Determination of Shape-Reactivity Relationships in Al-Nanoclusters

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Abstract. First-principles modeling of reactive materials offers a means of developing molecular-level understanding of adsorption processes. Geochemical surface science is in need of conceptual understanding of what substrate properties govern reactivity. Here, we review and expand upon some of our density functional theory modeling studies of ion adsorption on giant polyaluminum cation species. Where appropriate, we relate our findings to experimental information, and aim to generalize our results to enable future predictions.

1. Introduction
The partitioning of contaminant species between aqueous and solid phases influences bioavailability, transport, and fate in the environment. Fundamentally, ionic adsorption by solid phases is related to processes of importance to heterogeneous catalysis, electrochemistry, and corrosion. A reductionist approach to studying heterogeneous interface systems is to use well-defined simplified models, and then systematically increase complexity. In geochemical surface science, single-crystal surfaces have emerged as a popular model system, giving rise to more than a decade of experimental and theoretical work. However, it is not obvious how to advance these models to take into account defects that better represent natural surfaces while still employing the experimental and computational methods that rely on surface order. An alternative approach to geochemical surface science is to employ well-defined molecular models, such as polyaluminum cations based on the Baker-Figgis-Keggin structural motif. Such aluminum hydroxide nanoclusters are attractive geochemical models because they can be found in nature, are readily synthesized in the lab, and, between their size and crystal structure information, are also tractable at the atomistic modeling level. The cation $\text{Al}_{13}^{3+}$ has been identified in the $\delta$- and $\varepsilon$-isomers, with the $\varepsilon$-isomer being the most common form found in nature. Upon heating, the $\delta$-$\text{Al}_{13}$ cluster has been shown to form even larger complexes including $\text{Al}_{30}^{18+}$ and $\text{Al}_{32}^{20+}$, where two $\delta$-$\text{Al}_{13}$ are connected with Al$^{3+}$ linkers.

Arsenate and phosphate polyoxoanions share many properties and are important contaminants to target in water purification because of their impact on human health. In the environment, P(V) has become of greater concern because of phosphorous enrichment in fertilizers. Because it is toxic and a known carcinogen, As water contamination is a major health concern worldwide. Speciation of As and P in the
environment results in a variety of derivatives that are also of concern. [13-15] Recently, the arsenic uptake capacity of Al-nanoclusters was compared to other Al-based sorbents, including amorphous polyaluminum chloride and mineral Al phases. [16] It was shown that the Al-nanoclusters are the most efficient for arsenic removal from water. Polyaluminum cations are used as coagulants and adsorbents in water remediation processes. A number of studies have shown that 1 nm Al\textsubscript{13} clusters perform better than alum (KAl(SO\textsubscript{4})\textsubscript{2}·nH\textsubscript{2}O) as a clarifying agent, and 2 nm Al\textsubscript{13} performs even better over a wider range of pH and dosage. [16-19]

The growing empirical evidence of desirable adsorption properties possessed by Al-nanoclusters has motivated an ongoing collaborative “make and model” approach towards understanding the reactivity of this important geochemical model/water treatment sorbent. Here, we review and expand upon our recent studies, and discuss future research directions. An unexpected outcome of this body of work is that much of the conventional wisdom about metal hydroxide surface reactivity is at odds with the results. To briefly review, geochemical surface science has relied on the concept of bond-valence to rationalize structure-reactivity relationships. The bond-valence model of Brown, parametrized using bulk structures, suggests that oxygen functional group coordination and protonation states are key predictors of metal (hydr)oxide surfaces. [20] There are also considerations of adsorption based on the type of interaction between the ion and the surface. In inner-sphere (IS) adsorption, the adsorbate forms direct bonds to the surface, while in outer-sphere (OS) adsorption, the interaction is predominated by electrostatic interactions. Based on the different bonding in IS and OS adsorption, it is generally assumed that OS adsorption is relatively weak. [21]

2. Computational methods

Molecular structures for Al\textsubscript{13} and Al\textsubscript{30} were based on crystal structures. [11,22] Counter ions and molecular water not bound to the particles were removed, and the protonation state of under-coordinated oxygen atoms was deduced based on bond-valence. The molecular geometries were optimized using density functional theory (DFT), embedded in the conductor-like screening model (COSMO) dielectric continuum model, as implemented in the DMol\textsuperscript{3} code developed by Delley. [23,24] The DFT calculations are aperiodic, and include spin-polarization when adsorbates with an odd number of electrons are considered. The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) is used, [25] and the single-electron wavefunctions are expanded in a double-numeric-plus polarization atom-centered basis set. Because there was no significant difference in total energies, reaction energies, or the magnitude of the forces, the real-space basis set cut off of 3.5 Å was used. Further details of the methods, including benchmarking of geometries and relative energies using different computational parameters, can be found in our published studies. [10,26-28]

3.1 Trends in ion adsorption on Al\textsubscript{30}

In a purely theoretical study by Corum and Mason, [26] trends in cation and anion adsorption on Al\textsubscript{30} were explored. Based on studies of Al mineral surfaces, the cations Cu\textsuperscript{2+}, Pb\textsuperscript{2+}, and Zn\textsuperscript{2+} were assumed to adsorb to the particle surface in an IS bidentate fashion, while anions SO\textsubscript{4}\textsuperscript{2-} and Cl\textsuperscript{-} were assumed to adsorb in an OS fashion. Figure 1 summarizes the η-H\textsubscript{2}O functional group distinction of Rustad, [29] which is based on the distance of bound water from tetrahedral Al atoms in each end of the symmetric molecule. For convenience, we also refer to the particle region between the two δ-Al\textsubscript{13} building-blocks of Al\textsubscript{30} as the beltway; the flat ends of the δ-Al\textsubscript{13} sections are referred to as the caps.
Using DFT total energies and stoichiometric weights based on model adsorption reactions, we calculated theoretical adsorption energies, $E_{\text{rxn}}$. The results obtained show that Cu$^{2+}$ and Pb$^{2+}$ prefer adsorption through $\eta$-H$_2$O groups at the caps of Al$_{30}$ by 1.04 and 1.13 eV, respectively. On the other hand, SO$_4^{2-}$ and Cl$^-$ prefer OS adsorption in the beltway region, by 1.22 and 1.10 eV, respectively. The fact that the IS adsorption varies by $>1$ eV between oxygen functional groups of identical coordination/protonation violates the bond-valence interpretation of surface reactivity, and the fact that anion adsorption exhibits an opposite site preference to cation adsorption suggests variation in reactivity as a function of location on the particle surface. We found that the electrostatic potential ($V_{\text{el}}$) shown in Figure 2, offers an explanation for this behavior: $V_{\text{el}}$ is relatively negative on the molecular caps. On the other hand, in the beltway, the molecular shape gives rise to collective interactions of exposed water groups, leading to regions of relatively positive values of $V_{\text{el}}$. As the variation in $V_{\text{el}}$ has less to do with function group coordination and more to do with topography, we term the governance of $V_{\text{el}}$ on reactivity in Al$_{30}$ as a “shape-reactivity relationship.”

![Figure 1. Blue polyhedral representation of (Al$_{30}$O$_{30}$(OH)$_{36}$(H$_2$O)$_{26}^{18+}$), showing the locations of bound $\eta$-H$_2$O groups. Taken from Figure 1a in Ref. [10]. Copyright American Chemical Society 2013.](image1)

![Figure 2. Electrostatic potential, $V_{\text{el}}$, of Al$_{30}$ mapped onto a charge density isosurface. Taken from Figure 7 in Ref. [10]. Copyright American Chemical Society 2013.](image2)
3.2 Co-adsorption of Cu$^{2+}$ and SO$_4^{2-}$ on Al$_{30}$

The experimental determination of the structure of Cu$^{2+}$ bound to Al$_{30}$ (in two symmetry equivalent positions) provided an opportunity to use our modeling approach to rationalize the observed adsorbed geometry of the cation. The experimental crystal structure, Cu$_2$Al$_{30}$-S, is shown in Figure 3, and exhibits Cu$^{2+}$ in the beltway region, along with the counter ion used for crystallization, 2,6 naphthalene disulfonate (2,6-NDS). Immediately it is apparent that Cu$^{2+}$ adsorption in the presence of counterion conflicts with our theoretical result of Cu$^{2+}$ preferring adsorption at the cap sites. To explore this theoretically, we compare the separate adsorption of IS Cu$^{2+}$ and OS SO$_4^{2-}$ as discussed above, and compare that to modeled co-adsorption. We consider sulfate adsorption in place of the more complicated counterion used in the experiment to simplify the calculations, and note that sulfate is also a suitable counterion for Al$_{30}$ crystallization.

![Figure 3. Optimized geometry of Cu$_2$Al$_{30}$-S, which shows the two Cu$^{2+}$ cations near the beltway region with the sulfate group of the 2,6-NDS crystallizing agent. The color scheme for the Cu, Al, S, O, C, and H atoms are green, blue, orange, red, black, and gray, respectively. This atom labelling scheme is used throughout. Taken from Figure 3 in Ref. [10]. Copyright American Chemical Society 2013.](image)

As reported in our collaborative study, [10] while copper and sulfate separately prefer the caps and beltway sites by 1.04 and 0.95 eV, respectively, the DFT energetics show that co-adsorption is preferred in the beltway by 1.10 eV, congruent with the Cu$_2$Al$_{30}$-S crystal structure. The opposing trends of isolated ions has already been explained here in terms of $V_e$. The co-adsorption result can be further understood by comparing the strength of the OS SO$_4^{2-}$ adsorption compared to the IS Cu$^{2+}$ adsorption. As noted in the Introduction, OS adsorption is generally thought to be weaker than IS adsorption, as the former is dominated by electrostatics while the latter involves direct bonding. However, the DFT values of $E_{\text{rxn}}$ show that the most preferred value for IS Cu$^{2+}$ adsorption is -1.26 eV, while that of OS SO$_4^{2-}$ adsorption is -2.34 eV. This unusually strong OS SO$_4^{2-}$ adsorption is explored by visualizing the adsorption-induced charge density $\Delta \rho_{\text{SO4}}$ taken as $\rho_{\text{Al30/SO4}} - \rho_{\text{Al30}} - \rho_{\text{SO4}}$, shown in Figure 4. Qualitatively, it is apparent that there is a larger isosurface volume (at the same isosurface value) when sulfate adsorbs in the beltway (left) than at the caps (right). The plots of $\Delta \rho_{\text{SO4}}$ further support the concept of “shape-reactivity” relationships in Al$_{30}$. At the caps, the SO$_4^{2-}$ -- Al$_{30}$ interactions are sterically limited to a relatively small region of the particle surface, while the contours give rise to more extensive SO$_4^{2-}$ -- Al$_{30}$ interactions in the beltway.
Co-adsorption can be schematically summarized as shown in Figure 5: The topographical variations in $V_{el}$ (left) give rise to opposing trends in isolated cation/anion adsorption site preference, with Cu$^{2+}$ preferring the caps and SO$_4^{2-}$ preferring the beltway (middle). However, the unusually strong OS SO$_4^{2-}$ drives the site preference for co-adsorption in the beltway (right).

Figure 5. Schematic summary of coadsorption behavior of SO$_4^{2-}$ and Cu$^{2+}$ adsorption on Al$_{30}$, as described in the text.

3.3 As and P Adsorption on Al$_{30}$

More recently, we used the experimental crystal structure of [(TBP)$_2$Al$_2$(μ$_2$-O)$_8$(Al$_{28}$(μ$_2$-OH)$_{56}$(H$_2$O)$_{22}$)]$^{14+}$ shown in Figure 6 (where TBP = t-butylphosphonate (CH$_3$)$_3$CPO$_3$), as a basis for the DFT calculations to assess whether As(V) adsorption behavior follows that of P(V). We went on to explore if the beltway preference of the polyoxoanion forms of As(V)/P(V) could be changed through R-group substitution exploiting varying inductive effects. The R groups considered were tert-butyl (TB), methyl (M), benzene
(Ph), hydroxyl (OH), and methoxy (OCH₃). The Eigen-Wilkens (EW) mechanism [30,31] is shown in Scheme 1, where the net reaction is used to determine $E_{rxn}$.

Scheme 1. Eigen-Wilkens mechanism that proceeds by the initial formation of an outer-sphere ion pair followed by ligand exchange to form the final product

Step 1: Ion Pair Formation

$$Al_{30}O_8(OH)_{56}(H_2O)_{22} - (OH)_2(H_2O)_2^{16+} + 2 RXO_2OH^{1-} \rightarrow [Al_{30}O_8(OH)_{56}(H_2O)_{22} - (OH)_2(H_2O)_2^{16+}, 2 RXO_2OH^{1-}]^{14+}$$

outer-sphere ion pair

Step 2: Ligand Exchange

$$[Al_{30}O_8(OH)_{56}(H_2O)_{22} - (OH)_2(H_2O)_2^{16+}, 2 RXO_2OH^{1-}]^{14+} \rightarrow Al_{30}O_8(OH)_{56}(H_2O)_{22} - (RXO_2O)_{2}^{14+} + 4 H_2O$$

Net Reaction

$$Al_{30}O_8(OH)_{56}(H_2O)_{22} - (OH)_2(H_2O)_2^{16+} + 2 RXO_2OH^{1-} \rightarrow Al_{30}O_8(OH)_{56}(H_2O)_{22} - (RXO_2O)_{2}^{14+} + 4 H_2O$$

The values of $E_{rxn}$ show that the beltway configuration, congruent with the experimental crystal structure, is preferred by 0.42 eV for TBP and 0.51 eV for the arsenate analog. Ranges of 0.25 eV and 0.49 eV in $E_{rxn}$ were obtained as a function of R-group for P(V) and As(V) species respectively, with the most electron donating group (TB) showing the most favorable values and the most electron withdrawing group (OCH₃) showing the least favorable values. However, while the magnitude of $E_{rxn}$ was tunable in a fashion that followed predictions, it was always the case that the least favorable beltway adsorption of As or P was more favored than the most favorable cap adsorption of As or P. Thus we conclude that the beltway site preference can persist even as a function of large variation in arsenic or phosphorous speciation.
3.4 Heteroatom Substitution

Our adsorption studies have demonstrated shape-reactivity relationships in Keggin-based Al$_{30}$ reactivity. More generally speaking, there is great interest in polyoxometalate chemistry of structurally and compositionally diverse clusters. Recently, our collaborators succeeded in synthesizing a new gallium(III) substituted cluster with the formula [Ga$_2$Al$_{18}$O$_8$(OH)$_{36}$(H$_2$O)$_{12}$]$^{8+}$, or Ga$_2$Al$_{18}$. The Ga$_2$Al$_{18}$ cation contains a centrally-located GaO$_4$ tetrahedron, surrounded by octahedrally coordinated Al$_3^+$ atoms that arrange in trimers of the cluster. A question posed by our collaborators was whether or not the Ga substitution offered some sort of stability to the structure, as they were not able to isolate the pure Al analog, Al$_2$Al$_{18}$. To this end, we carried out DFT calculations on ε-Al$_{13}$ and ε-GaAl$_{12}$, both of which have been isolated experimentally, and compared the electronic structure of the Keggin tridecamers to the experimental Ga$_2$Al$_{18}$ structure and its hypothetical analog Al$_2$Al$_{18}$, electronic structure comparison shown in Figure 7. Based on a side-by-side comparison of the bulk atom-projected density of states that show a common electronic “fingerprint” across all four structures, we suggest that there is no unique stabilization provided by Ga substitution, and instead it may be kinetic or experimental factors that exclude the Al$_2$Al$_{18}$ species. [28]

4. Future Work

While our comparison of electronic structure as a function of heteroatom substitution did not reveal unique features from tetrahedral Ga(III), questions remain regarding heteroatom substitution in molecular clusters. Other aspects of the reactivity of Keggin clusters have been shown to depend on composition. For example, work done by Casey et al. has studied the oxygen-isotope exchange kinetics of the Al$_{13}$, GaAl$_{12}$, and GeAl$_{12}$ clusters; the core oxygen atoms are inert and can be tagged with $^{17}$O to allow for a comparison of all other oxygen atoms exchange rates. [30] The reactivity trend for isotopic exchange was determined to be GeAl$_{12}$ > ε-Al$_{13}$ > GaAl$_{12}$. [8,32] Therefore, in ongoing work, we are conducting a more detailed comparison of substituted tridecamer polycations, including more detailed electronic structure and vibrational analyses.
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References
[1] Eng PJ, Trainor TP, Brown GE, Waychunas GA, Newville M, Sutton SR, Rivers ML 2000 Science 288 1029
[2] Fenter P, Cheng L, Rihs S, Machesky M, Bedzyk MJ, Sturchio NC 2000 J Colloid Interf Sci 225 154
[3] Fenter P, Sturchio NC 2004 Prog. Surf. Sci. 77 171
[4] Catalano JG 2010 J. Phys. Chem. C 114 6624
[5] Catalano JG, Park C, Fenter P, Zhang Z 2008 Geochem. Cosmochim. Ac. 72 1986
[6] Rosso KM, Yanina SV, Gorski CA, Larese-Casanova P, Scherer MM 2010 Environ. Sci. Technol. 44 61
[7] Abadia M, Gonzalez-Moreno R, Sarasola A, Otero-Irurueta G, Verdini A, Floreano L, Garcia-Lekue A, Rogero C 2014 J. Phys. Chem. C 118 29704
[8] Casey WH, Rustad JR, Banerjee D, Furrer G 2005 J. Nano. Res. 7 377
[9] Furrer G, Phillips BL, Ulrich KU, Pothig R, Casey WH 2002 Science 297 2245
[10] Abeysinghe S, Corum KW, Neff DL, Mason SE, Forbes TZ 2013 Langmuir 29 14124
[11] Abeysinghe S, Unruh DK, Forbes TZ 2012 Cryst. Growth Des. 12 2044
[12] Abeysinghe S, Unruh DK, Forbes TZ 2013 Inorg Chem 52 5991
[13] Ilgen AG, Foster AL, Trainor T 2012 Geochem. Cosmochim. Ac. 94 128
[14] Wilson SC, Lockwood PV, Ashley PM, Tighe M 2010 Environ. Pollut. 158 1169
[15] Read EK, Ivancic M, Hanson P, Cade-Menun BJ, McMahon KD 2014 Water Res. 46 229
[16] Mertens J, Rose J, Wehrli B, Furrer G 2016 Water Res. 88 844
[17] Mertens J, Rose J, Kagi R, Chaurand P, Plotze M, Wehrli B, Furrer G 2012 Environ. Sci. Technol. 46 7310
[18] Mertens J, Casentini B, Mason A, Pothig R, Wehrli B, Furrer G 2012 Water Res. 46 53
[19] Mertens J 2011 Rev. Environ. Sci. Bio. 10 111
[20] Brown ID 2009 Chem. Rev. 109 6858
[21] Brown GE, Calas G 2011 Cr. Geosci. 343 90
[22] Johansson G 1960 Acta. Chem. Scand. 14 771
[23] Delley B 1990 J. Chem. Phys. 92 508
[24] Delley B 2000 J. Chem. Phys. 113 7756
[25] Perdew JP, Burke K, Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[26] Corum KW, Mason SE 2015 Mol. Simulat. 41 146
[27] Corum KW, Fairley M, Unruh DK, Payne MK, Forbes TZ, Mason SE 2015 Inorg. Chem. 54 8367
[28] Fairley M, Corum KW, Johns A, Unruh DK, Basile M, de Groot J, Mason SE, Forbes TZ 2015 Chem. Comm. 51 12467
[29] Rustad JR 2005 Geochem. Cosmochim. Ac. 69 4397
[30] Casey WH, Rustad JR 2007 Annual Rev. of Earth and Planet. Sci. 35 21
[31] Wilkins RG The study of kinetics and mechanism of reactions of transition metal complexes; Allyn and Bacon, Inc: Boston, MA, 1974
[32] Rustad JR, Casey WH 2012 Nat. Mater. 11 223