Supporting Information

Insights into the Surface Complexation of Dimethylarsinic Acid on Iron (oxyhydr)Oxides from ATR-FTIR Studies and Quantum Chemical Calculations

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1. Kinetics of DMA adsorption on FeOOH

Figure S1: Time-dependence of the absorbance at 840 cm^{-1} assigned to DMA(ads) on FeOOH.

2. ATR-FTIR spectra of DMA(aq) in H_2O and D_2O . Figure S2 (left) shows the ATR-FTIR spectra of 0.2 M DMA solution in D_2O at pD 10 and 4 (from top) and $I = 0.01$ M collected on a clean 60° ZnSe IRE according to the procedure described in our earlier work on p-arsanilic acid (p-AsA) (1). When D_2O is used as a solvent, the spectral components observed experimentally have minimal contributions from the librational mode of water molecules. Hence, features observed in Figure S2 are assigned as: 835 cm^{-1} (pD 10) to $\nu(\text{As}=\text{O})$ that blue shifts to 879 cm^{-1} (pD 4) upon protonation (2); 731 cm^{-1} (pD 4) to $\nu(\text{As-OD})$; and 879 and 900 cm^{-1} (pD 10) and 895 and 914 cm^{-1} (pD 4) to $\rho(\text{CH}_3)$. Experimental frequencies were correlated with those calculated for hydrated DMA clusters (Figure S2; right). Details on the calculations are provided below.

Figure S2: Left: ATR-FTIR absorption spectra of 0.2 M ($I = 0.01$ M KCl) DMA(aq) recorded at pD 10 and 4 (dashed lines), and pH 11 and 3 [solid lines, reproduced with permission from ref. (2)]. The dominant species at each pD is shown next to the corresponding spectra. Right: correlation between experimental and calculated As-O stretching vibrations (*vide infra*).

3. Quantification of DMA surface coverage (S_{DMA}) from ATR-FTIR spectra. The net absorbance of the component at 840 cm^{-1} observed in Figure 1 is proportional to the surface coverage of DMA(ads) (S_{DMA}). S_{DMA} is quantified according to:

$$S(\text{molecules} \cdot \text{cm}^{-2}) = \frac{A(\lambda)}{\epsilon(\lambda)N^2d_p(\lambda)\rho_{\text{bulk}}S.A_{\text{BET}}} \quad (\text{S1})$$

where: $A(\lambda)$ is the baseline-corrected absorbance at 840 cm^{-1} ,

$\epsilon(\lambda)$ is molar extinction coefficient in $\text{cm}^2/\text{molecule}$ obtained from the Beer's law fit to the calibration curve of aqueous DMA at pH 7 [$\epsilon(0.0012 \text{ cm}) = 6 \times 10^{-19} \text{ cm}^2 \cdot \text{molecule}^{-1}$],

N is the total number of reflections within the IRE [$N=3$],

d_p is the depth of penetration per reflection in cm [$d_p^{840 \text{ cm}^{-1}} = 2.3 \times 10^{-4}$ and $1.3 \times 10^{-4} \text{ cm}$ for $\alpha\text{-Fe}_2\text{O}_3$ - and $\alpha\text{-FeOOH}$ -coated IRE, respectively],

ρ_{bulk} is the bulk density in $\text{g}\cdot\text{cm}^{-3}$ of the porous Fe-(oxyhydr)oxides film deposited on the IRE calculated from its mass and measured thickness [$\rho_{\text{bulk}}=2.6$ and $1.8 \text{ g}\cdot\text{cm}^{-3}$ for $\alpha\text{-Fe}_2\text{O}_3$ - and $\alpha\text{-FeOOH}$ -coated IRE, respectively], and

$S.A._{\text{BET}}$ is the measured BET surface area of the Fe-(oxyhydr)oxides in $\text{cm}^2\cdot\text{g}^{-1}$ [$S.A._{\text{BET}}=1.86\times 10^5$ and $2.1\times 10^5 \text{ cm}^2\text{g}^{-1}$ for $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$, respectively].

Further details on the derivation of this model and calculations of pathlengths are provided in the Supporting Information of our earlier work on the thermodynamics of p-AsA adsorption on Fe-(oxyhydr)oxides(3).

Table S1 summarizes results from bulk measurements of S_{max} , which agree reasonably well with those derived above from ATR-FTIR absorbance (see *Environmental Significance* Section). Batch adsorption experiments were conducted by reacting ca. 0.5 g of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ particles with 10 mL of 0.8 mM DMA(aq) standard solution (60 ppm As) adjusted to pH 7 and $I = 0.01 \text{ M}$ (KCl). Particle suspensions were shaken for 24 hours using a vortex mixture (VWR), followed by centrifugation. Supernatants were filtered once in a $0.45 \mu\text{m}$ syringe filter and collected for analysis of total arsenic using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Besides cost-effectiveness, the main advantage of this *in-situ* determination of S_{DMA} compared with *ex-situ* bulk measurements of total adsorbed arsenic is the elimination of the “chemical digestion” step. This step is often employed to liberate adsorbed arsenic into the aqueous phase to quantify it using inductively couple plasma-atomic emissions spectroscopy (ICP-AES) for “total arsenic”.

Table S1: Total arsenic content from batch experiments on DMA binding to Fe-(oxyhydr)oxides at pH 7 and $I = 0.01$ M KCl

Substrate	[As] in supernatants (mg/L)	[As] adsorbed ^a (mg/L)	As/Fe molar ratio (mmol/mol)	DMA surface coverage (molecules/cm ²)
α -Fe ₂ O ₃	0.29	51.7	1.1	4.5×10^{13}
α -FeOOH	0.19	51.8	1.2	3.9×10^{13}

^a The amount adsorbed was calculated by subtracting [As] in supernatants from DMA standard solution (52 ppm As measured by ICP-AES added to ca. 50 g/L of each substrate.

4. pH-Envelope data for DMA(ads) from the component at 877 cm⁻¹

Figure S3: pH-envelopes of 1mM DMA adsorption on (a) α -Fe₂O₃, and (b) α -FeOOH particles as a function of $I = 0.001, 0.01$, and 0.1 M at 298 K. Experimental data (filled markers) are the baseline-corrected ATR absorbance at 877 cm⁻¹. Error bars are $\pm\sigma$ from averaging 3-4 experiments, each on a freshly-prepared film. Solid lines are guides to the eye.

5. DFT calculations of hydrated DMA complexes. Figure S4 shows the energy minimized equilibrium geometries of hydrated DMA clusters that are (a) fully deprotonated (8 explicit water), (b) fully protonated (8 explicit water), and (c) fully protonated (4 explicit water). Quantum chemical calculations were performed in Gaussian '09 using DFT(B3LYP/6-31G*) and the IEFPCM solvation model. Frequency calculations were performed on the optimized geometries of each hydrated DMA cluster shown in Figure S4. Calculated infrared spectral components with major contributions from $\nu(\text{As-O})$ are shown in Figure S2 (right). Cluster (a) in Figure S4 produced additional spectral components at 762, 802, 823, 847 and 857 cm^{-1} mainly due to H-bonding interactions with explicit water molecules. Simulations of these modes show that they are coupled to water and methyl group vibrations. The cluster containing four explicit water molecules produced values for $\nu(\text{As-O})$ that correlate very well with experimental ones (Figure S2; left).

Figure S4: Minimum energy equilibrium geometries of hydrated DMA clusters using DFT(B3LYP/6-31G*) and IEFPCM solvation model in Gaussian '09. Bond distances for (a) As-O1 = 1.70 Å, As-O2 = 1.71 Å, (b) As-O1 = 1.68, As-O2 = 1.77 Å, and (c) As-O1 = 1.67, As-O2 = 1.77 Å.

6. DFT calculations on hydrated DMA-iron oxide clusters.

Monodentate complexes

(A) DMA-Fe₂(OH)₅(OH₂)₄ 4H₂O (M=3)

(A') DMA-Fe₂(OD)₅(OD₂)₄ 4D₂O (M=3)

(B) [DMA-Fe₂(OH)₄(OH₂)₅ 4H₂O]⁺ (M=11)

(B') [DMA-Fe₂(OD)₄(OD₂)₅ 4D₂O]⁺ (M=11)

Bidentate complexes

(C) DMA-Fe₂(OH)₅(OH₂)₃ 4H₂O (M=3)

(C') DMA-Fe₂(OD)₅(OD₂)₃ 4D₂O (M=3)

(D) [DMA-Fe₂(OH)₄(OH₂)₄ 4H₂O]⁺ (M=11)

(D') [DMA-Fe₂(OD)₄(OD₂)₄ 4D₂O]⁺ (M=11)

Outer-sphere complexes

(E) DMA (4H₂O) Fe₂(OH)₅(OH₂)₅ (M=3)

(F) [DMA-H(4H₂O) Fe₂(OH)₄(OH₂)₆]²⁺ (M=11)

Figure S5: Energy-minimized equilibrium geometries of hydrated inner-sphere DMA-iron oxide clusters in the monodentate (top), bidentate-binuclear (middle) and outer-sphere (bottom) configurations, with multiplicity (M) > 1 . DFT calculations were performed using B3LYP/6-31G* in Gaussian '09 for normal and deuterated forms. Bond lengths and interatomic distances are listed in Table S2.

7. DFT calculations on hydrated iAs(V)-iron oxide cluster.

Figure S6: Minimum energy equilibrium geometry of iAs(V)-iron oxide cluster using DFT(B3LYP/6-31G*) in vacuum (Guassian '09) for comparison with cluster reported by Sherman and Randall(4). Bond lengths, interatomic distances and calculated $\nu(\text{As-O})$ frequencies are listed in Tables S2 and S3.

8. Summary tables of calculated geometrical and infrared frequencies in optimized structures of DMA- and iAs(V)-iron oxide clusters shown in Figures S5 and S6.

Table S2: Bond lengths and interatomic distances (Å). The number in parentheses represents multiplicity (M)

Calculated distances	As-O ₁	As-O ₂	As-Fe ₁	As-Fe ₂	As-C ₁	As-C ₂	Fe ₁ -O ₁	Fe ₂ -O ₂
Cluster in Figure 2								
(A,A') DMA-Fe ₂ (OH) ₅ (OH ₂) ₄ 4H ₂ O (3)	1.71	1.73	3.16	4.48	1.93	1.93	1.93	-
(B,B') [DMA-Fe ₂ (OH) ₄ (OH ₂) ₅ 4H ₂ O] ⁺ (11)	1.70	1.73	3.31	4.58	1.92	1.92	2.04	-
(C,C') DMA-Fe ₂ (OH) ₅ (OH ₂) ₃ 4H ₂ O (3)	1.71	1.72	3.19	3.19	1.93	1.92	1.93	1.99
(D,D') [DMA-Fe ₂ (OH) ₄ (OH ₂) ₄ 4H ₂ O] ⁺ (11)	1.72	1.71	3.34	3.24	1.93	1.92	2.15	2.05
(E) DMA (4H ₂ O) Fe ₂ (OH) ₅ (OH ₂) ₅ (3)	1.71	1.69	5.27	4.95	1.93	1.93	-	-
(F) [DMA-H (4H ₂ O) Fe ₂ (OH) ₄ (OH ₂) ₆] ²⁺ (11)	1.69	1.74	5.10	6.42	1.92	1.91	-	-
Comparison with iAs(V)-Iron Oxide Cluster [DFT/B3LYP(6-31G*)-Vacuum] – Figure S6								
[H ₂ AsO ₄ -Fe ₂ (OH) ₂ (OH ₂) ₆] ³⁺ (11) ^a	1.70	1.70	3.21	3.21	-	-	1.89	1.89

Notes: ^a As-O₃ = 1.72 Å and As-O₄ = 1.71 Å

Table S3: Assignment of calculated $\nu(\text{As}-\text{O})$ frequencies. The number in parentheses represents multiplicity (M)

	$\nu(\text{As}\equiv\text{O}\cdots\cdots\text{H})$ <u>d(Å): 1.69-1.70</u>	$\nu(\text{As}-\text{OFe})^a$ <u>d(Å): 1.71-1.74</u>	$\nu(\text{As}-\text{OH})$ <u>d(Å): 1.75</u>
(A) DMA-Fe ₂ (OH) ₅ (OH ₂) ₄ 4H ₂ O (3)	761, 814, 828	750, 804	
(A') DMA-Fe ₂ (OD) ₅ (OD ₂) ₄ 4D ₂ O (3)	808, 822	772, 777, 792, 822	
(B) [DMA-Fe ₂ (OH) ₄ (OH ₂) ₅ 4H ₂ O] ⁺ (11)	804, 848, 856	787	
(B') [DMA-Fe ₂ (OD) ₄ (OD ₂) ₅ 4D ₂ O] ⁺ (11)	827	798	
(C) DMA-Fe ₂ (OH) ₅ (OH ₂) ₃ 4H ₂ O (3)		804, 825, 828	
(C') DMA-Fe ₂ (OD) ₅ (OD ₂) ₃ 4D ₂ O (3)		779, 789, 795, 807, 839, 853	
(D) [DMA-Fe ₂ (OH) ₄ (OH ₂) ₄ 4H ₂ O] ⁺ (11)		744, 762, 788, 798, 823	
(D') [DMA-Fe ₂ (OD) ₄ (OD ₂) ₄ 4D ₂ O] ⁺ (11)		697, 707, 810, 823, 835	
(E) DMA (4H ₂ O) Fe ₂ (OH) ₅ (OH ₂) ₅ (3)	786, 812, 841, 844, 862		
(F) [DMA-H (4H ₂ O) Fe ₂ (OH) ₄ (OH ₂) ₆] ²⁺ (11)	848		768
Comparison with iAs(V)-Iron Oxide Cluster [DFT/B3LYP(6-31G*)-Vacuum] – Figure S6			
[H ₂ AsO ₄ -Fe ₂ (OH) ₄ (OH ₂) ₆] ³⁺		842, 882	778, 812

Notes: ^a multiple spectral components due to low symmetry of inner-sphere complexes.

9. Literature cited

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