XAS-based characterization of thioarsenates and their transformation to thioarsenites in acidic synthetic solutions

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Abstract. Recent ab initio calculations predict that As(III)- and As(V)-thioanions can occur simultaneously in sulfidic environments at ambient pH. However unambiguous structural characterizations for the two homologue series of thioarsenites or thioarsenates are still missing. In this study, the molecular structures of synthesized mono-, di-, and tetrathioarsenate were characterized by XRD and XAS in their solid state and in alkaline or near-neutral solution. The determined As(V)-S and As(V)-O bond distances of 2.13-2.18 Å and 1.70 Å, respectively, are consistent with the theoretical expectations for thioarsenates and can be clearly differentiated from the corresponding As(III)-bonds, with lengths of 2.24-2.34 Å and 1.78 Å, respectively. The XANES edge positions of the individual thioarsenates (mono- 11871 eV, di- 11870 eV, and tetrathioarsenate 11869.5 eV) lie between those of As2O5 (11872.3 eV) and As2O3 (11868.2 eV) and demonstrate that increasing sulfur substitution decreases bond energies and, consequently, absorption edge energy. Thioarsenates can be clearly distinguished from the species formed upon acidification of tetrathioarsenate to pH < 6.3. These species were identified as thioarsenites. Their XANES edge energy lies ca. 1 eV below that of As2O3, confirming the redox-state change from As(V) to As(III), which is also reflected in the increased As-S distance of 2.23-2.28 Å, corresponding to As(III)-S species. At pH 3, the detection of As-As-bonds indicates the beginning formation of colloids, most likely amorphous As2S3. Our results indicate that in synthetic solutions, thioarsenites can form as intermediate species between dissolved thioarsenates at near-neutral pH and AsS-precipitates formed under acidic conditions.

Introduction

Inter-elemental reactions and complex formation of arsenic and sulfur control arsenic solubility, mobility, and toxicity in sulfidic environments. As such environments are reducing, it is controversially discussed whether the As-S species formed are thioarsenites (As(III)-S species) (Helz et al., 1995, Bostick et al., 2005, Beak et al., 2008) or thioarsenates (As(V)-S species) (Stauder et al., 2005, Planer-Friedrich et al., 2007, Wallschlaeger and Stadey, 2007). The latest ab initio calculations even imply a co-occurrence of thioarsenates and thioarsenites in sulfidic environments at ambient pH (Helz and Tossell, 2008). Unambiguous characterization, however, is still missing, due to the lack of explicit structural data for any of these thioanions. This study focused on the structural characterization of synthesized thioarsenates with XAS, and the identification of species formed upon acidification of tetrathioarsenate.

Materials and Methods

Previously synthesized mono-, di-, and tetrathioarsenate (Wallschlaeger and Stadey, 2007) were analysed by XAS as solids and 10 mM solutions (liquid and flash-frozen) at the Rossendorf Beamline (ESRF, France). For the pH-dependent speciation studies, a 10 mM tetrathioarsenate solution was titrated (1 M HCl) to pH 9.5, 6.3, 5.8, and 2.8, flash-frozen and subjected to XAS. Preparation of all samples was done in a N2-atmosphere to avoid oxidation. XAS spectra were collected at the As K-edge (11867 eV) at room temperature (RT for liquid samples) and with a He-Cryostat at 15 K (solids and flash-frozen samples) in absorption (Oxford ionization chamber) and fluorescence mode (Canberra 13-element Ge-Detector). With the Software SixPack (Webb, 2005) the spectra were averaged, dead-time corrected, background subtracted, and normalized. EXAFS shell fitting on the Fourier transformations was performed using FEFF 7.02 and WinXAS 3.1.

Results

The As-O and As-S coordination numbers (Table 1) confirmed the structure as the expected mono-(As2O5 SΔ2), di-(AsO3S3), and tetrathioarsenates (AsS4 3-). The As-O bond
distances of 1.70 Å, comparable with arsenate and published thioarsenate XRD data (Sowerby, 1979), are clearly distinguishable from arsenite (1.78 Å) and thioarsenites with 1.77-1.82 Å (Helz et al., 1995, Bostick et al., 2005, Beak et al., 2008). The As-S distances with 2.13-2.18 Å were clearly shorter than those published for mineralized As(III)-sulfides (2.23-2.28 Å) and thioarsenites (2.23-2.24 Å) (Helz et al., 1995, Beak et al., 2008). The As-S distances with 2.13-2.18 Å were clearly shorter than those published for mineralized As(III)-sulfides (2.23-2.28 Å) and thioarsenites (2.23-2.24 Å) (Helz et al., 1995, Beak et al., 2008).

Table 1 Coordination of aquatic thioarsenate complexes determined at 15 K

<table>
<thead>
<tr>
<th>samples</th>
<th>O coordination</th>
<th>S coordination</th>
<th>ΔE0 [eV]</th>
<th>χ2 res [%]</th>
<th>CN R [Å]</th>
<th>σ2 [Å2] CN R [Å]</th>
<th>σ2 [Å2]</th>
</tr>
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<tbody>
<tr>
<td>AsO3S3-</td>
<td>pH 11.6</td>
<td>3.1 1.70 0.0018</td>
<td>1.1 2.18 0.0021</td>
<td>5.7</td>
<td>6.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsO2S2-3</td>
<td>pH 12.3</td>
<td>2.1 1.70 0.0014</td>
<td>1.9 2.16 0.0014</td>
<td>7.3</td>
<td>15.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsS4-3</td>
<td>pH 12.3</td>
<td>3.2 2.24 0.0054</td>
<td>7.9 19.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 2.8</td>
<td>3.8 2.28 0.0035</td>
<td>8.6 13.9</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

With increasing sulfur substitution XANES edge position decreases due to decreasing bond energies (Figure 1). A further shift in the edge position to ca. 1 eV below As2O3 occurred upon titration of the alkaline tetrathioarsenate at slightly acidic conditions (Figure 1). This shift is characteristic of a change in redox-state from As(V) to As(III). The increased bond distances (Table 1) to 2.24 Å and 2.28 Å confirm the formation of As(III)-S species, too. While the species formed at pH 5.8 can be assigned to thioarsenites as in prior publications (Beak et al., 2008), at pH 2.8 we observe a transitory stage to polymeric As-S species and AsS precipitates, shown by an emerging As-As coordination.

Discussion

Synthesized mono-, di-, and tetrathioarsenates were explicitly characterized with typical bond distances of 1.70 Å for As-O and 2.13-2.18 Å for As-S and XANES edge energies between As2O3 and As2O5. The individual thioarsenates are clearly distinguishable in their XANES and EXAFS spectra. Thioarsenates can also be distinguished from thioarsenites, due to their characteristic As(III)-S bond lengths of 2.24-2.28 Å and XANES edge positions between As2O3 and As2S3. The present data clearly show the transformation of thioarsenates predominant at alkaline to neutral pH via thioarsenites at slightly acidic pH to formation of polymeric As(III)-S species under acidic conditions, before precipitation of As(III)-sulfides.

References