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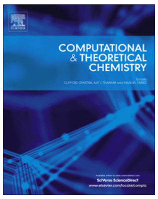

Density functional theory calculations on the adsorption of monomethylarsonic acid onto hydrated iron (oxyhydr)oxide clusters

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ABSTRACT

Monomethylarsonic acid (MMA) is an important arsenic pollutant that was extensively used as a herbicide/pesticide. Once introduced to the environment, MMA can enter the food chain or be recycled to the more mobile forms of arsenic that can contaminate nearby water sources. Density functional theory with dispersion corrections (DFT-D3) calculations provide a molecular-level understanding of the fate of pollutants such as MMA, particularly their interactions with reactive soil components such as iron (oxyhydr) oxides. Energies, optimal geometries, and vibrational frequencies for hydrated MMA complexes with iron (oxyhydr)oxide clusters were computed and ligand exchange reactions were constructed to investigate the thermodynamics of inner- and outer-sphere complex formation. The Gibbs free energies and enthalpies of adsorption show that both inner- and outer-sphere complex formation is thermodynamically favourable, with monodentate complexes being most favourable. The calculated As—Fe inter-atomic distances for MMA complexes are shown to be 3.23–3.55 Å for inner-sphere complexes and 5.17–5.75 Å for OS complexes. The calculated infrared frequencies were correlated to experimental values in the 740–900 cm^{-1} range containing stretching frequencies of As—O bonds. A comparison between MMA and other organoarsenicals reveals that adding methyl groups to arsenate affects the adsorption process and hence the mobility of organoarsenicals in the environment.

1. Introduction

Arsenic (As), present in hundreds of different minerals in the Earth's crust, is released to the environment by the weathering of rocks [1,2]. Under oxidizing conditions, arsenate is the dominant arsenic species and is strongly sorbed onto clays, iron (Fe), aluminum (Al) and manganese (Mn) (oxyhydr)oxides, as well as organic matter. Under reducing conditions, arsenite is the dominant arsenic species and is both more mobile and more toxic [3]. Bio-methylation of inorganic arsenic by organisms that live in the soil is prevalent in the environment and leads to the production of a variety of methylated arsenicals through the Challenger pathway [4–6]. Historically, monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and their sodium salts were the most common ingredients in herbicides and pesticides [7]. In the United States, monosodium methylarsonate (MSMA) was widely used as a herbicide in the 1990s, but has since been replaced by arsenic-free options [8]. In Canada, MMA was widely used in British Columbia to help suppress outbreaks of the mountain pine beetle in the 1990s, but has since been discontinued for fear of negative effects on wildlife. Blood samples from woodpeckers and other birds that feed on Mountain pine beetles from contaminated MMA trees showed elevated levels of total arsenic [9,10]. This shows that the accumulation and transfer of organic arsenic within the food chain could be toxic to other wildlife in general and avian species in particular.

Once in the environment, organoarsenicals form surface complexes with reactive soil components such as metal oxides. The nature of these surface complexes depends on the particular metal oxide surface. On amorphous aluminum oxides, MMA was reported to form bidentate binuclear (BB) complexes using extended absorption fine structure spectroscopy (EXAFS) [11]. The same type of complex formation was reported for the binding of MMA and DMA on goethite (α-FeOOH) using EXAFS [12]. However, using attenuated total internal reflection Fourier transform infrared spectroscopy (ATR-FTIR) and flow microcarlorimetry, MMA was reported to form mostly monodentate mononuclear (MM) complexes [13,14]. Also, it is likely that the presence of extra methyl groups on the arsenical affects the rate of adsorption [12,13]. Our earlier density functional theory (DFT) studies demonstrated that DMA forms more outer-sphere (OS) and MM

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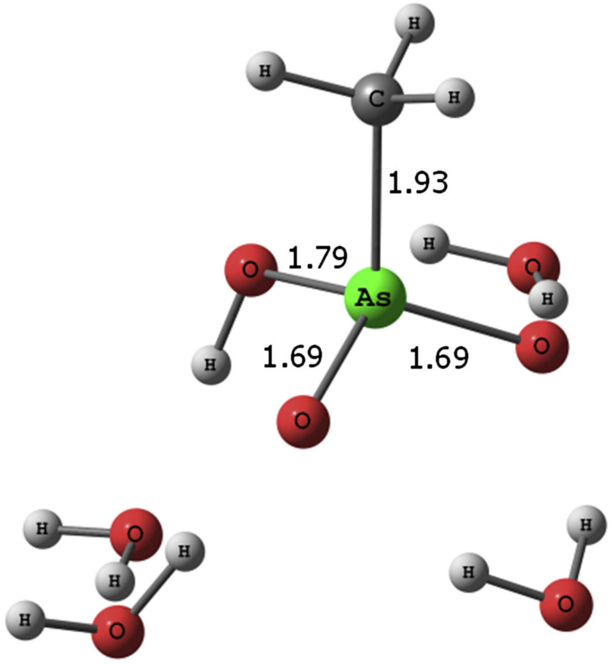

Fig. 1. Energy minimized structure of MMA with surrounding explicit waters. Calculated using B3LYP/6-311+G(d,p) with IEFPCM and GD3BJ dispersion.

complexes, and that a high activation barrier may hinder the formation of BB complexes [15–17]. Our latest DFT study showed that an extended metal oxide surface with four metal centers is desirable when dealing with MM and OS complexes [16]. This is because a metal oxide surface that has two metal centers allows the complexes to over-relax with the arsenical wrapping around the surface edge to find its minimum energy structure when the complex is optimized.

In this paper, we report DFT calculations on MMA surface complexes on an iron-(oxyhdyr)oxide cluster with four iron centers in a hydrated environment with dispersion corrections. Guided by the pKa of MMA (3.6,8.2) [18] and point of zero charge (PZC) of iron oxides (7–9) [19], we simulated only the interaction of singly protonated MMA and positively charged iron (oxyhydr)oxide clusters that are dominate under neutral pH conditions. This interaction could form three types of surface complexes: OS, MM and BB. We calculated the Gibbs free energies, enthalpies and entropies of adsorption for various types of ligand exchange reactions leading to the formation of the above complexes to determine which reactions are more thermodynamically favourable. The data is analyzed and compared to other well-known organoarsenical systems like p-arsanilic acid (pAsA) and DMA as mono- and disubstituted arsenicals, respectively.

2. Computational methods

Calculations were performed at the B3LYP/6-311+G(d,p) level of theory, on Gaussian 09, running on SHARCNET [20]. An initial geometry for the cluster of interest was built and energy optimization calculations were performed to find a geometry that is at an electronic energy (E_0) minimum on the potential energy surface (PES). To properly simulate a hydrated environment, explicit water molecules were added to form the first solvation shell, and the integral equation formalism polarizable continuum model (IEFPCM) [21], was used to incorporate long range solvation effects. Careful steps were taken to ensure that we are very close to the energy of a global minimum because of how the complexes were built. We first optimized in a vacuum and then added explicit water molecules one or two at a time in key locations so that they form favourable hydrogen bonds. Dispersion effects were included using Grimme's D3 method with Becke-Johnson (BJ) damping (GD3BJ). Inclusion of dispersion effects is known to improve inter-atomic distances [22] and hydrogen bonds lengths [23] and has been shown to be particularly important for OS complexes [16]. Table S1 in the Supplementary Material lists the Cartesian coordinates for the optimized structures with dispersion.

Calculating the vibrational frequencies enables a simulation of the infrared spectra, and also enables a simulation of thermodynamic properties, like the enthalpy, Gibbs free energy and the entropy at finite temperature [24]:

$$\Delta H^{\circ}_{\mathrm{ads}} = \sum (E_0 + H_{\mathrm{corr}})_{\mathrm{products}} - \sum (E_0 + H_{\mathrm{corr}})_{\mathrm{reactants}} \tag{1}$$

$$\Delta G^{\circ}_{\mathrm{ads}} = \sum (E_0 + G_{\mathrm{corr}})_{\mathrm{products}} - \sum (E_0 + G_{\mathrm{corr}})_{\mathrm{reactants}} \tag{2}$$

$$\Delta S^{\circ}_{\mathrm{ads}} = \left(\Delta H^{\circ}_{\mathrm{ads}} - \Delta G^{\circ}_{\mathrm{ads}}\right)/T \tag{3}$$

where H_{corr} and G_{corr} are the thermal corrections to enthalpy and Gibbs free energy, respectively. Because the calculations were performed at standard ambient temperature (298 K) and pressure (1 atm), the standard sign "°" is used in Eqs. (1)–(3).

Calculations for the Fe(III) surfaces were performed at high spin. Since, the electron configuration of Fe(III) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ and each electron in the 3d block is unpaired, the multiplicity of a cluster containing four Fe atoms is 21 (5 unpaired electrons for each of the 4 Fe atoms + 1) [25]. The lowest energies were also obtained for the highest spin (11) in two Fe clusters [25]. This analysis is inline with an earlier study on the electronic and optical properties of iron oxide clusters in vacuum and in simulated aqueous environments [26]. In all cases, the charge of the iron (oxyhydr)oxide cluster is kept at +1 because the point of zero charge for iron oxides is in the pH 7–9 range [19]. Together with the MMA anion with $pK_{a1} = 3.6$, $pK_{a2} = 8.2$ [18], neutral OS, MM and BB were simulated.

3. Results and discussion

3.1. MMA complexation with iron (oxyhydr)oxides

The optimized geometry of the hydrated, uncomplexed, and singly deprotonated MMA molecule is shown in Fig. 1. The As—O, As—OH and As—C bond distances are listed in Table 1. The adsorption of the negatively charged MMA molecule onto the positively

Table 1

Predicted As—O, Fe—O bond distances (Å) and As—Fe inter-atomic distances (Å) of OS, MM and BB complexes of MMA with 4Fe iron (oxyhydr)oxide cluster. These values are calculated using B3LYP/6-311+G(d,p) with the IEFPCM solvation and GD3BJ dispersion models.

MMA complexes	As—Fe$_1$	As—Fe$_2$	As—O$_1$	As—O$_2$	As—C	As—OH	Fe$_1$—O$_1$	Fe$_2$—O$_2$
MMA$^-\cdot(H_2O)_4$	–	–	1.69	1.69	1.93	1.79	–	–
OS(**4Fe**) complex	5.23	5.75	1.67	1.67	1.93	1.83	–	–
MM(**4Fe**) complex	4.92	3.55	1.67	1.67	1.92	1.82	–	1.98
MM(4Fe) without dispersion	5.01	3.60	1.67	1.68	1.93	1.83	–	2.00
BB(**4Fe**) complex	3.23	3.47	1.69	1.70	1.92	1.79	2.03	2.37