resins. In contrast to this, P1-Cu and P2-Cu did not adsorb any significant amount of Cd^{2+}. These results clearly verify that the metal binding sites were formed differently on each resin; the oleyl phenyl hydrogenphosphate moieties are implanted on the resin surface in such a way that they can match a desirable coordination around the template ion when they interact with the ion (Fig. 1). The Cu^{2+}-, Cd^{2+}-, and Zn^{2+}-imprinting may probably serve to place the phosphate groups in the square planar, tetrahedral and tetrahedral configurations, respectively. In this viewpoint, it should be noted that the Zn^{2+}-imprinted resins adsorbed moderate amounts of Cd^{2+} that has the same coordination configuration as Zn^{2+} (Fig. 6). On the nonimprinted resins, in contrast, oleyl phenyl hydrogenphosphate moieties are randomly distributed on their surface as determined by such conditions as pH, counter ion (Na^+) and co-surfactant (SDS) concentrations. Thus the nonimprinted resins showed only a small metal binding ability in all the cases.

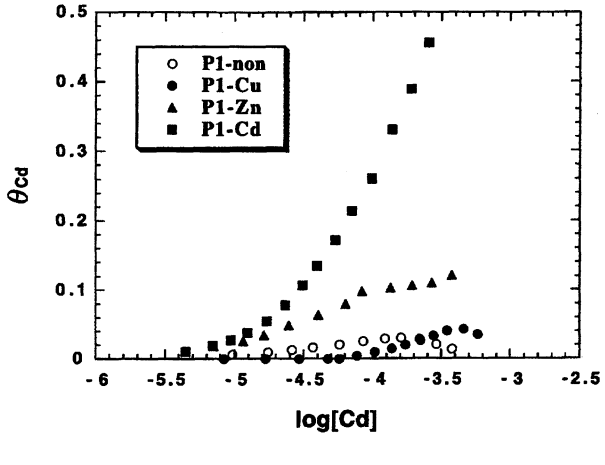


a) SDS 0.5 g

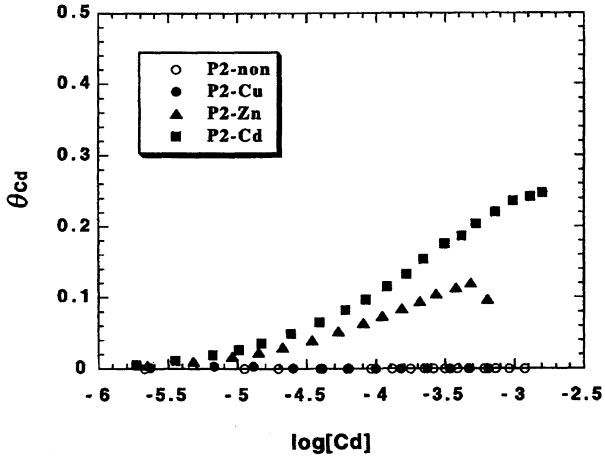


b) SDS 1.0 g

Fig. 5. Cu^{2+}-binding isotherms for the resins. (a) P1 resins; SDS as a co-surfactant, 0.5 g. (b) P2 resins; SDS, 1.0 g. ○, nonimprinted resin; ●, Cu^{2+}-imprinted resin; ▲, Zn^{2+}-imprinted resin; ■, Cd^{2+}-imprinted resin. Conditions; 0.5 g of resin and C_{KNO_3}=0.1 mM, at 25 °C for a potentiometric titration.



a) SDS 0.5 g



b) SDS 1.0 g

Fig. 6. Cd^{2+}-binding isotherms for the resins. (a) P1 resins; SDS as a co-surfactant, 0.5 g. (b) P2 resins; SDS, 1.0 g. ○, nonimprinted resin; ●, Cu^{2+}-imprinted resin; ▲, Zn^{2+}-imprinted resin; ■, Cd^{2+}-imprinted resin. Conditions; 0.5 g of resin and C_{KNO_3}=0.1 mM, at 25 °C for a potentiometric titration.

Interestingly, the optimal amount of SDS was different between the Cu^{2+}- and Cd^{2+}-imprinted resins in regard to the selectivity: the most superior resins were P2-Cu and P1-Cd that were prepared by using 1 g and 0.5 g of SDS, respectively. This is probably related to the surface activity of oleyl phenyl hydrogenphosphate (**1**) in the presence of template ions; the addition of suitable amount of co-surfactant gives a stable emulsion, while an excessive addition would result in the exclusion of the template ion-phosphate complex from the resin surface. In fact, the templated resins which were prepared with using 2 g of SDS showed low recovery of template ions after polymerization, in comparison with the resins prepared with using 0.5 or 1 g of SDS. For instance, Cu^{2+} was removed quantitatively (99% recovery) from P1-Cu by washing with a hydrochloric acid solution, whereas the similarly treated P3-Cu gave only 45% of Cu^{2+} added before polymerization. This may suggest that a population of accessible phosphate groups on the P3-Cu is smaller than on other resins. Apart from these considerations, the use of SDS as co-surfactant obviously offers a new technical advantage in the preparation of surface-imprinted resins.

In conclusion, we have prepared highly cross-linked polymers having a metal-complexing structure on the surface by the surface template polymerization technique. The binding strength and uptake capacity increased when we conduct the polymerization in the presence of template ions. The amount of SDS added as a co-surfactant during the polymerization was also a very important factor for the selectivity

of the resin. Nishide et al. have synthesized for the first time the ion exchange resins by a templating method.[7] Since then, there have been some successful examples of metal ion-imprinted resins.[8] However, the conventional template polymerization approaches have encountered problems including low binding selectivities, slow rebinding kinetics, and loss of selectivity with time.[9] In the present study, the surface templated resins exhibited rapid, reversible and unusually strong complexation with the target ion. As discussed previously,[3] these should be ascribed to the utilization of the surface as a field of molecular recognition.

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