

UCRL-JC-132856

PREPRINT

# Polymer Pendant Crown Thioethers for Removal of Mercury from Acidic Wastes

T. F. Baumann, J. G. Reynolds, G. A. Fox

This paper was prepared for submittal to the  
Waste Management '99 Conference  
Tucson, AZ  
February 28-March 4, 1999

December 22, 1998



Lawrence  
Livermore  
National  
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings.  
Since changes may be made before publication, this preprint is made available with  
the understanding that it will not be cited or reproduced without the permission of the  
author.

#### DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

## 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

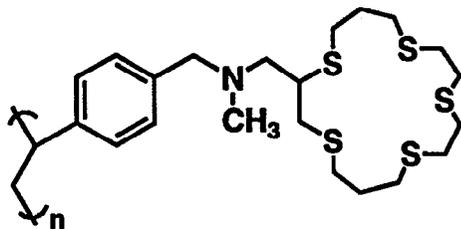
### ABSTRACT

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 thiacycrocrown polymer that has potential utility as a selective and cost-effective  $\text{Hg}^{2+}$  extractant. Copolymerization of a novel C-substituted thiacycrocrown, 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 thiacycrocrowns. Mercury extraction capabilities of the polymer were tested in acidic media (pH range: 1.5 to 6.2) and the extraction of  $\text{Hg}^{2+}$  was determined to be 95% with a mixing time of 30 minutes. The thiacycrocrown polymer was also determined to be selective for  $\text{Hg}^{2+}$ , even in the presence of high concentrations of competing ions such as  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Fe}^{3+}$ . The bound  $\text{Hg}^{2+}$  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  $\text{Hg}^{2+}$  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  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Pb}^{2+}$ . Removal of  $\text{Hg}^{2+}$  thus requires a robust and selective sequestering agent. To address this problem, we have synthesized polymer-pendant crown thioethers for the selective removal of  $\text{Hg}^{2+}$  from acidic aqueous media (Inset) (1). Crown thioethers (2) are well suited for this task due to the high affinity that sulfur crowns have for the  $\text{Hg}^{2+}$  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  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$ , directly from aqueous solutions (5). In this paper we show the extraction capabilities of the polymer pendant thiacycrocrown ether towards removal of mercury in aqueous acidic mixtures devised to simulate real waste streams, such as fuel reprocessing streams.

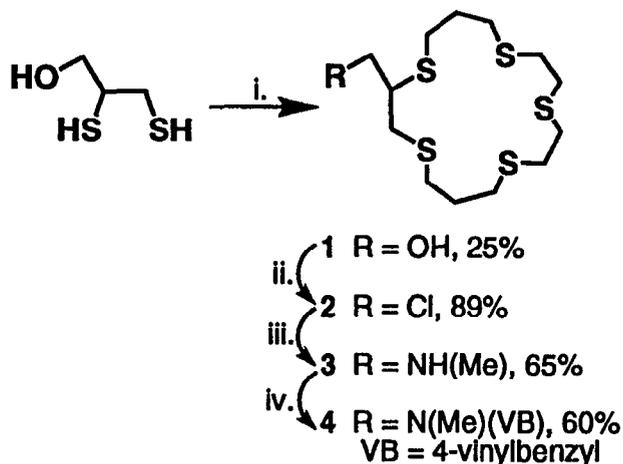
**Inset.**



## 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 cross-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,  $90^\circ C$ ; ii.  $SOCl_2$ ,  $CH_2Cl_2$ , RT; iii.  $MeNH_2$ ,  $Na_2CO_3$ , MeCN,  $0^\circ C$ ; iv. 4-vinylbenzyl chloride,  $Na_2CO_3$ , MeCN,  $81^\circ C$ .



The conditions for the  $Hg^{2+}$  extraction and recycling experiments have also been previously reported<sup>6</sup>. 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 diphenylthiocarbazon (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.<sup>a</sup>

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

<sup>a</sup>Each extraction was carried out at pH 3.6.

<sup>b</sup>Extraction (%) =  $100 - ([\text{remaining } Hg^{2+}]/[\text{starting } Hg^{2+}] \times 100)$ .

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

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

Initial $\text{Hg}^{2+}$ 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

<sup>a</sup>Each extraction was stirred for 30 minutes.

<sup>b</sup>Extraction (%) =  $100 - ([\text{remaining } \text{Hg}^{2+}]/[\text{starting } \text{Hg}^{2+}] \times 100)$ .

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

**Table 3.**  $\text{Hg}^{2+}$  ion selectivity data for thiocrown polymer<sup>a</sup>

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

<sup>a</sup>Each extraction was stirred for 30 minutes.

<sup>b</sup>Extraction (%) =  $100 - ([\text{remaining } \text{Hg}^{2+}]/[\text{starting } \text{Hg}^{2+}] \times 100)$ .

Polymer 5 was regenerated through the treatment of the  $\text{Hg}^{2+}$ -loaded polymer with dithizone in  $\text{CHCl}_3$ . Once the  $\text{Hg}(\text{dtz})_2$  complex was washed from the resin, the polymer was reused under the conditions described above to extract  $\text{Hg}^{2+}$  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  $\text{Hg}^{2+}$  and then reused without degradation, for at least one cycle.

## CONCLUSIONS

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

## 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*, 214<sup>th</sup> National Meeting of the American Chemical Society, Las Vegas, NV, Sept. 7-11, **1997**; ENV R 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.