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ORIGINAL PAPER

Can Fe^{3+} and Al^{3+} ions serve as cationic bridges to facilitate the adsorption of anionic As(V) species on humic acids? A density functional theory study

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Abstract A computational chemistry investigation was undertaken to shed light on the facilitatory role played by Fe^{3+} and Al^{3+} cations in the adsorption of anionic As(V) species by humic acids through the formation of so-called cationic bridges. Geometric and energetic parameters were obtained using density functional theory at the B3LYP/6-31G(d,p) level in conjunction with the polarizable continuum model (to account for the influence of bulk water). We found that, despite their similar molecular geometries, the adsorption energies of the As(V) species AsO_4^{3-} and H_2AsO^{4-} differ when Fe^{3+}, $FeOH^{2+}$, Al^{3+}, and $AlOH^{2+}$ participate in the bridge. We also found that effective adsorption of As(V) species by humic acids strongly depends on whether the considered cationic bridges are tightly coordinated by humic acids at the adsorption sites, as well as on the rigidity of these humic acid adsorption sites.

Keywords Anionic metals · Humic acid · DFT · PCM · Cationic bridge

Introduction

According to the World Health Organization, arsenic and its derivatives are among the most hazardous environmental contaminants. Due to anthropogenic activities such as mining, farming, and industrial processes, these species are present in toxic amounts in some groundwaters of Argentina, Cambodia, Chile, Mexico, the United States, Vietnam, India, and Bangladesh [1–4]. In the aquatic environment, arsenic exists in two chemical states: As(III), in derivatives of arsenous acid H_3AsO_3; and As(V), in derivatives of arsenic acid H_3AsO_4.

The environmental fate of As(III) and As(V) species in groundwater is dependent on their interactions with natural organic and inorganic matter. The current literature discusses three such scenarios:

(i) Microbial degradation of As(III) and As(V)—the ratio of As(III) to As(V) found in the environment is influenced by microbial activity [5]
(ii) Adsorption by mineral surfaces [6, 7]
(iii) Interaction with humic acids [8, 9]

Scenario (iii) is the topic of this paper. Thermodynamically feasible interactions between anions of both arsenic and arsenous acids and components of humic acids such as carboxylate and phenolate groups are the dominant topics in this context in the literature [8, 9]. However, it should be noted that both of these species (carboxylate/phenolate groups and anions of arseneous/arsenic acid) are negatively charged. Therefore, if they interact directly, they will actually repel each other. Consequently, a positively charged bridge between these anions is needed to initiate such interactions. Recently, it has been reported that Fe^{3+} plays this role when interacting with humic acids [10–13]. However, when As(III)/As(V) species are adsorbed by the surfaces of inorganic minerals, Fe^{3+} ions are not the only mediators of this binding mechanism. It was found that arsenic derivatives are adsorbed on the surfaces of iron(III) oxides and hydroxides such as goethite (see [14] and references therein), as well as on the surface of

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gibbsite (see [15] and references therein), which is an alumina-containing mineral. It was also found that, in the case of Suwannee River humic acid, neither Al^{3+} nor Ga^{3+} are able to serve as bridges [16], so they do not mediate the adsorption of As(V) species.

To shed more light on the specific roles of cations such as Al^{3+} and Fe^{3+} as bridges that potentially could mediate the adsorption of arsenic derivatives at adsorption sites on humic acids, we opted to investigate their roles using a computational chemistry approach. Specifically, we employed the anion of benzoic acid ($C_6H_5COO^-$) as a model humic acid adsorption site, Fe^{3+}, $FeOH^{2+}$, Al^{3+}, and $AlOH^{2+}$ as model cationic bridges, and the anions AsO_4^{3-} and $H_2AsO_4^-$ as model As(V) anionic species.

Computational methods

The Gaussian 09 program package was used for all of the calculations [17]. The geometries of all considered species were optimized using density functional theory at the B3LYP/6-31G(d,p) level. To establish that a minimum was observed for each optimized geometry, the harmonic vibrational frequencies were calculated for all obtained structures. The energy of the interaction was obtained with the inclusion of the gas-phase-calculated basis set superposition error (BSSE). Most of the adsorbed species considered here were expected to be quite flexible; to take this into account, the relaxation energy—the difference between the total energy of the isolated species and the energy of the species in the adsorbed state—was also calculated. The relaxation energy was considered a component of the adsorption energy. The influence of bulk water was taken into account using the polarizable continuum model (PCM) [18], assuming the static dielectric permittivity to be 80.

Since iron(III)-containing species can in principle possess several spin states, separate calculations for such iron-containing species as Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$, and $Fe(OH)_3$ were also performed. In all cases except for $Fe(OH)^{2+}$ (SCF convergence was not reached), a strong preference of the *d*-electron shell of iron for a sextet configuration was noted. Therefore, only the sextet configuration was used in further calculations.

Results and discussion

Before discussing the obtained results, we first explain why we chose our models. The anion of benzoic acid ($C_6H_5COO^-$) was selected as it is the most strongly interacting component of humic acids. $FeOH^{2+}$ and $AlOH^{2+}$ are species that mimic the geometric structure of an adsorption bridge close to neutral pH; Fe^{3+} and Al^{3+} mimic the structure of an adsorption bridge under acidic conditions. $H_2AsO_4^-$ is the most realistic structure of an anionic As(V) species, and AsO_4^{3-} is the anionic As(V) species that results from the full dissociation of $H_2AsO_4^-$ [10–13]. According to experimental data, adsorbed humic acid complexes that include a humic acid adsorption site, an anionic arsenic species, and a cationic bridge are ternary complexes, so those complexes were considered here. We also considered complexes that include two ($C_6H_5COO^-$) fragments and are formally quaternary complexes. This was done to reflect the fact that complexation of metal cations by humic acids actually results in the formation of multi-coordinate complexes due to the presence of other electron-donating groups such as –O, $-NH_2$, etc. The B3LYP-calculated structures of the complexes are presented in Fig. 1. Since the only available experimentally determined geometric parameter is the As–Fe interatomic distance, we present values of this in Fig. 1 along with values of the (similar) As–Al distance. All other geometric parameters can be obtained by analyzing the Cartesian coordinates of the species of interest, which are available upon request from the authors.

Useful experimental data on the structures of cation-bridge-mediated As(V) species are rather scarce [10–16]. As we have already mentioned, the only experimentally determined structural parameter is the As–Fe interatomic distance. Data on this distance allow us to categorize the complex as bidentate if this distance is ca. 2.9 Å and monodentate if this distance is ca. 3.2 Å [9, 12, 19]. Despite using monodentate structures as the initial geometries in all cases, the results of the analysis of As–Fe distances presented in Fig. 1 suggest that both monodentate and bidentate structures were obtained during the presented study. The calculations predict slightly shorter distances than the corresponding experimentally determined distances. This is probably because our models are very simple compared to the structures of real adsorption complexes. We would also like to highlight the similarity between the geometric structures of the Al^{3+}- and Fe^{3+}-containing species. According to the graphics presented in Fig. 1, those adsorption complexes are similar in shape and have comparable As–Fe and As–Al interatomic distances. However, since the ionic radius of Al^{3+} is slightly smaller than the ionic radius of Fe^{3+} (R_{ion}^{Al} = 0.67 Å, R_{ion}^{Fe} = 0.69–0.78 Å; see https://en.wikipedia.org/wiki/Ionic_radius), the As–Al distance is also slightly shorter than the corresponding value for As–Fe. In addition, we noticed that our calculations predict that both interatomic distances are only weakly sensitive to the coordination number by ligands.

Since we do not know how rigid the adsorption sites of humic acids are, Table 1 collates interaction energies calculated in two different ways: either the adsorption site was allowed to relax following interactions with AsO_4^{3-} and $H_2AsO_4^-$ or it was not.

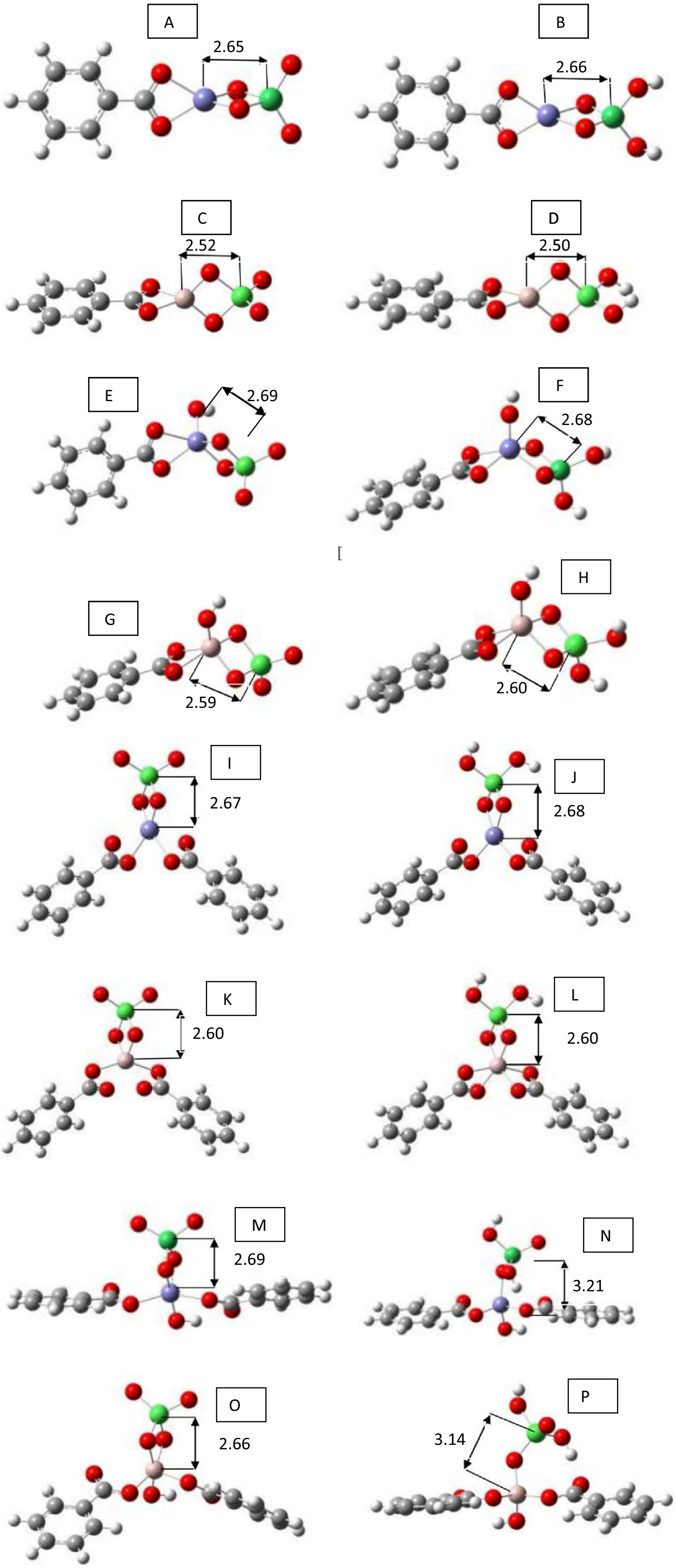

Fig. 1a–p Geometric structures of the models considered in this work: **a** $Fe^{3+}C_6H_5COO^-AsO_4^{3-}$, **b** $Fe^{3+}C_6H_5COO^-H_2AsO_4^-$, **c** $Al^{3+}C_6H_5COO^-AsO_4^{3-}$, **d** $Al^{3+}C_6H_5COO^-H_2AsO_4^-$, **e** $[FeOH]^{2+}C_6H_5COO^-AsO_4^{3-}$, **f** $[FeOH]^{2+}C_6H_5COO^-H_2AsO_4^-$, **g** $[AlOH]^{2+}C_6H_5COO^-AsO_4^{3-}$, **h** $[AlOH]^{2+}C_6H_5COO^-H_2AsO_4^-$, **i** $Fe^{3+}(C_6H_5COO^-)_2AsO_4^{3-}$, **j** $Fe^{3+}(C_6H_5COO^-)_2H_2AsO_4^-$, **k** $Al^{3+}(C_6H_5COO^-)_2AsO_4^{3-}$, **l** $Al^{3+}(C_6H_5COO^-)_2H_2AsO_4^-$, **m** $[FeOH]^{2+}(C_6H_5COO^-)_2AsO_4^{3-}$, **n** $[FeOH]^{2+}(C_6H_5COO^-)_2H_2AsO_4^-$, **o** $[AlOH]^{2+}(C_6H_5COO^-)_2AsO_4^{3-}$, **p** $[AlOH]^{2+}(C_6H_5COO^-)_2H_2AsO_4^-$. The atoms are color-coded as follows: *purple* iron, *green* aluminum, *red* oxygen, *gray* carbon, *white* hydrogen

Table 1 Basis set superposition error (BSSE)-corrected interaction energies (ΔE_{BSSE}), relaxation-energy-corrected interaction energies ($\Delta E_{\mathrm{BSSE}}{}^{\mathrm{rel}}$), and relaxation energies (ΔE_{rel}) in a bulk water solution (all energies are in kcal/mol)

Fe^{3+} and Al^{3+} bridges	$AsO^{3-}{}_4$			$H_2AsO^{-}{}_4$		
	$\Delta E_{\mathrm{BSSE}}{}^{a}$	$\Delta E_{\mathrm{BSSE}}{}^{\mathrm{rel}}$	$\Delta E_{\mathrm{rel}}{}^{b}$	ΔE_{BSSE}	$\Delta E_{\mathrm{BSSE}}{}^{\mathrm{rel}}$	$\Delta E_{\mathrm{rel}}{}^{b}$
$Fe^{3+}C6H5COO^{-}$	−162.7	−152.8	9.9	−53.7	−49.4	4.3
$Al^{3+}C6H5COO^{-}$	−301.5	−292.5	9.0	−183.4	−178.6	4.8
$Fe^{3+}OH^{-}C6H5COO^{-}$	−121.3	−109.0	12.30	−34.9	−31.5	3.4
$Al^{3+}OH^{-}C6H5COO^{-}$	−168.9	−120.6	48.3	−81.2	−52.3	28.9
$Fe^{3+}(C6H5COO^{-})_2$	−125.0	−108.2	16.8	−34.7	−28.6	6.1
$Al^{3+}(C6H5COO^{-})_2$	−151.7	−94.1	57.6	−67.1	−30.6	36.5
$Fe^{3+}OH^{-}(C6H5COO^{-})_2$	−69.8	−28.3	41.5	−9.2	8.6	17.8
$Al^{3+}OH^{-}(C6H5CO^{-})_2$	−74.5	15.6	90.1	−21.1	31.2	52.3

[a] Due to SCF nonconvergence, the BSSE of $H_2AsO^{-}{}_4$ was used instead

[b] Relaxation energy in kcal/mol

The data presented in Table 1 suggest that, despite the very similar ionic radii of Al^{3+} and Fe^{3+}, the interaction energies differ significantly for Al^{3+} and Fe^{3+}, especially when the coordination number is low. It is clear that interactions with sites that have Fe^{3+} and Al^{3+} ions with low coordination numbers (i.e., $Fe^{3+}C_6H_5COO^{-}$, $Al^{3+}C_6H_5COO^{-}$, $Fe^{3+}OH^{-}C_6H_5COO^{-}$, and $Al^{3+}OH^{-}C_6H_5COO^{-}$) result in unrealistically high interaction energies, especially in the case of $AsO_4{}^{3-}$; such values would never be observed in adsorption experiments. This is the case regardless of how the interaction energy is calculated (i.e., with or without adsorption site relaxation). In reality, free coordination sites are saturated by the same or other humic acid fragments or by surrounding water molecules. Indeed, if we consider the interaction energies for $Fe^{3+}(C_6H_5COO^{-})_2$, $Al^{3+}(C_6H_5COO^{-})_2$, $Fe^{3+}OH^{-}(C_6H_5COO^{-})_2$, and $Al^{3+}OH^{-}(C_6H_5COO^{-})_2$, it is clear that they are much lower than those for the other Al^{3+} and Fe^{3+} species, especially in the case of the $H_2AsO_4{}^{-}$ anion, which, as mentioned above, is the most realistic As(V) species. It is evident from Table 1 that calculations which do not include the relaxation energy only predict the bonding situations for the Fe^{3+} and Al^{3+} species considered. However, when the relaxation energy is included in the calculations, they predict both the bonding (negative interaction energy) and nonbonding (positive interaction energy) situations. As we have already mentioned, both of these cases (bonding and nonbonding) are observed experimentally [10–16]. This means that adsorption sites of some humic acids with Fe^{3+} or Al^{3+} bridges sometimes cannot adsorb an As(V) species due to the unfavorable bonding contribution of the relaxation energy. This phenomenon could be explored in more depth by considering more realistic models of humic acid adsorption sites.

Conclusions

We have performed a computational study of the efficiencies of cationic bridges formed by Fe(III) and Al(III) species at facilitating the adsorption of As(V) species by humic acids. Simple molecular models were developed. The adsorption energies of $AsO_4{}^{3-}$ and $H_2AsO_4{}^{-}$ were predicted for scenarios where the adsorption is mediated by Fe^{3+} and Al^{3+} bridges coordinated by active sites on humic acids. Both bridges were found to have similar molecular structures and to display similar trends in the change in interaction energy with increasing coordination number. Increasing the coordination number caused the interaction energy to decrease. Including the relaxation energy in the calculation of the interaction energy changes the bonding situations for both the Fe^{3+} and the Al^{3+} derivatives, in agreement with available experimental data. Therefore, we speculate that the relaxation energy is an influence on the roles played by Fe^{3+} and Al^{3+} cationic bridges in the adsorption of As(V) species by humic acids.

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