Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Zeng, Xiangfei and Murray, G. M.(1996) 'Synthesis and Characterization of Site-Selective Ion-Exchange Resins Templated for Lead(II) Ion', Separation Science and Technology, 31: 17, 2403 — 2418
To link to this Article: DOI: 10.1080/01496399608001056
URL: http://dx.doi.org/10.1080/01496399608001056

SEPARATION SCIENCE AND TECHNOLOGY, **31**(17), pp. 2403–2418, 1996

Synthesis and Characterization of Site-Selective Ion-Exchange Resins Templated for Lead(II) Ion

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ABSTRACT

Ion-exchange resins that exhibit enhanced selectivity for the Pb(II) ion have been synthesized by the copolymerization of styrene with lead(II) vinylbenzoate. Removal of the Pb(II) ion by acid washing left cavities templated for the Pb(II) ion. Sorption characteristics of the template resins have been studied over a large range of template loadings by varying the degrees of crosslinking, and with or without the use of ultrasonification during copolymerization. The capacity of the lead templated resins increases logarithmically with the increase of template complex content for levels of lead template content below 5 mol%. The complexation equilibrium constants of the resins reach a maximum at 3 mol% template complex content. The resins show marked preference for binding the Pb(II) ion. The selectivity, $\alpha_{Pb,Cd}$, has been found to be 174 for the 1 mol% templated polymer. In comparison to untemplated resins, the template process enhances the selectivity by roughly a factor of 3 over Cu^{2+} and 2 over Cd^{2+}. The selectivity enhancement is mainly ascribed to "coordination-geometry selectivity."

INTRODUCTION

The toxic effects of the exposure to lead on living organisms are well known. The use of coal and oil for combustion and, more significantly, the wide application of lead and its compounds in industrial processes has resulted in the deposition of a large amount of lead in the environment. Children are especially susceptible to lead exposure (1). Lead uptake by human beings results in accumulation in the bone, liver, kidney, and other parts of body, which affects the functioning of the hematopoietic, nervous,

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renin-angiotensin, and reproductive systems (2). The growing public awareness and interest in environmental quality combined with tougher governmental regulations have made it necessary to develop technologies for the analysis and control of lead contamination.

Many techniques have been proposed for the preconcentration, separation, and removal of metals from various natural and industrial fluids and wastewater. Among these methods the use of ion-exchange resins, especially chelating resins, has proven to be very efficient. However, the lack of selectivity of the available chelating resins has made separation processes complicated (3).

In the last decade the concept of molecular recognition has drawn the attention of chemists (4). By recording the shapes of template molecules in a matrix of polymer, it is possible to create new kinds of chemical sieves, sensors, and even catalysts (5). Many successful applications of molecular templating in the separation of organic compounds have been reported (6, 7). Much less work has been done for inorganic ions.

The application of the template approach to synthetic ion-exchange resins is based on the exact recognition characteristics of self-assembled molecules. Ligands and specific metal ions are congregated by self-recognition to form supermolecules during polymerization. The information of the specific metal ion encoded in the natural self-assembling process is retained even though the metal ions no longer remain in the polymeric construction (8, 9). Thus, high selectivity, a direct result of self-recognition, is achieved.

The two approaches used in the manufacture of templated ion-exchange resins vary in the order of synthesis. The first approach is the more traditional in that an existing resin, often in the form of porous beads, is first functionalized and the template ion is introduced. Next the template ion polymer complex is crosslinked further with the expectation that the subsequent removal of the template molecule will leave site-specific cavities (8). The second method begins with a template molecule and ligating molecules complex. The entire assemblage is copolymerized together with a suitable monomer for the polymeric backbone and a compatible crosslinking agent (9). Again, when the metal ions are removed, site-specific cavities remain. Although both methods have been demonstrated to produce resins with enhanced metal ion selectivity for the templated species, the second method is less likely to produce nonspecific exchange sites. However, the second method can lead to greater synthetic difficulty since it is harder to make all the monomers miscible in the correct proportions to make a useful resin.

In the present paper an ion selective resin templated for Pb(II) ion is reported. The resin was synthesized by the copolymerization of styrene monomers with lead vinylbenzoate complexes and crosslinked with divinylbenzene. Removal of Pb(II) ion by acid washing left cavities templated for Pb(II) ion. Chemical insights into the characteristics of a good coordination site were used to guide the synthesis of lead(II) ion templated resins. These insights include coordination number and geometry, ionic size and shape, as well as thermodynamic affinity. We have extended and amended the early methodologies used to synthesize templated resins by the application of *ultrasonification* during polymerization, by the use of a lower feed ratio of crosslinker, by exploring a much larger range of feed ratio of template complex, and by the selection of a functional group already selective for the Pb(II) ion.

EXPERIMENTAL

Reagents and Analysis

Unless otherwise indicated, materials were obtained from commercial suppliers and used without further purification. Vinylbenzoic acid (VBA) was freshly prepared from *p*-carboxybenzyl bromide by a Wittig reaction, mp = 142°C (lit. 142–143°C), yield 50% (10).

Trace metal analyses were performed using a Varian Model AA-1475/GTA95 Atomic Absorption Spectrometer with a graphite furnace atomizer, using single element Pb, Cu, and Cd lamps. Compositional analyses were performed using a Perkin-Elmer Model 5500B Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Standard solutions of the metal ions were prepared by dilution of 1000 ppm standard solutions purchased from Fisher Scientific. pH measurements were made on a model 350 Corning pH/Ion Analyzer. Infrared spectra (IR) were recorded on a Perkin-Elmer Model 1310 IR Spectrophotometer. Samples for IR analysis were prepared as KBr pellets after grinding with a Wig-L-Bug Amalgamator from Crescent Dental Manufacturing Company. Melting points were measured in Pyrex capillaries by using a Thomas-Hoover apparatus.

Lead vinylbenzoate complex was prepared by dissolving the freshly prepared VBA in a 1 N NaOH solution. Dilute HNO_3 was carefully added to adjust the solution pH to about 5. Any undissolved material was removed by filtration. A stoichiometric amount of 1 M $Pb(NO_3)_2$ was added with rapid stirring. A white precipitate formed immediately, and was collected by vacuum filtration after 15 minutes of stirring. The product was washed with acidified demineralized water (pH ~ 6.0), acetone, and finally toluene, then dried in a vacuum desiccator. The product yield was 44%; IR(KBr): 3400 (br, H_2O), 3050 (br), 1600–1700, 1510, 1400, 850 cm^{-1}; elemental analysis (ICP-AES), 41.8 ± 0.5% Pb (calc. 41.3%). Nickel vinylbenzoate complex was prepared by the same procedure as used for the lead vinylbenzoate complex: yield 86%.

Synthesis of Templated Polymers

The chemical steps involved in the synthesis of the Pb^{2+} templated resins is outlined in Fig. 1. A predetermined amount of template complex compound was weighed into a screw cap vial. For the untemplated polymers (blank), an equivalent amount of VBA was used. The matrix monomer styrene and the cross-linker divinylbenzene (DVB) were then added to the vial. The DVB concentration varied from 1 to 4 mol%. As little pyridine as possible was added to dissolve the complex compound mixture. Finally, 1 mol% of the initiator, azobisisobutyronitrile (AIBN), was added, and the solution was thoroughly mixed by a Vortex-Genie mixer for about 1 minute. Nitrogen was bubbled through the mixture to remove oxygen from the solution, and the vial was filled with nitrogen to serve as an inert atmosphere. The vial was then sealed by closing it with a screw cap, placed in an ultrasonic bath, and sonicated for ca. 4 hours. The vial was moved to an oil bath at 60°C for another 20 hours to complete the polymerization.

The polymerized product was ground as finely as possible in a stainless steel mill vial with a Wig-Bug Model 6 ball mill after first freezing with liquid nitrogen. Ground polymer was washed with acetone, then slowly exposed to water by subjecting it to a gradient elution of acetone with a

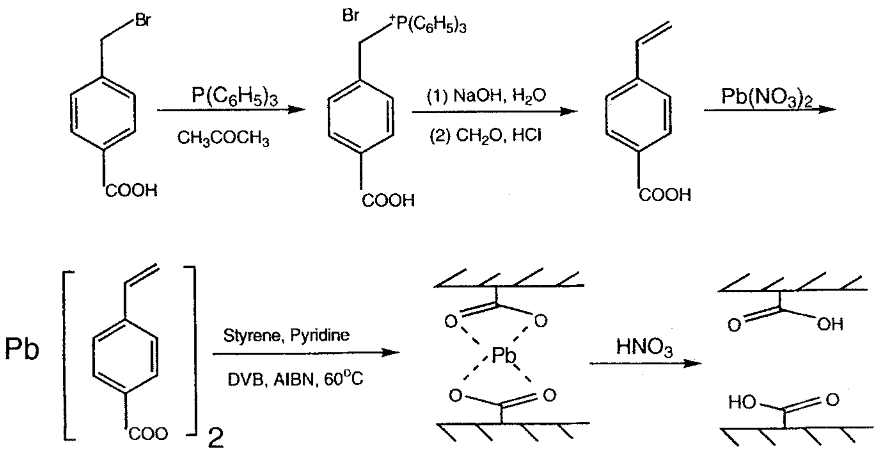

FIG. 1 Synthesis route for Pb^{2+} templated resins.

steadily increasing water content. Hydrated polymer was washed with 1 N HNO_3 until no Pb^{2+} was detected in the wash solution. The hydrogen form of the polymer was washed with water to remove excess acid until the pH of the wash solution became greater than 4.

Metal-free templated resins were loaded with metal ion by the following procedure. The polymers were weighed into 30 mL glass fritted Buchner funnels and a solution of 3.0 mL of a 0.1 M metal nitrate solution diluted to 15.0 mL was allowed to drip through. This process was repeated, and the polymers were left standing overnight in contact with the adsorbed metal ion solution. The resulting resins were rinsed with water until the eluted water was found to be metal free. After air drying, the samples were weighed into plastic Nalgene bottles and combined with water. The pH of each mixture was adjusted to 2.6–2.8 by addition of dilute HNO_3. The mixture was equilibrated at 30°C for 24 hours. A portion of the solution was removed for the determination of acid and metal ion content. The pH of the remaining solution was further adjusted to less than 1.0 by addition of concentrated nitric acid. After a second overnight equilibration, the concentration of the metal ion in solution was determined by AAS. After washing with deionized water, the resins can be reused.

The metal ion recovery of the resins was determined by loading the resin with a predetermined, accurate amount of metal ion, which should be lower than the capacity of the resin. After air drying, the sample was weighed into plastic Nalgene bottles and combined with water. The solution pH was adjusted to less than 1 by addition of concentrated nitric acid. After an overnight equilibration at 30°C, the concentration of metal ion in solution was determined by AAS.

RESULTS AND DISCUSSION

The ligand was selected primarily on the basis of thermodynamic affinity. The selected ligand coordinates Pb^{2+} ion with a large affinity, and there is a maximum difference in affinity for typical competing metal ions. A maximum affinity is desirable for stability under the polymerization conditions, and a maximum difference in affinity for competing metal ions aids selectivity. A thorough examination of the chemical literature (11) led to the choice of 4-vinylbenzoic acid (VBA).

The effect of the crosslinker on the exchange capacity, DVB, was determined by measurement of the capacities of resins with varying degrees of crosslinking and was found to be proportional to the DVB mole percent composition of the polymer. The results of the measurements are summarized in Table 1. The capacity reaches a maximum around 2 mol% DVB. This value is much lower than that of a polystyrene-sulfonic acid resin

TABLE 1
The Effect of Crosslinking on Lead Ion Capacity

Polymer ID	Complex (mol%)	DVB (mol%)	Capacity[a] (μmol/g)
P-1	1	1	0.179 ± 0.01
P-2	1	2	0.231 ± 0.05
P-3	1	4	0.127 ± 0.02

[a] Determinate error.

(PSSA). It is reported that PSSA resins reach a capacity maximum around 8 to 12 mol% DVB (12). This difference may be due to the preorganization of ligands in the template process, which is particularly sensitive to the variation of the local environment. Considering the homogeneity and flexibility of the polymers produced, an amount of 1–2 mol% DVB was used in following work.

The dissolution of the complex/monomer mixture has historically been a difficult step (8). In this study, ultrasonification was used in copolymerization with the expectation that ultrasonification may result in more complete and more uniform incorporation of the metal ion complex in the copolymer. In addition, ultrasonification has the serendipitous effect of maintaining the temperature of 60°C which is the recommended temperature for chemically initiated free radical polymerization using AIBN. The experimental results show that for otherwise identical polymers, 1% of template complex and 2% of DVB content, the capacity of resin was increased from 0.146 μmol/g in a mineral oil bath to 0.231 μmol/g by use of an ultrasonic bath. The visual homogeneity of the copolymers produced was also improved by the use of ultrasonification.

Metal Ion Capacity and Equilibrium Constant

Templated polymers were subjected to batch mode equilibration conditions (Fig. 2). The data acquired from the procedure described above were used in the following equations to calculate the metal ion capacity and the equilibrium constant:

$$\text{Capacity} = \frac{[M^{2+}]_1 V_2 + [M^{2+}]_2 V_3}{W_1} \tag{1}$$

$$K = \frac{[H^+]^2(\text{capacity} - [M^{2+}]_1 V_1/W_1)}{[M^{2+}]_1(2[M^{2+}]_1 V_1/W_1)^2} \tag{2}$$

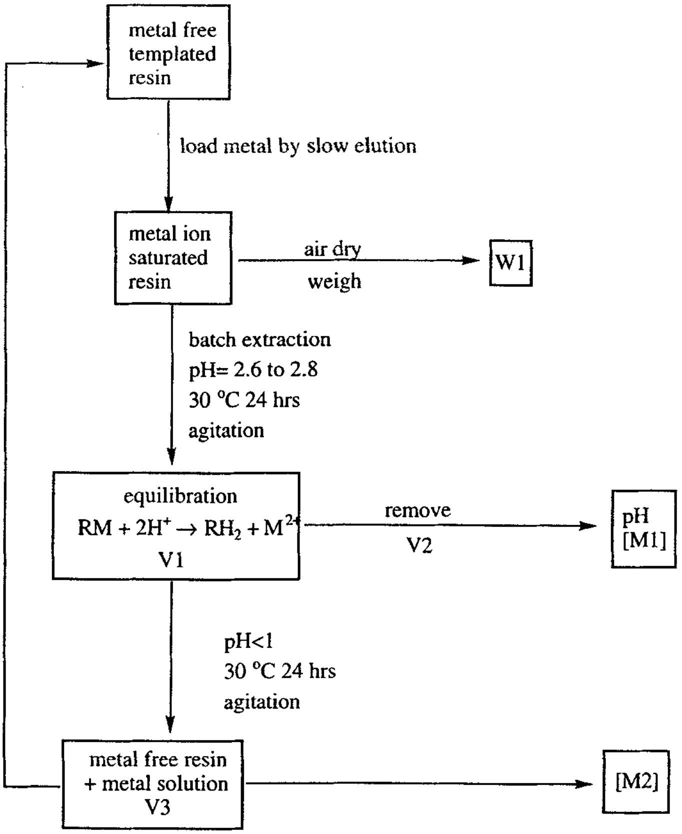

FIG. 2 Batch mode equilibrium conditions for the characterization of resins.

for the reaction

$$M^{2+} + 2HR \rightarrow MR_2 + 2H^+ \tag{3}$$

where W_1 is the amount of dry polymer weighed into the vial; $[M^{2+}]_1$ and $[M^{2+}]_2$ are the concentrations of the metal ion in the solutions for the first and second overnight equilibrations; $[H^+]$ is the concentration of acid in solution; and V_1, V_2, and V_3 are the volumes of the solution for first overnight extraction, the solution removed after first overnight extraction, and the solution for second overnight extraction, respectively.

The metal ion capacities of polymers with differing amounts of template complex are summarized in Table 2. A plot of lead capacity versus tem-

TABLE 2
The Effect of Template Complex Content on the Lead Ion Capacity

Polymer ID	Complex (mol%) (mol% ligand)[a]	DVB (mol%)	Lead capacity[b] (μmol/g)
P-11	(3)	1	0.0599 ± 0.00
P-0	(4)	1	0.112 ± 0.006
P-12	(5)	1	0.198 ± 0.01
P-1	1	1	0.179 ± 0.01
P-5	2	1	0.373 ± 0.01
P-6	3	1	0.752 ± 0.03
P-7	4	1	2.128 ± 0.08
P-8	5	1	3.065 ± 0.07
P-9	7	1	5.741 ± 0.05
P-10	10	1	8.035 ± 0.07

[a] Equivalent mole percent of ligand in untemplated polymer.
[b] Determinate errors.

plate complex content is illustrated in Fig. 3. A remarkable feature of the lead templated resins is that increasing the mole fraction of template complex produced a logarithmic increase in the resin capacity for the level of template content below about 5%. In like fashion, the untemplated polymers gave a similar logarithmic increase as the ligand monomer contents increased from 3 to 5%, but the plot for untemplated polymers lagged about one logarithmic unit below the plot for the templated polymers. The increase in capacity of the untemplated polymers is likely due to the increase of the accessible binding sites. If this is the case, a 10-fold higher capacity of templated polymer over untemplated polymer must result from the template process.

The grinding of the bulk polymer results in a powder consisting of small, roughly spherical particles. These particles are sieved to give a sample of uniform size. The theoretical capacity is the exchange capacity expected if the entire amount of template complex in the polymer feed is utilized for exchange. The measured capacity of the resins is considerably smaller than the theoretical capacity, since much of the template complex is buried inside the particle. A semiquantitative estimate of the active or accessible depth of the surface of the polymer particles can be calculated on the assumption that all of the template complex used in the copolymerization reaction is homogeneously dispersed in the bulk polymer. The calculation is based on the following equations.

$$V = \frac{4}{3}\pi r^3; \qquad dV = 4\pi r^2 dr; \qquad \frac{dV}{V} = 3\frac{dr}{r} \tag{4}$$

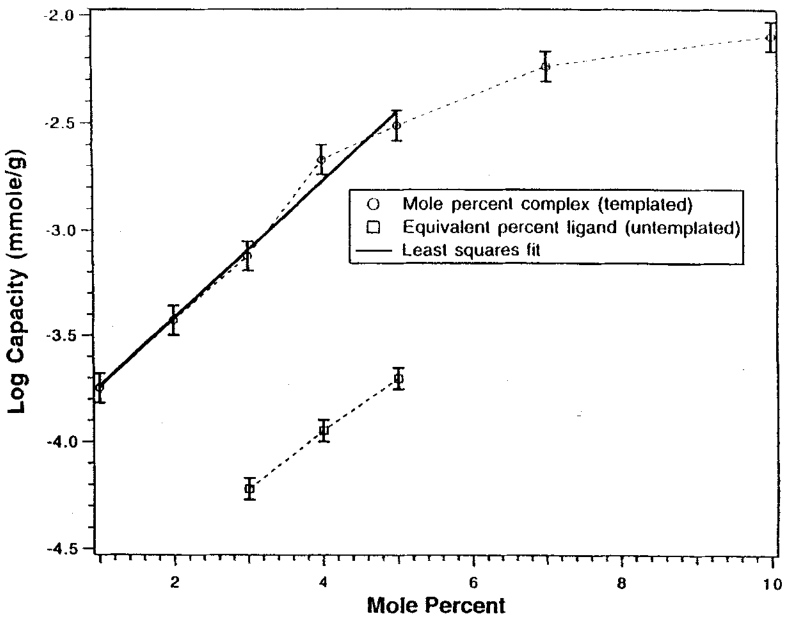

FIG. 3 Capacity of resins as a function of template content (monomer ligand content).

The calculation consists of assigning the measured capacity as the portion of the volume accessible to exchange (*dV*), the theoretical capacity to the total volume (*V*), and solving for the depth (*dr*) associated with the effective exchange volume. The experimental value for the capacity of the 5 mol% resin is 3.1 μmol/g. The amount of complex loading based on the polymer feed is 418 μmol/g. The volume of 100 mesh beads (r = 0.0100 in. = 2.54×10^{-2} cm = 254 μm) is calculated to be 7.45×10^{-3} cm^3. The portion of the surface volume equal to the experimental exchange capacity yields an active surface depth of about 6.3×10^{-5} cm or 630 nm. This depth corresponds to a distance of the order of 10 template complex molecules. The model suggests that the polymer particles can be viewed as similar to a interwoven mass of fibers whose frayed ends are accessible for ion exchange.

The above hypothesis was examined using a scanning electron microscope equipped with an x-ray analyzer. The electron micrograph of the resin particles (Fig. 4) shows that the sieved particles are of fairly uniform size with a diameter of slightly more than 200 μm. Analysis of x-rays emitted by the particles shows that at low accelerating voltages, no lead appears to be present. As the acceleration voltage is increased, resulting

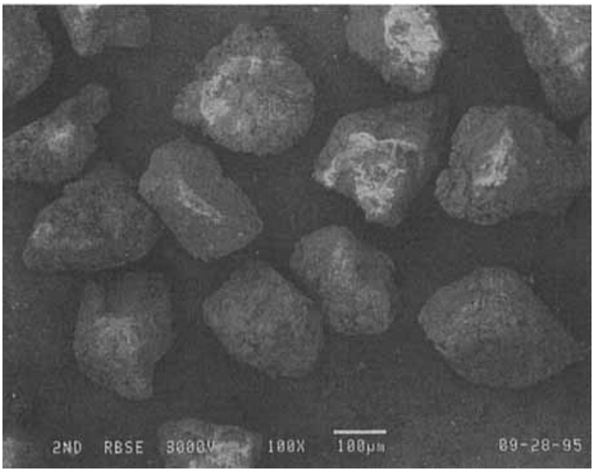

FIG. 4 Scanning electron micrograph of 100 mesh resin particles (scale bar is 100 μm).

in a deeper penetration of the electron beam, a clear lead signal is obtained (Fig. 5). The micrograph reveals a rough granular structure that may tend to give the calculations a low estimate on the surface area of the particle. This may suggest that the depth of exchange is somewhat less than the depth calculated.

When the template content is higher than 5%, the capacity increases more slowly (linearly). Examination of the physical appearance of the polymers shows that up to 5 mol% template complex, a transparent homogenous copolymer is formed. For template contents greater than 5%, the polymer appearance changes to a more granular texture. The change in physical form with increasing amounts of template complex suggests that the complexes were no longer distributed evenly in the styrene–DVB matrix or an entirely different set of physical characteristics was being produced (crystallinity). A reason for the relatively low capacity for heterogeneous polymers may be that more of the functional groups are buried in the interior of the polymer and are physically inaccessible to the metal ions and eluents. Heterogeneous polymers have been shown to yield low fractional recovery by Shea (13). The fractional recovery of template molecules had been reported to be only 24% for DVB polymers (13).

Recovery values were determined in a chromatographic mode. Dynamic capacity is usually lower than the effective capacity because equilibrium may not be completely attained under chromatographic conditions. The lead ion was loaded in amounts of the effective capacity. Recoveries were

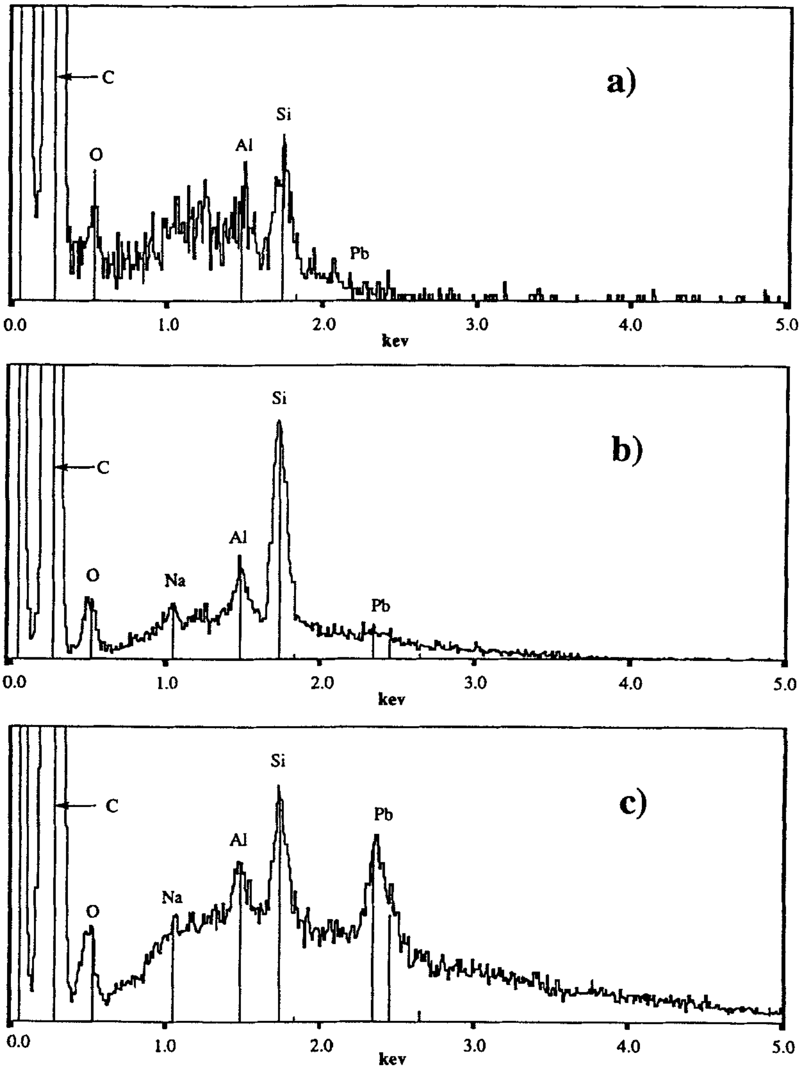

FIG. 5 Electron beam x-ray fluorescence spectra of the resin particles obtained at different acceleration voltages; a) 3 kV, b) 7 kV, and c) 9 kV.

found to be 100% for 2 mol% Pb ion templated resin and 88% for 5 mol% Pb ion templated resin. The smaller recovery in 5 mol% templated polymer suggests that the kinetics of the process for this resin are more complex and relatively slower.

The equilibrium constants of the polymers are presented in Table 3. The equilibrium constant, log K = 5.21 for the 3 mol% template polymer, implies that the templated polymer is capable of strongly binding Pb^{2+}, even in the acidic region. Unlike the capacity values, the equilibrium constants reach a maximum at template complex of 3%. When the template content is higher than 3 mol%, K decreases as template content increases. This decreasing trend of equilibrium constants with template content was reported by Harkins and Schweitzer (9, 14). They found that equilibrium constants were inversely related to capacities for their nickel and copper ion templated polymers.

The equilibrium constant was determined using Eq. (3) as follows:

$$K = \frac{[R_2M][H^+]^2}{[M^{2+}][RH]^2} = \left(\frac{[R_2M]}{[M^{2+}][R^-]^2}\right) \times \left(\frac{[R^-]^2[H^+]^2}{[RH]^2}\right) = K_s \times K_a^2 \qquad (5)$$

where K_s is the association constant of the metal ligand complex and K_a is the dissociation constant of the polymeric acid.

Owing to the different Donnan potentials, both K_a and K_s will vary with template content. In general, K_s increases and K_a decreases with increasing template content. The equilibrium constants are proportional to K_s and to the square of K_a. Therefore, the equilibrium constants normally decrease as template content increases, as seen in the Harkins case (14). Furthermore, at high levels of template content, increasing template content may directly lower the K_s because the template assembly would make a significant contribution to the gross structural rigidity of the polymeric solid, thus the hydrolysis of the template ion may disrupt the three-dimensional lattice and the micro-environment of the binding sites (13). No

TABLE 3
The Effect of Template Complex Content on the Equilibrium Constant

Polymer ID	Complex (mol%), (mol% ligand)[a]	DVB (mol%)	Log K
P-0	(4)	1	2.31
P-1	1	1	4.93
P-5	2	1	4.83
P-6	3	1	5.21
P-7	4	1	3.67
P-8	5	1	3.29
P-9	7	1	3.09
P-10	10	1	3.07

[a] Equivalent mole percent of ligand in untemplated polymer.

matter which reason is the major one for the decrease of equilibrium constants, the increase of equilibrium constants up to 3% template content may be attributed to a significant template effect due to the preorganization of ligands and size-match.

Selectivity

Metal ion recognition and selective binding ability of the templated polymer are two of its major properties and are evaluated by both single ion exposure and multiple ions exposure experiments. The selectivity values are calculated according to following equation:

$$\alpha_{Pb^{2+},M^{2+}} = \frac{\text{capacity } Pb^{2+}}{\text{capacity } M^{2+}} \tag{6}$$

Table 4 summarizes the results for single ion exposure experiments. Cd^{2+} and Cu^{2+} were selected as competing ions due to their relative high stability with benzoic acid (11). In addition, Cd^{2+} and Cu^{2+} are general interferences in Pb^{2+} determination (15). Examination of Table 4 reveals that resins prepared with benzoate ligands are already selective for Pb^{2+}. The template process enhances the selectivity by roughly a factor of 2 over Cd^{2+} and 3 over Cu^{2+}.

The selectivity of the untemplated polymer implies that the "intrinsic" stability of the $Pb(VBA)_2$ complex may play an important role in selectivity. It is also noted that the capacities of polymers for Cu^{2+} are higher than for Cd^{2+}, despite the fact that the ionic radius of Cd^{2+} (0.095 nm) is closer to Pb^{2+} (0.118 nm) than the ion radius of Cu^{2+} (0.073 nm).

TABLE 4

Capacity and Selectivity of Untemplated and Pb Templated Resins toward Pb, Cu, and Cd in Single Exposure Experiments

Polymer ID	Complex (mol%), (mol% ligand)	Rebinding ion	Metal capacity (μmol/g)	Selectivity $\alpha_{Pb,M}$
P-0	(4)	Pb	0.112	
P-0	(4)	Cd	0.00112	100
P-0	(4)	Cu	0.0233	5
P-1	1	Pb	0.179	
P-1	1	Cd	0.00103	174
P-1	1	Cu	0.0113	16
P-8	5	Pb	3.065	
P-8	5	Cd	0.0191	161
P-Ni	3	Pb	0.0467	
P-6	3	Pb	0.751	

However, the intrinsic stability of the metal ion–ligand complex cannot be the only reason for selectivity. A Ni^{2+} templated polymer was synthesized for comparison. Though the stability constant of $Pb(VBA)_2$ is larger than that of $Ni(VBA)_2$, the resin shows a capacity for Pb^{2+} that is 16 times lower than that of Pb^{2+} templated polymer under the same conditions. It is noted that the lead capacity of Ni^{2+} template polymer is even lower than that of the untemplated one, which suggests that the template process may produce binding sites complimentary to Ni^{2+} ion and less accessible to Pb^{2+} ion. There are two possible explanations for the selectivity enhancement. One is the "hole-size selectivity." That is, the size of Pb^{2+} ion exactly fits the cavity size of Pb^{2+} templated polymer but is too large to fit the cavity of Ni^{2+} templated polymer. This "hole-size selectivity" does have an impact on selectivity but cannot be the dominate reason. As mentioned above, Cd^{2+} has an ion size closer to Pb^{2+} and still the resin exhibits a lower capacity. The second reason is that the Pb^{2+} template polymer can provide the ligand groups arranged in a suitable way required for coordination of Pb^{2+} ion. This "coordination-geometry selectivity" may dominate in the selectivity enhancement. A coordination environment complimentary to the metal ion would, of course, result in favorable bonding interactions, while the "wrong" ion can produce repulsive interactions and is inaccessible to binding site. Dahl et. al. (16) found that the orientation of the binding sites is the primary source of binding selectivity in their metal-complexing polymers.

The results for multiple ion exposure experiments are summarized in Table 5. Examination of Table 5 reveals that the selectivity values for multiple ion exposures are smaller than those for single exposures. This fact suggests that Cd^{2+} and Cu^{2+} can compete with Pb^{2+} for some binding sites. The competitive binding may be either a kinetic effect or a thermodynamic one. The majority of the binding sites are not accessible to Cd^{2+} and Cu^{2+} because single exposure experiments do not exhibit high capaci-

TABLE 5

Capacity and Capacitive Selectivity of Untemplated and Pb Templated Resins toward Pb, Cu, and Cd in Multiple Exposure Experiments

Polymer ID	Pb capacity (μmol/g)	Cd (μmol/g)	$\alpha_{Pb,Cd}$	Cu (μmol/g)	$\alpha_{Pb,Cu}$
P-0	0.162	0.00463	35		
P-1	0.119	0.00220	54		
P-5	0.107	0.00120	90	0.00931	12

ties for these ions. There may be a number of different kinds of sites, each with a unique affinity for each metal ion. The majority of the sites may exhibit the strongest binding with ion used as template, while a minority of sites exhibit high affinity for other ions. The higher the abundance of sites that are preorganized for templated ion, the higher the selectivity will be.

CONCLUSIONS

Lead ion selective resins containing carboxylic acid ligands in a PS–DVB copolymer matrix have been synthesized by the template synthesis method. Characterization of the resins shows that the selectivity of the templated resins for original template Pb^{2+} ion is considerably higher than that of the untemplated resins. The selectivity, $\alpha_{Pb,Cd}$, has been found to be 174 for the 1 mol% templated polymer. The high preference for binding the original template ion demonstrates that the template method indeed makes the cavities lined by functional groups retain some of the coordination and size information originally present in the template assembly.

The factors that affect selectivity are the intrinsic thermodynamic affinity and preorganization of ligands in the binding cavity as well as the size of the cavity. The results of the metal ion rebinding studies suggest that preorganization of the ligands may be the major explanation for the selectivity enhancement of templated resins. The evidence of the importance of coordination geometry selectivity may be of use in the design of synthetic polymers that are selective for other metal ions.

A remarkable feature of the lead templated resins is that increasing the percent complex produces a logarithmic increase in the resin capacity for levels of complex below 5 mol%. When the template complex is greater than 5 mol%, the capacity increases linearly. The trend observed for equilibrium constants reached a maximum at 3 mol% of the template complex.

Ion-exchange synthesis procedures based on the template synthesis method seem to offer unexplored opportunities and may deserve serious attention. Scientists concerned with environmental analysis and decontamination may soon have a selective means to remove or measure hazardous metal ions. This work shows that the template synthesis method may be a simple and efficient way to synthesize high selectivity resins. These synthetic resins should have many applications in environmental science.

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Received by editor November 20, 1995