METAL ION-IMPRINTED RESINS WITH NOVEL BIFUNCTIONAL MONOMER BY SURFACE TEMPLATE POLYMERIZATION

MASAHIRO YOSHIDA, KAZUYA UEZU,
MASAHIRO GOTO AND FUMIYUKI NAKASHIO
*Department of Chemical Science and Technology,
Kyushu University, Hakozaki, Fukuoka 812-81, Japan*

Key Words: Adsorption, Ion Exchange, Separation, Molecular Imprinting, Surface Template Polymerization

Introduction

Molecular recognition has drawn much attention with regard to separation chemistry. One of the promising approaches to create molecular-recognizing materials is the "molecular imprinting" method (Mosbach, 1994; Wulff, 1995), the concept of which was proposed by Wulff *et al.* about twenty years ago (Wulff and Sarahan, 1972). The new methodology does not require a precise molecular design and multi-step procedures to construct highly-selective polymers. In the technique, imprint (template) molecules are bound to functional monomers in matrix-forming monomers. The monomers are then polymerized under conditions that lead to formation of a highly cross-linked matrix with chains in a fixed arrangement. Removal of the imprint molecules leaves behind cavities, whose structure and arrangement of the functional monomers are predetermined by the chemical nature of the template. However, this technique has some fundamental drawbacks; for example, complexation between imprint molecules and functional monomers is not always fast, and water-soluble substances cannot be employed as imprint molecules. During the past couple of years, we have proposed a novel molecular imprinting technique, which is called "surface template polymerization," to conquer the drawbacks of metal ion-selective resins (Tsukagoshi *et al.*, 1993; Uezu *et al.*, 1994).

We found that the interfacial activity of functional monomers is the dominant factor to succeed in preparing imprinted resins. (Uezu *et al.*, 1994). It is also important to fix the recognition sites rigidly and to create strong interactions between the functional monomers and imprint molecules. In the present study, we have designed 1,12-dodecanediol-O,O'-diphenyl phosphonic acid having two functional groups in the molecular structure as a recognition monomer, and prepared a highly-selective metal ion resin by surface template polymerization with a W/O emulsion. The separation of zinc and copper ions with the resins

was conducted, and the template effect was characterized by comparing with that in ordinary solvent extraction for the metal ions.

1. Experimental Sections

1.1 Reagents

The new bifunctional monomer, 1,12-dodecanediol-O,O'-diphenyl phosphonic acid (abbreviated with DDDPA), and *L*-glutamic acid dioleylester ribitol (abbreviated with 2C₁₈ Δ⁹GE) were synthesized according to previous works (Goto *et al.*, 1996; Goto *et al.*, 1987). **Figure 1** exhibits the molecular structure of DDDPA. Divinylbenzene (abbreviated as DVB, Wako Pure Chemical Industries, Ltd.) was employed after treatment with silica gel to remove an inhibitor. Other reagents were commercially available grades.

1.2 Preparation of Resins

The preparation scheme of a metal ion-imprinted resin by surface template polymerization is illustrated in **Fig. 2**. A 40 cm³ solution of DVB, in which DDDPA (60 mol/m³) and 2C₁₈ Δ⁹GE (3 mol/m³) were dissolved, was mixed with 20 cm³ of toluene. A 30 cm³ aqueous solution containing 10 mol/m³ Zn(NO₃)₂ (pH = 3.0, buffered with 100 mol/m³ nitric acid-100 mol/m³ acetic acid-100 mol/m³ sodium acetate) was added, and the mixture was sonicated for 4 min to obtain a W/O emulsion. After 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 55 °C for 2 h under a nitrogen atmosphere. The resin obtained was dried *in vacuo* and ground to an appropriate size. The resin was washed with 1000 mol/m³ hydrochloric acid solution to remove zinc ions and then filtered off. This procedure was repeated several times until the zinc ions in the filtrate could not be detected. Finally, the zinc ion-imprinted resins (abbreviated with Zn-imprinted resin) were dried *in vacuo*.

1.3 Adsorption experiment of zinc and copper ions

The adsorption equilibrium of zinc and copper ions onto the resins was examined in a batchwise method. 0.1

* Received on November 2, 1995.

Correspondence concerning this article should be addressed to F. Nakashio

Fig. 1 Structures of novel functional monomer 1,12-dodecanediol-O, O'-diphenyl phosphonic acid (DDDPA)

Fig. 2 Schematic illustration of surface template polymerization with DDDPA

g of the resin was placed in a sealed test tube (10 cm³ volume), to which was added a 5 cm³ mixed solution containing 0.1 mol/m³ Zn(NO₃)₂ and 0.1 mol/m³ Cu(NO₃)₂. The pH was adjusted to a desired value between 1.0 and 6.0 with 100 mol/m³ nitric acid-100 mol/m³ acetic acid-100 mol/m³ sodium acetate. The mixture was shaken in a thermostated water bath at 303 K for 24 h. Then the resins were filtered off through a cellulose nitrate membrane (DISMIC-25, Tokyo Roshi Kaisha, Ltd.). The concentrations of zinc and copper ions in the filtrate were analyzed by an atomic absorption spectrophotometer (SAS-760, Seiko Instrument Inc.).

1.4 Solvent Extraction of zinc and copper ions

An organic and an aqueous solution were prepared in a similar way as the resin was prepared. A mixture of a 10 cm³ organic solution and a 5 cm³ aqueous solution was shaken in a thermostated water bath at 303 K for 24 h. After the phase separation, the concentration in equilibrium of zinc or copper ions in the aqueous solution was analyzed by an atomic absorption spectrophotometer.

2. Results and Discussion

A highly cross-linked imprinted resin was prepared by surface template polymerization. Zinc ion was employed as an imprint molecule because of its high interaction with the bifunctional monomer, DDDPA. DVB, 2C₁₈ Δ⁹GE, and toluene were used as a matrix-forming monomer, an emulsion stabilizer, and a diluent, respectively. After polymerization, the imprint molecules were removed from the resin, on which selective recognition sites were formed. The Zn-imprinted resins were ground into particles, whose volume-averaged diameters were ca. 40 μm. The yield was ca. 80 %.

Fig. 3 pH dependence in adsorption of zinc (●) and copper (○) ions with a Zn-imprinted resin using DDDPA

Fig. 4 pH dependence in solvent extraction of zinc (●) and copper (○) ions using DDDPA

Figure 3 shows the pH dependence of the adsorption of zinc and copper ions on the Zn-imprinted resins with DDDPA. The percent adsorption increased with increasing pH for both ions. The ability of the Zn-imprinted resins to adsorb zinc ions is significantly higher, which is due to the interfacial activity of DDDPA and the strong interaction between zinc ions and DDDPA. The Zn-imprinted resins adsorbed zinc ions much more effectively than copper ions over the entire pH range. It is surprising that zinc and copper ions were completely separated in the vicinity of pH 3. The high selectivity is considered to be produced by the Zn-memorized cavity on the surface of the resins. The pH dependence in liquid-liquid extraction for zinc and copper ions using the same extractant DDDPA was shown in Fig. 4. In the solvent extraction system, an

effective selectivity was not observed compared with that of the imprinted resins. Because the functional monomers (extractants) in the solvent extraction can take both the tetrahedral configuration for zinc ions and the planar configuration for copper ions due to high mobility in the organic solvent, the selectivity towards the ions only depends on the stability of the complex between the extractants and the ions. In contrast, the functional monomers on Zn-imprinted resins are fixed in the tetrahedral configuration, therefore the ability to recognize zinc ions is considered to be extremely high.

Conclusion

Metal-imprinted resins with the novel bifunctional monomer, DDDPA, have been prepared by surface template polymerization with a W/O emulsion. The imprinted resin exhibits a tremendously high selectivity towards zinc ions over copper ions. It is concluded that the bifunctional monomer enables recognition sites to be rigid. Surface template polymerization will be to an ideal method to construct new molecular-recognizing materials for various water-soluble substances.

Acknowledgement

This work was partially supported by the research fund from the Power Reactor and Nuclear Fuel Development Corporation and the Salt Science Foundation.

References

- Goto, M., S. Matsumoto, F. Nakashio, K. Yoshizuka and K. Inoue; "Design of novel organophosphorus extractants having two functional groups for the extraction of Rare Earth Metals," *Proc. ISEC' 96* (Australia) in Press (1996)
- Goto, M., M. Matsumoto, K. Kondo and F. Nakashio; "Development of new surfactant for liquid surfactant membrane process," *J. Chem. Eng. Jpn.*, **20**, 157-164 (1987)
- Mosbach, K.; "Molecular imprinting," *TECHNIQUES*, 9-14 (1994)
- Tsukagoshi, K., K. Y. Yu, M. Maeda and M. Takagi; "Metal ion-selective adsorbent prepared by surface-imprinting polymerization," *Bull. Chem. Soc. Jpn.*, **66**, 114-120 (1993)
- Uezu, K., H. Nakamura, M. Goto, M. Murata, M. Maeda, M. Takagi and F. Nakashio; "Novel metal ion-imprinted resins prepared by surface template polymerization with W/O emulsion," *J. Chem. Eng. Jpn.*, **27**, 436-438 (1994)
- Wulff, G.; "Molecular imprinting in cross-linked materials with the aid of molecular templates - a way towards artificial antibodies," *Angew. Chem. Int. Ed.*, **34**, 1812-1832 (1995)
- Wulff, G. and A. Sarhan; "The use of polymers with enzyme-analogous structures for the resolution of racemates," *Angew. Chem. Int. Ed.*, **11**, 341-341 (1972)