POLYMER PENDANT CROWN THIOETHERS FOR REMOVAL OF MERCURY FROM ACIDIC WASTES

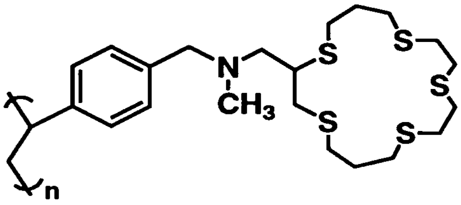
Theodore F. Baumann,* John G. Reynolds, and Glenn A. Fox
Lawrence Livermore National Laboratory
University of California
P.O. Box 808, Livermore, CA 94551

ABSTRACT

Removal and immobilization of mercury ions from industrial waste streams is a difficult and expensive problem requiring an efficient and selective extractant that is resistant to corrosive conditions. We have now developed an acid-resistant thiacrown polymer that has potential utility as a selective and cost-effective Hg^{2+} extractant. Copolymerization of a novel C-substituted thiacrown, N,N-(4-vinylbenzylmethyl)-2-aminomethyl-1,4,8,11,14-pentathiacycloheptadecane, with DVB (80% divinylbenzene) using a radical initiator generated a highly cross-linked polymer containing pendant thiacrowns. Mercury extraction capabilities of the polymer were tested in acidic media (pH range: 1.5 to 6.2) and the extraction of Hg^{2+} was determined to be 95^{+}% with a mixing time of 30 minutes. The thiacrown polymer was also determined to be selective for Hg^{2+}, even in the presence of high concentrations of competing ions such as Pb^{2+}, Cd^{2+}, Al^{3+}, and Fe^{3+}. The bound Hg^{2+} ions can then be stripped from the polymer, allowing the polymer to be reused without significant loss of loading capacity.

INTRODUCTION

We have been interested in designing polymer bound extractants for Hg^{2+} remediation in mixed waste streams generated at U.S. Department of Energy facilities. Some of these waste streams are not only very acidic, but also contain a wide variety of other metal ions, such as Al^{3+}, Fe^{3+}, and Pb^{2+}. Removal of Hg^{2+} thus requires a robust and selective sequestering agent. To address this problem, we have synthesized polymer-pendant crown thioethers for the selective removal of Hg^{2+} from acidic aqueous media (**figure** 1). Crown thioethers (2) are well suited for this task due to the high affinity that sulfur crowns have for the Hg^{2+} ion (3) as well as their resistance to degradation under acidic conditions (4). As pendant ligands on solid supports, the crown thioethers have been shown to remove soft metal ions, such as Ag^{+}, Hg^{2+} and Pb^{2+}, directly from aqueous solutions (5). In this paper we show the extraction capabilities of the polymer pendant thiacrown ether towards removal of mercury in aqueous acidic mixtures devised to simulate real waste streams, such as fuel reprocessing streams.



5

Figure 1.

EXPERIMENTAL

The synthesis of the thiacrown polymer has been previously described (1). Scheme 1 summarizes the preparation of thiacrown polymer precursor. Copolymerization of pendant arm crown **4** and divinylbenzene using a radical initiator (AIBN) generated the highly crossed-linked thiacrown polymer **5**. Elemental analysis of **5** showed that each gram of the polymer contained 1.5 mmol of thiacrown (based on % by weight of sulfur).

Scheme 1. *Reagents and Conditions*: i. $S(CH_2CH_2SCH_2CH_2CH_2OTs)_2$, Cs_2CO_3, DMF, 90°C; ii. $SOCl_2$, CH_2Cl_2, RT; iii. $MeNH_2$, Na_2CO_3, MeCN, 0°C; iv. 4-vinylbenzyl chloride, Na_2CO_3, MeCN, 81°C.

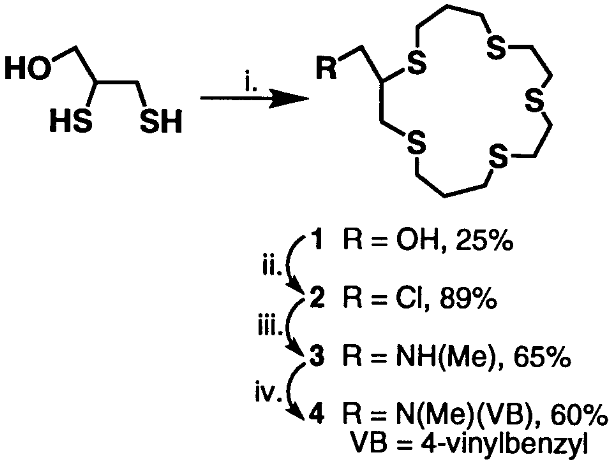


Figure 2.

The conditions for the Hg^{2+} extraction and recycling experiments have also been previously reported[6]. The thiacrown polymer (20 mg) was mixed with solutions (5 mL) of mercury nitrate at various pH values and Hg^{2+} concentrations for a variety of mixing times. For metal ion competition studies, a known concentration of the competing ion is added to the extraction solution. After the mixing is complete, the polymer is filtered and the concentration of Hg^{2+} remaining in solution is determined spectrophotometrically. This is performed by extracting the aqueous solution with a solution of diphenylthiocarbazone (dithizone or dtz) in $CHCl_3$ and determining the $Hg(dtz)_2$ $[Hg(C_{13}H_{11}N_4S)_2]$ content at $\lambda_{max} = 490$ nm. For the polymer recycling experiment, the Hg^{2+}-loaded polymer was washed with acetone to remove residual water and dried. The polymer was then treated with H_2dtz in $CHCl_3$, filtered and washed with $CHCl_3$ to remove the $Hg(dtz)_2$ complex. The dried thiacrown polymer could then be used to extract more Hg^{2+} without a significant loss of loading capacity.

RESULTS

Table 1 shows the Hg^{2+} extraction results for thiacrown polymer **5** at pH 3.6 at various reaction times. The data clearly shows that the polymer is very efficient for the removal of Hg^{2+} for reaction times as short as 30 minutes. Shorter reaction times were not possible due to experimental limitations.

Table 1. Extraction of Hg^{2+} from aqueous solution by thiacrown polymer as a function of time.[a]

Initial Hg $^{2+}$ Concentration, ppm	Reaction Time, h	Percent Extraction
4.3	18	98
4.3	3	95
4.3	1	95
4.3	0.5	95
34	0.5	99

[a] Each extraction was carried out at pH 3.6.
[b] Extraction (%) = 100 – ([remaining Hg^{2+}]/[starting Hg^{2+}] x 100).

Table 2 summarizes the Hg^{2+} extraction results as a function of pH and Hg^{2+} concentrations. Again, the data shows that the polymer is very effective in extracting Hg^{2+} from aqueous solution in the pH range of 1.5 to 6.1 at concentrations of 4 and 30 ppm. The polymer is also effective in removing Hg^{2+} concentrations of 4 ppm to 200 ppm at low pH. To ascertain the Hg^{2+} binding capacity of the resin, polymer **5** was treated with 400 ppm of Hg^{2+} at pH 2.5 and the results show that only 50% of the Hg^{2+} was extracted from solution. From this experiment, it was determined that the resin has ~0.5 mmol of Hg^{2+} binding sites per gram resin. Assuming that each Hg^{2+} ion complexes with a single crown, that number suggests that only ~ 30% of the thiacrowns are involved in Hg^{2+} extraction. This number may be higher, however, since there could be cooperative binding of the Hg^{2+} ions, meaning that sulfur donors from two or more crowns may be involved in binding a single Hg^{2+} ion.

Table 2. Extraction of Hg^{2+} from aqueous solution by **5** as a function of pH.

Initial Hg $^{2+}$ Concentration, ppm	pH	Percent Extraction
3.7	1.45	99
4.1	2.59	99
4.3	3.60	98
3.5	6.12	97
32	1.49	99
34	2.58	98
34	3.60	99
32	6.12	97
170	1.45	91
400	2.58	50

[a] Each extraction was stirred for 30 minutes.
[b] Extraction (%) = 100 – ([remaining Hg^{2+}]/[starting Hg^{2+}] x 100).

The selectivity of polymer **5** for Hg^{2+} was tested in the presence of competing metal ions (Al^{3+}, Cd^{2+}, Fe^{3+}, Pb^{2+}) and the results are summarized in Table 3. The data shows that the thiacrown polymer preferentially binds Hg^{2+} even at large molar ratios of competing metal ions.

Table 3. Hg^{2+} ion selectivity data for thiacrown polymer[a]

Metal	pH	Molar Ratio (M^{n+}/Hg^{2+})	Percent Extraction[b]
Pb^{2+}	1.40	5	98
Cd^{2+}	1.51	5	97
Fe^{3+}	1.53	10	98
Al^{3+}	1.62	100	95

[a] Each extraction was stirred for 30 minutes.
[b] Extraction (%) = 100 – ([remaining Hg^{2+}]/[starting Hg^{2+}] x 100).

Polymer **5** was regenerated through the treatment of the Hg^{2+}-loaded polymer with dithizone in $CHCl_3$. Once the $Hg(dtz)_2$ complex was washed from the resin, the polymer was reused under the conditions described above to extract Hg^{2+} from acidic aqueous solution without a significant loss of loading capacity. While this procedure may not be the ideal method to regenerate the polymer, it does show that polymer **5** can be stripped of the bound Hg^{2+} and then reused without degradation, for at least one cycle.

CONCLUSIONS

A novel thiacrown polymer has been synthesized and used to successfully extract Hg^{2+} from acidic aqueous solution. The removal of Hg^{2+} from solution was determined to be 95^{+}% over a wide range of pH (1.5 to 6.1) and Hg^{2+} concentrations (4 to 200 ppm). The thiacrown polymer is also selective for Hg^{2+} in the presence of competing metal ions. The polymer can be stripped of the Hg^{2+} and reused to extract more Hg^{2+}.

ACKNOWLEDGMENT

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

REFERENCES

1. (a) T. F. BAUMANN, J. G. REYNOLDS, and G. A. FOX. *Chem. Commun.* **1998**, 1637–1638 (b) T. F. BAUMANN, J. G. REYNOLDS, and G. A. FOX. *Synthesis of Novel Pendant Arm Crown Thioethers for Mercury Removal from Mixed Waste Streams*, *Abstracts of Papers*, 214th National Meeting of the American Chemical Society, Las Vegas, NV, Sept. 7-11, **1997**; ENVR 117.
2. S. R. COOPER. *Acc. Chem. Res.* **1988**, *21*, 141.
3. (a) D. SEVDI´C, and H. MEIDER. *J. Inorg. Nucl. Chem.* **1981**, *43*, 153. (b) D. SEVDI´C, L. FEKETE, and H. MEIDER. *J. Inorg. Nucl. Chem.* **1980**, *42*, 885. (c) D. SEVDIC, and H. MEIDER. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1409.
4. B. A. MOYER, G. N. CASE, S. D. ALEXANDRATOS, A. A. KRIGER. *Anal. Chem.* **1993**, *65*, 3389.
5. (a) K. YAMASHITA, K. KURITA, K. OHARA, K. TAMURA, M. NANGO, and K. TSUDA. *React. Funct. Polymers* **1996**, *31*, 47. (b) M. TOMOI, O. ABE, N. TAKASU, and

H. KAKIUCHI. *Makromol. Chem.* **1983**, *184*, 2431. (c) M. OUE, K. KIMURA, and T. SHONO. *Analyst* **1988**, *113*, 551. (d) E. I. TROANSKY, M. S. POGOSYAN, N. M. SAMOSHINA, G. I. NIKISHIN, V. V. SAMOSHIN, L. K. SHPIGUN, N. E. KOPYTOVA, and P. M. KAMILOVA. *Mendeleev Commun.* **1996**, 9.

6. T. F. BAUMANN, J. G. REYNOLDS, and G. A. FOX. **1998**. Inorg. Chem., submitted for publication.