Structure, acidity, and metal complexing properties of oxythioarsenites in hydrothermal solutions

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ABSTRACT

In the pursuit of understanding the aqueous chemistry of oxythioarsenites (i.e., H_3AsO_2S and H_3AsOS_2) on a microscopic scale, first principles molecular dynamics (FPMD) simulations were performed to investigate the hydration structures, acidity constants, and metal-complexing properties of these species in aqueous solutions at temperatures up to 573 K. The simulations showed that the oxythioarsenite species are stable and have trigonal pyramidal structures in both low- and high-temperature fluids. Their solvated structures were characterized in detail and it was found that the S or H atoms of the SH ligands form very weak H-bonds with the solvating water molecules and the OH ligands form H-bonds with water as both donors and acceptors. Furthermore, the dangling S or O sites act as strong acceptors to form H-bonds. Their acidity constants were calculated by using the FPMD-based vertical energy gap method. Together with our previous work (Liu et al., 2015, *Chemical Geology*, 411, 192–199), we found that in the arsenite-thioarsenite series (i.e., $H_3AsO_{3-x}S_x$ for x varying from 0 to 3), the pK_a values of the oxythioarsenite species (H_3AsO_2S and H_3AsOS_2) were always located between those of the end members, H_3AsO_3 and H_3AsS_3, and decreased with the increasing temperature up to 573 K. Based on the calculated acidity constants, the speciation versus pH distributions were obtained at temperatures ranging from ambient temperature to 573 K. It was found that both $H_2AsO_2S^-$ and $H_2AsOS_2^-$ are the predominant species at near neutral pH for H_3AsO_2S and H_3AsOS_2 species, respectively. In addition, the structures and the dissociation free energy of the oxythioarsenite-metal complexes at 573 K indicated that these As-S moieties are effective ligands for complexing with ore-forming metals in geological fluids.

1. Introduction

Arsenic has become a focus of attention because of its toxic effect on humans as well as the ubiquitous occurrence in the environment, such as in hydrothermal ore deposits, and ground and surface water (Chakrabarty, 2016; Nordstrom, 2002; O'Day, 2006; Oremland and Stolz, 2003; Smedley and Kinniburgh, 2002). It is also found in minerals such as As-rich pyrite, which may act as a sink for noble metals because As is commonly associated with the ores of metals like gold, silver, and copper (Marini and Accornero, 2006; Pokrovski et al., 2014; Seward et al., 2014). Therefore, a more comprehensive understanding of arsenic speciation is important for improving both low- and high-temperature geochemical models that explore and predict the arsenic distribution in geo-fluids. Furthermore, the molecular-scale formation mechanism of the complexation of arsenic and ore-forming metals in hydrothermal fluids is crucial for understanding the key ore-forming processes of the arsenic-bearing deposits.

It is generally accepted that inorganic arsenic predominantly binds with oxygen and sulfur to form *aquo* species such as arsenites, arsenates, (oxy)thioarsenites, and (oxy)thioarsenates (Guo et al., 2017; Perfetti et al., 2008; Zakaznova-Herzog and Seward, 2012). Owing to the typically low oxidation potential in hydrothermal fluids, arsenic exists in the +3 state in its hydroxide and sulfide complexes (Bundschuh and Maity, 2015; Pokrovski et al., 1996). With various sulfur activities, the members of the arsenite-thioarsenite series (i.e., $H_3AsO_{3-x}S_x$ for x varying from 0 to 3) and their deprotonation species can be regarded as common and simple arsenic species in the aqueous solutions (Beak et al., 2008; Zakaznova-Herzog and Seward, 2012). Herein, the acidity constant (pK_a) is a fundamental thermodynamic parameter of this series (Watts et al., 2014). The ionization constants of the end members have been measured experimentally and computationally at room temperature. The pK_{a1} of arsenous acid has been determined to be 9.2–9.3 and the successive pK_a values of the thioarsenites lie in the ranges 3.8–4.2, 6.5–7.6, and 9.3–10.3 (Liu et al., 2015; Raposo et al., 2003; Yamazaki et al., 1993; Zakaznova-Herzog and Seward, 2012; Zakaznova-Herzog et al., 2006). This data has been

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successfully expanded up to a temperature of 573 K for both H_3AsO_3 and H_3AsS_3 (Liu et al., 2015; Zakaznova-Herzog et al., 2006).

Recently, some studies have been performed to elucidate the stoichiometric and stability aspects of the oxythioarsenite species. Using IC-ICP-MS in dilute sulfidic waters, Wilkin et al. (2003) reported the stoichiometry and presence of various arsenite species, including the arsenite-thioarsenite series and $As(HS)_4^-$. The detection of $As(HS)_4^-$ could be explained by the incipient oxidation of As^{3+} taking place during the elution/solution handling procedural steps (Zakaznova-Herzog and Seward, 2012). In reductive solutions ($\Sigma(As + S) = 0.1$ M, S/As = 1–5, and pH = 7–10.3), Bostick et al. (2005) identified a dithioarsenite species (i.e., $H_2AsOS_2^-$) using XANES/EXAFS spectra. Later, Beak et al. (2008) performed a XANES/EXAFS study and reported the presence of oxythioarsenite species ($H_nAsOS_2^{n-3}$ and $H_nAsO_2S^{n-3}$) in more dilute solutions at S/As < 3. The study of the solubility of As_2S_3 by Vlassopoulos et al. (2010) provided detailed insights into the formation and ionization constants of mono-, di-, and trithioarsenites by nonlinear least squares optimization at room temperature. Besides, quantum chemical studies have also been used to investigate the structures and pK_a values of the arsenite-thioarsenite series (Helz and Tossell, 2008; Tossell, 2003; Tossell, 1997; Tossell and Zimmermann, 2008; Zimmermann and Tossell, 2009). While the structural characterization of oxythioarsenic molecules was successfully achieved in these studies, some pK_a values show significant discrepancies from the experimentally determined values (Zakaznova-Herzog and Seward, 2012). The main reason for the discrepancy is that the static quantum chemistry calculations with continuum solvent models cannot accurately take the solvent effects into account (Marenich et al., 2014; Rustad et al., 2000). To the best of our knowledge, the microstructures and pK_a values of the oxythioarsenite species under wide ranging T-P conditions have not been systematically studied to date.

Although the association of arsenic and ore-forming metals in sulfur hydrothermal systems has long been recognized (O'Day, 2006; Oremland and Stolz, 2003; Seward et al., 2014), it is still poorly understood. It has been previously reported that the solubility of Cu increases by several orders of magnitude because of the formation of $CuAsOS_2H_2^-$ in sulfur-containing solutions ($\Sigma S = 0.001$–0.1 mM) (Clarke and Helz, 2000). By using a combination of the empirical and ab initio methods, Tossell et al. further confirmed the high stability of $MAsS_2OH_2^-$ (where M = Cu^+, Ag^+, Au^+, etc.) in the gas phase (Tossell, 2000a; Tossell, 2000b; Tossell, 2001). Nevertheless, the microscopic formation and reactive process of the As-metal combination in aqueous solutions, especially at elevated T-P, have not been reported until now.

The first principles molecular dynamics (FPMD) method has been proven to be an effective way to explore the complexation and coordination of species in aqueous solutions (Brugger et al., 2016; Sherman, 2010). In recent years, FPMD has been successfully applied to the speciation studies of metal/metalloid complexes such as those of Au^+, Ag^+, Cu^+, Zn^{2+}, Ca^{2+}, As^{3+}, Y^{3+}, Zr^{4+}, and Hf^{4+} (Jahn et al., 2015; Liu et al., 2010; Liu et al., 2011; Mei et al., 2014; Mei et al., 2013; Mei et al., 2015; Pokrovski et al., 2015; Pokrovski et al., 2013; Sherman, 2007; Sherman, 2010; Vuilleumier et al., 2014), which are consistent with the experimental data as well. As a result, the FPMD method acts as a promising complement to the experiment performed at low- and high-temperatures. Recently, the FPMD-based vertical energy gap method has been developed for predicting the pK_a values (Costanzo et al., 2011; Sulpizi and Sprik, 2008). This state-of-the-art technique has also been applied to a large set of molecular acids with an accuracy of 2.0 pK_a units (Cheng et al., 2009; Costanzo et al., 2011; Mangold et al., 2011; Sulpizi and Sprik, 2008; Sulpizi and Sprik, 2010). In particular, we calculated the pK_a values of molybdic acid, arsenite, and thioarsenite species at different temperatures, ranging from ambient temperature to 573 K, within the error range of 1.0 unit (Liu et al., 2013; Liu et al., 2015). These results indicate that the method is also valid at high-

T solutions.

In this study, FPMD simulations were carried out to investigate the microstructures, acidity constants, and metal complexing properties of oxythioarsenites (H_3AsO_2S and H_3AsOS_2) from ambient temperature to 573 K. The FPMD-based vertical energy gap method was also applied to calculate the acidity constants of oxythioarsenites. According to the calculated pK_a values, the speciation distributions versus pH were derived over the investigated temperature range. Furthermore, the structures of $H_2AsO_2S^-$-M (M = Cu^+, Ag^+, Au^+) complexes were calculated at 573 K and the dissociation free energy of $H_2AsO_2S^-$-CuHS was further estimated to quantify the stability of As-M complexing at the same temperature. Thus, this study provides new insights for understanding the transport of arsenic and metals in the S-bearing hydrothermal fluids.

2. Methods

2.1. Systems

In all initial configurations, the investigated species was placed in the simulation cell and the water molecules were inserted randomly. The simulation cells for the oxythioarsenite species were periodically repeated cubic boxes with a side length of 12.43 Å. The number of water molecules and the corresponding T-P conditions are listed in Table 1. The temperatures chosen for study were ambient temperature, 473 K, and 573 K. In order to avoid the glassy behavior at lower temperatures, the temperature at ambient conditions was controlled at 330 K (VandeVondele et al., 2005). The pressures at 473 K and 573 K in Table 1 were the saturated vapor pressures and should be viewed as approximations because pressure was not controlled in the simulations (see below).

The cell sizes for the simulations of As-S-metal complexes (i.e., $H_2AsO_2S^-$-MHS (where M = Cu^+, Ag^+, Au^+) and Ag_3AsS_3) were 15 Å × 15 Å × 15 Å. The temperature was controlled at 573 K. There were 76 and 73 water molecules in the $H_2AsO_2S^-$-MHS and Ag_3AsS_3 systems, respectively.

The number of water molecules in a system shown above was determined by estimating the number of water molecules one As-containing complex could exclude from pure liquid water. The number of water molecules in pure liquid water was obtained from the equation of state of water at the corresponding T-P conditions (Wagner and Pruß, 2002). The hydration structures of the complexes (except $H_2AsO_2S^-$-MHS) and water molecules in liquid water were considered as tetrahedrons. Accordingly, we found that H_3AsOS_2, H_3AsO_2S, and Ag_3AsS_3 can replace approximately 4, 4, and 8 water molecules, respectively. The MHS group of $H_2AsO_2S^-$-MHS can exclude one H_2O molecule.

2.2. FPMD details

In this study, the CP2K/QUICKSTEP package (http://www.cp2k.org) (VandeVondele et al., 2005) was applied to the FPMD simulations. Density functional theory (DFT) was implemented with a mixed Gaussian and plane waves approach (Lippert et al., 1997). Goedecker-Teter-Hutter (GTH) pseudopotentials (Goedecker et al., 1996) were used to avoid the core state calculation. The BLYP density functional (Becke, 1988; Lee et al., 1988) was employed and the DZVP basis sets were used for O, H, S, As, Au, Ag, and Cu. A cutoff of 280 Ry was set for the

Table 1
T-P conditions and number of water molecules in the boxes.

T-P conditions	Acid	Number of water molecules (N)
Ambient	H_3AsO_2S/H_3AsOS_2	60
473 K–1.55 MPa	H_3AsO_2S/H_3AsOS_2	52
573 K–8.59 MPa	H_3AsO_2S/H_3AsOS_2	42