Polymer Pendant Ligand Chemistry. 3. A Biomimetic Approach to Selective Metal Ion Removal and Recovery from Aqueous Solution with Polymer-Supported Sulfonated Catechol and Linear Catechol Amide Ligands[1a]

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The design of organic ligands to selectively remove and recover metal ions from aqueous solution is a new and important area of environmental inorganic chemistry. One approach to designing organic ligands for these purposes is to use biological systems as examples for selective metal ion complexation. Thus, we report on our results on the synthesis of several biomimetically important polymer-supported, sulfonated catechol (**PS-CATS**), sulfonated bis(catechol) linear amide (**PS-2–6-LICAMS**), and sulfonated 3,3-linear tris(catechol) amide (**PS-3,3-LICAMS**) ligands that are chemically bonded to modified 6% cross-linked macroporous polystyrene-divinylbenzene beads (**PS-DVB**) for selective removal and recovery of environmentally and economically important metal ions from aqueous solution, as a function of pH. The Fe^{3+} ion selectivity was dramatically shown for **PS-CATS**, **PS-2–6-LICAMS** and **PS-3,3-LICAMS** polymer beads in competition with a similar concentration of Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Mg^{2+}, Al^{3+}, and Cr^{3+} ions at pH 1–3, while metal ion selectivity could be changed at higher pH values in the absence of Fe^{3+} (for example, Hg^{2+} at pH 3). Rates of removal and recovery of the Fe^{3+} ion with the **PS-CATS**, **PS-2–6-LICAMS** and **PS-3,3-LICAMS** polymer beads were also studied as well as relative equilibrium selectivity coefficient (K_m) values for all metal competition studies. The chelate effect for the octahedrally predisposed **PS-3,3-LICAMS** polymer pendant ligand, as shown for the homogeneous ligand, appears to be the reason that this polymer pendant ligand has a more pronounced selectivity for Fe^{3+} ion in comparison to the **PS-CATS** polymer beads, while the square planar predisposed **PS-2–6-LICAMS** series of polymer pendant ligands were more selective to divalent metal ions, Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, and Mg^{2+}, than either **PS-CATS** or **PS-3,3-LICAMS**, although Fe^{3+} ion still dominated in competition with other divalent and trivalent metal ions. It is interesting to note that changing the cavity size from two CH_2 groups to six CH_2 groups in the **PS-2–6-LICAMS** polymer pendant ligand series did not affect the order of metal ion selectivity.

There is a growing need, in the relatively new area of environmental inorganic chemistry, to design organic ligands in order to selectively remove and recover environmentally and economically important metal ions from aqueous solution. One approach to designing organic ligands for these purposes is to look at biological systems for examples on selective metal ion complexation.[2] Thus, the biomimetic approach has provided an array of organic ligands that fulfill the requirements of high selectivity to certain metal ions, especially for the Fe^{3+} ion, due to their preference for octahedral coordination.[3]

However, the selective removal and recovery of metal ions from environmental aqueous solutions must be cost-effective and, therefore, the anchoring of these selective ligands to solid supports is mandatory for continual reuse.[4] In previous polymer pendant ligand chemistry studies, we reported on the synthesis of a polymer bound catechol ligand for non-aqueous solution metal ion complexation.[5] Since diffusion of the metal ions into the hydrophobic polymer macropore/gel phases is so important, it is highly desirable to modify the catechol ligands with a hydrophilic group, such as a sulfonic acid substituent, to increase the kinetics and capacities of metal binding in aqueous solution, while also preventing the catechol ligand from being oxidized to the weaker metal binding *o*-quinone ligand.

With regards to a previous synthesis of a polymer pendant sulfonated catechol ligand, Griesbach and Lieser[6] described a

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(2) Martell, A. *Organic Sequestering Agents*; John Wiley & Sons, Inc: New York, 1959; Chapter 8, p 416.

(3) (a) Raymond, K. N. *Coord. Chem. Rev.* **1990**, *105*, 135 and references therein. (b) Stack, T. D. P.; Karpiskin, T. B.; Raymond, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1512. (c) Stack. T. D. P.; Hou, Z.; Raymond, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 6466. (d) Pierpont, C. G.; Lange, C. W. The Chemistry of Transition Metal Complexes Containing Catechol and Semiquinone Ligands. In *Progress in Inorganic Chemistry*, Karlin, K. D., Ed.; John Wiley & Sons Publishers: New York, 1994; Vol. 41, p 331.

(4) (a) Warshawsky, A. Modern Research in Ion Exchange. In *Ion Exchange: Science and Technology*; Rodrigues, A., Ed.; Martinus Nijhoff Publishers: Dordrecht, The Netherlands, 1986; p 67. (b) Blasius, E.; Brazio, B. Chelating Ion Exchange Resins. In *Chelates in Analytical Chemistry*; Flaschka, H. A., Barnard, J. A., Eds; Marcel Decker: New York, 1967.

(5) (a) Fish, R. H.; Tannous, R. S. *Inorg. Chem.* **1985**, *24*, 4456. (b) Fish, R. H.; Thormodsen, A. D.; Belser, R. Jr.; Friedman, G.; Reynolds, J. G. *React. Polym.* **1987**, *6*, 255.

(6) (a) Griesbach, M.; Lieser, K. H. *Fresenius Z. Anal. Chem.* **1980**, *302*, 109. (b) Griesbach, M.; Lieser, K. H. *Fresenius Z. Anal. Chem.* **1980**, *302*, 181. (c) Griesbach, M.; Lieser, K. H. *Angew. Makromol. Chem.* **1980**, *90*, 143.

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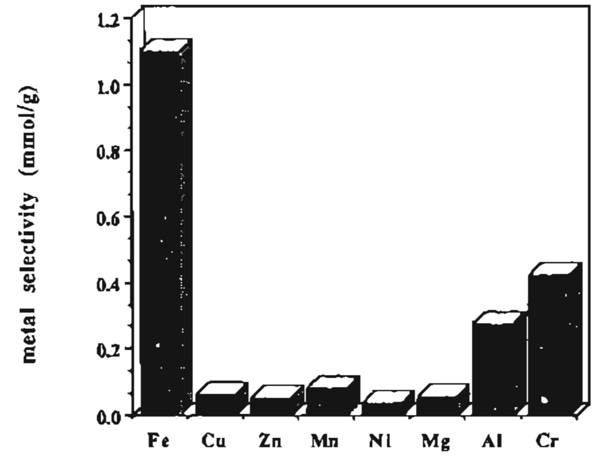


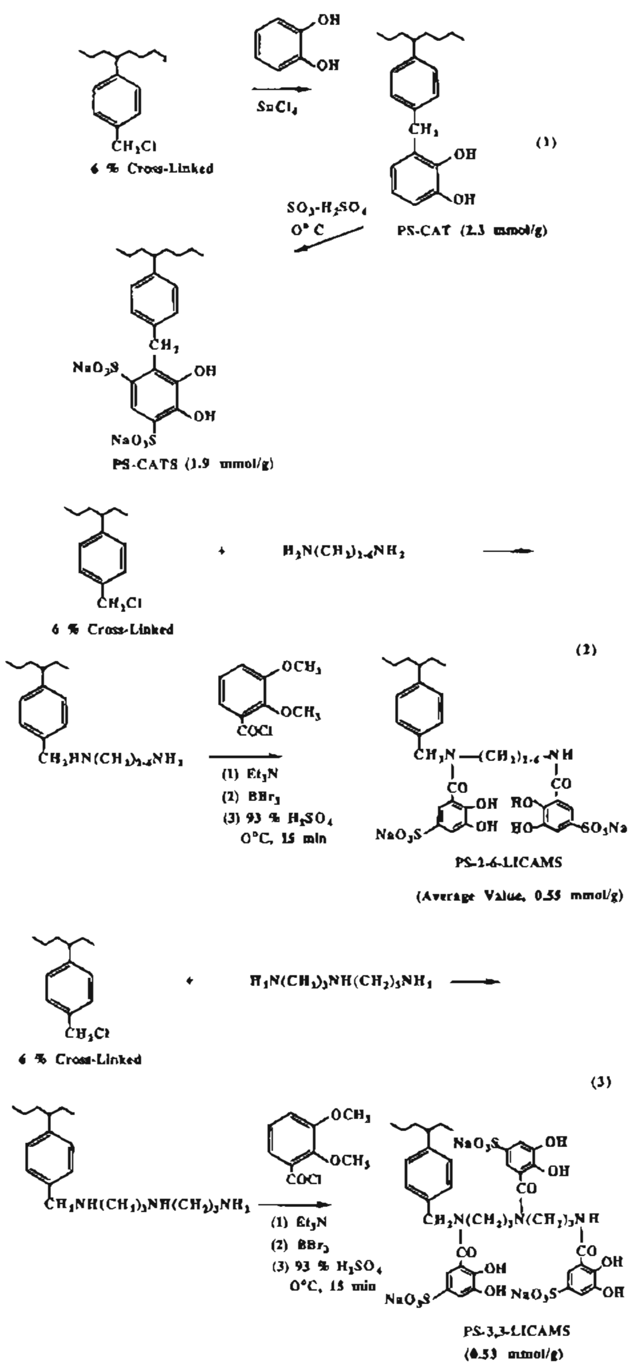
Figure 1. Metal Selectivity of the **PS-CATS** Ligand (1.9 mmol/g) at pH 2.1.

number of organic ligands that were chemically bound to 2–3% cross-linked polystyrene–divinylbenzene beads (**PS-DVB**) via an azo group linkage reaction. Among the many ligands attached using this procedure, the 3,5-disulfonatecatechol ligand (**TIRON**) was also described. However, we feel that the stability of the azo linkage at low pH is suspect, while the metal ion selectivity found for the polymer-supported azo-linked **TIRON** ligand appears different from the data we report in this paper for a polymer-supported methylene-linked **TIRON** ligand.

Therefore, we wish to present our recent results on the synthesis of several biomimetically important sulfonated catechol (**PS-CATS**), sulfonated 2–6-linear catechol amide (**PS-2–6-LICAMS**), and sulfonated 3,3-linear catechol amide (**PS-3,3-LICAMS**) ligands that are chemically bonded to modified 6% cross-linked polystyrene–divinylbenzene beads (**PS-DVB**) for selective removal and recovery of environmentally and economically important metal ions from aqueous solution, as a function of pH. To our knowledge, this is the first reported example of the synthesis of sulfonated linear catechol amide ligands that are chemically bonded to modified **PS-DVB** beads for selective metal ion complexation from aqueous solutions. We will demonstrate that the concept of predisposition of a polymer-supported pendant ligand, as demonstrated for the solvent soluble versions,[3] allows for a far greater selectivity to Fe^{3+} ions in comparison to a non-predisposed ligand; i.e., **PS-3,3-LICAMS** ≫ **PS-CATS**, while the **PS-2–6-LICAMS** ligands were more selective to divalent metal ions than either the **PS-3,3-LICAMS** or **PS-CATS** ligands.

Results

Synthesis of PS-CATS, PS-2–6-LICAMS and 3,3-LICAMS Polymer Pendant Ligands. The precursor polymer pendant ligands, **PS-CAT**, **2–6-LICAM**, and **3,3-LICAM**, were synthesized by standard techniques[5,7] using a 6% cross-linked chloromethylated **PS-DVB** polymer, while selective sulfonation of these precursor polymer-supported catechol ligands was accomplished with 23% fuming sulfuric acid (**PS-CAT**, 0 °C, 3h; 25 °C, 2h), or for **2–6-LICAM/PS-3,3-LICAM** with 93% sulfuric acid (0 °C, 15 min; 25 °C, 30 min). Elemental analysis, FT-IR spectra, and, in selected cases, 100 MHz CP-MAS ^{13}C NMR studies (See Experimental Section), all supported the structures for the **PS-CATS** (1.9 mmol/g), **2–6-LICAMS** (average value, 0.55 mmol/g) and **PS-3,3-LICAMS** (0.53 mmol/g) polymer pendant ligands bound to modified 6% **PS-DVB** beads (eqs 1–3).



PS-CATS Metal Ion Selectivity, Relative Selectivity Coefficient Values (K_m), and Kinetic Studies, as a Function of pH. Since the homogeneous versions of the **PS-CATS** (known commercially as **TIRON**) and **PS-3,3-LICAMS** ligands have been shown to selectively complex Fe^{3+} ion in aqueous solution,[8,9] we decided to study the selectivity of the polymer pendant versions with Fe^{3+} ion (0.02 M) in the presence of a similar concentration of Cu^{2+}, Zn^{2+}, Mn^{2+}, Al^{3+}, Ni^{2+}, Cr^{3+}, and Mg^{2+} ions. Figure 1 shows the selectivity of the **PS-CATS** polymer to Fe^{3+} ion in the presence of the above-mentioned

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(7) Butler, A.; de la Rosa, R.; Zhou, Q.; Jhanji, A.; Carrano, C. J. *Inorg. Chem.* **1992**, *31*, 5072 and references therein.

(8) Reference 2, p 515.

(9) The 3,3-LICAMS ligand was shown in our studies to be highly selective to Fe^{3+} ion in aqueous acidic solutions (unpublished results of S.-P.H.). For similar Fe^{3+} ion selectivity for a 3,3-LICAMS analog, 3,4 -LICAMS, see: Weitl, F. L.; Harris, W. L.; Raymond, K. N. *J. Med. Chem.* **1979**, *22*, 1281.

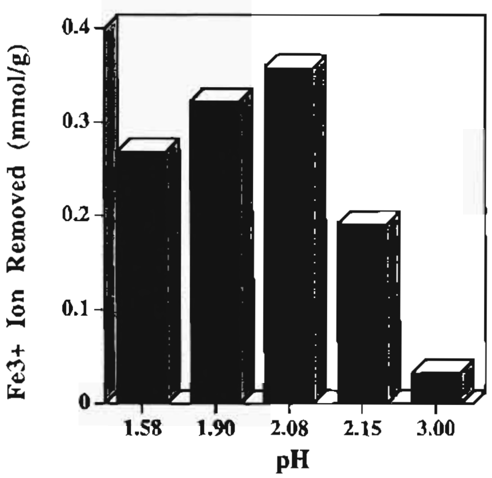
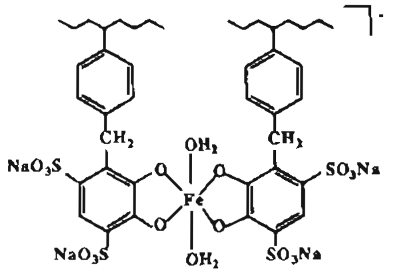


Figure 2. pH profile of Fe^{3+} removal by the **PS-CATS** ligand. Samples of 100 mg of **PS-CATS** polymer beads were allowed to react with 10 mL of a 0.02 M Fe^{3+} solution with rigorous shaking for 30 min at different pH values.

metal ions at pH 2.1, where maximum Fe^{3+} ion removal from aqueous solution was observed (Figure 2). The relative equilibrium selectivity coefficients (K_m values) were found,[10] with Mg^{2+} as the standard, to be: (M^{n+}/Mg^{2+}); 171 (Fe^{3+}); 66 (Cr^{3+}); 43 (Al^{3+}); 5.0 (Mn^{2+}); 0.8 (Cu^{2+}); 0.8 (Zn^{2+}); 0.3 (Ni^{2+}); 1 (Mg^{2+}) and further demonstrates **PS-CATS** high selectivity for Fe^{3+} in competition with other metal ions.

The ratio of **PS-CATS/Fe^{3+}** at equilibrium was found to be close to 2:1, presumably with H_2O molecules occupying the other octahedral sites around Fe^{3+} (Fe^{3+} removal capacity at equilibrium was found to be 1.1 mmol/g). The bonding of the **[(PS-CATS)$_2$Fe]$^-$** complex appears to be exclusively to the catechol groups rather than the sulfonic acid substituents via its FT-IR spectrum (free sulfonic acid bands, $\nu_{S=O}$, at 1220 and 1175 cm^{-1}) and, more importantly, for the fact that **PS-CATS** and the unsulfonated **PS-CAT** polymers have similar selectivities for Fe^{3+}. We depict the polymer-supported **[(PS-CATS)$_2$Fe]$^-$** complex as follows:



The kinetic experiments for rates of Fe^{3+} ($[Fe(SCN)_4]^-$, λ 460 nm) removal from solution, via a ligand exchange reaction, with the **PS-CATS** beads at pH 2.1 were readily accomplished by a UV–vis technique using a thermostated cuvette equipped with a stirring bar, from which linear plots of ln *A* (absorbance) vs *t* (sec) provided a pseudo first order rate constant of 4.2×10^{-4} s^{-1} at 25 °C (Figure 3). The hydrophilic **PS-CATS** beads cooperate by sinking to the bottom of the cuvette before they reacted with $[Fe(SCN)_4]^-$, unlike the beads with the unsulfonated version, **PS-CAT**, that float on the surface, and dramatizes the fact that maximum diffusion of Fe^{3+} occurs into the macropores/gel phase when a sulfonic acid group is bonded to the catechol ligand.

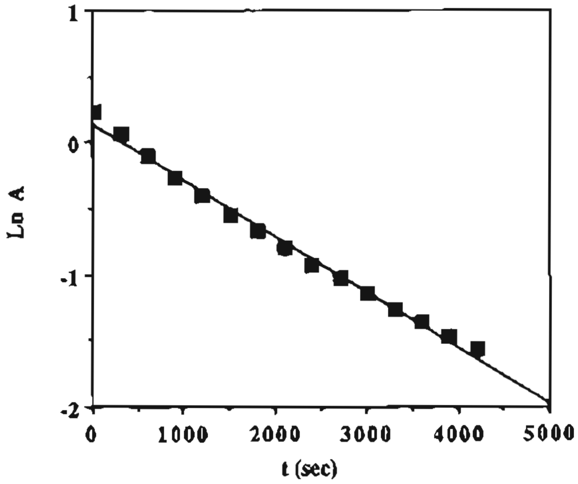


Figure 3. Kinetic plot of ln *A* vs *t* (sec) for Fe^{3+} ion removal with the **PS-CATS** ligand at 25 °C and pH 2.1. The Fe^{3+} ion removal kinetic rates were followed by the decay of the absorption maximum at 460 nm using UV–vis spectrometry.

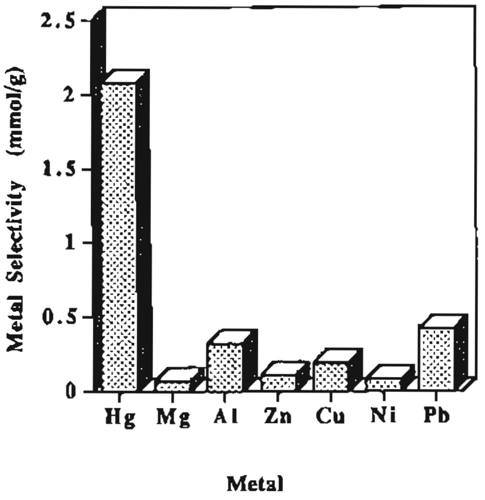


Figure 4. Metal Selectivity of the **PS-CATS** ligand at pH 3.0.

As well, by raising the pH to 3.0, and replacing Fe^{3+} (insoluble at pH >3.0) with Hg^{2+}, the **PS-CATS** selectivity was changed to Hg^{2+} in the presence of Mg^{2+}, Al^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} (Figure 4). It is interesting to note that at equilibrium, the **PS-CATS/Hg^{2+}** ratio was close to 1:1 (Hg^{2+}-capacity on the **PS-CATS** beads at equilibrium was 2.4 mmol/g). Thus, selectivity to other metal ions is possible, as a function of pH.

PS-3,3-LICAMS Metal Ion Selectivity, Relative Selectivity Coefficient Values (K_m), and Kinetic Studies, as a Function of pH. Similar experiments with **PS-3,3-LICAMS**, a ligand that is predisposed for possible octahedral Fe^{3+} complexation, provided an even greater selectivity for Fe^{3+} ion in comparison to **PS-CATS** in the presence of Cu^{2+}, Zn^{2+}, Mn^{2+}, Al^{3+}, Ni^{2+}, and Mg^{2+} ions (0.02 M) at pH 2.1, where maximum Fe^{3+} ion removal from solution was observed. The selectivity for Fe^{3+} ion in the presence of competitors is dramatically shown in Figure 5. The relative equilibrium selectivity coefficients (K_m values) were also found, with Mg^{2+} as the standard, to be as follows: (M^{n+}/Mg^{2+}); 1817 (Fe^{3+}); 443 (Cr^{3+}); 121 (Al^{3+}); 4 (Cu^{2+}); 2 (Zn^{2+}); 6 (Mn^{2+}); 3 (Ni^{2+}); 1 (Mg^{2+}). This demonstrates the **PS-3,3-LICAMS** unique selectivity for Fe^{3+} in competition with other metal ions. Moreover, the relative

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[10] (a) Grimshaw, R. W.; Harland, H. *Ion Exchange: Introduction to Theory and Practice*; Monograph for Teachers 29; The Chemical Society: London, 1975; p 73. (b) Sahni, S. K.; Reedijk, J. *Coord. Chem. Rev.* **1984**, *59*, 1.

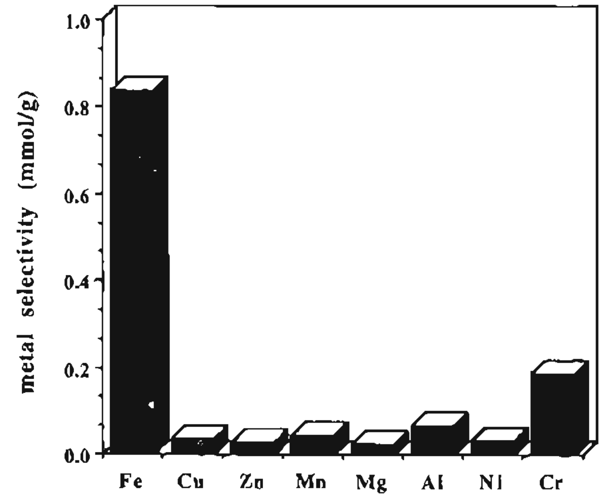
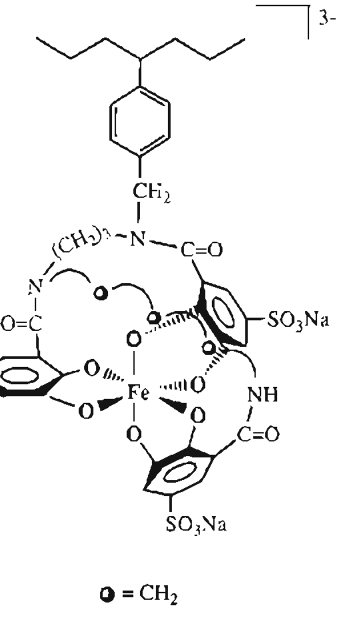


Figure 5. Metal Selectivity of the **PS-3,3-LICAMS** Ligand (0.53 mmol/g) at pH 2.1.

equilibrium selectivity coefficient for **PS-3,3-LICAMS** was ~11 times greater than **PS-CATS** for Fe^{3+}, clearly demonstrating that possible octahedral predisposition of the pendant ligand in the polymer matrix provides the thermodynamically more stable Fe^{3+} complex.

It is interesting to note that at equilibrium, the **PS-3,3-LICAMS**/Fe^{3+} ratio was 0.63:1 (Fe^{3+} removal capacity at equilibrium was found to be 0.84 mmol/g), which indicates that complexes other than the 1:1 complex may be formed on the polymer. The bonding of the proposed 1:1 complex, [(**PS-3,3-LICAMS**)Fe]$^{3-}$ also appears to be exclusively to the catechol groups rather than the sulfonic acid substituents, via FT-IR spectra, with the free sulfonic acid bands, $\nu_{S=O}$, at 1223 and 1175 cm^{-1}, while the catechol ν_{C-O} stretch is shifted from 1270 cm^{-1} for the polymer bound ligand to 1257 cm^{-1} for the Fe^{3+} complex. We depict the structure for the 1:1 [(**PS-3,3-LICAMS**)-Fe]$^{3-}$ complex as shown:



[PS-(3,3-LICAMS)Fe]$^{3-}$

The rates of Fe^{3+} removal by the **PS-3,3-LICAMS** beads at pH 2.1 were also studied by UV–vis techniques, which provided a pseudo-first-order rate constant of 7.2 × 10^{-4} s^{-1} at 25 °C.

Table 1. Divalent and Trivalent Metal Ion Selectivity (mmol/g) for the **PS-2-6-LICAMS** Ligands[a]

PS-LICAMS	Ni^{2+}/Cu^{2+}	Zn^{2+}/Cu^{2+}	Mn^{2+}/Cu^{2+}	Fe^{3+}/Cu^{2+}
PS-2-LICAMS	0.354/0.409	0.346/0.393	0.384/0.352	0.737/0.069
PS-3-LICAMS	0.375/0.436	0.359/0.411	0.382/0.349	
PS-4-LICAMS	0.363/0.427	0.361/0.411	0.411/0.379	
PS-5-LICAMS	0.347/0.406	0.370/0.419	0.377/0.349	
PS-6-LICAMS	0.351/0.406	0.332/0.392	0.408/0.379	0.776/0/0.069

[a] See the Experimental Section for details.

The kinetic results clearly indicate that sulfonation of either the **PS-CAT** or **PS-3,3-LICAM** ligands, in comparison to their unsulfonated analogs, is more important for rates and capacities (10-fold increase for each parameter) of metal removal, since it helps eliminate diffusional effects in aqueous solution; i.e., sulfonation makes the catechol ligand more hydrophilic, while lowering the pK_a of catechol (OH) ionization and raising the oxidation potential for *o*-quinone formation. It should be noted that global sulfonation of polymer backbones[4a] was previously utilized to increase the overall polymer hydrophilicity, but does not always lead to selective metal ion reactions; we found that nonselective sulfonation caused a dramatic loss in metal ion selectivity of the **PS-3,3-LICAM** ligand. However, the new concept of selective sulfonation on the polymer pendant catechol ligand site, as demonstrated in these studies, preserves the metal ion selectivity when comparisons are made to the unsulfonated analog, while providing the added beneficial properties that were described above.

PS-2–6-LICAMS Metal Ion Selectivity, Relative Selectivity Coefficient Values (K_m), and Kinetic Studies, as a Function of pH. The synthesis of a series of bis-linear catechol amides, PS-2–6-LICAMS (eq 2), allowed us to change the cavity size (2-CH_2 to 6-CH_2) between the two catechol groups on the linear amide chain and to ascertain whether this modification allowed a selectivity to different divalent metal ions. Table 1 compares the **PS-2–6-LICAMS** derivatives with several divalent and trivalent metal ions and clearly shows the lack of selectivity; all the **PS-2–6-LICAMS** derivatives provided very similar removal capacities for the variety of metal ions studied.

While there appears to be no selectivity differences between the divalent metal ions (Table 1), the selectivity to trivalent metal ions, such as Fe^{3+}, Cr^{3+}, and Al^{3+}, still dominates in this series of polymer pendant ligands as it did in both the **PS-CATS** and **3,3-LICAMS** beads and is shown in Figure 6. Interestingly, the average mmol/g values for divalent metal ion removal for the **PS-2–6-LICAMS** series, in comparison to the **PS-3,3-LICAMS** and the **PS-CATS** ligands, indicates that the potentially predisposed, square-planar **PS-2–6-LICAMS** ligands have a higher selectivity for the divalent metal ions.

The relative equilibrium selectivity (K_m) values were also found, with Mg^{2+} as the standard, to be as follows: (M^{n+}/Mg^{2+}); 65 (Fe^{3+}); 28 (Cr^{3+}); 6 (Al^{3+}); 1 (Cu^{2+}); 1 (Zn^{2+}); 1 (Mn^{2+}); 1 (Ni^{2+}); 1 (Mg^{2+}).

These results further demonstrate the higher selectivity to the divalent metal ions compared to the **3,3-LICAMS** and **PS-CATS** ligands via the fact that selectivity to Fe^{3+} is concomitantly diminished in the **PS-2–6-LICAMS** series with Fe^{3+} K_m ratios of **3,3-LICAMS/PS-2–6-LICAMS** = 28 and, interestingly, the **PS-CATS/2–6-LICAMS** ratio was found to be 2.6. Moreover, comparing the K_m ratios, Cu^{2+}/Fe^{3+}, for all the polymer pendant ligands studied, again emphasizes the fact that the **PS-2–6-LICAMS** series of ligands are more selective to Cu^{2+}, and therefore, to all divalent metal ions (Figure 7).

The rates of Fe^{3+} ion removal by the **PS-2-LICAMS** ligand at pH 2.1 was also studied by UV–vis techniques, which

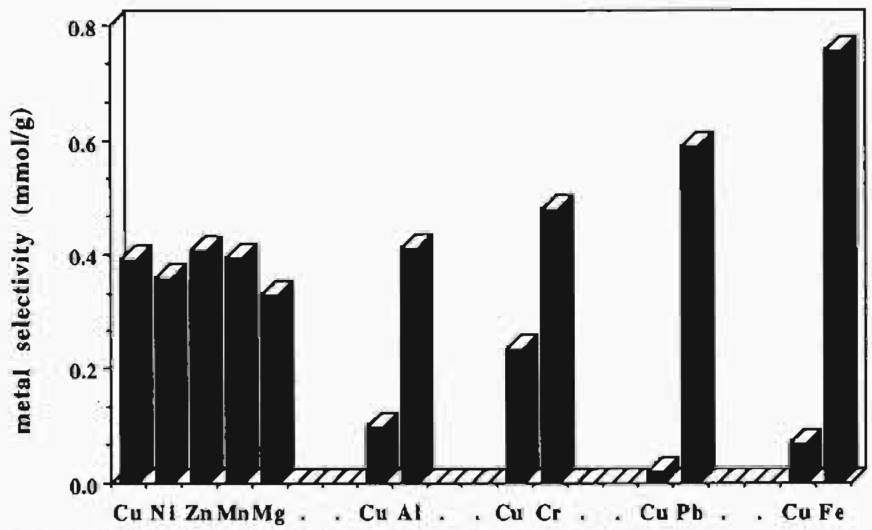


Figure 6. Metal Selectivity of the **PS-2–6-LICAMS** Ligand (average, 0.55 mmol/g) at pH 2.1.

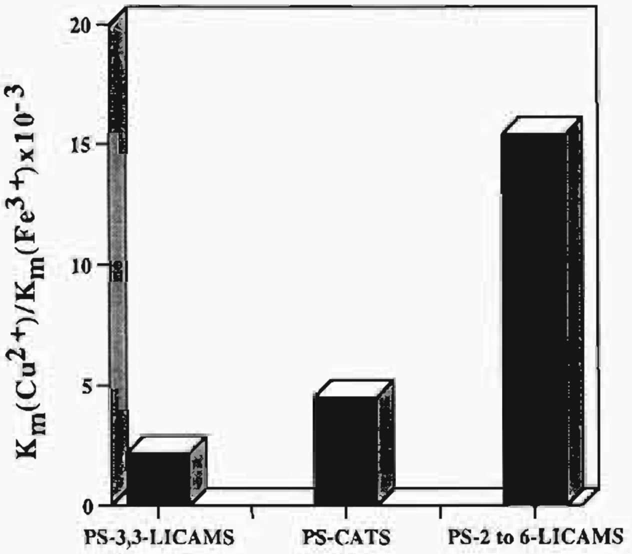
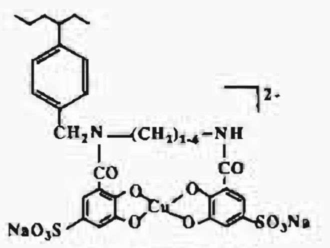


Figure 7. Comparison of K_m Cu^{2+}/Fe^{3+} ratios for **PS-CATS**, **PS-3,3-LICAMS**, and **PS-2–6-LICAMS** Ligands.

provided a pseudo-first-order rate constant of 2×10^{-4} s^{-1} at 25 °C. Thus, the order of the rate of removal of Fe^{3+}ion from a pH 2.1 solution is **3,3-LICAMS** > **PS-CATS** > **PS-2-LICAMS** with a rate ratio of 4: 2: 1, respectively.

We depict an example of a divalent metal complex (Cu^{2+}) with the **PS-2–6-LICAMS** series of beads as follows:



$[PS\text{-}2\text{-}6\text{-}LICAMS\text{-}Cu]^{2-}$

Recovery of the Complexed Fe^{3+} From PS-CATS and 3,3-LICAMS Polymer Beads by Sulfuric Acid Treatment. The total recovery of Fe^{3+} ions from the **PS-CATS** and **3,3-LICAMS** beads, for continual reuse, was readily accomplished with 2 N H_2SO_4 as shown in Figure 8. Removal (pH 2.1) and subsequent recovery (2 N H_2SO_4) of Fe^{3+} from aqueous solution with both **PS-CATS** or **3,3-LICAMS** beads was accomplished several times without loss of selectivity or capacity, demonstrating the effectiveness of these materials for future environmental or analytical applications.

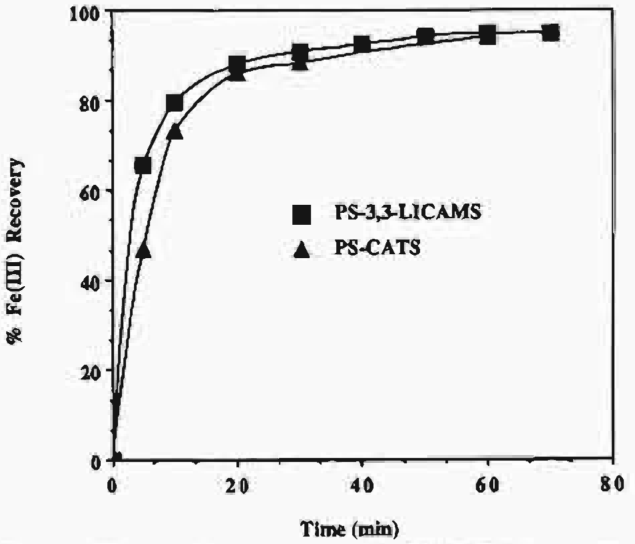


Figure 8. Percent Fe^{3+} recovery rates from **PS-CATS–Fe** and **PS-3,3-LICAMS–Fe** ligands with 2 N H_2SO_4.

Discussion

The major finding in this extensive study of selectivity to trivalent and divalent metal ions, with polymer pendant ligands that have a biomimetic connection to the structures of biological ligands, is that the concept of predisposition that was successfully applied to the solvent soluble versions[3] of these ligands, especially for Fe^{3+}, is also a viable concept for the polymer-supported analogues. This concept is clearly demonstrated by comparing the selectivity of the potentially octahedrally, predisposed **PS-3,3-LICAMS** ligand with the nondisposed **PS-CATS** ligand for Fe^{3+} ions as reflected in the 11-fold relative selectivity coefficient (K_m) ratio (**PS-3,3-LICAMS/PS-CATS**) in favor of the polymer-supported, biomimetic enterobactin analogue, **PS-3,3-LICAMS**.

This concept is further demonstrated in the kinetics of Fe^{3+} ion removal from a pH 2.1 solution, where the rate (k) ratio of **PS-3,3-LICAMS/PS-CATS** was ~2, while the rate ratio of **PS-3,3-LICAMS/PS-2–6-LICAMS** was 4. In addition, the potentially square-planar **PS-2–6-LICAMS** series of ligands were more selective to divalent metal ions compared to the **PS-3,3-**

LICAMS and **PS-CATS** ligands, while no selectivity for any divalent metal ions was observed within the **PS-2–6-LICAMS** series, clearly signifying that this series of polymer pendant ligands have maximum flexibility to accommodate these metal ions.

The trivalent metal ions for all the polymer pendant ligands studied were more readily removed from aqueous solution in comparison to the divalent metal series, with the following order of selectivity: $Fe^{3+} > Cr^{3+} > Al^{3+}$. This trivalent metal ion selectivity was similar for all the polymer pendant ligands studied. Therefore, it is interesting to compare our **PS-CATS** results with those of Griesbach and Lieser[6] for an azo linked **TIRON** polymer pendant ligand. They reported that the K_d value for Cu^{2+} removal is higher than that for Fe^{3+} at a pH of ~2.3, while our results are diametrically opposite. We find that the K_m ratio of Fe^{3+}/Cu^{2+} for **PS-CATS** is 214 at pH 2.1, while they report a K_d ratio of 0.03 for Fe^{3+}/Cu^{2+}. Our speculation on the reason for the selectivity differences between these polymer-supported 3,5-sulfonate catechol ligands is that the azo linkages are not spectator ligand and, in fact, they are more selective to Cu^{2+} than Fe^{3+}. This premise correlates with their reported data and provides a warning that control experiments need to be run if reactive linkages are to be used to anchor other polymer pendant ligands.

It is also important to note that by changing the pH of the solution, as exemplified with **PS-CATS**, from 2.1 to 3.0, that the selectivity could be changed to Hg^{2+}, in the absence of Fe^{3+} and in the presence of Mg^{2+}, Al^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} ions. This demonstrates the wide utility of these polymer pendant ligands for future environmental remediation applications.

The recovery of the metal ions from the polymer pendant ligands, an important step for reusing these polymer beads, was also found to be a very facile process with a 2N H_2SO_4 treatment providing >95% of the bound Fe^{3+}. This was demonstrated with **PS-CATS** and **PS-3,3-LICAMS** for the Fe^{+} ion and shows the rapid recovery of the metal ion from the polymer beads (Figure 8). Thus, selective removal and facile recovery of metal ions from aqueous solutions have been demonstrated and this biomimetic approach appears to be viable for a variety of environmentally and economically important metal ions.[11]

Conclusions

In conclusion, we have demonstrated that the novel polymer-supported **PS-3,3-LICAMS, PS-2–6-LICAMS** and **PS-CATS** ligands have similar Fe^{3+} ion selectivities as their homogeneous analogs in competition with other metal ions. The sulfonic acid substituent, bonded directly to the polymer pendant catechol ligand, dramatically improved the kinetics and capacities of Fe^{3+} ion removal for all the polymer-supported ligands studied (10-fold) in comparison to their unsulfonated analogs, while the thermodynamic parameter of predisposition of catechol ligands (chelate effect) appears to be more important for the improved selectivity of **3,3-LICAMS** toward Fe^{3+} ion (higher K_m value) removal from aqueous acidic solutions in comparison to the **PS-CATS** ligand. As well, the **PS-2–6-LICAMS** ligands were also more selective to divalent metal ions due to their predisposition for square planar coordination, but no differences were observed within the series itself. Future reports on polymer pendant ligand chemistry will include selectivity studies for radionuclides with the **PS-CATS**, **2–6-LICAMS**, and **3,3-LICAMS** ligands,[12a] Al^{3+} selectivity with a **PS-2-QA** (quinaldic acid) ligand,[12b] and Ag^{+} selectivity with an **PS-SED** ligand, ethylenebis(dithiocarbamate).[12c]

Experimental Section

The purchased chemicals in this study were used as obtained. Solvents were purified and degassed, while all manipulations were performed in air, unless otherwise noted.

Physical Measurements. UV–vis spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer. FT-IR spectra were determined as a solid, in a KBr matrix, in the mid-IR region (400–4000 cm^{-1}) with the use of a computer-controlled Nicolet Impact 400 FT-IR spectrometer. Elemental analyses were carried out by either the Department of Chemistry Microanalytical Laboratory at the University of California, Berkeley, CA, or Galbraith Laboratories, Inc., Knoxville, TN. Metal analyses were carried out by either X-ray fluorescence spectrometry or by atomic absorption spectrometry. The CP-MAS ^{13}C NMR spectra were obtained on a 100 MHz solid state NMR spectrometer instrument,built by the Reimer group, Department of Chemical Engineering, University of California, Berkeley, CA, and operating at a field strength of 2.3 T at 25.1 MHz for ^{13}C NMR. The ^{13}C NMR spectra were obtained with a spectral width of 10K Hz, a line-broadening of 5 Hz, an aquisition time of 26 ms, last delay of 3 s, and a cross polarization of 3 ms.

Chloromethylation of Amberlite-XE-298A. This was carried out with a procedure described by Warshawsky.[13] In a typical reaction, a sample of dry Amberlite-XE-298A polymer beads (20.0 g, 6% cross-linked, Rohm and Haas) was swelled in a CH_2Cl_2 solution (140 mL) consisting of 3 M $ClCH_2OCH_2(CH_2)_6CH_3$ for 30 min. After $SnCl_4$ (4.0 mL) was added, the reaction was stirred at room temperature for 6 h. The polymer was then washed with CH_2Cl_2, dioxane, H_2O, and MeOH and dried under vacuum at 60 °C for 24 h. Elemental analysis showed 6.33% Cl (1.78 mmol/g).

Sulfonation of PS-CAT. PS-CAT (catechol, 2.3 mmol/g) was synthesized using a procedure described in the literature.[5] Fuming sulfuric acid (18–22%) was purchased from Aldrich with no further purification. All reactions were carried out under an inert atmosphere. The **PS-CAT** (5 g, 2.3 mmol/g) beads were added in portions to the fuming sulfuric acid (20 mL) in a flask immersed in an ice bath. The mixture was left standing at 0 °C for ~3 h, then warmed up to room temperature. After 2 h, the mixture was poured onto ice. The beads were filtered and washed in the following order: H_2O, 5% Na_2CO_3 solution, H_2O, CH_3OH, and diethyl ether. The **PS-CATS** beads were finally dried at 60 °C overnight in vacuo.

Analysis for **PS-CATS**: 1.9 mmol/g of catechol, 12.4% S (3.9 mmol/g of sulfonic acid substituents). The FT-IR data for **PS-CATS** (KBr, cm^{-1}): 1292 (C-O); 1220 and 1075 (S=O). CP-MAS ^{13}C NMR data (referenced to TMS, ppm): 138.31, 132.08, 127.40 (for comparison a CP-MAS ^{13}C NMR spectrum for **TIRON** is as follows: 144.55, 134.03, 120.39).

Kinetics Procedure for PS-CATS and PS-3,3-LICAMS with Fe^{3+} Ions. Experiments were run at 25 °C at various pH values using a thermostated cuvette in an HP 8452A UV–vis spectrophotometer. A typical procedure is as follows: The **PS-CATS** or **PS-3,3-LICAMS** beads (10 mg) were added to a cuvette with a small magnetic stirring bar and charged with 4 mL of a solution of $Fe(NO_3)_3$ (20 mM) and KSCN (0.8 mM); $[Fe(SCN)_4]^-$. The rate of Fe^{3+} removal was measured using the HP kinetic software package from the decay of the absorbance at 460 nm for the **PS-CATS** and 452 nm for **PS-3,3-LICAMS**, every 5 min for 70 min and every 2 min for 30 min, respectively.

The general equation for a first-order reaction was used to calculate the rate constants: $C = C_0 e^{-kt}$, where C is the concentration at time t, and C_0 is the concentration at time 0, while k is the first order rate constant. The UV–Vis measures absorbance, which is a linear function of concentration. The slope of the ln A vs time plot gives the rate constant, k. For the initial rate we can assume that Fe^{3+} uptake is

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[11] Fish, R. H. Patent Applications submitted by DOE.

[12] (a) Bowen, S. M.; Attrep, M., Jr.; Li, W.; Huang, S-P.; Fish. R. H. Manuscript in preparation. (b) Li, W.; Fish. R. H. Submitted for publication. (c) Huang, S-P.; Franz, K. J.; Fish. R. H. Submitted for publication.

[13] Warshawsky, A.; Deshe A.; Gutman, R. *Br. Polym. J.* **1984**, *16*, 234.

pseudo first order as the kinetics slow down considerably after about a half hour. This decrease, we speculate, is due to the saturation of the beads present in the cuvette or to diffusion factors. The Fe^{3+} removal pseudo-first-order rate constants for both the **PS-3,3-LICAMS** and **PS-2−6-LICAMS** ligands were normalized due to the concentration differences between them and the **PS·CATS** ligand.

K_m, Relative Selectivity Coefficient Determination Procedure. A typical experiment follows: The **PS-CATS** (50 mg) beads were added to a solution (50 mL) of $Fe(NO_3)_3$ (0.02 M) and $M(NO_3)_x$ (0.02 M). The mixture was shaken for ~14 h to ensure complete reaction. The **PS-CATS** beads were filtered, washed with H_2O, CH_3OH, and ether, and dried in vacuo. The beads were analyzed for Fe^{3+} and M^{n+} using X-ray fluorescence (XRF) analysis. The concentrations of Fe^{3+} and M^{n+} in the solution were calculated from the mass balance.

The relative selectivity coefficients (K_m) were calculated for each metal according to the following method:

$$n\mathrm{Fe}^{3+} + \overline{3\mathrm{M}^{n+}} \leftrightarrow 3\mathrm{M}^{n+} + \overline{n\mathrm{Fe}^{3+}}$$

(bar indicates resin phase)

$$\mathrm{K}_{\mathrm{Fe/M}} = \frac{(q_{\mathrm{Fe}})^n (C_{\mathrm{M}})^3}{(C_{\mathrm{Fe}})^n (q_{\mathrm{M}})^3}$$

q = equilibrium concentration on the bead

C = equilibrium concentration in solution

Final K_m values were normalized by allowing $K_{Mg} = 1$. For example $K_{Fe/Mg} = 1817$, so $K_{Fe} = 1817$ for **PS-3,3-LICAMS**.

Recovery Procedure for Fe^{3+} Ions. The **PS-CATS-Fe** for **PS-3,3-LICAMS-Fe** polymer beads (50 mg) were added to 2 N H_2SO_4 (40 mL). The percent Fe^{3+} removal from the beads was calculated from the residual concentration of Fe^{3+} on the beads using XRF analysis.

Preparation of PS-3,3-LICAM Beads. To 20.0 g (35.6 mmol) of chloromethylated Amberlite-XE-298A beads, swelled in 100 mL of dioxane for 1 h, was added dropwise, under N_2, 14.0 g (106.8 mmol) of 3,3-iminobis(propylamine), $[H_2N(CH_2)_3NH(CH_2)_3NH_2]$, in 30 mL of dioxane. After being stirred at room temperature for 30 h, the beads were washed with dioxane, H_2O/dioxane (1:1), H_2O, and MeOH, and then dried under vacuum at 60 °C for 15 h. We obtained 22.94 g of off-white beads. Elemental analysis showed 3.01% N (0.72 mmol/g of 3,3-iminobis(propylamine) and 1.49% Cl, 64% yield). To 20.0 g (14.4 mmol) of the above-mentioned aminated Amberlite-XE-298A beads in 100 mL THF was added dropwise 50 mL of a THF solution containing 10.8 g (53.8 mmol) of 2,3-dimethoxybenzoyl chloride followed by a dropwise addition of a 20 mL THF solution containing 7.0 g (69.3 mmol) of triethylamine. The reaction was kept at 50 °C with gentle agitation for 2 days. After the triethylamine hydrochloride precipitate was decanted from the solvent, the polymer was washed with dioxane/MeOH (1:1), MeOH, H_2O, and MeOH.

The product beads were dried under vacuum at 60 °C for 10 h and weighed 26.6 g (92% yield). This product was then swelled in 150 mL of CH_2Cl_2 for 30 min and to this was added dropwise at 0 °C 25.0 g of BBr_3 (25.0 g, 99.8 mmol) in 50 mL of CH_2Cl_2. After the reaction was stirred under N_2 at 0 °C for 14 h, the solvent was decanted, and 100 mL of deionized H_2O was slowly added. The polymer was then soaked in H_2O for 10 h and washed with MeOH and then dried under vacuum at 60 °C for 20 h. The **PS-3,3-LICAM** polymer beads, thus obtained, analyzed for 2.46% N (0.59 mmol/g of the **3,3-LICAM** ligand).

Sulfonation of the PS-3,3-LICAM Beads. Thus, 5.0 g of **PS-3,3-LICAM** beads were swelled in 50 mL of CH_2Cl_2 for 1 h, then filtered and air-dried for 2 h. The solvent-treated polymer was added to 50 mL of cold 93% H_2SO_4 and kept at this temperature for 15 min to allow for diffusion of the acid into the polymer structure. After the reaction was allowed to warm up to room temperature during a 30 min time period, the polymer was filtered, and neutralized with a mixture of 200 g of ice containing 10 g of Na_2SO_4 and 1 g of NaOH. After thorough washing with deionized H_2O, the polymer beads were rinsed with MeOH and finally dried under vacuum at 60 °C for 14 h. The product thus obtained, **PS-3,3-LICAMS** polymer beads, showed 2.26% N (0.53 mmol/g of ligand or 1.62 mmol/g of catechol) and 5.59% S (1.75 mmol/g of sulfonic acid substituents). FT-IR data for **PS-3,3-LICAMS** (KBr, cm^{-1}): 1460 (C—C); 1641(C=O); 1270 (C—O); 1229 and 1179 (S=O).

Table 2. Analytical Data for the **PS-2-6-LICAMS** Ligands[a]

PS-LICAMS	N %	ligand concn (mmol/g)	S %	$-SO_3Na$ concn (mmol/g)	ratio SO_3Na/catechol
2-LICAMS	1.49	0.53	4.35	1.36	1.28
3-LICAMS	1.54	0.55	3.57	1.11	1.01
4-LICAMS	1.50	0.54	4.04	1.26	1.17
5-LICAMS	1.57	0.56	3.18	0.99	0.88
6-LICAMS	1.61	0.58	4.13	1.29	1.11

[a] The sulfonation reactions for **PS-2** to **6-LICAM** beads were run similarly to the **PS-3,3-LICAM** beads, except that a 20 min warmup time was used.

Selectivity Studies with PS-3,3-LICAMS. Solutions were made that were 0.02 M in both Fe^{3+} and M^{n+} (M = Al^{3+}, Zn^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, and Cu^{2+}). Nitrate salts were used for all metals except Mn^{2+}, where $MnCl_2$ was used. Reagent grade water was used to make the solutions. All solutions were adjusted to pH = 2.1, and to each one was added 100 mg of the 3,3-LICAMS beads. The flasks were placed on a wrist-action shaker and allowed to shake for 16 h, by which time the equilibrium was well established. The beads were washed with deionized water and acetone, vacuum-dried, and analyzed using X-ray fluorescence for analysis of all metals except Mg^{2+} and Al^{3+}, which were done by atomic absorption spectrophotometry.

Preparation of PS-2 to 6-LICAM Beads. These polymer pendant ligands were made using a similar procedure as described above for the synthesis of the **PS-3,3-LICAM** beads. Typically, a sample of chloromethylated Amberlite-XE-298A beads (5.0 g, 8.9 mmol) was allowed to react with $H_2NCH_2(CH_2)_nCH_2NH_2$ (n = 0−4, 28.0 mmol) in dioxane under N_2. The aminated Amberlite-XE-298A polymer was then allowed to react with 2,3-dimethoxybenzoyl chloride (1.8 g, 9.0 mmol) in THF in the presence of triethylamine (1.2 g, 12.0 mmol). After demethylation in CH_2Cl_2 with BBr_3 (4.0 g, 16.0 mmol) under N_2 at 0 °C, the product was hydrolyzed with H_2O, washed with MeOH, and dried under vacuum at 60 °C for 20 h. The ligand concentration was found to be ~0.61mmol/g (an example of an analysis for N: 1.71% N for the **4-LICAM** polymer beads).

Sulfonation of PS-2 to 6-LICAM Beads. Table 2 provides the analytical data that were obtained for the **PS-2−6-LICAMS** beads.

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