Mercury Speciation in the Presence of Polysulfides

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Introduction

The methylation of mercury is known to occur chiefly in anoxic waters and is thought to be generally mediated by sulfate-reducing bacteria, the major agents of this process in aquatic systems. Consequently, there has been much recent interest in quantifying the chemical speciation and lipid solubility of mercury in the presence of sulfide and polysulfides, which form by reaction of sulfide with elemental sulfur or as intermediates in sulfur cycling. We quantify a large increase in the solubility of cinnabar (HgS_{(s)}) in the presence of elemental sulfur, particularly at high pH. Based on our data and those of Paquette and Helz, we propose that the complex, Hg(S_{(aq)})^{2+}, dominates the speciation of Hg(II) in such waters. At lower sulfide concentrations and at high pH, the data are best fitted by considering also the formation of the species HgS_{(aq)}^{+}. Octanol–water distribution (D_{ow}) experiments confirm the charged nature of the dominant mercury–polysulfide complexes and imply the presence of a minor lipophilic polysulfide complex, such as HgS_{2}. The recently reported decrease in D_{ow} with increasing sulfide concentration also occurs in the presence of polysulfides.

Experimental Methods

Solubility Experiments. The solubility of cinnabar in the presence of sulfide and elemental sulfur was measured in duplicate bottles at conditions ranging from pH 6 to 10 and S(− I)_{T} concentrations from 2 μM to 5 mM (measured by iodometry). S(− I)_{T} (by iodometry) and total mercury measurements were taken after equilibration in triplicate in most cases and duplicate as a minimum. Aliquots from several bottles were withdrawn and remeasured on different days.

Environmental mercury methylation appears modulated by sulfide concentrations, possibly via changes in mercury availability to sulfate-reducing bacteria, the major agents of this process in aquatic systems. Consequently, there has been much recent interest in quantifying the chemical speciation and lipid solubility of mercury in the presence of sulfide and polysulfides, which form by reaction of sulfide with elemental sulfur or as intermediates in sulfur cycling.

The solubility of cinnabar in the presence of polysulfides up to 0.1 mM has been measured in the Lower Mystic Lake, MA (19). Although there is some uncertainty in the literature regarding the existence of S_{6}^{2−} as well as the equilibrium constants for particular polysulfide species, the total concentrations of polysulfides predicted by the various models are similar. (We have used the equilibrium constants reported by Bouillé and Michard (20).) In this article, S(− I)_{T} represents the total concentration of H_{2}S, H_{2}S^{−}, S_{2}^{−}, S_{3}^{2−}, S_{4}^{3−}, S_{5}^{4−}, H_{2}S_{4}^{−}, and H_{2}S_{5}^{−}, since each polysulfide chain can be envisioned as possessing one sulfur atom of oxidation state (−II).

In this study we extend the study of Paquette and Helz by studying the effect of polysulfides on cinnabar solubility at lower S(− I)_{T}. Our results combined with those of Paquette and Helz lead us to propose a new chemical speciation scheme for mercury in the presence of polysulfides. We also extend the results of Benoit et al. (2) by measuring the octanol–water partitioning of mercury in the presence of polysulfides.

### Table 1. Constants Used in This Study for Mercury–Sulfide Interactions

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<tr>
<th>Formation reactions for mercury–sulfide species</th>
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<tr>
<td>HgS_{(aq)} + H_{2}S^{−} = HgS_{2}^{2−} + H^{+}</td>
<td>−13.0</td>
</tr>
<tr>
<td>HgS_{(aq)} + H_{2}S^{−} = HgS_{3}^{3−} + H^{+}</td>
<td>−4.5</td>
</tr>
<tr>
<td>HgS_{(aq)} + HS^{−} + H_{2}S^{−} = Hg(SH)_{2}</td>
<td>+1.0</td>
</tr>
<tr>
<td>HgS_{(aq)} + H^{+} = HgS_{2}^{2−}</td>
<td>−16.81</td>
</tr>
<tr>
<td>HgS_{(aq)} = HgS_{2}^{2−} + S_{2}^{−}</td>
<td>−53.5</td>
</tr>
<tr>
<td>HgS_{(aq)} = HgS_{aq}^{0}</td>
<td>−9.3</td>
</tr>
</tbody>
</table>

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† Massachusetts Institute of Technology.
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confirm that sulfide and total dissolved mercury concentrations were stable.

While serum bottles containing 0.1 g of cinnabar (Johnson Matthey) and 0.1 g of orthohombic elemental sulfur (Mallinckrodt) were purged with deoxygenated (passed through a heated column of copper filings) high-purity nitrogen through a 30 cm long Teflon needle, 50 mL of deoxygenated buffer (pH 7 and 8 Hydron buffers contained sodium phosphate and potassium phosphate, and pH 9 and 10 Hydron buffers contained sodium carbonate and sodium bicarbonate, Aldrich) was transferred to each bottle. Triage strength was approximately 0.3 M, and resazurin was added as a redox indicator. Each bottle was capped with a Teflon-faced butyl rubber septum (or a butyl rubber septum when faced butyl rubber septum (or a butyl rubber septum when the bottle was equilibrated, unstirred, in a nitrogen-filled flask, with 1% stannous chloride reductant. Mercury was added in sufficient quantities so that the sample retained its identity of possible complexes by assuming analogous behavior with the mercury–sulfide system. Given equilibrium among polysulfide species (all expected to be soft-sphere ligands), it is likely that the increased cinnabar solubility observed when polysulfides are present is a result of many different complexes. We inferred the identity of possible complexes by assuming analogous behavior with the mercury–sulfide system.

**Results**

**Cinnabar Solubility in the Presence and Absence of Polysulfides.** Measurements of dissolved mercury after 3, 10, and approximately 30 days in the presence of cinnabar at pH 8 showed no significant variations with time (data not shown); thus, equilibrium between the dissolved and solid phases appears to be achieved within a few days. As will be discussed later, our dissolved mercury measurements in the absence of S(0) agree with previous data and published thermodynamic constants.

At high S(−II)T, (≥1 mM) in the presence of S(0) (and consequently, the presence of polysulfides), our data generally agreed with those of Paquette and Helz. At low pH, the dissolved mercury concentration in the presence of S(0) was approximately 3-fold higher than in the absence of S(0). At high pH, this increase went up to about 200-fold (Figure 1a).

The dissolved mercury concentration decreased along with S(−II)T. (Figure 1b,c); the trend of increasing solubility with pH became more pronounced at the lower S(−II)T. (Note that in Figure 1 some scatter in the points results from lumping the data for a range of S(−II)T in each graph.)

As can be seen in Figure 1, the data obtained at high pH differed significantly from the model proposed by Paquette and Helz; the measured solubility was up to 100 times larger than predicted by their model. To improve the speciation model, we considered the formation of several possible mercury–polysulfide complexes besides HgS(0), which was proposed by Paquette and Helz. We chose the species by analogy with the complexes that have been proposed for the reaction between mercury and polysulfide (Table 1). As seen in Table 2, the species that gave the best fit of the data (smallest WSOS/DF; see Experimental Methods) was Hg(S−II)T.2⁻. Note that the model calculations are unable to distinguish between complexes of the various polysulfides (x = 3, 4, 5, 6). The species Hg(S−II)T.2⁻ gave the best fit for the Paquette and Helz data set as well as for that set combined with ours.

Including the previously proposed species, HgS(0), along with Hg(S−II)T.2⁻ did not improve the model fit. This was true for the other species as well, except for HgS(OH), which gave a small improvement in the fit. The role of this species in accounting for the high solubility of cinnabar at low S(−II)T and high pH can clearly be seen in Figure 1b,c. Including the species HgS(OH)2⁻ (along with Hg(S−II)T.2⁻ and HgS(OH)− at their optimal formation constants) resulted in no improvement of the model; the fit degraded above a Kformation of HgS(OH)− = 4.0.

As a general measure of the quality of the fit obtained with our speciation model (Hg(S−II)T.2⁻ and HgS(OH)−) and that of Paquette and Helz (HgS(0)), we plotted for all available
Octanol–Water Partitioning. The octanol–water distribution coefficient ($D_{ow} = Hg_{tot}/Hg_{oct}$) was determined at pH 8 for various $S(-II)$, in the absence of $S(0)$. Our results were in good agreement with the model of Benoit et al. (Figure 4), showing a large decrease in $D_{ow}$ with increasing sulfide concentration. The model calculates $D_{ow}$ by summing up expected contributions to $D_{ow}$ from uncharged species, $HgS^{0(aq)}$ and $Hg(SH)_2$, according to the equation

$$D_{ow} = \sum \chi_i K_{ow} \alpha_i$$  \hspace{1cm} (1)$$

where $\chi_i$ represents the mole fraction of species $i$ at equilibrium in the aqueous phase, and $K_{ow}$ equals 25 for both $HgS^{0(aq)}$ and $Hg(SH)_2$. (2).

The presence of $S(0)$ in the system resulted in insignificant changes in the octanol solubility of mercury; both the magnitude of $D_{ow}$ and its decrease with $S(-II)$ were the same with and without $S(0)$ (compare Figure 4a,b). This result is surprising since the concentration of $HgS^{0(aq)}$, the species which is presumably responsible for most of the octanol solubility (2, 3), should not be affected by the presence of polysulfides and its contribution to the total dissolved mercury (which increases with the addition of polysulfides) should decrease along with the ratio $HgS^{0(aq)}/HgT$ (see Figure 4b). Indeed, calculations based on Benoit et al.’s model predict much smaller $D_{ow}$’s than observed. Thus it appears that, at least in the presence of polysulfides, some species other than $HgS^{0(aq)}$ and $Hg(SH)_2$ may partition significantly into the octanol.

The simplest way to account for our result is to consider that some uncharged mercury–polysulfide species present at a minor concentration may have a significant octanol water partitioning. We assumed the presence of $HgS_n$ for $n > 2$ is predicted to be the dominant polysulfide. Based on Hansch and Leo’s additive method, and starting with $HgS^{0(aq)}$ and $Hg(SH)_2$ as starting points (to estimate a range), assuming alternating single and double bonding between sulfur atoms (25, 26), the resulting value for $K_{ow, HgS_n}$ is between 900 and $11 \times 10^4$. To account for the observed data, the species $HgS_5$ must thus be present at approximately 10–100 pM in equilibrium with cinnabar and elemental sulfur (see Supporting Information for further discussion). Importantly, the concentration of this species does not change with $S(-II)$, and it can account for the increase in $D_{ow}$ at all three $S(-II)$ (Figure 4).

Discussion

It is clear that polysulfides increase the solubility of cinnabar, especially at high pH. Based on our results and those of Paquette and Helz, we propose a new mercury–polysulfide speciation model that includes the species $HgS_{n-2}^{2-}$ and $Hg(SH)_4^{2-}$, with the equilibrium constants, $10^{-11.7}$ and $10^{-15.7}$, respectively. To exemplify the importance of these species to mercury speciation, we have compared the solubility of mercury and its speciation in the presence of cinnabar at pH 8 as a function of sulfide in both the presence and absence of $S(0)$ (Figure 5). Shown in the figure are our measurements of total dissolved mercury under both conditions, which agree well with the model. In the presence of $S(0)$, the polysulfide complexes account for most of the dissolved mercury and substantially increase its solubility.

The calculated solubility and speciation of mercury as a function of pH in the presence of cinnabar and $S(0)$ at 1 mM $S(-II)$ is shown in Figure 6, along with some of our measured data. In the speciation model presented in Figures 5 and 6, we have included not only the dominant mercury–polysulfide species $HgS_n^{2-}$ and $Hg(SH)_4^{2-}$, but also the proposed minor uncharged species $HgS_n$. Insofar as our octanol–water partitioning results in the absence of elemental sulfur confirm
those of Benoit et al., they support the presence of a hydrophobic mercury—sulfide species such as HgS\(_0\)(aq) dominant at lower sulfide concentrations (we are unable to make a stronger statement regarding the existence of this species as it would not be dominant under the conditions we tested.)

Although we have no direct evidence for the species Hg(S\(_x\))\(_2\)\(^{-}\) and HgS\(_x\)OH\(^{-}\), the indirect evidence provided by the variations in cinnabar solubility with pH and S(−II)\(_T\) is fairly strong. The evidence for HgS\(_x\) is more indirect since it is based on octanol—water partition data. Further, the equilibrium constant for this species is also dependent on the value estimated for its K\(_{ow}\) since we used a fragment approach, whether the sulfur atoms are singly or doubly bonded to each other would result in a difference of a factor of 10 in the estimated K\(_{ow}\) and, hence, a factor of 10 in its equilibrium constant. (Note that the prediction of K\(_{ow}\) for Hg(SH)\(_2\) by the fragment method does not agree particularly well with the data of Benoit et al.)

From the point of view of the toxicology of mercury, the most important process is its methylation, which, presumably, depends on the concentrations of mercury species and their permeability through biological membranes. Under conditions where mercury is at equilibrium with cinnabar (the case shown in Figures 5 and 6) the presence of polysulfides could serve to increase mercury bioavailability

<table>
<thead>
<tr>
<th>formation reactions for new Hg−S(_x) species</th>
<th>P&amp;H data</th>
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<tr>
<td>HgS(_{cinn}) + HS(^{-}) + (x−1)S(0)(orth) = HgS(_x)HS(^{-})</td>
<td>log K</td>
<td>WSOS/DF</td>
</tr>
<tr>
<td>HgS(_{cinn}) + (x−1)S(0)(orth) = HgS(_0)</td>
<td>−3.9</td>
<td>12.7</td>
</tr>
<tr>
<td>HgS(_{cinn}) + HS(^{-}) + (x−1)S(0)(orth) = HgS(_x)S(^2)(^{-}) + H(^+)</td>
<td>−5.9</td>
<td>11.1</td>
</tr>
<tr>
<td>HgS(_{cinn}) + (x−1)S(0)(orth) + H(_2)O = HgS(_x)OH(^{-}) + H(^+)</td>
<td>−11.7</td>
<td>4.28</td>
</tr>
<tr>
<td>HgS(_{cinn}) + HS(^{-}) + 2(x−1)S(0)(orth) = Hg(S(_x))(_2)(^{-}) + H(^+)</td>
<td>−11.8</td>
<td>3.2</td>
</tr>
<tr>
<td>HgS(_{cinn}) + HS(^{-}) + (x−1)S(0)(orth) + H(_2)O = HgS(_x)OH(^{-}) + H(^+)</td>
<td>did not converge</td>
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* Species bolded in formation reaction. The model proposed here is shown in the last two rows (WSOS/DF from a simultaneous optimization). Reported for I = 0.3 M.

**FIGURE 2.** Log of the ratio (predicted Hg\(_T\)/observed Hg\(_T\)) where Hg\(_T\) is the total soluble mercury in equilibrium with cinnabar, for all data points in the both data sets under two modeling scenarios. Circles depict this parameter using the Paquette and Helz data set, while diamonds represent data from this study. Open symbols represent results from modeling calculation using the previous mercury—polysulfide model, allowing HgS\(_x\)HS\(^{-}\) as the only mercury—polysulfide complex, and closed symbols depict calculation using the model proposed in this study (Hg(S\(_x\))\(_2\)\(^{-}\) and HgS\(_x\)OH\(^{-}\)).

**FIGURE 3.** Residual error calculated by FITEQL as the formation constants for Hg(S\(_x\))\(_2\)\(^{-}\) and HgS\(_x\)OH\(^{-}\) are varied, keeping all other values constant. Both Paquette and Helz data and those from this study were used in this analysis.

**FIGURE 4.** Experimentally determined octanol—water distribution coefficients (D\(_{ow}\)) (dark bars) for dissolved mercury species at pH 8 in equilibrium with cinnabar in the absence (a) and presence (b) of S(0). For comparison, the predicted contribution to D\(_{ow}\) from HgS\(_x\)HS\(^{-}\) and Hg(SH)\(_2\) is shown by the white column (using the measured values of K\(_{ow}\) for both (2)). Error bars represent one standard deviation, propagated error. In the presence of S(0), shaded bars depict the D\(_{ow}\) predicted including the above species, as well as 10 pM HgS\(_x\) (estimated K\(_{ow}\) of 1.000). Duplicate experiments were performed at 4 × 10\(^{-4}\) M S(−II)\(_T\).

**TABLE 2.** Formation Constants and Weighted Sum of Squares over Degrees of Freedom (WSOS/DF) for Various Likely Mercury—Polysulfide Complexes

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high Kfides may have two competing effects on mercury bioavailability; due to their differences in size, polysulfide species would diffuse equally well through membranes, however, that uncharged mercury species. At sulfide concentrations below 10^{-6} M, the presence of polysulfides results in an overall decrease (approximately 3-fold) in the predicted D_{ow} of mercury. At higher sulfide, a slight (up to 2-fold) increase in overall D_{ow} is predicted.

While speculations of the effects of polysulfides on methylation are certainly reasonable, their validity will ultimately need to be tested by direct measurements of methylation rates in the presence and absence of S(0).

Acknowledgments
The authors wish to thank Lynn Roberts and Rob Mason for their initial inspirations at the conception of this study, their technical guidance through rigorous laboratory methods, and their continuing advice. Also, we greatly appreciate the invaluable comments of Cindy Gilmour and Janina Benoit and the meticulous laboratory assistance of Karen Murray. We are grateful to Dan Brabander, Miriam Chirico, Samantha Roberts, Dianne Newman, Nicole Keon, David Senn, and three anonymous reviewers for their helpful comments on the manuscript. This work was supported by the NIEHS Superfund Basic Research Fund (Grant P42-ES4675-08) and a GE Graduate Fellowship to Jenny Ayla Jay.

Supporting Information Available
The full data set and FITEQL tables, further information concerning K_{ow} calculations for HgS_{2}, and a sensitivity analysis of the model to HgS_{5}^{2-}. This material is available free of charge via the Internet at http://pubs.acs.org.

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