Ferrocyanide-Templated Resins Prepared by Surface Template Polymerization

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The ferrocyanide-templated resin was prepared by the "surface template polymerization method", using ferrocyanide ion as a template, oleylamine as a functional surfactant monomer and divinylbenzene as a matrix-forming monomer. Decyltrimethylammonium chloride (DTAC; quarternary ammonium salt) was found to be suitable as an auxiliary surfactant, when preparing the templated resin: DTAC stabilized the emulsion and was easily removed from the resin by washing with alkaline solution after the polymerization. The templated resin adsorbed ferrocyanide ions about 2 times as much as the non-templated resin. Although the structure of the complex between ferrocyanide and amino groups on the resin surface remains for further study, we found preparation conditions of the anion-templated resin using oleylamine and DTAC.

Keywords Surface template polymerization, oleylamine, decyltrimethylammonium chloride, emulsion polymerization, divinylbenzene

Imprinting polymerization is a method of preparing the resin that has a great affinity and selectivity to the guest molecule. This method is based on polymerization of the functional monomer (host) with the matrix monomer surrounding the guest molecule; the guest is removed from the resultant resin to give a cavity, which has the structure complementary to the guest molecule. We may utilize the cavity as the guest recognizable place. This method was proposed by Wulff^{1,2} for the separation of optically active compounds two decades ago. In contrast to "supra-molecules" such as crown ethers, cryptands and cyclodextrins, this method does not need a precise design of a host compound to catch the guest molecule, since the functional monomers spontaneously assemble around the guest molecule by interacting with it. The cavity of the imprinted resin memorizes the shape and chemical properties of the guest molecule. Recently, the imprinting polymerization method has been studied for many molecules and ions. Nishide *et al.* prepared the metal-chelating-resins to collect the target metal selectively.^{3,4} Mosbach *et al.* prepared the resin to separate the organic cations⁵ as well as anions.⁶ Shea *et al.* prepared the resin for column adsorbents to concentrate some drugs.⁷

On the other hand, there have been some other methods of imprinting polymerization, by which the template site is formed on the resin surface.^{8,9} The resins prepared by these methods have an excellent property of adsorbing target molecules with a much

shorter period than conventionally prepared resins. The surface template polymerization method⁸ depends on the facts that the functional surfactant (monomer) and the guest molecule interact with each other at an oil-water interface in the O/W emulsion and that the host-guest complex is immobilized by polymerization of matrix monomer. Since the spherical micro-particles are produced, grinding and sieving of the particles are not needed. This method can be applied to any water-soluble guest that cannot be used in the conventional method. The copper-imprinted resin was prepared with a functional monomer such as oleic acid⁸ and dioleoyl phosphoric acid¹⁰, and with divinylbenzene as a matrix monomer by the surface template polymerization method.

In this study, since there has been no report on a templated resin for inorganic anions, we tried to prepare an anion-imprinted resin. The resin was prepared by the surface template polymerization method that can be applied to a water soluble inorganic anion, using ferrocyanide ion as a template, oleylamine as a functional surfactant monomer, divinylbenzene as a matrix forming monomer, and quaternary ammonium surfactant as an auxiliary surfactant. Figure 1 shows in schematic form the surface template polymerization method with the aid of an auxiliary surfactant. The auxiliary surfactant was used to increase emulsion stability and to support a construction of the imprinting field on the emulsion surface. It can be removed from the resin after polymerization to give only the primary amino groups

Fig. 1 Schematic illustration of surface template polymerization using oleylamine as a host monomer, quarternary ammonium as an auxiliary surfactant, divinylbenzene as a resin forming monomer and ferrocyanide ion as a template. The quarternary ammonium surfactant was removed after polymerization, and only amino groups remained on the resin surface.

due to oleylamine on the resin. The adsorption behavior of ferrocyanide on the templated resins was studied in comparison with that on non-templated resins.

Experimental

Reagents and apparatus

Oleylamine, cetyltrimethylammonium chloride (CTAC), and decyltrimethylammonium chloride (DTAC) were purchased from Tokyo Kasei Kogyo Co., Ltd. V-65 (2,2'-azobis(2,4-dimethylvaleronitrile)) (Wako Pure Chemical Industries, Ltd.) was used as an initiator. Divinylbenzene (DVB) (a gift from Nippon Steel Chemical Co., Ltd.) was used after treatment with silica gel to remove an inhibitor. The ferrocyanide solution was prepared by dissolving potassium ferrocyanide just before the experiments. Pure water was obtained from a Milli-Q Water Purification System (Nippon Millipore Ltd.). Other reagents were of commercially available grade. Iron concentration was determined by an SAS 760 Atomic Adsorption Spectrophotometer (Seiko Instruments Inc.). The DU-70 spectrophotometer (Beckman Co., Ltd.) was used for the determination of an auxiliary surfactant. Resin particles were observed by Scanning Electron Microscopy ABT-32 type (Akaishi Beam Technology).

Preparation of the resins

A divinylbenzene solution containing oleylamine and an initiator, 0.1 mol dm⁻³ hydrochloric acid, and an aqueous solution of potassium ferrocyanide (the template guest) and auxiliary surfactant were put into a three necked flask (300 cm³) under a nitrogen atmosphere. The mixture was sonicated for 3 min to give an emulsion, and polymerization was started by

placing the flask in a water bath at 48°C. The polymerization period was 6 h. The reaction was stopped by removing the flask from the bath and the suspension in the flask was put into 0.1 mol dm⁻³ potassium hydroxide solution (300 cm³), so that the resins formed aggregates. The mixture was stirred for 12 h. Then the resin was filtered and was washed with 0.1 mol dm⁻³ potassium hydroxide solution (300 cm³) three times to remove the template. The resin was further washed with pure water until the filtrate solution became neutral. The resin was dried for 7 d at 40°C and then was preserved in a desiccator. The recovery of the template guest was determined by the measurement of ferrocyanide concentration in the filtrate.

Non-templated resin was prepared by the same procedures as for the templated resin but without using the template.

Determination of recovery of the auxiliary surfactant

The concentration of quaternary ammonium surfactants (CTAC, DTAC) in the filtrate was determined by a spectrophotometric method¹¹ by measuring the absorbance of an ionically associated complex consisting of the quaternary ammonium and Orange II.

Determination of adsorbed ferrocyanide

A 0.100 g amount of the templated resin and 10 cm³ volume of 0.1 mmol dm⁻³ ferrocyanide solution (ionic strength, 0.1 mol dm⁻³, with potassium chloride) were taken into a plastic tube. The pH of the solution was adjusted with hydrochloric acid or potassium hydroxide solution. The relation of the amount of ferrocyanide adsorbed and the shaking time was examined: the adsorption amount became constant after 10 h shaking.

Table 1 The conditions of the resin synthesis

Run	Divinylbenzene/g	0.1 M HCl ^a /g	Oleylamine/mmol	Ferrocyanide/mmol	Auxiliary surfactant/mmol	V-65 ^b /g
1	9.2	100	5.0	0.20	—	0.1
2	26	130	1.0	0.50	4.0 ^c	0.5
3	13	65	0.5	0.25	2.0 ^d	0.25

a. With the amounts of hydrochloric acid used in this table, the pH values of the emulsion mixture are about 1.7 (run 1), 1.3 (run 2), and 1.3 (run 3). b. 2,2'-Azobis(2,4-dimethylvaleronitrile); an oil-soluble initiator. c. Auxiliary surfactant is cetyltrimethylammonium chloride (CTAC). d. Auxiliary surfactant is decyltrimethylammonium chloride (DTAC).

So the shaking time was fixed at 12 h in the present experiments. After the shaking, the pH of the suspension was measured and the resin was filtered with a filter (DISMIC-25, Toyo Roshi Kaisha, Ltd.). Then the ferrocyanide ion concentration in the filtrate was measured. The adsorption percentage of the ferrocyanide ion was calculated from the amount of ferrocyanide initially added.

Results and Discussion

Preparation of the resin using oleylamine alone

Before preparing resins by emulsion polymerization, the stability of the emulsion was investigated. In the present imprinting study, oleylamine was used as a surfactant, since oleylamine has a primary amino group which interacts with anions and has an unsaturated double bond for a possible copolymerization with matrix monomers. The emulsion state was visually examined for several different conditions after sonication for 3 min and successive standing for more than 12 h. In this examination, "stable emulsion" means that the emulsion was not broken down into oil and water within 12 h after the mixture was emulsified.

First, oleylamine was used alone as a surfactant. The polymerization condition of water/divinylbenzene (oil phase) ratio was fixed to be 10/1, and the ratio of the surfactant/divinylbenzene was investigated. As 10 cm³ of divinylbenzene were added into the aqueous surfactant solution at pH 2, the emulsion was observed to be stable when 5 mmol of oleylamine was used; under such conditions, the molar ratio of divinylbenzene/oleylamine was 14/1. When the amount of oleylamine was smaller than 5 mmol, the emulsion became more stable. So, the molar ratio of divinylbenzene/oleylamine was fixed at 14/1, and the pH dependence of the emulsion stability was investigated. Oleylamine was not well dispersed at pH values over 3, while the emulsion was not stable at pH values lower than 1; the latter effect is probably due to an increase in ionic strength. So the emulsion mixture suitable for polymerization was formed at pH values from 1 to 3. The effect of molar ratio of oleylamine/template on the emulsion stability was also investigated. At pH 2 and with divinylbenzene/oleylamine molar ratio of 14/1, the stable emulsion was observed when the molar ratio of oleylamine/ferrocyanide (template) was larger than 10.

Fig. 2 The adsorption percentage of ferrocyanide ion on the resin which was prepared from oleylamine and divinylbenzene. ●, non-templated resin; ○, templated resin; 10 cm³ of 1.0 mM potassium ferrocyanide solution (*I*=0.1 M (KCl)) and 0.100 g of resin were shaken for 12 h at 25°C.

Considering the conditions for stable emulsion formation as studied above, we determined the polymerization conditions as follows: the volume ratio of water/divinylbenzene=10/1, the molar ratio of divinylbenzene/oleylamine=14/1, pH=1–3 and the molar ratio of oleylamine/template=25/1. The oil soluble initiator, V-65, was used for these series of experiments.¹² Thus, the polymerization was performed with a mixture of DVB (9.2 g), 0.1 mol dm⁻³ HCl (100 g), oleylamine (5 mmol), potassium ferrocyanide (0.2 mmol) and V-65 (0.1 g) (run 1 in Table 1).

After the polymerization, the template recovery was measured and was found to be 50%. This result means that the template anion could not be well washed out. The adsorption behavior of ferrocyanide was measured at pH 2–10. As seen in Fig. 2, the non-templated resin adsorbed ferrocyanide more effectively than the templated resin did. This suggests that a considerable portion of amino groups (oleylamines) used in the resin preparation was not available for adsorption on the templated resin since 50% of the template anion remained on the resin surface and/or inside the resin particle, presumably forming ion-paired association complexes with the cationic amino groups. This indicates the failure or limitation of the surface imprinting procedure that uses a functional monomer as a sole surfactant.

Preparation of the resin using an auxiliary surfactant

In the former experiments, ferrocyanide could not be removed completely from the templated resin, so that the template effect was not observed. In the emulsion suspension leading to such resin preparations, ferrocyanide ions carrying four negative charges should be strongly associated with positively charged protonated oleylamine molecules on the oil/water interface. Some of such complexes seem to somehow be buried deep in the oil droplet and are unable to be dissociated by simple washing after polymerization, as experimentally suggested above.

The maneuver using a functional monomer as both surfactant (emulsion stabilizer) and cationic host (to interact with anionic guest) is also conceptually not simple in designing the surface imprinting polymerization system. A complexity exists in that the emulsion stability has to be sustained by the balance of surface activity of the resultant host-guest complex and the unreacted remainder of cationic surfactant host. In order to avoid such complexity, we thought of introducing a co-surfactant or an auxiliary cationic surfactant, which keeps the emulsion stable during polymerization and also hopefully can be removed by simple washing after polymerization. Such an auxiliary surfactant should be one that carries a permanent charge independent of pH conditions. In addition, it should be such that many interact with an anionic guest through an ion-pair type electronic force, but should not interact through dipolar interactions such as hydrogen bonding with the guest; a dipolar type interaction can not be excluded between ferrocyanide ion and the unprotonated oleylamine in DVB when the anion is in effect "extracted" in DVB by protonated oleylamines.

In the present work, CTAC was first selected for auxiliary surfactant, since CTAC is a quarternary ammonium salt with high surface activity. CTAC has a positive charge which allows an additional attraction with ferrocyanide ion. The stable emulsion was obtained in the acidic region when adding the equimolar amount of CTAC to that of oleylamine under the former conditions (run 1, Table 1). The oil/water mixture was easily emulsified by hand-shaking after adding CTAC.

The effect of the oil/water ratio on the emulsion stability was investigated in the presence of CTAC. CTAC stabilized the emulsion from the mixtures with an oil/water molar ratio less than 1/3. When the oil/water molar ratio was fixed to 1/5, the molar ratio of the oleylamine/CTAC=1/4 and the molar ratio of template/oleylamine=1/2 were found to be appropriate for emulsion polymerization. The templated resin was prepared using CTAC under the conditions of run 2 in Table 1. After the preparation of the resin, the recoveries of the template ion and CTAC were investigated. The recovery of the template was 46%, and those of CTAC at the templated resin and non-templated resin were 0.03 and 6.3%, respectively.

The ferrocyanide adsorption was investigated on the resin prepared in the presence of CTAC. The non-

Fig. 3 The adsorption percentage of ferrocyanide ion on the resin which was prepared from oleylamine, cetyltrimethylammonium chloride and divinylbenzene. ●, non-templated resin; ○, templated resin; 10 cm³ of 0.1 mM potassium ferrocyanide solution ($I=0.1$ M (KCl)) and 0.100 g of resin were shaken for 12 h at 25°C.

templated resin was found to adsorb ferrocyanide more efficiently than the templated resin (Fig. 3). This is probably due to the fact that ferrocyanide was not completely removed from the resin by washing; the ammonium sites on the resin are already occupied by bound-ferrocyanide. In addition, the non-templated resin adsorbed ferrocyanide over a wide pH region ranging from pH 2 to 12, although the amino group on the resin could be reasonably assumed to be unprotonated at pH values above 10. This phenomenon is to be explained by the presence of surface-bound CTAC which should adsorb anionic ferrocyanide over the entire pH region. Thus the stability of the emulsion was improved by using CTAC, but a problem evolved that CTAC could not be removed at all from the resin after polymerization.

DTAC as an auxiliary surfactant

In the former experiment, CTAC was tightly immobilized on the resin. This is to be ascribed to its long methylene chain, which presumably is anchored deep in the oil phase. As decyltrimethylammonium chloride (DTAC) has a shorter aliphatic chain than CTAC, the former was next employed as an auxiliary surfactant. Since DTAC makes an emulsion stable to an extent similar to the case with CTAC under the relevant polymerization conditions, the resin was synthesized using DTAC under conditions of run 3 in Table 1.

The recoveries of DTAC from the templated resin and the non-templated resin were now 85 and 100%, respectively, after washing. The recovery of DTAC was thus much higher than in the case of CTAC. The recovery of the template was 78%; a value which is also much improved from the case using CTAC. However, a small amount of the template anion still remained in the

Fig. 4 Scanning electron micrograph of the templated resin prepared from oleylamine, divinylbenzene, and decyltrimethylammonium chloride (DTAC).

Fig. 5 The adsorption percentage of ferrocyanide ion on the resin which was prepared from oleylamine, decyltrimethylammonium chloride and divinylbenzene. ●, non-templated resin; ○, templated resin; 10 cm³ of 0.1 mM potassium ferrocyanide solution ($I=0.1$ M (KCl)) and 0.100 g of resin were shaken for 12 h at 25°C.

resin. Both the templated and non-templated resins were spherical fine particles and had diameters in the 0.05–1.0 μm range (Fig. 4).

The adsorption of ferrocyanide on the resin prepared by using DTAC was investigated (Fig. 5). The templated resin adsorbed ferrocyanide 2 times greater under optimum conditions than the non-templated resin did. The template effect was clearly observed in this system. The amount of adsorption was dependent on pH; the maximum adsorption was observed at pH 3. Under alkaline and neutral pH conditions, there is no ferrocyanide ion adsorption for either templated or non-templated resins. As the pH of the solution is lowered, amino groups on the resin are protonated so that the adsorbed amount of ferrocyanide anion increases. However, when the pH value becomes lower than 3,

ferrocyanide ion is also protonated and changes its molecular structure; this leads to the diminished amount of adsorption. However, it is recalled that the detailed nature of the interaction between the ferrocyanide and amino groups is still not fully understood. A quantitative equilibrium consideration should be made on the binding process of ferrocyanide ion with the amino groups on the resin.

In conclusion, we prepared the inorganic anion-imprinted resin by the surface template polymerization, using oleylamine as a surfactant monomer, divinylbenzene as a matrix-forming monomer and DTAC as an auxiliary surfactant. Template effect was observed only when using DTAC; CTAC did not work well for this purpose. Use of oleylamine alone did not produce any template effect. With DTAC improving the emulsion stability, the complexes between protonated amino group of (protonated) oleylamine and ferrocyanide ion somehow more effectively fixed at the oil and water interface. DTAC was easily removed from the resin by washing with aqueous alkaline solution. The DTAC-assisted templated resin adsorbed ferrocyanide 2 times as much as the non-templated resin did.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan. A contribution from the Asahi Glass Foundation is also acknowledged.

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(Received March 4, 1996)

(Accepted May 2, 1996)