Metal Ion Selectivity of Surface Templated Resins
Carrying Phosphate Groups

Masaharu Murata, Mizuo Maeda and Makoto Takagi

Department of Chemical Science and Technology, Faculty of Engineering,
Kyushu University, Hakozaki, Higashi, Fukuoka 812-81, Japan

Abstract: The metal ion selective resins were prepared by surface template polymerization using monooleyl phosphoric acid (1), oleyl methyl phosphoric acid (2) or oleyl ethyl phosphoric acid (3) as an amphiphilic host surfactant. The Cu^{2+}-imprinted resins prepared in the presence of Cu^{2+} adsorbed Cu^{2+} much more effectively than did their reference resins. On the other hand, the Cu^{2+}-imprinted resins showed much less binding ability to Zn^{2+}. The template-dependent selectivity should be ascribed to a favorable placement of the surface-anchored metallophilic groups for multidentate coordination to specific metal ion.

Keywords: Surface template polymerization, ion exchange resin, phosphoric acid, divinylbenzene, selective metal ion adsorption.

1. Introduction

Polymeric resins carrying phosphate groups have attracted much attention. The main reason is that these groups can form stable complexes with metal ions including lanthanides and actinides [1]. However, the selectivity among those metals are not very satisfactory, since the random introduction of the metallophilic groups in the resin does not make their placement favorable for multidentate coordination. On the selective metal adsorbent, more than two phosphate coordinating groups must be placed appropriately to form a stable complex with the metal ion.

On the other hand, 'molecular imprinting' (or 'template polymerization') has attracted considerable attention as means of producing polymers which exhibit molecular recognition properties [2]. This technique involves prearrangement of coordinating groups in the presence of a print molecule and fixation of the arranged structure by polymerization.

Recently, we proposed the "surface template polymerization" technique as a well sophisticated version of such imprinting methods [3-5]. This approach involves a preorganization of surfactants with a coordinating group (amphiphilic host monomers) on oil-water emulsion surface by interacting cooperatively
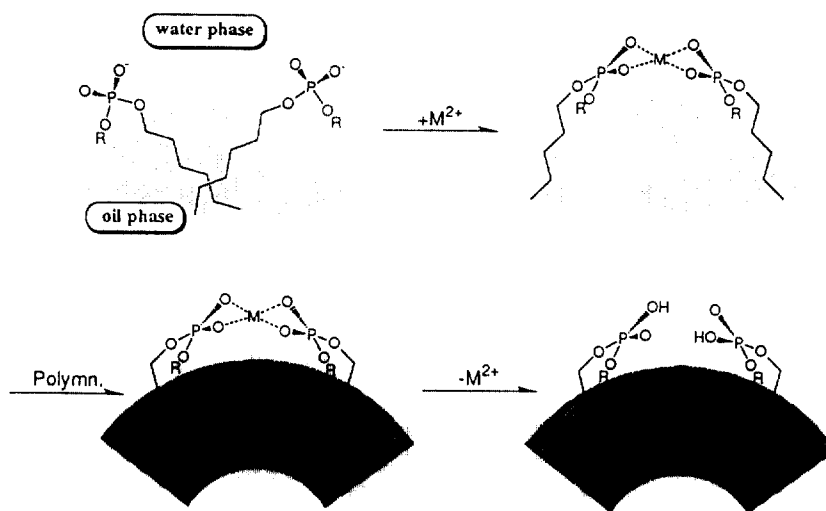
Figure 1   Schematic illustration of surface template polymerization using phosphoric acid as an amphiphilic host monomer, divinylbenzene as a resin-forming monomer (oil phase) and Cu^{2+} as a target.

with the target (template guest) in aqueous phase. The organized structure from the template and the 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 coordinating groups appropriately placed on their surface.

We prepared a surface-templated resin 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]. As a result, Cu^{2+}-imprinted resin showed the highly-effective binding to Cu^{2+} as compared with that of a reference (non-imprinted) one. The organophosphate-carrying resins were also prepared by using dioleyl phosphoric acid as an amphiphilic host, in the presence or in the absence of Cu^{2+} or Zn^{2+} [4]. In this study, the dependence of selectivity on the template was clearly demonstrated by the result that 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 non-imprinted. However, the metal ion selectivity of the surface templated resins between the targeted metal and the un-targeted metals has not been clearly demonstrated.

In this work, we studied the metal ion selectivity of Cu^{2+}-imprinted resins which were prepared by surface template polymerization using monooleyl phosphoric acid (1), oleyl methyl phosphoric acid (2) or oleyl ethyl phosphoric acid (3) as an amphiphilic host surfactant (*Fig. 1*). These amphiphiles have high surface activity which allows a stable emulsion formation during polymerization. Therefore, it was not needed to add a co-surfactant in the polymerization mixture, in contrast to our previous case [4]. Binding capacity of the resins were determined for Cu^{2+} and Zn^{2+}. As a result, all of the Cu^{2+}-templated resins adsorbed Cu^{2+} more efficiently than did the resins prepared in the absence of Cu^{2+}. On the other hand, the Cu^{2+}-imprinted resins showed much less binding ability to Zn^{2+}. The results suggest that the surface template polymerization technique gives resins with the metal ion selective feature for the template ion.

2. Experimental

Reagents and Apparatus.   Monooleyl phosphoric acid (1) as a coordinating surfactant was synthesized as follows: Oleyl alcohol (90.0g, 0.335mol) was added dropwise in 90 min to phosphorus oxychloride (50g,

0.326mol) with vigorous stirring at room temperature, and the mixture was continuously agitated for further 60 min. Then, the temperature was raised to 50 ℃ and maintained at this temperature with stirring overnight. The reaction mixture was poured dropwise into 300 cm³ of cold water, which was stirred overnight at room temperature. The organic phase was extracted repeatedly with ether (3 × 100 cm³), 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, 18%. Anal. Calcd for $C_{18}H_{37}O_4P$: C, 62.09; H, 10.63. Found: C, 61.57; H, 10.82 %.

Oleyl methyl phosphoric acid (2) and Oleyl ethyl phosphoric acid (3) were synthesized in analogous manner by phosphorylation of oleyl alcohol with methyl phosphorodichloridate and ethyl phosphorodichloridate, respectively, instead of phosphorus oxychloride. Yields and analytical data of these compounds were as follows: 2: Yield, 25%. Anal. Calcd for $C_{19}H_{39}O_4P$: C, 63.01; H, 10.77. Found: C, 63.38; H, 11.18 %. 3: Yield, 34%. Anal. Calcd for $C_{20}H_{41}O_4P$: C, 63.80; H, 10.98. Found: C, 63.19; H, 11.23 %. The products, 1-3, were viscous liquid at room temperature.

$$CH_3-(CH_2)_7-CH=CH-(CH_2)_8-O-P(=O)(OH)(OH)$$

1

$$CH_3-(CH_2)_7-CH=CH-(CH_2)_8-O-P(=O)(OH)(OCH_3)$$

2

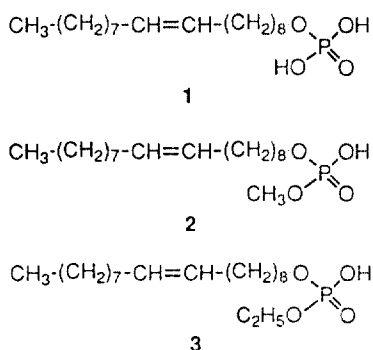$$CH_3-(CH_2)_7-CH=CH-(CH_2)_8-O-P(=O)(OH)(OC_2H_5)$$

3

Figure 2   Structures of amphiphilic host surfactants employed in this study. (1) monooleyl phosphoric acid, (2) oleyl methyl phosphoric acid, (3) oleyl ethyl phosphoric acid.

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. 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 grade. Scanning electron microscopic study was made by an ABT-32 type instrument from Akashi Beam Technology. The metal-ion concentration was determined by SAS 760 Atomic Absorption Spectrophotometry (Seiko Instruments Inc.).

Resin Preparation.   Resins were prepared according to the conditions indicated in *Table 1*. As a typical example, the preparation of **P1-Cu** is described: A 10 cm³ solution of DVB containing 0.4 mmol of 1 with 100 cm³ aqueous solution of 2 mM $Cu(CH_3COO)_2$ (pH6, buffered with 50 mM MES-sodium hydroxide), and the mixture was treated by a probe-type sonicator 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. The resin was washed with the hydrochloric acid solution in order to exchange the bound metal ion with a proton, and then filtered. 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 was synthesized similarly but without Cu^{2+}. The overall yield of the resin was in typical cases *ca.* 90 % (based on 1 and DVB as starting compounds).

Metal Adsorption Studies.   The adsorption equilibrium of metal ions 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 $Cu(CH_3COO)_2$ (1 mM). The pH was adjusted to 6 with 25 mM MES-sodium hydroxide. The mixture was shaken at 25 ℃ for 12 h. The equilibrated mixture was centrifuged (10000 rpm, 3 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+} by atomic absorption

Table 1   Resins prepared in this study.

Polymer code [a]	Monomer [b]	Template	Particle size (μm) [c]
P1-BL	1	none	0.1-2.0
P1-Cu	1	Cu^{2+}	0.1-2.5
P2-BL	2	none	0.1-2.0
P2-Cu	2	Cu^{2+}	0.5-3.0
P3-BL	3	none	0.1-2.0
P3-Cu	3	Cu^{2+}	0.5-2.5

a) Polymers that were different only in the template used during polymerization are indicated with the same number. The templated ion is indicated after the resin number (absence of template is indicated by BL = blank).
b) 1, monooleyl phosphoric acid; 2, oleyl methyl phosphoric acid; 3, oleyl ethyl phosphoric acid.
c) Approximate range in particle size estimated from electron microscopic observation.

spectrophotometry. The amount of metal ion adsorbed onto the resin was taken as the difference between the amount initially added and that determined after equilibrium in the aqueous phase. Similarly, the adsorption of Zn^{2+} to the resins at pH7 (buffered with 25 mM HEPES-sodium hydroxide) was evaluated.

3. Result and Discussion

Polymers with molecular imprints against Cu^{2+} were prepared, using three compounds (1-3) as ion-complexing amphiphile. By the surface template approach, the phosphate groups are spatially arranged on the resin surface to facilitate the binding of Cu^{2+} (Fig. 1). DVB that was added in large excess to the ion-complexing amphiphile plays a role in cross-linking agent. In general, adsorptivity and wettability of ion exchange resin should decrease with increasing cross-linking since the resident functional groups would be less accessible to the metal ions [6]. However, the surface templated resins exhibit rapid, reversible and unusually strong complexation with the target ion. As discussed previously [3], these are endorsed by utilization of the surface as a field of molecular recognition.

Resin morphology may influence on tractability and adsorptivity of the resin [7]. The imprinted polymers are usually obtained as blocks that need to be

ground and sieved before use [8]. This results in irregular particles, poor adsorptivity and a loss of unsized material. In contrast, surface template polymerization based on emulsion polymerization produces spherical particles [4]. In this study, resins were obtained as globular particles having diameter of 0.1-3.0 μm as determined by scanning electron microscopic observations (Table 1).

Fig. 3 shows the amounts of Cu^{2+} and Zn^{2+} adsorbed on the Cu^{2+}-imprinted and unimprinted (reference) resins in the presence of excess metal ions. P1-BL which was prepared using monooleyl phosphoric acid in the absence of Cu^{2+} adsorbed 68×10^{-7} mol-Cu^{2+}/g-resin for Cu^{2+} and 54×10^{-7} mol-Zn^{2+}/g-resin for Zn^{2+}. The amount of adsorbed ions by the unimprinted resins follows the common trend of complexation, $Cu^{2+} > Zn^{2+}$, which is in turn on the Irving-Williams series. On the other hand, P1-Cu prepared in the presence of Cu^{2+}adsorbed a slightly more amount of Cu^{2+} relative to the P1-BL, while the binding capacity of P1-Cu for Zn^{2+} decreased to 34×10^{-7} mol-Zn^{2+}/g-resin. This reduced capacity for Zn^{2+} relative to the unimprinted resin clearly indicates that the templating has affected the distribution of phosphate groups on the resin. The phosphoric acid groups on the reference resin are randomly distributed on the resin as determined by such conditions as pH and counter ion (Na^+) concentration. On the other hand, on the Cu^{2+}-imprinted resin, it appears that the phosphate groups are
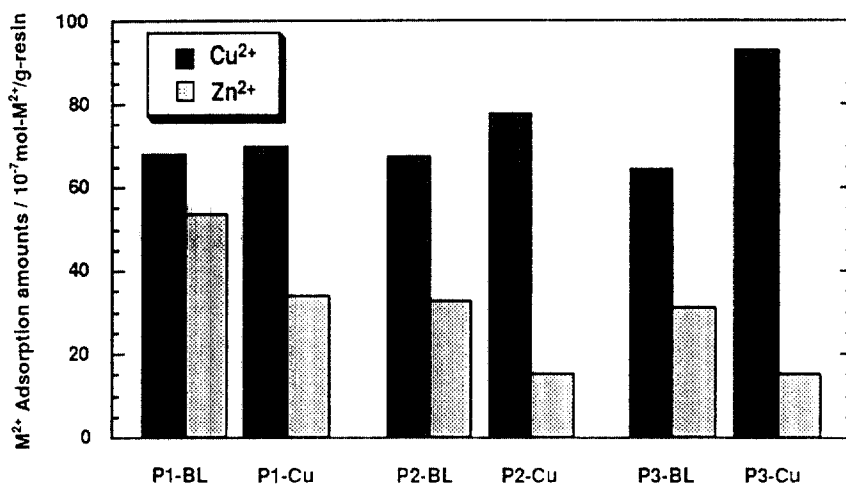
Figure 3 Metal ion binding by the imprinted and unimprinted resins under saturation rebinding conditions.

implanted in such a way that they can match a desirable coordination (probably the square planar one) around the Cu^{2+}. Consequently, placements of the phosphate groups on Cu^{2+}-imprinted resin did not favor the accommodation of Zn^{2+} (probably in the tetrahedral configuration).

The similar phenomena were observed in P2 and P3 resins that were prepared using oleyl methyl phosphoric acid (2) and oleyl ethyl phosphoric acid (3), respectively. **P2-Cu** and **P3-Cu** prepared in the presence of Cu^{2+} adsorbed Cu^{2+} much more effectively than did their reference resins (**P2-BL** and **P3-BL**, respectively). In contrast, binding capacities for Zn^{2+} of the **P2-Cu** and **P3-Cu** decreased to approximately one half of the reference resins. This clearly reveals a negative templating effect to un-targeted metal ion.

Adsorption on selectivity (α) of Cu^{2+} compared with Zn^{2+} is defined as; $\alpha = Q_{Cu^{2+}} / Q_{Zn^{2+}}$ (where $Q_{Cu^{2+}}$ and $Q_{Zn^{2+}}$ are the binding capacities for Cu^{2+} and Zn^{2+}, respectively). In order to separate the nonspecific effect due to the intrinsic nature of respective surfactant from the template effect with a metal ion, α value of the Cu^{2+}-imprinted resins was compared with that of their reference resins (α'= (α on imprinted resin) / (α on reference resin)). α' value of the Cu^{2+}-imprinted resins increased in order of **P1-Cu** < **P2-Cu** < **P3-Cu** (α'; 1.6 < 2.5 < 2.9, respectively). It is interesting that this order is in agreement with that of bulkiness of complexing

group with metal ion in the host surfactant (1; -OH < 2; -OCH₃ < 3; -OC₂H₅). This result suggests that molecular structure of host surfactant would also influence the template effect.

In conclusion, the results obtained here indicate that the adsorption of metal ions is a specific event due to the organized distribution of phosphate groups on the resin surface. The adsorption capacities for the template ion increased when performing the polymerization in the presence of that ion. In contrast, the binding capacities for other metal ion decreased significantly. By using the technique of surface template polymerization, metal-complexing groups are placed in a favorable position to rebind the template ion. Molecular structure of a host surfactant was found to be also an important factor for the template effect.

Acknowledgement

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